A Dissertation

Entitled

Spectroscopic Ellipsometry Studies of Ag and ZnO Thin Films and Their Interfaces for Thin Film Photovoltaics

by

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Many modern optical and electronic devices, including photovoltaic devices, consist of multilayered thin film structures. Spectroscopic ellipsometry (SE) is a critically important characterization technique for such multilayers. SE can be applied to measure key parameters related to the structural, optical, and electrical properties of the components of multilayers with high accuracy and precision. One of the key advantages of this non-destructive technique is its capability of monitoring the growth dynamics of thin films in-situ and in real time with monolayer level precision.

In this dissertation, the techniques of SE have been applied to study the component layer materials and structures used as back-reflectors and as the transparent contact layers in thin film photovoltaic technologies, including hydrogenated silicon (Si:H), copper indium-gallium diselenide (CIGS), and cadmium telluride (CdTe). The component layer materials, including silver and both intrinsic and doped zinc oxide, are fabricated on crystalline silicon and glass substrates using magnetron sputtering techniques. These thin films are measured in-situ and in real time as well as ex-situ by spectroscopic ellipsometry.
in order to extract parameters related to the structural properties, such as bulk layer thickness and surface roughness layer thickness and their time evolution, the latter information specific to real time measurements. The index of refraction and extinction coefficient or complex dielectric function of a single unknown layer can also be obtained from the measurement versus photon energy. Applying analytical expressions for these optical properties versus photon energy, parameters that describe electronic transport, such as electrical resistivity and electron scattering time, can be extracted. The SE technique is also performed as the sample is heated in order to derive the effects of annealing on the optical properties and derived electrical transport parameters, as well as the intrinsic temperature dependence of these properties and parameters. One of the major achievements of this dissertation research is the characterization of the thickness and optical properties of the interface layer formed between the silver and zinc oxide layers in a back-reflector structure used in thin film photovoltaics. An understanding of the impact of these thin film material properties on solar cell device performance has been complemented by applying reflectance and transmittance spectroscopy as well as simulations of cell performance.
To Dawan Bazar, Bhojpur, Nepal, where I was born.

To my parents and parents-in-law; grandparents; uncles-aunties; brother; brothers-in-law and sisters-in-law; relatives; friends; families; wife and two sons.
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Chapter 1

Introduction

1.1 Thin Film Photovoltaics

The photovoltaic (PV) effect was first observed by Edmund Becquerel in 1839 (Becquerel, 1839). In his studies of electrolytic cells consisting of platinum electrodes immersed in an acidic solution of silver chloride, Becquerel recognized that when the cell was illuminated, a voltage and current were generated. Thus, the term “photovoltaic” refers to the generation of current or voltage upon exposure to photons, in the modern day context in reference to the exposure of two materials that form a junction. Solar cells are the devices that operate on the basis of this effect. Solar modules are made from solar cells connected in series and/or parallel in a packaged form in order to achieve desired operating voltages and currents. The first viable solar cell was based on a crystalline silicon p-n junction and was fabricated at Bell Telephone Laboratories in 1954. Since then, various junction material combinations and fabrication techniques have been developed for highest efficiency solar cells and modules. Over time, research and development activities have focused on achieving low PV system cost, with the ultimate goal of competing with conventional sources of electric power.
Silicon remains the dominant technology in the PV industry because of its status as a very mature materials and device technology arising from its applications in the microelectronics industry. One of the drawbacks of crystalline silicon PV technology, and the driving force behind thin film PV technology development over the last few decades, has been the high silicon materials cost and limited availability. In the past few years, however, such issues have been addressed and silicon solar modules have rebounded as among the lowest in cost across the photovoltaics industry. One approach for further reducing the cost of solar electricity is to use a smaller quantity of material in the fabrication process. In silicon technology, that implies thinner wafers and direct wafer fabrication, the latter avoiding sawing from ingots and the resulting kerf loss. A completely different approach involves the development of thin film solar cells and modules, called second generation PV technology, which has the potential to reduce costs even lower than those of crystalline silicon, albeit with a reduction in efficiency. So far, the only technology that has reached that goal is heterojunction CdS/CdTe deposited on low cost glass coated with a transparent conducting oxide, a technology perfected by First Solar Corporation, a Toledo area company.

In this section, the most basic operating principles of a solar cell are presented. Then an introduction to each of the thin film PV technologies is described since this dissertation research has touched on each such technology, with the focus being on the optical properties of the conductive contacting materials, both front (sun side) and back. Finally, spectroscopic ellipsometry is introduced as an invaluable tool to assist in the characterization and optimization of solar cell material components and multilayer device structures.
1.1.1. Operating Principle of the Solar Cell

A solar cell is fabricated as a semiconductor diode, which is a $p$-$n$ junction. When a photon having an energy greater than the semiconductor bandgap is absorbed, an electron-hole pair is generated. The goal of an operational solar cell is to ensure that photon absorption occurs in the junction region so that the photogenerated electron and hole can be separated and individually transported to the neutral regions or electrode where their recombination with the opposite charge carrier draws current into the device through an external circuit. Thus, an important semiconductor materials characteristic for photogeneration of electron-hole pairs is its bandgap energy $E_g$. Only photons with energy $h\nu > E_g$ will contribute to the photogeneration of charge carriers. (Here $h$ is Planck’s constant and $\nu$ is frequency of the light wave associated with the photon.) The fact that the energy difference $h\nu - E_g$ is lost as heat due to electron and hole thermalization, however, implies that there will be an optimum solar cell material band gap and a maximum efficiency which is $\sim 1.35$ eV and $\sim 34\%$, respectively, for a single semiconductor junction. This efficiency is described as the Shockley-Queisser Limit for a solar cell with $1.35$ eV bandgap (Shockley and Queisser, 1961).

A space charge region and internal electric field forms spontaneously in a solar cell device where the p and n type materials are in contact. Free holes in the p-type material diffuse to the n side and recombine there due to the high concentration of electrons, leaving negatively charged dopant atoms on the p-side. Similarly, free electrons from the n-type material diffuse to the p-type side, leaving positively charged dopant atoms on the n-side. Thus, the electric field in the space charge region is directed from the n-side to the p-side. The space charge region is also called the depletion region.
because it is depleted of free charge due to the recombination of diffusing carriers. When photons generate electron-hole pairs within the space charge region between the p and n-type materials, electrons will drift under the influence of the field to the n-type side of the device whereas holes will drift to the p-type side.

Contacts are required at the top or sun side and the back of the solar cell. For thin film solar cells, the top contact is typically a layer of transparent conducting oxide such as fluorine-doped tin oxide (SnO$_2$:F; FTO), tin-doped indium oxide (In$_2$O$_3$:Sn; ITO), or aluminum doped zinc oxide (ZnO:Al; AZO) with current-collecting grid lines deposited on top. The back contact is usually an opaque metal, such as aluminum, chromium, molybdenum, silver, or gold designed to make an ohmic contact to the semiconductor. The two contact layers enable a dc current in the external circuit with the goal being high shunt and low series resistances. In some device structures with partial absorption in the semiconductor material, the back contact metal layer can also serve as a back-reflector, which provides an opportunity for photon absorption in a second pass through the semiconductor.

The efficiency $\eta$ of the solar cell is the ratio of the generated electrical power $P_{\text{out}} = I_m V_m$ to the incident sunlight power $P_{\text{in}} \sim (1000 \text{ W/m}^2)$A, where A is the area of the cell or $\eta = I_m V_m / P_{\text{in}}$. In these expressions $I_m$ and $V_m$ are the current and voltage at the maximum power point of solar cell operation. One can proceed to find that $\eta (\%) = (\text{FF})(J_{\text{sc}})(V_{\text{oc}})$, where $J_{\text{sc}}$ is the short-circuit current density in mA/cm$^2$ (at $V = 0$) and $V_{\text{oc}}$ is the open-circuit voltage in V (at $J = 0$). The quantity FF is the fill-factor, which is defined according to $\text{FF} = J_m V_m / J_{\text{sc}} V_{\text{oc}}$. The efficiency is limited not only by incomplete
collection of the energy of each photon, but also by electrical loss mechanisms (Hubbard, 1989).

The major factors limiting the efficiency of a solar cell include the inability to collect photons below the gap; the inability to collect the thermalization energy of the electrons and holes; loss of light by reflection from the cell surface and absorption by inactive components such as contacts; shading by the top electrical grids; inability to achieve a voltage equal to the band gap (in V); loss of electrons and holes via recombination, which can occur due to point defects and grain boundaries in thin film materials; and high series resistances and low shunt resistances that reduce the FF, caused in the former case by non-ohmic or blocking contacts and in the latter case by contaminants at grain boundaries and pinholes in thin films.

1.1.2 Amorphous Silicon Solar Cells

Although solar cells made from crystalline silicon are highly efficient, as high as 25% in the laboratory, the lowest production cost achievable in the future will likely be limited by the materials cost due to the quantity of high quality silicon material required in high efficiency modules. An alternative to crystalline silicon PV technology that has been explored for decades is thin film hydrogenated silicon (Si:H) technology, which encompasses solar cells made from thin films of hydrogenated amorphous silicon (a-Si:H), hydrogenated amorphous silicon-germanium alloys (a-Si$_{1-x}$Ge$_x$:H), and hydrogenated nanocrystalline silicon (nc-Si:H). These thin film materials are fabricated by plasma-enhanced chemical vapor deposition using SiH$_4$, Si$_2$H$_6$, and GeH$_4$ gases as the Si and Ge sources, and PH$_3$ and B$_2$H$_6$ as the most common dopant atom sources. The amorphous thin film materials exhibit a much higher optical absorption coefficient in
the visible range of the solar spectrum than crystalline silicon, and thus total material thicknesses less than 1 μm can be used to fabricate a solar cell of optimum performance, as compared to 50 μm or greater for crystal silicon (Shah et al., 1999, Nelson, 2003). The increase in absorption coefficient for a-Si:H results from the amorphous structure. Optical transitions that are forbidden in indirect gap single crystal silicon, due to the requirement of crystal momentum conservation, become allowed in a-Si:H as a result of the relaxation of this conservation law for a disordered material.

In such thin film Si:H cells, reducing recombination losses due to defects related to the disordered structure is a priority. In particular, the doped forms of Si:H are highly defective. For this reason, Si:H-based solar cells are fabricated in the superstrate/p-i-n and substrate/n-i-p structures, whereby p represents a thin (~ 100 Å) p-type doped layer, i represents a thicker (0.3-0.5 μm) intrinsic layer (which acts as the active layer for photogeneration), and n is a thin (~ 200-400 Å) n-type doped layer. The superstrate/p-i-n configuration typically uses transparent conducting oxide (TCO) coated glass as the starting superstrate for rigid cell or module fabrication. The substrate n-i-p configuration typically uses stainless steel foil for flexible cells or modules and a TCO coating on the top.

To increase the efficiency of the a-Si:H solar cell, generally a multijunction cell structure is used whereby the additional stacked cells use lower bandgap nc-Si:H or a-Si1-xGex:H i-layers in the p-i-n or n-i-p structures. The p-i-n or n-i-p cells are stacked on top of one another with the i-layer band gap decreasing in the direction of the incoming photons. Irrespective of the configuration (superstrate/p-i-n or substrate/n-i-p), the structure is designed so that the light enters through the p-layer. This design is due to
the lower mobility of holes which need not travel as far on average as electrons in this
design (Deng and Schiff, 2003).

A schematic of a triple-junction hydrogenated amorphous silicon-based solar cell
is shown in Fig. 1.1 (left). The light passes through the transparent ITO top contact first
and the largest fraction of the transmitted light is absorbed successively in the three i-
layers with typical band gaps of 1.8 eV (a-Si:H), 1.6 eV (a-Si_{1-x}Ge_{x}:H), and 1.4 eV
(a-Si_{1-x}Ge_{x}:H). Typical thicknesses range from 500 to 2000 Å, selected to match the
current generated in each cell of the multijunction. The doped layers are made as thin as
possible to minimize absorption losses due to these layers since electron-hole pairs
generated in the doped layers recombine there and do not contribute to collection. A
photograph is provided on the right side of Fig. 1.1 that depicts a flexible solar module
fabricated by the former United Solar Corp. using precisely the same configuration as is
shown at the left. This company is no longer in existence due to their inability to
compete on efficiency and manufacturing cost, considering the rapid drop in the prices of
imported crystalline silicon modules.
Figure 1-1: (Left) A schematic of the triple-junction substrate/n-i-p type flexible solar cell is shown (Deng and Schiff, 2003). (Right) A photograph of a 68 W flexible self-adhesive solar module is provided. This module was manufactured by United Solar Corp. using the configuration at left. For a module, several triple-junction a-Si:H-based solar cells are connected in series.

One of the primary drawbacks of the Si:H-based multijunction solar cell is the low efficiency inherent to the i-layer material properties. In particular, the mobility of the electron and especially that of the hole are low in amorphous semiconductors due to the presence of disorder which generates band tail states whose energies lie below the conduction band edge and above the valence band edge that can trap and temporarily immobilize charge carriers. The density of defects states that can serve as recombination centers is also high relative to crystalline materials. In addition, the a-Si:H cell loses efficiency after initial exposure to the solar irradiance. One simple theory of light-induced degradation contends that dangling bonds form in the intrinsic layer of the solar cell due to the breaking of weak Si-Si bonds when electrons and holes recombine and
release energy. The advantage of a-Si:H PV technology is that the solar cells can be deposited at low temperatures (<200°C) relative to other technologies, and so a variety of low cost substrates, not just glass and metal foil, but also polymer film and fabrics can be used, thereby giving it an edge for wide variety of building integrated and consumer-related applications. Thin film Si:H modules that use metal foils and polymers as substrates are ideal for applications in which light weight, portability, and ease of installation is more important than high efficiency.

1.1.3 Cadmium Telluride Solar Cells

Cadmium telluride (CdTe) is another useful and important thin film semiconductor material for photovoltaics applications. CdTe has an advantage over crystalline silicon due to its direct bandgap, having an energy of $E_g = 1.49$ eV, and its associated strong optical absorption. Although single crystal wafers of CdTe are exceedingly expensive, polycrystalline CdTe can be deposited very inexpensively as a thin film from CdTe powder by various evaporation and vapor transport methods. Because of its direct bandgap, a thickness of 2-3 microns of CdTe can absorb almost all of the incoming light above its bandgap. The structure of a CdTe solar cell developed at University of Toledo is presented in Fig. 1.2 (left) along with a photograph of a module fabricated by First Solar Corporation (right). In the structure at left, a 2 µm layer of CdTe serves as the p-type semiconductor and a thinner ~0.1 µm layer of CdS serves as the n-type semiconductor in order to form the p-n junction. In CdTe, native defects such as Cd vacancies, along with Cu which can substitute for Cd, impart p-type character, and similarly, native defects in CdS such as Cd interstitials impart n-type character. In the highest efficiency University of Toledo solar cell, the transparent conducting oxide
(TCO) aluminum doped zinc oxide (ZnO:Al) is used as the top contact, and in fact a bi-layer of TCOs, including a thinner undoped layer adjacent to the solar cell is effective at increasing the shunt resistance. A tin oxide bi-layer is used commercially, yielding the structure SnO$_2$:F/SnO$_2$/CdS/CdTe.

One issue that has impacted the international use of CdTe thin film PV technology is the toxicity of cadmium. CdTe is considered harmless when properly encapsulated, specifically as a thin layer between sheets of glass in a module. Researchers from Brookhaven National Laboratory have found that the fabrication of CdTe PV modules, which are used widely in this nation’s utility scale solar PV plants, do not produce any pollutants and do not pose risks to health and the environment (Fthenakis, 2004). Furthermore, First Solar has established a program for recycling the modules after their useful life in further efforts to eliminate any environmental concerns.

Figure 1-2: (Left) A schematic is shown that depicts the layers of a superstrate type CdTe solar cell developed at University of Toledo. The solar irradiance enters through the glass side. (Right) First Solar's 60 cm x 120 cm CdS/CdTe photovoltaic module is shown, observed from the glass side.
1.1.4 Copper Indium Gallium Diselenide Solar Cells

Copper indium gallium diselenide (CuIn$_{1-x}$Ga$_x$Se$_2$; CIGS) is a direct bandgap polycrystalline semiconductor that forms the basis of a third thin film photovoltaics technology. For the alloy composition of $x = 0.3$, which is the optimal PV material, the band gap is ~ 1.2 eV. CIGS is similar to CdTe and Si:H in that it is strongly absorbing in the visible range and, thus, requires very little material (~ 2 $\mu$m thickness) compared to wafer silicon. The native defects in CIGS, predominantly Cu vacancies, impart p-type character. Thus, the CIGS solar cell is fabricated as in CdTe technology, by making a junction with CdS whose native defects impart n-type character. Some CIGS solar cells and modules have shown an instability problem different in nature than that reported for a-Si:H (Shah et al., 1999). The stability problem in CIGS generally occurs in hot and humid environments and has been attributed to changes in the ZnO layers which serve as the top transparent conducting oxide.

A schematic of a typical CIGS solar cell is shown in Fig. 1.3 along with a photograph of a flexible module produced by Global Solar Energy, Inc. In contrast to CdTe technology, which applies the superstrate configuration with light entering through the glass first, CIGS cells and modules are fabricated in the substrate configuration, which allows the use of optically opaque substrate materials such as metal foils. Among the thin-film solar cells, CIGS has the highest conversion efficiency of 21.7 % as reported by the researchers from Zentrum für Sonnenenergie- und Wasserstoff-Forschung (ZSW) in Stuttgart, Germany (ZSW Press Release, 2014). Because CIGS is a thin film technology, the resulting modules are also produced inexpensively, and the potential of CIGS for high efficiencies have displaced thin film Si:H from the market for flexible PV
in building integrated applications. Although CIGS cells can be "printed" on flexible substrates using solution-derived precursors, the highest efficiencies are obtained in high temperature (> 500ºC) vacuum deposition processes using evaporation sources for the four individual elements. In the fabrication of CIGS, stoichiometric control of Cu is required such that \( y = \frac{[\text{Cu}]}{[\text{In}]+[\text{Ga}]} = 0.9 \), and the Cu deficiency leads to vacancies that impart the p-type character. The large number of vacancies is compensated by the ordered defect complex \( 2\text{V}_{\text{Cu}} + \text{In(Ga)}_{\text{Cu}} \), which is neutral and represents two Cu vacancies with an In or Ga atom residing at one of the two empty sites. The required stoichiometric and alloy compositional control, such that \( x = \frac{[\text{Ga}]}{[\text{In}]+[\text{Ga}]} = 0.3 \), pose challenges in optimization and scale-up that are greater for CIGS technology than for Si:H and CdTe.

![Multilayer Structure](image)

Figure 1-3: (Left) A schematic multilayer structure is shown for a typical CIGS solar cell fabricated on a glass substrate. (Right) A flexible CIGS module is depicted, as fabricated by Global Solar Energy, Inc. on a stainless steel substrate.

### 1.2 Transparent Conducting Oxide and Back Reflectors

Transparent conducting oxides (TCOs) are important components of thin film photovoltaic devices. These thin films serve as electrodes or contacting components that
transmit light but may have other functions as well. They may serve as barriers against atomic diffusion, templates for structural control of overlying films, and ohmic contacts with work function control (Fortunato et al., 2007). TCOs used in PV devices have desirable characteristics similar to those found in flat-panel display and touch screen technology. These characteristics include high optical transparency, not only throughout the visible range, but also into the near-ultraviolet and near-infrared, and low sheet resistance. Additionally, the capability must exist to deposit these materials over large areas at low cost for wide applications in terrestrial PV.

The first TCO to be studied was cadmium oxide (CdO), discovered and reported by K. Badeker in 1907. CdO is n-type, as is the case for most TCOs, due to the presence of native defects such as cation interstitials and anion vacancies. Currently the three most important TCOs commercially include indium oxide (In$_2$O$_3$), tin oxide (SnO$_2$), and zinc oxide (ZnO), which have bandgaps of 3 eV or more. Generally, even though the oxides are not intentionally doped, they show sufficiently high n-type conductivity as a result of their native defects to enable electron transport through the TCO layer thickness in PV devices. Thus, undoped TCOs are used as so-called HRT or high resistivity transparent layers in CdTe and CIGS technologies as a component of the bi-layers in order to increase shunt resistance. They are also used as conductive diffusion barrier layers between a metal back contact and the semiconductor, in particular, as part of a back-reflector.

Further doping is usually required for these transparent conducting oxides to be used for planar transport over the area of the PV devices (as opposed to transport through the thickness). Such doped TCOs are used as the second component of the bi-layers for
the transparent top contact in CdTe and CIGS PV technologies. The most common doped TCOs include In$_2$O$_3$:Sn (ITO), SnO$_2$:F (FTO), and ZnO:Al (AZO). In ITO and AZO, the n-type doping is achieved by substitution of the cation with an element having one excess valence electron, whereas for FTO, the doping is achieved instead through anion substitution. The substitutional dopants increase the free carrier concentration sufficiently to shift the Fermi level from an energy at or just below the conduction band minimum, which is the situation for undoped materials, to an energy higher into the conduction band. In this dissertation, ZnO and ZnO:Al will be explored for their optical and electrical properties, investigated by applying the Drude theory of free electrons in a solid. This theory is applicable when the Fermi energy lies within a high density of band states as is the case for doped ZnO.

Another aspect of this dissertation is the study of ZnO integrated into the back-reflector (BR) as applied in Si:H PV technology. There are two types of back-reflector configurations used in Si:H PV technology, one being the superstrate/p-i-n in which the ZnO/Ag layers are deposited in succession on the n-layer of the p-i-n cell and the other being the substrate/n-i-p in which the ZnO is deposited on the substrate/metal-contact before deposition of the n-i-p cell. The Si:H-based substrate/n-i-p solar cell configuration is the one studied in detail in this dissertation.

In the configuration of this study, the n-i-p cell is deposited on a back-reflector consisting of a metal-contact/ZnO two-layer structure. Either Ag or Al is chosen as the metal contact whose purpose is two-fold, namely to serve as a highly conducting plane and also to reflect the light not absorbed in the cell in the first pass so that it can be absorbed in the second and successive passes. The metal layer also incorporates
macroscopic roughness to allow for oblique scattering and longer optical path lengths upon reflection. The ZnO layer on top of the metal prevents diffusion of metal into the cell, acts as an optical spacer, and also transfers the roughness from the metal contact to the ZnO/n-layer interface in order to generate an additional source of light scattering for the rays entering and exiting the back-reflector.

When this back-reflector is integrated into the multijunction Si:H-based solar cell, the cell can experience a gain as large as 25-30% in short-circuit current due to the increase in near-IR (~1.2–1.7 eV) absorption. This effect is demonstrated in Fig 1.4 which depicts the quantum efficiency spectra for two identically-deposited a-Si1-xGex:H solar cells. One was deposited on top of uncoated stainless steel and the other was deposited on top of stainless steel coated with a Ag/ZnO back-reflector. A current density enhancement from 17.3 mA/cm² to 23.7 mA/cm² was achieved (Yang et al., 2003).

![Figure 1-4: Quantum efficiency spectra and short-circuit current densities are compared for two identically-deposited a-Si1-xGex:H solar cells. One was deposited directly on top of stainless steel (SS) whereas the other was deposited on top of stainless steel that was coated with a Ag/ZnO back-reflector (Yang et al., 2003).](image)
The operation of Ag/ZnO back-reflectors is not perfect, however, which leads to opportunities for their improvement and, thus, increases in the efficiency of Si:H based thin film solar cells. Optical absorption losses are associated with Ag/ZnO back-reflectors that reduce their reflectance. These losses include (i) the intrinsic optical absorption in the bulk metal and ZnO layers, (ii) physical intermixing due to microscopic roughness at the metal/ZnO interface that leads to Ag protrusions and confined free electron or plasmon resonances in the interface layer optical properties, (iii) propagating plasmons on the Ag side of the interface that are excited as a result of macroscopic roughness through grating coupling that enables both energy and momentum conservation; (iv) chemical intermixing at the metal/ZnO interface, leading to new compositions that are formed as a result of the energetic bombardment of the Ag surface in the initial stages of ZnO magnetron sputter deposition. In this dissertation, the losses in the Ag/ZnO back-reflector structures will be studied systematically using real time, in situ, and ex situ spectroscopic ellipsometry by depositing ZnO on the smoothest possible Ag surface first, and then on Ag of gradually increasing surface roughness until the level of surface roughness found in commercial solar cells is reached.

1.3 **Spectroscopic Ellipsometry**

Spectroscopic ellipsometry is a technique that derives its name from a measurement of the most general state of polarized light, which is elliptical. In the most common use of an ellipsometer, the change in polarization state of an electromagnetic wave is measured upon oblique reflection of the wave from a specularly reflecting interface of interest. The ellipsometry measurement is strongly influenced by the addition of a layer at a reflecting interface, such as an oxide layer at the interface between
a polished silicon wafer and the ambient. The sensitivity to fractions of a monolayer arise due to the differences in phase shift upon reflection of the linearly polarized p and s waves, having electric fields parallel and perpendicular to the plane of incidence, respectively (Collins and Vedam, 1993). Because ellipsometry measures polarization, or p-s relative fields, rather than absolute irradiance, the technique is not sensitive to isotropic surface defects that scatter incident specular light.

The ellipsometer is ideal for measurement of the optical properties of reflecting solids and the thickness and optical properties of all types of thin films. Because of these properties, ellipsometry is a natural fit for materials and device analysis in thin-film photovoltaics. As the schematics of solar cells presented earlier clearly show, thin film solar cells include at minimum four layers (top TCO, p-type and n-type semiconductors, and metallic back contact) and as many as twelve layers for a triple-junction Si:H-based device. In the optimization of PV devices, the first step involves incorporating the proper material components, which requires knowledge of the films’ optical properties, quantified by the index of refraction n and extinction coefficient k. The second step involves optimization of layer thicknesses such that light can be absorbed predominantly by the active layer with the resulting electrons and holes separated and collected. Thus, ellipsometry performed spectroscopically over the wavelength range of solar cell operation provides these two key PV materials and device characteristics. The challenges of amorphous and polycrystalline thin films arise because thin film material properties can change considerably with the conditions of deposition and with the nature of the underlying films and the substrate/superstrate. In addition, as different layers of materials are deposited on top of one another, interface layers are formed that can exhibit unique
properties, especially when one of the two layers incorporate free electrons. The spectroscopic ellipsometer is a powerful tool to identify these unique properties and as a result uncover new physics associated with thin film structures.

1.4 Optical Properties of Solids

The key parameters that determine light propagation within a solid state medium are the index of refraction $n$ and the extinction coefficient $k$. The index of refraction describes the phase speed and wavelength of the electromagnetic wave in the medium, according to $v = c/n$ and $\lambda = \lambda_0/n$, where $c$ and $\lambda_0$ are the phase speed and the wavelength of the wave in vacuum. The extinction coefficient describes how the electric field amplitude associated with the wave decreases with distance $z$ within the medium according to $E = E_0 \exp(-2\pi kz/\lambda_0)$. The uniqueness of spectroscopic ellipsometry is the ability to determine $n$ and $k$ of an unknown material from a single oblique reflection measurement at an interface between a known ambient medium and the unknown material. The complex relative electric permittivity or dielectric function $\varepsilon = \varepsilon_1 + i\varepsilon_2$ is obtained by squaring the complex index of refraction, which has as its real part $n$ and as its imaginary part $k$, according to $\varepsilon = \varepsilon_1 + i\varepsilon_2 = (n + ik)^2$.

1.4.1 Silver

Silver (Ag) is a noble metal, meaning that the d-bands are filled with electrons and the conduction is controlled by the single electron per atom residing in s-like bands. In fact, the d-band electrons lie well below the Fermi energy and so do not participate in conduction, and this accounts for the high electrical conductivity. Ag crystallizes in the face-centered cubic (FCC) structure with a lattice constant of $a = 0.409$ nm (Wyckoff, 1963). The J. A. Woollam Company database of optical properties cites Palik (1985) for
the optical properties of Ag, and the real and imaginary parts of the dielectric function from that database are plotted in Fig. 1.5. The data were collected using a polarimetric method applied to a polycrystalline silver sample of 99.999% purity that was electrolytically and chemically polished (Winsemius et al., 1976). In the spectra of Fig. 1.5, two distinct regions can be observed. At low photon energies, intraband electronic transitions dominate the spectra, whereas at higher energies, interband electronic transitions are evident.

In order to characterize these two types of electronic transitions, the dielectric function can be parameterized by using a complex analytical function with multiple terms. Since the low energy transitions involve free electrons, a Drude term is incorporated that includes as parameters an amplitude and a broadening energy from which the plasma energy and scattering time can be deduced. On the other hand, because the higher energy transitions involve bound electrons, a term consisting of a generalized critical point (CP) oscillator is incorporated. The parameters of such an oscillator term include an amplitude, resonance and broadening energies, a phase, and an exponent. For metals, the resonance energy of interband absorption reflects the electronic transitions from the Fermi level to the next higher empty band or from a lower lying filled band to the Fermi level (Ehrenreich and Philipp, 1962). In the case of silver, the latter situation accounts for the interband transitions whereby the electronic transitions occur from the filled $d$ bands to the Fermi level. From the structure of the dielectric function, the interband absorption onset can be clearly observed at $\sim 4$ eV. Dielectric functions of silver similar in form are obtained in this dissertation research for the various deposition and processing conditions.
1.4.2 Zinc oxide

G.E. Jellison, Jr., et al. have applied spectroscopic ellipsometry to study an undoped single crystal of ZnO (Jellison and Boatner, 1998). Because ZnO crystallizes in the wurtzite structure as shown in Fig. 1.6, it exhibits uniaxial optical properties, meaning that the dielectric function differs for optical electric fields parallel to the crystal’s c-axis, yielding the extraordinary dielectric function, and perpendicular to the c-axis, yielding
the ordinary dielectric function. In fact, for a uniaxial crystal, the dielectric response can be described as a second rank tensor which is diagonalized in a coordinate system having z parallel to the c-axis of the crystal. In this coordinate system, the x and y diagonal components of the dielectric response are equal and define the ordinary dielectric function; the z diagonal component is the extraordinary dielectric function.

By using an advanced ellipsometer and a suitably cut and polished single crystal of ZnO, a single measurement is adequate to determine the ordinary and extraordinary dielectric functions as shown in Fig. 1.7 (Jellison and Boatner, 1998). Applying a physics-based analytical model for the optical transitions, two distinct band gap critical points of $3.372 \pm 0.004$ eV and $3.405 \pm 0.004$ eV can be determined from the ordinary and extraordinary dielectric functions, respectively. In addition, the amplitude of the

![Diagonalization of dielectric response](image)

Figure 1-6: Characteristics of the wurtzite crystal structure are shown along with lattice parameters for various II-VI and III-V semiconductors including ZnO. Two atoms representing Zn (corner and center cell positions) and two atoms representing O (edge and top positions) of the crystallographic basis are circled (adapted from: http://cmt.dur.ac.uk/sjc/thesis_mcg/node47.html).
extraordinary dielectric function resonance is larger, giving larger amplitudes of $\varepsilon_1$ and $\varepsilon_2$ for E-fields parallel to the c-axis over the range of photon energies above the bandgap. Jellison et al. have claimed that their spectroscopic ellipsometry method provides the most accurate values of the dielectric function components of single crystal ZnO above the band gaps (> 3.4 eV). In fact, below the bandgap, where the single crystal is transparent and transmits light, the results of Jellison et al., spanning the range 1.45 to ~2.8 eV, agree with minimum deviation measurements on single crystal ZnO prisms (Bond, 1965). The minimum deviation method is generally more accurate than the ellipsometry method, but is limited to bulk transparent solids ($\varepsilon_2 = 0$), and only those from which one can fabricate an optically polished prism.

Figure 1-7: (Left) The complex ordinary and extraordinary dielectric function components and absorption coefficients of a ZnO single crystal are shown as measured at room temperature by spectroscopic ellipsometry; (right) the same data are shown for the 3.1-3.5 eV range. The solid and dashed lines in the right panel are fits to the data using an analytical expression (Holden, et al. 1997) that provides the bandgaps (Jellison and Boatner, 1998).
In this dissertation research, the relatively weak anisotropy that characterizes single crystal ZnO is ignored based on the fact that the films are polycrystalline and tend to exhibit random orientation of the individual grains. Thus, it is assumed that the spectroscopic ellipsometry measurements obtain a spatial average of the weighted ordinary and extraordinary components associated with individual grains which can be understood in terms of an isotropic dielectric function. In the neighborhood of the band gap, where the differences in the two dielectric function components are the largest, the shape of the absorption onset, especially the broadening of the dielectric function, is most strongly affected by the anisotropy. If the crystallites in the ZnO film are not random, however, but preferentially oriented with the c-axis normal to the substrate, for example, then the assumption that spatial averaging leads to isotropy breaks down and the thin film itself is optically anisotropic. For a strongly refracted ellipsometry beam, however, in the example of c-axis preferential orientation, the ellipsometry experiment tends to probe the ordinary dielectric function which exhibits the narrower bandgap.

1.5 Dissertation Organization

Previously in Chapter 1 of this dissertation, three different thin film technologies have been introduced that are being actively studied in the photovoltaics community, as well as in this research. A brief introduction to spectroscopic ellipsometry, the measurement tool used throughout this dissertation, was also provided. The main components of this dissertation describe research on the back-reflector, composed of a silver thin film coated with a transparent conducting oxide, zinc oxide, whose optical properties have also been introduced in this chapter. Chapter 1 concludes with this brief description of the dissertation organization chapter by chapter.
Chapter 2 describes spectroscopic ellipsometry (SE) and other experimental techniques used in this dissertation research. First, the basic optics of reflection and transmission at an interface are summarized, and effective medium theories are introduced. These topics are important for an understanding of SE measurements of interfaces that are imperfect due to the presence of microscopic roughness. Next, the basic concepts and principles of SE are presented. SE is an indispensable tool in determining the optical properties and thickness of a thin film material. An example demonstrating the determination of the dielectric function of a molybdenum back-contact in the CIGS solar cell has been presented in this chapter as a case study. All of the thin film materials in this research have been deposited using RF magnetron sputtering, and a short introduction to this method is presented in Chapter 2. Other experimental techniques, such as transmission and reflection (T&R) measurement and simulation, are also introduced in Chapter 2. The role of optical simulation in guiding the design of the TCO layer in CdTe solar cell optimization is given as an example.

Chapter 3 focuses primarily on silver thin film depositions. In this chapter, the unique ability of real time spectroscopic ellipsometry (RTSE) to describe the structural evolution of silver thin films is presented for different deposition conditions, including elevated substrate temperatures. The bulk of Chapter 3 is devoted to presenting the dielectric functions of silver films deposited under the different conditions and modeling the dielectric functions using analytical expressions. This section also describes experiments in which substrate heating is performed before deposition of the silver film and annealing of the film is performed after deposition. The effect of these steps on the film’s dielectric function have been explored. The dielectric functions obtained from
spectroscopic ellipsometry as described in this chapter have been fit using expressions incorporating both free and bound electron contributions, the latter described in terms of one or more oscillators. As a result, insights into the origins of the observed optical and electrical properties of the materials can be obtained.

Zinc oxide is the main focus of Chapter 4, considering its role along with underlying silver as a component of the back-reflector in Si:H n-i-p photovoltaics technology. In this role, intentional doping is not necessary as the native defects ensure sufficiently low n-type resistivity. Because doped zinc oxide is also used as a transparent conducting oxide top contact for in-plane conduction in both CdTe and CIGS solar cells, the most common doped form, aluminum doped zinc oxide, is discussed in Chapter 4 in addition to intrinsic zinc oxide. Chapter 4 focuses on the bulk optical properties of intrinsic and aluminum doped zinc oxide deposited under various conditions as well as on different substrates. The effects of annealing and measurement temperature on the optical properties of intrinsic as well as doped zinc oxide are also presented.

As the first component of Chapter 5, differences in the structural evolution of zinc oxide films deposited on top of silver films are described. Here again, the usefulness of RTSE and SE as optical probes in thin film photovoltaics research is demonstrated clearly. As the second component of Chapter 5, the interfaces formed between silver and zinc oxide layers are analyzed. This component exploits the unique capability of ellipsometry as a tool to characterize the optical properties of thin interface layers. In this chapter, the results of studies of interfaces formed under a variety of conditions are reported. By parameterizing the optical properties of the interface layer using an analytical function, various optical characteristics including free and bound electron
resonance amplitudes, energies, and broadening parameters have been determined. The results enable one to identify bands associated with localized plasmons and their characteristic energies. The possible role of such plasmons in the dissipation and scattering of incident radiant energy has also been studied using transmittance and reflectance (T & R) spectroscopy. Corresponding SE and T & R studies are also used to compare an industry standard textured back-reflector for thin film a-Si:H solar cells with those fabricated at University of Toledo. Finally, by using the ellipsometry derived dielectric functions of interface layers, an optical model has been developed to calculate how much current will be lost due to the non-idealities associated with real solar cell structures.

In Chapter 6, an investigation of the screening effect of zinc oxide on the plasmon bands is described. In this investigation, etching of the back-reflector is performed in order to completely remove the ZnO, exposing uncoated Ag. The differences in the dielectric functions of back-reflectors before and after etching are explored. This comparison shows how a low refractive index material can be used to blue-shift the plasmon resonances so that absorption losses can be reduced. The chapter concludes with a comparison of the normal incidence reflectance of back-reflectors before and after etching away the ZnO layer.

Chapter 7 presents a summary of the primary observations and conclusions drawn from this dissertation research. A general conclusion is that spectroscopic ellipsometry can be applied to achieve a greater understanding of complex thin film photovoltaics structures and to identify methods by which the quantum efficiency spectra of thin film solar cells can be improved. The dissertation will conclude with a description of the
future work that is needed to advance the performance of back-reflectors, and the optics of thin film PV in general, based on the insights from this research. Photovoltaics installations are very rapidly increasing in number and in total energy production. For this expansion in photovoltaics to reach terawatt targets, leading to reductions in carbon emissions that cause climate change, significant improvements in materials, device, and system performance as well as reductions in cost are needed. Continuing research along the lines described in this dissertation will make progress toward these targets.
Chapter 2

Theory and Instrumentation for Optical Measurements with Case Studies

2.1 Introduction to Optics and Ellipsometry

Ellipsometry is a nondestructive optical measurement technique that uses polarized light to probe matter. The instrument that performs ellipsometry, the ellipsometer, is applied to measure the relative amplitude ratio \( \tan \psi \) and the phase shift difference \( \Delta \) for two orthogonal electric field components of a polarized light wave when it reflects from a planar interface between two media. In this section, the basic optics necessary to understand the spectroscopic ellipsometry experiment will be reviewed.

Light is a self-sustaining transverse wave consisting of perpendicularly oriented electric field \( \mathbf{E} \) and magnetic induction \( \mathbf{B} \) vectors requiring no medium in order for the wave to propagate. A time-varying \( \mathbf{E} \)-field generates a \( \mathbf{B} \)-field perpendicular to \( \mathbf{E} \) and vice versa. When a light wave enters into and travels through a solid state medium, however, the atoms at its surface and within it refract the wave, reduce its phase velocity, and absorb energy from the wave. These effects can be quantified by the complex refractive index of the medium. When light travels through an isotropic, transparent, i.e. non-absorbing, medium as a plane wave, the electric field amplitude of the wave can be represented by the following equation (Azzam and Bashara, 1977):

\[ \]
$E = E_{to} \exp \left[ i \left( \frac{2\pi n}{\lambda} x + \delta \right) \right]. \quad (2.1)$

In this equation, $E_{to}$ is the maximum in the electric field amplitude within the transparent medium; $\omega$ is the angular frequency of the wave; $\lambda$ is the wavelength of the wave in vacuum, with $\lambda_t = \lambda/n$ being the wavelength in the transparent medium; $x$ is the propagation direction; and $\delta$ is the initial phase of the wave at $x = 0$. The optical properties of the medium are described by the real number $n$, which is the refractive index of the medium and describes the phase velocity of the wave $v = c/n$, with $c$ being the speed of light in vacuum. When light propagates through an isotropic absorbing medium, the equation for the optical electric field becomes:

$$E = E_{ao} \exp \left( -\frac{2\pi k}{\lambda} x \right) \exp \left[ i \left( \omega t - \frac{2\pi n}{\lambda} x + \delta \right) \right], \quad (2.2)$$

where $E_{ao}$ is the maximum in the electric field amplitude, considered versus time at $x=0$ within the absorbing medium, and $k$ is the extinction coefficient. The refractive index $n$ completely describes the propagation of electromagnetic waves in an isotropic transparent medium, but for any medium that absorbs energy from the waves, $n$ is insufficient to describe the process and one must introduce the extinction coefficient $k$. Together, the complex refractive index $N$ is defined as

$$N \equiv n - ik. \quad (2.3)$$

With this definition the electric field equation returns to the form of Eq. 2.1:

$$E = E_0 \exp \left[ i \left( \omega t - \frac{2\pi N}{\lambda} x + \delta \right) \right].$$

From the form of Eq. (2.2), it is clearly seen that within the absorbing medium, the amplitude of the electric field of the electromagnetic wave decreases exponentially along
the propagation direction $x$. In addition, the irradiance decreases according to $I = I_0 \exp(-\alpha x)$ where $\alpha$, the absorption coefficient, is $\alpha = 4\pi k/\lambda$.

The complex refractive index $N(\omega)$ is a frequency dependent measure of the dielectric polarization generated within a homogeneous isotropic medium by an optical electric field oscillating at frequency $\omega$, and is often defined instead with respect to the complex dielectric function $\varepsilon$ of the medium, according to:

$$N^2 \equiv \varepsilon \equiv \varepsilon_1 - i\varepsilon_2. \quad (2.4)$$

The dielectric function relates the displacement field $D$ and electric field according to $D = \varepsilon_0 \varepsilon E$, where $\varepsilon_0$ is the electric permittivity of vacuum. As a result of Equation (2.4), the real and imaginary parts of the complex dielectric function, $\varepsilon_1$ and $\varepsilon_2$, respectively are given by

$$\varepsilon_1 = n^2 - k^2; \quad (2.5a)$$

$$\varepsilon_2 = 2nk. \quad (2.5b)$$

Inverting these equations, the real and imaginary parts of the complex refractive index become:

$$n = \sqrt{\frac{\varepsilon_1^2 + \varepsilon_2^2 + \varepsilon_1}{2}}; \quad (2.6a)$$

$$k = \sqrt{\frac{\varepsilon_1^2 + \varepsilon_2^2 - \varepsilon_1}{2}}. \quad (2.6b)$$

For a transparent medium, $k = 0$ which implies that $\varepsilon_2 = 0$ and $\varepsilon_1 = n^2$.

For an anisotropic transparent medium, $n = \varepsilon_1^{1/2}$ depends on the direction of propagation in the medium and the wave polarization, often characterized in the form of the index ellipsoid of $n$ versus the direction of $\mathbf{k}$. Thus, for an anisotropic medium, the
processes of both dispersion and absorption depend on the direction of the wave. In this case, the complex dielectric function of the medium is expressed as a complex second-rank tensor. The tensor representation as a 3 x 3 matrix is diagonal in a principal axes coordinate system that aligns with the unit cell axes of the crystal structure when considering single crystal media with orthorhombic symmetries and higher (Fujiwara, 2007).

The complex refractive index of an isotropic medium at a given, selectable optical range frequency can be determined from the reflectance/transmittance method using a sample consisting of two plane parallel specularly reflecting/transmitting surfaces. Using this method, data analysis can be a challenge due to the superposition of the multiple reflections between the sample surfaces. In addition, in order for this method to be successful, the sample must not be opaque at any frequencies within the range of interest; otherwise the transmittance capability is lost.

In contrast, the ellipsometry method is unique to the extent that it allows direct measurements of the complex refractive index from a single reflected beam using a simple analytical expression. When an obliquely-incident, quasi-monochromatic, polarized plane wave of light is reflected from the top surface of the isotropic sample and no light returns from the back surface of sample, then the ellipsometry methodology provides the change in the polarization state that occurs upon reflection. The reflected light wave (and transmitted wave, as well) are resolved into p and s linearly polarized waves according to the direction of oscillation of their electric fields. The component with its direction of oscillation parallel to the plane of incidence is p-polarization and that with its direction perpendicular to the plane of incidence is s-polarization. The details of
the reflected and transmitted field components for the single interface are shown in
Figure 2.1. In this figure, it is assumed that the reflecting interface occurs between

Figure 2-1: Electric field $E$ and magnetic induction $B$ for linear states of (a) p-
polarization and (b) s-polarization. In these figures, $B$ in (a) and $E$ in (b) are
perpendicular to the plane of the page. Here the subscripts $i$, $r$, and $t$ identify incident,
reflected, and transmitted waves (Fujiwara, 2007). The co-planar propagation vectors for
the incident, reflected, and transmitted plane waves $k_i$, $k_r$, and $k_t$ are shown, establishing
the z-axes of right-handed coordinate systems with the corresponding $E$ (as $x$) and $B$ (as
$y$).

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an isotropic non-absorbing ambient medium of real index of refraction $n_i$ and an isotropic absorbing medium of complex index of refraction $N_t = n_t - i k_t$. In general, the same formalism can be applied to interfaces between two absorbing media, and this more general assumption applies to the equations to be provided in the next paragraph.

Applying the boundary conditions requiring that the components of $E$ and $B$ parallel to the interface are continuous across it, then one can describe the effect of the sample on the incident linearly polarized waves in terms of complex amplitude reflection coefficients. Assuming the most general interface between homogeneous, isotropic absorbing media having complex indices of refraction $N_i = n_i - i k_i$ and $N_t = n_t - i k_t$, these reflection coefficients for p- and s-polarized light waves are given, respectively, by

$$r_p \equiv \frac{E_{rp}}{E_{ip}} = \frac{N_i \cos \theta_i - N_i \cos \theta_t}{N_i \cos \theta_i + N_i \cos \theta_t} = |r_p| \exp(i\delta_p), \quad (2.7a)$$

$$r_s \equiv \frac{E_{rs}}{E_{is}} = \frac{N_i \cos \theta_i - N_i \cos \theta_t}{N_i \cos \theta_i + N_i \cos \theta_t} = |r_s| \exp(i\delta_s), \quad (2.7b)$$

where the subscripts $r$, $i$, and $t$ refer to reflected, incident, and transmitted characteristics, e.g., notation appropriate for electric fields, media, or angles. Thus, the resulting relative E-field amplitudes (reflected relative to incident) are $|r_p|$ and $|r_s|$, and the phase shifts of the E-field components upon reflection are $\delta_p$ and $\delta_s$. The right-most expressions in the above equations describe the amplitude coefficients in a polar coordinate representation. In a similar manner, one can express the amplitude transmission coefficients for p- and s-polarized light waves as follows:

$$t_p \equiv \frac{E_{tp}}{E_{ip}} = \frac{2N_i \cos \theta_i}{N_i \cos \theta_i + N_i \cos \theta_t} = |t_p| \exp(i\delta_p); \quad (2.8a)$$
The set of Equations (2.7) and (2.8) for $r_p$, $r_s$, $t_p$, and $t_s$ are called the Fresnel equations. Further information to assist in calculating the amplitude coefficients derives from Snell's Law:

$$N_i \sin \theta_i = N_t \sin \theta_t$$  \hspace{1cm} (2.8c)

in which case the angles of incidence and transmittance are in general complex. The Fresnel equations and Snell's Law form the simple foundational optics for all ellipsometry studies of homogeneous, isotropic media with plane-parallel, specular surfaces/interfaces.

The Fresnel equations can be understood qualitatively as follows. When a plane light wave is incident from vacuum onto the surface of a medium, its electric field will polarize the charges of the transmitted medium. This polarization generates dipoles which oscillate with the field. Every oscillating dipole emits radiation, and for an incident plane wave, the resulting dipole radiation interferes to generate reflected and transmitted plane waves as long as the interface is atomically flat and smooth. Because of the difference in electric dipole radiation for incident p- and s-polarized light, the amplitude reflection coefficients $r_p$ and $r_s$ differ; $t_p$ and $t_s$ also differ. This difference in $r_p$ and $r_s$ can be seen in both the amplitude and phase of the coefficients for p- and s-polarized light. The ellipsometry method is used to obtain measures of the p-to-s ratio of the relative field amplitudes (reflected as a ratio to incident) and the p-to-s difference in the field phase shifts (reflected shifted relative to incident) ($\psi$, $\Delta$), which are defined by

$$\rho \equiv \tan \psi \exp(i \Delta) = \frac{r_p}{r_s}.$$  \hspace{1cm} (2.9)
Thus, \( \tan \psi \) can be referred to as a relative amplitude ratio and \( \Delta \) can be referred to as a phase shift difference. If the amplitude reflection coefficients are expressed in polar coordinates, then it follows that

\[
\tan \psi = \frac{|r_p|}{|r_s|} \quad \text{and} \quad \Delta = \delta_{rp} - \delta_{rs} .
\] (2.10)

Next, Fig. 2.1 is considered to represent a model for the ideal measurement situation of a reflecting interface that is abrupt and precisely planar on the atomic scale. If the model includes an isotropic, non-absorbing ambient medium of real index of refraction \( n_i \) and an isotropic, absorbing reflecting medium of complex index of refraction \( N_t = n_t - i k_t \), then the measured ellipsometric angles \( (\psi, \Delta) \) can be expressed in terms of \( n_i \) and \( N_t \) and the angles of incidence and refraction \( \theta_i \) and \( \theta_t \) (Azzam and Bashara, 1977). Using Equations 2.7 and 2.9, the ratio of complex amplitude reflection coefficients \( \rho \) which defines \( (\psi, \Delta) \) becomes:

\[
\rho = \frac{r_p}{r_s} = \frac{\left( \frac{N_t \cos \theta_t - n_i \cos \theta_i}{N_t \cos \theta_i + n_i \cos \theta_t} \right)}{\left( \frac{n_t \cos \theta_t - N_t \cos \theta_i}{n_t \cos \theta_i + N_t \cos \theta_t} \right)} .
\] (2.11)

In this equation, \( \cos \theta_t \) can be eliminated by expressing it in terms of optical properties of the two media and the angle of incidence through the complex form of Snell's Law [Equation (2.8c)] and a simple trigonometric relation:

\[
\cos \theta_t = \pm \sqrt{\frac{N_t^2 - n_i^2 \sin^2 \theta_i}{N_t}} .
\] (2.12)

The result is given by:
\[ \rho = \frac{n_i \sin^2 \theta_i \mp \cos \theta_i \sqrt{N_i^2 - n_i^2 \sin^2 \theta_i}}{n_i \sin^2 \theta_i \pm \cos \theta_i \sqrt{N_i^2 - n_i^2 \sin^2 \theta_i}}. \]  

(2.13)

The above equation can be solved for the square of the complex refractive index of reflecting medium, yielding the following:

\[ N_i^2 = n_i^2 \sin^2 \theta_i \left[ 1 + \tan^2 \theta_i \left( \frac{1-\rho}{1+\rho} \right)^2 \right]. \]  

(2.14a)

Finally, the dielectric function can be written as:

\[ \varepsilon_i = \varepsilon_i \sin^2 \theta_i \left[ 1 + \tan^2 \theta_i \left( \frac{1-\rho}{1+\rho} \right)^2 \right], \]  

(2.14b)

by applying its definition from Eq. (2.4). The key final result demonstrates that the complex dielectric function of the reflecting medium, \( \varepsilon_t \), can be found from a relatively simple equation if one knows (i) the dielectric function of the ambient \( \varepsilon_i \), (ii) the angle of incidence \( \theta_i \), and (iii) the measured ellipsometric angles \( (\psi, \Delta) \). It should be kept in mind, however, that the experimental situation for this measurement must approach as closely as possible the optical model of a perfect interface as in Fig. 2.1. If such an interface is present between vacuum and a transparent isotropic medium, then the phase shift difference \( \Delta \) is either 0° or 180°, depending on whether the angle of incidence is above or below the Brewster angle of the reflecting medium, respectively. In this case, the refractive index \( n_t \) of the reflecting medium can be expressed as a function of the relative amplitude ratio parameter \( \psi \) through Eq. (2.14a).

The complex amplitude reflection ratio \( \rho \), can also be described theoretically for a model optical system consisting of a single layer or multiple layers with perfect interfaces according to \( \rho = r_{p,m+1}/r_{s,m+1} \), where \( m \) is the number of layers. For example, considering
a single-layer sample consisting of two ideal atomically-smooth, planar interfaces and three different media (ambient/film/substrate), the reflection coefficients denoted \( r_{p2} \) and \( r_{s2} \), where ‘2’ designates the number of interfaces, are given by

\[
\begin{align*}
    r_{p2} &= \frac{r_{p,af} + r_{p,fs}Z_f}{1 + r_{p,af}r_{p,fs}Z_f}, \\
    r_{s2} &= \frac{r_{s,af} + r_{s,fs}Z_f}{1 + r_{s,af}r_{s,fs}Z_f},
\end{align*}
\]  

(2.15a)

(2.15b)

where

\[
Z_f = \exp\left\{ \frac{4\pi id_f}{\lambda} \left( \varepsilon_f - \varepsilon_a \sin^2 \theta \right)^{1/2} \right\}.
\]  

(2.15c)

In Eqs. (2.15a) and (2.15b), \{\( r_{p,af}, r_{s,af} \)\} and \{\( r_{p,fs}, r_{s,fs} \)\} are the p and s complex amplitude reflection coefficients as in Eqs. (2.7) for the individual ambient/film (af) and film/substrate (fs) interfaces, respectively. In the pairs of expressions analogous to Eqs. (2.7), the angle of transmission for the af interface \( \theta_{t,af} \) is equal to the angle of incidence for the fs interface \( \theta_{i,fs} \). Thus, successive applications of Snell’s Law can be used to determine the beam angles throughout the sample structure as long as one knows \( \theta_{i,af} = \theta_i \), the angle of incidence at the first ambient/film interface, the index of refraction of the ambient medium \( n_a \), and the complex indices of refraction of the film and substrate, \( N_f \) and \( N_s \), respectively. Thus, \( n_a \sin \theta_{i,af} = N_f \sin \theta_{t,af} = N_f \sin \theta_{i,fs} = N_s \sin \theta_{t,fs} \), where \( \theta_{t,fs} = \theta_t \) is the angle of transmission at the film/substrate interface, and \( N_f = n_f - ik_f \) and \( N_s = n_s - ik_s \) with \( (n_f, k_f) \) and \( (n_s, k_s) \) as the real indices of refraction and extinction coefficients of the film (f) and substrate (s) media. In addition in Eq. (2.15c), \( \varepsilon_f = \varepsilon_{1f} - i\varepsilon_{2f} \), \( d_f \), and \( \lambda \) are the complex dielectric function of the film, the thickness of the film, and the wavelength of the incident light in vacuum, respectively. Finally, the analogues
of Eqs. (2.15) for an $m$-layer structure with $m > 1$, yielding $r_{p,m+1}$ and $r_{s,m+1}$, can be derived using matrix methods to perform the required manipulations.

Because there are no closed-form expressions for Eq. (2.15) analogous to that of Eq (2.14b) for either $\varepsilon_f$ or $d_f$ in the two interface problem, determination of these sample properties from $(\psi, \Delta)$ requires numerical inversion of Eqs. (2.15). For example, if $d_f$ is known, or a trial value is assumed for $d_f$, then $(\psi, \Delta)$ can be subjected to numerical inversion to determine $\varepsilon_{f1}$ and $\varepsilon_{f2}$. The fundamental data analysis problem in ellipsometry, characterization of a single thin film applying Eqs. (2.15), however, involves determining all three parameters $\varepsilon_{1f}$, $\varepsilon_{2f}$, and $d_f$ from the measured $(\psi, \Delta)$ values using the presumed known values of $\varepsilon_a$, $\varepsilon_s$, $\theta_i$, and $\lambda$. Because three sample parameters cannot be deduced from only two measured parameters, multiple measurements of $(\psi, \Delta)$ are needed – at different wavelengths, for example. Acquiring a pair of $(\psi, \Delta)$ measurements at each additional $\lambda$ value, however, introduces two additional unknown parameters $\varepsilon_{1f}$, $\varepsilon_{2f}$ at that $\lambda$. Thus, the number of unknowns will always be one larger than the number of measurements. There are several ways to address this data analysis problem. In one approach, the $\varepsilon_{1f}$ and $\varepsilon_{2f}$ spectra are described as analytical functions of $\lambda$ with a much smaller number of wavelength-independent parameters than the number of $\varepsilon_{1f}$ and $\varepsilon_{2f}$ values themselves. Then the analysis problem reverts to least square regression. Examples of this approach will appear throughout the thesis. Additional approaches and issues in data analysis will be presented in Sec. 2.3.3.

For a thin film at a reflecting interface between ambient and substrate media, measurements of the angle $\Delta$ provide extreme sensitivity to changes film thickness, on the order of 0.1 Å for the highest precision ellipsometers. Figure 2.2 shows how the
experimentally determined phase shift difference $\Delta$ changes when a 7 Å thickness of silver (Ag) is deposited at the interface between the ambient and a crystalline silicon (c-Si) wafer substrate which is in turn covered with its native oxide. Thus, this example presents an experimental study of a three-interface, four-medium sample: vacuum/Ag (7 Å)/SiO$_2$ (19 Å)/Si. Maximum changes in $\Delta$ of $\sim 6^\circ$ over a relatively large range of photon energy are observed with the addition of the monolayer scale Ag film, an effect that is easily characterized with the multichannel ellipsometers used in this research.

Figure 2-2: Very high sensitivity of the ellipsometry phase shift difference $\Delta$ to thin layers at surfaces and interfaces is demonstrated here. In situ measurements were performed before (solid line) and after (dotted line) the deposition of an estimated 7 Å layer of silver on the top of a crystalline silicon substrate which was in turn covered with a 19 Å layer of native oxide. The acquisition time was 1 s for each pair of ($\psi$, $\Delta$) spectra, corresponding to an average over 62 optical cycles of the rotating-compensator multichannel ellipsometer.
2.2 Effective Medium Theories

Solar cells and a plethora of semiconductor devices use multilayer solid state structures. Between any two layers of materials, generally an interface region is formed whose properties are extremely important in determining device function. In fact, Nobel Prize winner Herbert Kroemer emphasized in his Nobel lecture: "Often, it may be said that the interface is the device" (Mannhart et al., 2010). Furthermore, even a single layer of thin film material deposited on an atomically-smooth dissimilar substrate is likely to exhibit some roughness at its surface, i.e. at the interface to the ambient air. Such roughness ensures that deviations occur from the assumptions implicit in the derivation of the Fresnel equations. Surface roughness as well as interface roughness can be described optically within the framework of the Fresnel equations as a layer with mathematically abrupt interfaces consisting of a physical mixture or composite of underlying and overlying materials. In the case of surface roughness, the roughness can be considered as a single topmost layer, consisting of a composite of void and the underlying layer material itself. Spectroscopic ellipsometry is very sensitive to roughness related structures, and great success has been made possible by treating the roughness as a layer distinct from the so-called "bulk" layer having a dielectric function determined from an effective medium theory (EMT).

The general expression of the EMT for an isotropic composite of two isotropic component materials can be written as (Fujiwara, 2007; Aspnes et al., 1979):

\[
\frac{\varepsilon - \varepsilon_h}{\varepsilon + 2\varepsilon_h} = f_a \frac{\varepsilon_a - \varepsilon_h}{\varepsilon_a + 2\varepsilon_h} + f_b \frac{\varepsilon_b - \varepsilon_h}{\varepsilon_b + 2\varepsilon_h},
\] (2.16)

where \(\varepsilon\) is the effective dielectric function of the composite material, \(\varepsilon_h\) is the host dielectric function, \(\varepsilon_a\) and \(\varepsilon_b\) are the dielectric functions of the two constituent materials,
and \( f_a \) and \( f_b \) are the volume fractions of the constituent materials such that \( f_a + f_b = 1 \). With such an expression, the inclusions of the constituent materials in the host are assumed to be spherical. Several special cases arise associated with specific assumptions, and these are summarized below.

(a) The Lorentz-Lorentz (LL) model is based on the assumption that \( \varepsilon_h = 1 \), i.e., the host is free space. Thus, for this approximation, the ambient surrounding the two constituent materials is vacuum, or the ambient medium. Equation (2.16) then becomes:

\[
\frac{\varepsilon - 1}{\varepsilon + 2} = f_a \frac{\varepsilon_a - 1}{\varepsilon_a + 2} + f_b \frac{\varepsilon_b - 1}{\varepsilon_b + 2}.
\] (2.17)

(b) In the Maxwell Garnett (MG) model, the dielectric function of composite materials is described by setting \( \varepsilon_h = \varepsilon_a \) if material "a" is dominant (i.e. \( f_a > f_b \)). The new EMT equation then becomes:

\[
\frac{\varepsilon - \varepsilon_a}{\varepsilon + 2\varepsilon_a} = f_b \frac{\varepsilon_b - \varepsilon_a}{\varepsilon_b + 2\varepsilon_a}.
\] (2.18)

Here the constituent material "b" is completely surrounded by material "a". For this EMT, if \( \varepsilon_a \) is exchanged with \( \varepsilon_b \), the effective dielectric function \( \varepsilon \) will be different.

(c) The Bruggeman model is the most widely used EMT in spectroscopic ellipsometry studies, and is often simply called the effective medium approximation (EMA). The EMA is based on the assumption that \( \varepsilon_h = \varepsilon \), i.e., that the host medium dielectric function becomes the effective dielectric function:

\[
0 = f_a \frac{\varepsilon_a - \varepsilon}{\varepsilon_a + 2\varepsilon} + f_b \frac{\varepsilon_b - \varepsilon}{\varepsilon_b + 2\varepsilon}.
\] (2.19)

These effective medium theories have a limited range of validity. First, the scale of the structure, i.e., the length scale over which the composite varies from one component to
another (h, a, b), must be much smaller than the wavelength of the light in the effective medium ($\lambda_m = \lambda / n_{\text{eff}}$, where $n_{\text{eff}}$ is the effective medium index of refraction). If this scale is exceeded by the structure, then light scattering is one of the phenomena that will be encountered that invalidates the analysis approach. Second, the scale of the inclusions in the host, and the size scale of the host, should not be so small that their electronic structure and optical properties are modified by size. This latter requirement can be overcome by incorporating size modified dielectric functions in the effective medium theories.

The EMT approach can also be applied to characterize the plasmon band arising from roughness layers at metallic surfaces and interfaces. One can substitute the Drude expression into the Maxwell-Garnett (MG) EMT to determine the optical nature of the resulting composite. For this case, the MG EMT of Eq. (2.18) can be rewritten by replacing the constituent material 'b' with a metallic component 'm', yielding:

$$\frac{\varepsilon - \varepsilon_a}{\varepsilon + 2\varepsilon_a} = Q_m \frac{\varepsilon_m - \varepsilon_a}{\varepsilon_m + 2\varepsilon_a},$$

where $Q_m$ is the volume fraction of the metal component. Solving this equation for $\varepsilon$ in turn yields:

$$\varepsilon = \varepsilon_a \left[ \frac{2\varepsilon_a (1 - Q_m) + \varepsilon_m (1 + 2Q_m)}{\varepsilon_a (2 + Q_m) + \varepsilon_m (1 - Q_m)} \right]. \quad (2.20)$$

The following Drude expression for the dielectric function of the metal can be substituted for $\varepsilon_m$ in Eq. (2.20):

$$\varepsilon_m = \varepsilon_{\text{vo}} - \frac{E_p^2}{E(E + i\Gamma)}, \quad (2.21)$$
where $\varepsilon_{1o}$ is the energy-independent contribution to the real part of the dielectric function, $E_p$ is the plasma energy associated with the free electrons in the bulk metal, $\Gamma$ is the broadening parameter, and $E$ is the photon energy. The resulting equation is

$$
\varepsilon = \varepsilon_a + B^2 \left( 1 - \frac{(\varepsilon_{1o} - \varepsilon_a)}{E_p} \frac{E(E + i\Gamma)}{E_p^2} \right),
$$

(2.22)

where the following substitutions have been made:

$$
B^2 = \frac{3\varepsilon_a Q_m E_p^2}{1 - Q_m^2},
$$

(2.23)

and

$$
E_0 = \sqrt[2]{\frac{E_p}{\varepsilon_{1o} + \varepsilon_a \left( \frac{2 + Q_m}{1 - Q_m} \right)}}.
$$

(2.24)

It is informative to note that a standard form of the Lorentz oscillator expression is

$$
\varepsilon_{LO} = \varepsilon_{0LO} + \frac{B^2}{(E_0^2 - E^2) - i\Gamma E},
$$

(2.25)

where $\varepsilon_{0LO}$ is the energy-independent contribution to the real part of the dielectric function, $B^2$ describes the amplitude, $E_0$ is the resonance energy, and $\Gamma$ is the broadening parameter. Similarities can be observed in a comparison of Eq. (2.22) with the Lorentz oscillator expression of Eq. (2.25). In fact, if the following assumptions are made:

$$
(\varepsilon_{1o} - \varepsilon_a) \frac{E_p^2}{E_p} << 1 \quad \text{and} \quad (\varepsilon_{1o} - \varepsilon_a) \frac{E \Gamma}{E_p^2} << 1.
$$

(2.26)

and if $\varepsilon_a$ does not depend on wavelength, which is strictly only the case for an ambient medium of vacuum or air, then the Lorentz oscillator equation results directly from the
MG EMA. Under these circumstances, one can observe that the amplitude $B$, and the resonance energy $E_0$ of the Lorentz oscillator can be used to estimate the metal volume fraction in the interface layer via Eq. (2.23). Then Eq. (2.24) can be used as a check for consistency of the theory by comparing the predicted and observed resonance energies. If the above inequalities do not apply, or if $\varepsilon_a$ shows dispersive behavior, then a feature near $E_0$ of Eq. (2.24) may be still observable but the lineshape will be no longer Lorentzian.

Simulations applying the Maxwell-Garnett and the Bruggeman effective medium theories were performed in order to acquire physical insights into the plasmon features, including the low energy resonances, which have been found to occur in the imaginary parts of the dielectric function spectra $\varepsilon_2$ in the various studies of this dissertation research. The dielectric functions required for these simulations were obtained both from Chapter 3 for Ag, specifically sample DS005, below the interband transitions thus including only the Drude term, and from Chapter 4 for ZnO, specifically sample PVIC (University of Toledo), below its band gap. First the Maxwell-Garnett simulations were performed using void with $\varepsilon = 1$ as the host and Ag as the guest metal with different metal volume fractions $Q_m$. Then simulations were then repeated by replacing void with ZnO as the host. The dielectric functions generated in this manner are shown in Fig. 2.3.
Figure 2-3: Shown in the left panels are the real and imaginary parts of the dielectric functions simulated by using the Maxwell-Garnett effective medium theory with void as the host and Ag as the guest metal constituent. The right panel shows the dielectric functions generated by using the Maxwell-Garnett effective medium theory with ZnO as the host and Ag as the guest metal constituent. These simulations have been performed with various metal volume fractions $Q_m \leq 0.5$. The simulation for a Ag volume fraction of $Q_m = 0.01$ has been multiplied by five so that it becomes visible in the data set.

The calculations were repeated in separate simulations using void or vacuum and ZnO as the dominant media with volume fractions greater than 0.5, but instead applying the Bruggeman EMA rather than the Maxwell-Garnett theory. It should be recalled that in the Bruggeman EMA the host is assigned as the effective dielectric function irrespective of the constituent volume fractions. The resulting simulated dielectric functions results using the Bruggeman EMA are shown in Fig. 2.4.
Figure 2-4: Shown in the left panels are the real and imaginary parts of the dielectric functions simulated by using the Bruggeman EMA with void or vacuum as the dominant medium (having volume fractions greater than or equal to 0.5) and Ag as a metal constituent. The right panel shows the dielectric functions generated by using the Bruggeman EMA with ZnO as the dominant medium. Various metal volume fractions with $Q_m \leq 0.5$ are used in the simulations.

The simulations of Figs. 2.3 and 2.4 were repeated using volume fractions of Ag given by $Q_m \geq 0.5$. For the Maxwell-Garnett effective medium theory in this range of $Q_m$, it is now reasonable to assign Ag as the host and void or vacuum and ZnO as the guest constituents. These simulations are shown in Fig. 2.5. Finally, the Bruggeman EMA simulation with Ag volume fractions given by $Q_m \geq 0.5$ are shown in Fig. 2.6.
Figure 2-5: Shown in the left panels are the real and imaginary parts of the dielectric functions simulated by using the Maxwell-Garnett effective medium theory with Ag as the host and void or vacuum as the guest constituent medium. The right panel shows the dielectric functions generated by using Maxwell-Garnett effective medium theory with Ag as the host and ZnO as the guest constituent medium. Various metal volume fractions with $Q_m \geq 0.5$ are used in the simulations.

Figure 2-6: Shown in the left panel are the real and imaginary parts of the dielectric functions generated by using the Bruggeman EMA simulation with Ag as the dominant medium and void as a second constituent medium. The right panel shows the dielectric functions generated by using the Bruggeman EMA with Ag as the dominant medium and ZnO as the second constituent medium. Various metal volume fractions with $Q_m \geq 0.5$ are used in the simulations.
From the results of Fig. 2.3 for the Maxwell-Garnett simulation, the photon energy at which the maximum in the imaginary part of the dielectric function $\varepsilon_2$ occurs is plotted versus the metal volume fraction in Fig. 2.7. For both cases of air or vacuum and ZnO serving as hosts, the energy at which the maximum in $\varepsilon_2$ occurs decreases with increasing metal volume fraction. One also observes that the maxima in $\varepsilon_2$ are much higher in photon energy for the same metal volume fractions when vacuum or air is the host relative to when ZnO is the host. The plasmon Equation 2.24 is also used to generate the resonance $E_0$ as a function of the Ag metal volume fraction. The resulting values match very well the energies of maximum $\varepsilon_2$ for the Maxwell-Garnett simulation with the air or vacuum as the host. For the Maxwell-Garnett simulation with ZnO as the host, however, Eq. (2.24) generates a resonance that is slightly different in energy with a discrepancy that increases with increasing metal volume fraction. This is likely due to the dispersion in the ZnO dielectric function, which is neglected in Eq. (2.24).
Figure 2-7: The photon energy at which the maximum in the imaginary part of the dielectric function $\varepsilon_2$ occurs is plotted versus metal volume fraction using the results of Fig. 2.3 for the Maxwell-Garnett simulation. The points locate the energies of these maxima in $\varepsilon_2$ versus Ag metal volume fractions for both air or vacuum (squares) and ZnO (circles) as the host media. The corresponding solid lines are results that identify the location of the resonance $E_0$ using Equation 2.24.

Similarly, from the results of Figs. 2.4 and 2.6 for the Bruggeman EMA simulation, the photon energy at which the maximum in imaginary part of the dielectric function, $\varepsilon_2$, occurs versus metal volume fraction is plotted in Fig. 2.8. In this case, the photon energy of the maximum decreases monotonically toward zero until the metal volume fraction reaches $\sim 0.30$-$0.35$. Then it increases monotonically again for higher metal volume fractions.
Figure 2-8: The photon energy at which the maximum in the imaginary part of the dielectric function $\varepsilon_2$ occurs is plotted versus metal volume fraction using the results of Figs. 2.4 and 2.6 for the Bruggeman EMA simulation. The points locate the energies of these maxima in $\varepsilon_2$ versus Ag metal volume fractions for both air or vacuum (squares) and ZnO (circles) as the host media.

2.3 Spectroscopic Ellipsometry (SE)

In this section, the arrangement of the instrument for spectroscopic ellipsometry will be discussed with a brief history of its development. The procedure for data analysis in SE will be further discussed, demonstrating an application in which the dielectric function of the back contact metal in the CIGS solar cell is determined.

2.3.1 History

The first ellipsometric studies were performed by Paul Drude in 1887 at the University of Leipzig in Germany. As is known, Drude established the model that bears his name and describes the frequency dependence of the optical properties of metals. The
term "ellipsometry" was coined in 1945 by Alexandre Rothen who was performing research on biological thin films in the Laboratories of The Rockefeller Institute for Medical Research located in New York (Rothen, 1945). Ellipsometers were operated manually until D. E. Aspnes and A.A. Studna of Bell Laboratories realized the fully automated spectroscopic ellipsometer in 1975 by exploiting a laboratory minicomputer for data collection, calibration, data reduction, and analysis (Aspnes and Studna, 1975).

The first real-time monitoring experiments using a spectroscopic ellipsometer were reported in 1984 by R. H. Muller and J. C. Farmer of Lawrence Berkeley Laboratories (Muller and Farmer, 1984). They used the self-nulling principle in an instrument having the polarizer-compensator-sample-analyzer configuration, and scanned the wavelength serially from the visible to ultraviolet (370 - 720 nm) at a maximum scan rate of 114 nm/s for a total spectral acquisition time of ~ 3 s. Improvements in the speed of the real-time spectroscopic ellipsometry measurement came in 1990 from R. W. Collins and his group at The Pennsylvania State University by introducing a multichannel detection system in which a photodiode array (PDA) detector measures light irradiances at multiple wavelengths simultaneously (Kim et al., 1990). This effort, for the first time, led to high speed real time spectroscopic ellipsometry (RTSE) with the capability of monitoring thin film growth on the atomic scale with a minimum spectral acquisition time of 15 ms. With such instrumentation, Kim et al. reported the measurement of the optical properties and growth of a monolayer gold oxide film formed on polycrystalline gold surfaces in an electrochemical environment.
2.3.2 Construction of the Spectroscopic Ellipsometer

The ellipsometer consists of two arms, one containing the light source and the other containing the detector, whose individual optical axes lie in a single plane. The point on the sample surface to be measured lies at the intersection of the individual co-planar optical axes, and the sample normal lies in the same plane as the two axes. Because the instrument is designed to operate in specular reflection, the normal to the surface is set to bisect the angle between the two optical axes. A photograph of the spectroscopic ellipsometer in the configuration used for this research in the ex-situ mode of operation is shown in Fig 2.9 (top). A schematic of the same ellipsometer and sputter chamber used for RTSE studies is also shown in Fig 2.9 (bottom). The spectroscopic ellipsometer, model M2000-DI, was manufactured by J. A. Woollam Company. This model is a rotating-compensator multichannel ellipsometer with a photon energy range from 0.74 to 6.5 eV including 706 spectral points.

In Fig 2.9 (bottom), the lower right corner shows the light source arm of the ellipsometer, which also serves as the polarization generation and modulation arm. This arm incorporates a dual light source (deuterium and quartz tungsten halogen lamps) and a collimator (not shown) for the generation of an unpolarized plane wave having a wide photon energy range. Also included are a fixed polarizer and a rotating compensator. As the light passes through the polarizer, it is converted to linearly polarized light with high degree of polarization (extinction ratio: \( \sim 1 \times 10^{-5} \)). The compensator then generates a phase difference between two orthogonal electric field components, parallel and perpendicular to the fast axis of the compensator. A compensator is a retarding device made from one or more optical elements of birefringent material. When light passes
through the compensator, the two orthogonal electric field components experience different indices of refraction and thus different phase velocities. Thus a phase shift is introduced between the two components; however, their amplitudes are not affected in an ideal compensator. The polarization detection components of the spectroscopic ellipsometer are shown in the lower

Figure 2-9: (Top) The M2000-DI spectroscopic ellipsometer used in this study is shown as mounted on a base for ex-situ analysis. (Bottom) For real time analysis, the same ellipsometer is shown schematically mounted to a sputtering chamber. In the lower right corner, the polarization generation and modulation components consist of a dual light source and its collimator (not shown), a fixed polarizer, and a rotating compensator. In the lower left corner, the polarization detection components consist of a fixed analyzer and a spectrograph with dual gratings and irradiance detectors. A computer calculates and stores spectra in \((\psi, \Delta)\) by analysis of the detector output (Li, 2010).
left corner of the bottom schematic of Fig. 2.9. These components consist of a fixed analyzer, which is simply another linear polarizer, a wide spectral range (0.74 to 6.5 eV) spectrograph that uses two gratings to disperse the light over the length of two irradiance detector arrays, one consisting of InGaAs photodiodes and the other a silicon charge coupled device (CCD).

The compensator used in this ellipsometer system rotates continuously at an angular frequency of ~ 190 rad/s, corresponding to a mechanical rotation frequency of 30 Hz and a mechanical period of 33 ms. Since a rotation of 180° in a compensator generates a single optical cycle, spectra in the ellipsometric angles ($\psi$, $\Delta$) over the entire range available (0.74 - 6.5 eV) can be collected within ~ 16 ms. A minimum of two optical cycles are necessary to acquire full spectra in ($\psi$, $\Delta$) at high accuracy, due to the mechanical inequivalence of two successive optical cycles that can differ due to slight optical misalignments. In the RTSE applications used for this thesis research, which involve monitoring the depositions of Ag, ZnO, and ZnO:Al thin films, acquisition times from 1 to 3 seconds were used so that a higher precision in the measured ($\psi$, $\Delta$) could be achieved. Moreover, in the ex-situ SE applications, even greater precision was ensured by increasing the acquisition time to a value within the range from 10 to 15 seconds.

For the source beam to pass from the source through to the detector, stress free fused silica windows are used on the walls of chamber as shown in Fig. 2.9. These fused silica windows are designed to minimize the polarization modification due to stress built into the silica as a result of its manufacture and mounting. Furthermore, the calibration process performed before the measurement is also capable of correcting the data for weak polarization modification effects. In addition to the acquisition time in RTSE, the angle
of incidence is another measurement parameter which must be set and recorded. For the RTSE measurements performed in this research, the angle of incidence was generally set near 70°. For ex situ measurements on a static sample, this parameter is varied from 45° to 75° in 5° or 10° increments in a methodology described as variable-angle SE (VASE).

2.3.3 Data Analysis

Ellipsometry is an indirect optical characterization technique. In fact, such techniques nearly always involve indirect measurements since a light beam simply cannot be used to measure film thickness or dielectric functions directly without the steps of iterative model development and evaluation (Tompkins & McGahan, 1999). Already this has been pointed out in Sec. 2.1 in reference to the two-interface, single-layer analysis problem. As a result, the data collected on the sample must be analyzed, sometimes quite intensively, to extract parameters of interest. As described earlier, the measured quantities in ellipsometry are the two angles (ψ, Δ), and data analysis must be applied with a proper model for the sample to extract its layer thicknesses and optical properties (ε₁, ε₂).

There are two broad approaches for optical data analysis. The first approach involves an exact calculation of the parameters of interest in the model for the sample from the measured (ψ, Δ) data. A well-known procedure used in this exact approach is the direct numerical inversion of ellipsometric (ψ, Δ) spectra to obtain a single unknown complex dielectric function of an unknown material component of the sample. The process is referred to as numerical inversion because the (ψ, Δ) spectra are mathematically transformed to (ε₁, ε₂) spectra by determining the matrix elements in multilayer analysis and applying an iterative procedure for solving non-linear equations such as Newton's method. The second approach is based on least squares regression
analysis fitting whereby a number of photon energy independent parameters of interest in the model (less than the number of measured \( \psi \) and \( \Delta \) values) are varied systematically so as to match the calculated \((\psi, \Delta)\) spectra for the model to the measured \((\psi, \Delta)\) spectra as closely as possible. A simplified flow-chart of the regression analysis procedure that can be used for spectroscopic ellipsometry (SE) is illustrated in Fig 2.10.

Figure 2-10: A simplified flow-chart of the least-squares regression procedure used in spectroscopic ellipsometry data analysis (Chen, 2010). In this chart, \( E \) is photon energy in SE and MSE is the mean square error, a measure of the fit quality.
Once the data are acquired, initial optical model development involves identification of the physical sequence of layers in the sample, a mathematical expression for the complex dielectric function with photon-energy-independent parameters, as well as the thickness, for each layer that serves as an unknown to be characterized. The known values include the angle of incidence, the photon energy corresponding to each data point along the \((\psi, \Delta)\) spectra, and in most cases the optical properties and thicknesses of the components that establish the assumed previously measured structure that serves as the substrate of the unknown layer(s). Since regression analysis is an iterative process, we must assign initial estimated values to each thickness and to each photon energy independent parameter that describes any unknown dielectric function. This parameter set starts the iteration and can be used to calculate the \((\psi, \Delta)\) spectra for comparison with the experimental \((\psi, \Delta)\) spectra. The set of photon energy independent unknown parameters are adjusted iteratively until the difference spectra between simulated and measured \((\psi, \Delta)\) spectra are minimized.

It is crucial here that the initial estimate of the unknown parameters should not be substantially different from the overall best fit solution; otherwise the regression algorithm may fail. As a result, it is effective to perform one or more initial grid searches before starting the automated iteration sequence. Otherwise the algorithm may either diverge or converge to a local minimum in the quality of the fit. In the latter circumstance the difference between the calculated and experimental spectra may be substantial. On the other hand, when the initial parameter estimates are close to the global best fit solution as established by the grid searches, the regression algorithm readily identifies the global minimum in the quality of the fit through iterative corrections, as
long as the minimum is well-defined. The result should be closely matched calculated
and experimental \((\psi, \Delta)\) spectra if the model has been selected appropriately. In many
circumstances, several different models with different layer structures and different
dielectric function expressions must be evaluated to find the one that generates an overall
best fit. The process is clearly seen in the flow chart of Figure 2.10 where the iteration
steps are taken not only from the assigned initial variables toward the best fit variables,
but also from the initial, usually simplest, optical model toward more detailed models
incorporating additional parameters in a step-by-step manner.

In summary, the least-squares regression method is used not only to determine the
film thickness, but is equally useful also for extracting the complex dielectric function of
one or more materials in the model. If the unknown dielectric function is expressed as an
analytically-defined function of various photon energy independent variables such as
resonance energies, broadening parameters, and amplitudes, then the iterative fitting
procedure becomes analogous to that of fitting for unknown thickness. Known
parameters such as those that characterize a previously measured substrate structure are
fixed in the model whereas the unknown energy-independent parameters such as those
that characterize a deposited film stack on the substrate, including the layer thicknesses,
are varied. Then, the iterative algorithm will adjust the unknown parameters until a
measure of the difference spectra between the simulated and experimental ellipsometry
spectra \((\psi, \Delta)\) are minimized.

The validity of the model and the quality of the fit is judged by the mean squared
error (MSE). When the MSE reaches its global minimum, the iterations are terminated.
A commonly used MSE is defined in terms of the error-weighted standard deviations between calculated and measured spectra according to:

\[
MSE = \frac{1}{2N - M} \sum_{i=1}^{N} [\left(\frac{\psi_{i,\text{cal}} - \psi_{i,\text{exp}}}{\sigma_{\psi,i}}\right)^2 + \left(\frac{\Delta_{i,\text{cal}} - \Delta_{i,\text{exp}}}{\sigma_{\Delta,i}}\right)^2], \tag{2.27}
\]

where the superscripts "cal" and "exp" refer to calculated and experimentally measured values. In the above equation, \(N\) is the total number of measured \((\psi, \Delta)\) pairs, \(M\) is the number of fitting parameters, and \(\sigma_{\psi}\) and \(\sigma_{\Delta}\) are the standard deviations of the measured \((\psi, \Delta)\) spectra. The division by the standard deviations (i.e., random errors obtained from multiple measurements of the sample) ensures that low precision data points, such as points with lower signal-to-noise ratio that typically occur at the lowest and highest photon energies of the spectra, are weighted less heavily in the fitting procedure. Assuming all systematic errors in the \((\psi, \Delta)\) spectra are eliminated at their sources, an appropriate model should have an MSE near unity. When the MSE is much greater than unity, one can conclude that the model does not fit the data, and as a result should be adjusted. If the MSE is much less than unity, it would suggest that the errors are overestimated or that noise features themselves are being fit.

Once the best fit parameters are found for a given model and the MSE is well above unity, a number of different models should be tested in attempts to improve the global fit to the data. Generally, for a single deposited layer on a substrate, the fit starts with a simple model that includes just that one layer. Then depending upon the structural nature of the film and substrate, more complex structural models may be attempted that incorporate surface and interface roughness and other complexities such as graded properties in the layer in order to improve the fit. The starting model for the optical properties may include a Drude contribution and one or more Lorentz oscillators such
that the number of free optical parameters is \( M_o = 2 + 3N_o + 2N_p + 1 \). Here, the first
value of two represents the number of parameters associated with the Drude term. Next,
\( 3N_o \) is the number parameters associated with \( N_o \) Lorentz oscillators with absorption
within the spectral range. The contribution \( 2N_p \) is the number of parameters associated
with \( N_p \) oscillators that do not generate absorption due to these resonances being well
outside the spectral range. Finally, the unit parameter is due to a photon energy
independent offset in the real part of the dielectric function \( \varepsilon_1 \). More complex models
may use a more general critical point oscillator expression in which case each oscillator
introduces five parameters, rather than three for the Lorentz oscillator. In any case, for a
complicated structural/optical model with many fitting parameters, each final best fit
parameter must be evaluated for its confidence limits and its correlation coefficients with
other parameters. When the correlation coefficients between two or more parameters are
near unity it may explain the inability of the regression algorithm to converge with a
reasonable number of iterations.

2.3.4 Case Study: Determination of Dielectric Function of the Mo Back-

Contact in a CIGS Solar Cell

The thin-film photovoltaics (PV) technology based on the I-III-VI_2 (or
chalcopyrite) polycrystalline semiconductors has reached the highest laboratory
efficiency among all potentially low-cost thin-film technologies – 21.7% for
\( \text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2 \) (CIGS) fabricated using a modified co-evaporation process [ZSW,
Germany Press Release, 2014]. Because this PV technology presents significant
challenges in industrial scale-up, spectroscopic ellipsometry (SE) can play an important
role in better understanding the materials fabrication processes. In this case study, the in-
situ SE measurement has been performed to extract the complex dielectric function of the molybdenum (Mo) thin films currently used as the metallic back contact in these solar cells. The molybdenum thin film studied here was deposited by radio-frequency (rf) magnetron sputtering onto an unheated soda-lime glass (SLG) substrate (see Sec. 2.4). The sputter deposition was performed using an rf power of 100 W and Ar gas (99.999%) at a pressure of $10^{-2}$ Torr.

The thin film polycrystalline Mo back contact used in CIGS solar cells plays a key role in enabling the diffusion of Na atoms from the underlying soda-lime glass (SLG) substrate interface to the Mo surface for further diffusion into the overlying CIGS, where the Na is known to improve the electronic properties of the CIGS (Scofield et al., 1994). Because the diffusion of Na is believed to occur along the grain boundaries of the Mo film, characterization of the grain structure of the Mo is very important for the optimization of these films for CIGS solar cell applications. Other important characteristics of the Mo back contact film are its void content, lattice strain, and its ability to adhere to the SLG. These characteristics are important since the stress that develops during film growth can lead to delamination and void introduction at elevated Ar pressure can relax the stress.

Figure 2.11 presents the complex dielectric functions of Mo at two bulk layer thicknesses of 33 Å and 1073 Å, as determined by exact inversion of spectra collected in real time during Mo growth on soda-lime glass substrates (Marsillac et. al, 2008). The bulk layer thicknesses used in the inversions were determined through a global fit to spectra collected over a narrow time range (An et al., 1991).
Figure 2-11: Complex dielectric functions $\varepsilon = \varepsilon_1 + i\varepsilon_2$ are shown for a Mo thin film deduced at bulk layer thicknesses of 33 Å (left) and 1073 Å (right). The substrate used in this study was unheated soda-lime glass.

In these analyses, narrow time ranges of $\sim 36$ s and $\sim 70$ s are selected for the two thicknesses shown in Fig. 2.11, with the inversion point $t^*$ chosen at the center of those time ranges. At $t^*$, initial trial values of the bulk and surface roughness layer thicknesses are assumed, which enables inversion of the dielectric function at $t^*$. This dielectric function is assumed to be unchanged over the narrow time range, enabling least squares regression to determine the evolution of the two thicknesses over the time range. Thus, the least squares regression analysis performed at a given time uses only two free parameters. The critical result of this analysis is the sum of the MSE values for the individual fits taken over the selected time range. The correct dielectric function, obtained with the correct trial values of the bulk and roughness layer thicknesses at $t^*$, minimizes this sum of MSE values. Thus, the method for determining the two bulk layer thickness values in Fig. 2.11 is quite involved, combining iterations of inversion to
extract dielectric functions and least-squares regression analysis to identify the proper thicknesses at which the inversion is to occur. The surface roughness in this analysis was found to be negligible (< 5 Å).

Clear differences in $\varepsilon$ are observed for the two thicknesses. These differences are qualitatively consistent with differences in the Drude free-electron relaxation time $\tau$. This observation is further supported by the results of Fig. 2.12, in which the spectra in $\varepsilon_1$ for three different thicknesses are compared on the same plot. The increase in relaxation time with increasing thickness leads to the abrupt decrease in $\varepsilon_1$ (0.75 eV) from 9 to $-22$ in Fig. 2.12.

The dielectric function spectra deduced by inversion could be fit over the low energy range (0.75 - 3 eV) by combining the Drude equation:

$$\varepsilon(E) = \varepsilon_{1o} - \frac{2E_p^2}{\left(E + i\Gamma\right)}.$$  \hspace{1cm} (2.28 a)

with a single Lorentz oscillator expression:

$$\varepsilon(E) = \frac{-A^2}{E^2 - E_0^2 + i\Gamma E}.$$  \hspace{1cm} (2.28 b)

In the Drude equation, $E$ is the photon energy, $E_p$ is the free electron plasma energy, and $\Gamma$ is the broadening parameter, given in terms of the free electron relaxation time by $\tau = \hbar / \Gamma$, where $\hbar$ is Planck's constant. Finally, $\varepsilon_{1o}$ is the energy-independent contribution to the real part of the dielectric function due to oscillators well above the high energy limit of the fitting range. The Lorentz oscillator has a similar form as the Drude expression, but with an electron resonance energy term $E_0^2$ in the denominator. In addition, the constant contribution to the real part of the dielectric function of the Lorentz oscillator is assumed to be absorbed into $\varepsilon_{1o}$ of the Drude equation. The resulting best fit Drude broadening
Figure 2-12: Comparison of $\varepsilon_1$ spectra is shown for a Mo film measured at three different thicknesses using real time spectroscopic ellipsometry. The substrate used in this study was unheated soda-lime glass.

parameter $\Gamma$ and relaxation time $\tau$ for the Mo film are shown as a function of its bulk layer thickness $d_b$ in the inset and the main part of Fig. 2.13, respectively.

Figure 2-13: Broadening parameter $\Gamma$ (inset) and relaxation time $\tau$ are shown for free electrons in Mo plotted versus the bulk layer thickness obtained using real time spectroscopic ellipsometry. The solid line fit to $\tau$ is obtained using Eq. (2.29) based on the assumption that the mean free path of electrons is equal to the average grain radius $R_g$ which is assumed to increase with bulk layer thickness according to $R_g = d_b/2$. In addition, the grain boundary reflection coefficient in the fit is taken as $\Re = 0.5$. The solid line in the inset connects the data points.
These results can be interpreted using two different models. The first model is that of Mayadas and Shatzkes (Kasap, 2006) in which it is assumed that the relaxation time is controlled by scattering of free electrons at grain boundaries, giving rise to the expression:

\[ \tau^{-1} = \tau_b^{-1} + 3\Re \nu_F / [2(1-\Re)\lambda_g] \]  

(2.29)

where \( \tau_b = 1 \times 10^{-14} \) s is the relaxation time in the limit of large grains, \( \lambda_g \) is the mean free path due to grain boundary scattering - assumed to be equal to the grain radius \( R_g \), \( \Re \) is the grain boundary reflection coefficient, and \( \nu_F = 1.7 \times 10^6 \) m/s is the Fermi velocity of Mo. If the grain diameter is assumed to be equal to the thickness of the film, then a reasonable fit to the data of Fig. 2.13 is obtained with a grain boundary reflection coefficient of \( \Re = 0.5 \). The second model is that of Fuchs-Sondheimer (Kasap, 2006) in which it is assumed that surface and interface scattering play a dominant role. The resulting expression has the same form as Eq. (2.29), but with the second term on the right replaced by \( 3\nu_F(1-p)/8d_b \), where \( p \) is the fraction of surface collisions that are elastic. When this model is applied to fit the data, a physically unrealistic (negative) value of \( p \) is obtained. This demonstrates that the effect of the Mo bulk layer thickness on the relaxation time is much larger than would be predicted based on surface/interface scattering effects alone. Thus, grain boundary scattering is believed to be the dominating effect.

2.4 RF Magnetron Sputtering

In this research, all the component thin films of the back reflectors and contacts, including metals and transparent conducting oxides (TCOs) such as Mo, Ag, ZnO:Al, and ZnO, are deposited by RF magnetron sputtering. This section briefly describes the
magnetron sputter deposition technique. In this technique, a thin film is fabricated by ejecting (or sputtering) atoms or molecules from a solid state target material and collecting them on a substrate where they chemisorb, bonding to the substrate atoms and accumulating to form the thin film (Wasa and Hayakawa, 1992). By varying the deposition process and conditions, and even modifying these conditions in real time during deposition, thin films and their interfaces can acquire a range of desirable properties, in particular their thickness that may not be accessible to bulk materials. As a result, sputtered thin films are used extensively in integrated circuits, electronic and optical devices, multilayer optical coatings, and hard and decorative coatings.

There are numerous methods for depositing thin films, and sputtering is one of the most widely used in research and development as well as in industrial applications. Expressed in the simplest terms, sputtering is the ejection of surface atoms of a target by bombardment with energetic ions (generally Ar+). The phenomenon was first observed in a dc gas discharge tube by Grove in 1852. During the operation of a gas discharge, Grove observed the effect whereby energetic ions bombard the cathode surface of the tube with the result being the ejection of atoms from the cathode surface. These atoms were subsequently deposited onto the inner wall of the tube. A simplified schematic diagram for the configuration used in RF magnetron sputter deposition is shown in Fig 2.14, designed specifically to enhance the effect first observed by Grove for high thin film deposition rates.
In a vacuum chamber, the target made from the material to be deposited as a thin film is bonded to the cathode and the substrate onto which the thin film is to be deposited is attached to the anode with the capability of substrate heating. A controlled flow of inert gas (or a mixture of inert and reactive gases) is brought onto the chamber after it is pumped to high vacuum (< $10^{-6}$ Torr). The deposition of thin films by sputtering occurs when positive ions from the plasma of the pure inert gas (typically Ar) or the gas mixture are accelerated toward a target material that acquires a negative bias. The surface atoms of the target are ejected by momentum transfer if the energy of the impinging ions is greater than the sputtering threshold energy. In the specific case of sputtering in Ar, the ions are generated by a radio frequency (RF) glow discharge that is ignited between the two electrodes thereby producing Ar$^+$ ions. These Ar$^+$ ions are accelerated toward the surface of the target by the electric field in front of the cathode. Moreover, a magnetic
field around the cathode confines the discharge plasma to a torus-like shape in front of the target. The magnetic field strength is adjusted in such a way that it will influence the electrons significantly but not the ions. This will force electrons to follow cycloidal orbits in the region of orthogonal intersection of the electric and magnetic fields. In this configuration, the electrons are trapped in a channel. The number of ionized gas atoms thus will increase significantly enabling a low gas pressure for sputtering. Although the plasma can be sustained at pressures below $10^{-6}$ Torr, typical pressures used in this research are in the 4-100 mTorr range.

2.5 Spectroscopic Transmission & Reflection (T & R)

Almost all thin film samples studied in this thesis research were measured not only by spectroscopic ellipsometry but also by reflectance and transmittance spectroscopy. In transmittance spectroscopy, a monochromatic light beam is passed through a sample and the resulting measured irradiance $I_t$ is divided by the irradiance of the light beam that has passed through the ambient in the absence of the sample $I_i$. Thus, the transmittance is given by $T = I_t/I_i$. In reflectance spectroscopy, the light irradiance that has been reflected from a sample $I_r$ should be normalized to the irradiance from a completely reflective sample $I_i$. In this case, the reflectance would be given by $R = I_r/I_i$. Since such a sample does not exist, calibration with a sample of known reflectance is performed according to the expression $R_{\text{cal}} = I_{r,\text{cal}}/I_i$. Since $I_i$ is not known, the reflectance of the unknown sample is determined in terms of that of the known sample by $R = R_{\text{cal}} I_r/I_{r,\text{cal}}$. In general, spectroscopic transmittance T (or reflectance R) spectroscopy involves four basic steps (Ferreira, 2004) : (a) generating a collimated broadband incident light beam, (b) transmitting the light beam through (or reflecting it
from) a sample, (c) collecting the transmitted (or reflected) beam irradiance spectroscopically, and (d) calculating beam/sample interaction parameters, i.e., transmittance (or reflectance) by using spectra that includes irradiance from background radiation and from a transmittance (or reflectance) reference, specifically no sample, for example, (or a crystal silicon wafer substrate).

The procedures to be described next include the possibility of a background signal which can arise due to ambient light, dark current in the detector, or offsets from zero in the electronics. The procedures also assume a crystalline silicon calibration sample. To determine the transmittance, the transmitted irradiance $I_t$ is measured first by collimating the broadband light from the lamps before directing it through the sample, and then by collecting the transmitted light with focusing optics before directing it to the spectrograph/detector system. The procedure is repeated with the sample removed to measure the total incident irradiance $I_o$. Finally, the background irradiance $I_b$ is measured by blocking the light source with a shutter immediately after the source. From the three measured spectra, the transmittance is calculated using the formula:

$$T = \frac{r_p^2 + r_s^2}{2} = \frac{I_t - I_b}{I_o - I_b}.$$  \hspace{1cm} (2.30)

In a similar manner, the reflectance is measured, but in this case the second measurement, yielding $I_{Si}$ is performed in reflection from the reference sample, a crystalline silicon wafer substrate. The reflectance can therefore be described similarly as:

$$R = \frac{r_p^2 + r_s^2}{2} = R_{Si} \left( \frac{I_r - I_b}{I_{Si} - I_b} \right) ,$$  \hspace{1cm} (2.31)

where $I_r$ is the reflected irradiance from the sample and $R_{Si}$ is the reflectance (known in advance) of the crystalline silicon substrate.
2.6 Optical Modeling of Reflectance and Transmittance

2.6.1 Modeling Approach and Capabilities

Optical modeling with custom-developed software is used to simulate reflectance, transmittance, and absorption spectra of various multilayer stacks of solar cells. The same program is also used to generate the quantum efficiency that describes the absorption in the active layers of the thin film solar cells. The modeling is generally performed for a normal angle of incidence using the dielectric function library extracted from the materials deposited specifically for this research. The program does not incorporate optical scattering phenomena as it assumes that solar cell structures are specularly reflecting and transmitting, i.e., all interfaces are perfectly abrupt on the macroscopic scale with no roughness on this scale and no non-uniformity. Optimization results for the transparent conducting oxide (TCO) layers of a CdTe solar cell are presented here as a case study of optical modeling capabilities. Details of this work can be found in Podraza et al. (2005).

2.6.2 Case Study: Optimization of TCO for CdTe Solar Cell

Optical modeling of CdTe solar cells has been performed in order to determine the potential of index of refraction tailoring of the TCO and TCO/CdS interface for improved cell performance. The modeling has focused on the design of a multilayer that serves as an anti-reflection coating in specular models of single-junction CdTe devices. This multilayer is inserted between the glass superstrate and the CdS/CdTe solar cell and serves the dual function of transparent top contact and antireflection coating. The primary focus of the optical simulations is simple, namely, to determine how the presence of such a multilayer can reduce losses by reflection from the top glass/SnO$_2$:F interface,
and to demonstrate the associated quantum efficiency of the solar cell and the resulting short-circuit current gains. The simulations have suggested that solar cell performance can be improved by a properly placed anti-reflection multilayer including (i) a low index SnO$_2$:F layer (L-SnO$_2$:F) between the glass superstrate and a high index SnO$_2$:F layer (H-SnO$_2$:F), as well as (ii) a controlled thickness of interface roughness between the high index SnO$_2$:F (H-SnO$_2$:F) layer and the CdS, as shown in the index of refraction depth profile at 700 nm in Fig. 2.15.

Typical commercial SnO$_2$:F coated glass exhibits ~300 Å of surface roughness, which then appears as interface roughness between the SnO$_2$:F and the over-deposited CdS in the completed solar cell. Thus, incorporation of a H-SnO$_2$:F/CdS interface roughness layer has provided a more realistic model of the current collection in the solar cell; however, controlling the thickness of this layer provides a means for optimization of light collection in the CdTe layer for improved solar cell performance. In the optical modeling, it is found that increases in this surface roughness provide a direction for improvement of glass industry products for CdTe photovoltaics applications. In fact, a 500 Å thick roughness layer thickness demonstrates an overall reduction of reflectance loss, leading to an increase in quantum efficiency and a current density gain of 0.44 mA/cm$^2$ in the solar cell.

An additional reduction in reflectance loss was accomplished by placing an L-SnO$_2$:F layer between the glass superstrate and the H-SnO$_2$:F layer. Optimizations varying the thicknesses of the L and H-SnO$_2$:F layers, as well as the optical properties of the L-SnO$_2$:F layer have demonstrated that a combination of a 300 nm L-SnO$_2$:F layer with an index of refraction n of 1.66 at 700 nm and a 300 nm H-SnO$_2$:F with n = 1.89 at
700 nm has yielded the greatest reduction in reflectance loss [Fig. 2.16 (a)] and consequent increase in quantum efficiency [Fig. 2.16 (b)]. This broadband antireflection layer has demonstrated a current gain of 0.39 mA/cm$^2$ for a cell structure without the H-SnO$_2$:F/CdS interface layer. Combining the optimized SnO$_2$:F/CdS roughness and the antireflecting layer yields a current gain of 0.80 mA/cm$^2$. This represents an increase of 3.6% in device performance, and a potential improvement in absolute efficiency of 0.5%. Obviously more sophisticated approaches are possible that incorporate graded layers and even higher gains may be forthcoming.

Figure 2-15: Profile in the index of refraction at $\lambda = 700$ nm is shown for the top or sun side layers of a CdTe solar cell. The broken line is for the "standard cell" with abrupt interfaces and the solid line includes a two layer SnO$_2$:F TCO and an optimized SnO$_2$:F/CdS interface roughness layer.
Figure 2-16: (a) (top) Spectral reflectance and (b) (bottom) quantum efficiency are shown for two different optical models of the CdTe solar cell, corresponding to the two index of refraction profiles in Fig. 2.9. The apparent R ~ 0.04-0.06 baseline in (a) is due to the loss from the ambient/glass side of the superstrate.
Chapter 3

Structural Evolution and Optical Properties of Ag Thin Films

3.1 Motivation and Introduction

Silver metal films are important components of thin film hydrogenated amorphous silicon (a-Si:H) solar cells as back-reflector layers in both p-i-n superstrate and n-i-p substrate configurations. In this chapter, the discussion will focus on the structural evolution of silver films deposited on Si wafer substrates as studied using real time spectroscopic ellipsometry (RTSE). Later in the chapter, the discussion will turn to the optical properties of the silver films as obtained in the analysis using the same RTSE data set. The chapter will begin with a motivation which will explain some of the challenges associated with the development of high performance back-reflectors that incorporate silver.

A widely-used back-reflector (BR) for thin film a-Si:H solar cells in the substrate/BR/n-i-p layer sequence consists of opaque metal (Ag or Al), followed by a ~1500 - 3000 Å thick layer of ZnO transparent conducting oxide (TCO). In most laboratories, both layers are deposited by sputtering onto a low-cost substrate such as stainless steel or polymer (Deng and Schiff, 2003). Quantum efficiency enhancement in the solar cell over the red-to-near-infrared range (620 to 780 nm; 1.6 to 2.0 eV), where
the a-Si:H absorption is weak, arises due to reflection of near-infrared wavelengths back into the cell for possible absorption during additional passes. Back-reflectors for hydrogenated nanocrystalline silicon operate over a range of longer wavelengths (typically 780 to 1000 nm; 1.2 to 1.6 eV). Furthermore, the Ag/ZnO interface is designed to be macroscopically rough so that the light rays are scattered upon back-reflection for increased path lengths. It is generally recognized that as macroscopic roughness is incorporated, however, absorption losses in the rough Ag at the Ag/ZnO interface are enhanced. Thus, incorporating macroscopic roughness leads to a trade-off between increased optical path lengths and increased interface absorption. It should be noted that in this application, macroscopic roughness is defined as that having in-plane scales within an order of magnitude of the wavelength of light, such that scattering occurs.

Unexpected losses in the back-reflectors used in a-Si:H-based multijunction solar cells arise from the non-ideality of their interfaces. In the limit of an atomically smooth starting metal film, an overdeposited TCO may interact with the metal to form both a chemical mixture and possibly roughening at the interface. This mixture may occur through a chemical reaction even if the deposition of the TCO is via a low energy process such as thermal evaporation that avoids bombardment-induced intermixing. In the sputtering process of the TCO, which is typically ZnO, however, there will be ion impact of sufficient energy to cause atomic displacements and ion-bombardment-induced atomic intermixing. The atomically-mixed layers formed either chemically due to a reaction or physically due to bombardment reduce the reflectance from that expected for an ideal interface, and can give rise to optical losses particularly because the back reflector relies on multiple reflections at the metal/TCO interface.
When microscopic roughness exists on the metal surface, then various effects can occur in the deposition process of the overlying TCO. First the roughness can promote additional reaction between the metal and TCO via diffusion, leading to a thicker chemically reacted layer and greater optical losses. In addition, the modulated metal/TCO interface may give rise to plasmon resonances and associated absorption due to the confinement of electrons in the metal protrusions of the modulated interface. For modulations that are very small on an in-plane scale (~100 Å), these resonances will typically occur near the visible range and thus will not contribute to losses in the infrared range where the BR must operate. As the in-plane scale of the roughness increases, such resonances will shift to the near-infrared range where losses detrimental to the solar cell performance may occur (Muller et al., 2004; Haug et al., 2008).

The goal of this research is to explore the different types of losses that can occur due to imperfect interfaces in the metal/TCO back reflector, and then develop proposals to minimize these losses through optimized processing conditions. The initial focus involves the losses that occur when ZnO is deposited on top of the smoothest possible specular Ag. The second focus involves the effects of microscopic roughness of increasing thicknesses on the absorption losses at the Ag/ZnO interface. The third focus considers the effect of macroscopic roughness (or so-called "texture") on these losses, as the texture increases in magnitude. Here the dividing line between the microscopic and macroscopic roughness in terms of thickness is ~ 100-200 Å or approximately one-tenth the wavelength of the shortest wavelength used in the RTSE experiments.
3.2 Variation of Deposition Parameters

The Ag films were deposited by RF magnetron sputtering in an argon atmosphere. The substrates were c-Si wafers covered with native and thermally grown oxides (d_{ox} \sim 15 - 120 \text{ Å}) to prevent Si/Ag inter-diffusion and possible silicide formation. In addition, c-Si/SiO_{2} is atomically smooth, and ultra-smooth Ag deposition is possible on these substrates under specific conditions. The base pressure was on the order of 10^{-6} \text{ Torr} prior to argon flow into the chamber at 10 sccm. The pressure was raised above 100 mTorr in order to ignite the sputtering plasma. After plasma ignition, the pressure was reduced to the operating value, which was 4 mTorr in most cases. For selected depositions, the pressure was reduced from the ignition value to 7 or 10 mTorr. Pre-sputtering over a period of 2 to 4 minutes was performed in order to remove contamination from the target surface. During pre-sputtering, a shutter in front of the sputtering target remained closed, with the purpose of blocking the pre-sputtered flux to the substrate. An RF plasma power of 50 W was used for most of the samples, but for selected samples, the depositions were performed at lower and higher power levels of 25 and 100 W, respectively.

During each entire thin film deposition process, including plasma ignition for pre-sputtering, shutter removal for growth, and plasma extinction, real time spectroscopic ellipsometry was performed using a rotating-compensator multichannel instrument with a spectral range of 0.75 – 6.5 eV. The smoothest Ag film exhibits a surface roughness thickness of d_{s} = 4 \pm 1 \text{ Å}, as deduced by RTSE at the end of the deposition (typically after \sim 1500 \text{ Å in Ag bulk layer thickness}). The procedure for obtaining these values is described in the next section. These smoothest films in this study are obtained on room
temperature substrates using the lowest gas pressure of ~ 4 mTorr and the intermediate power level of 50 W. The smoothest final surfaces also involve annealing the substrate at 200ºC prior to Ag deposition. By elevating the temperature of the substrate to the highest value explored, 190ºC, and depositing at that temperature, a much thicker surface roughness layer with $d_s = 105 \, \text{Å}$ is obtained by the end of the Ag film deposition. The deposition conditions for the Ag films are summarized in Table 3.1 below.

Table 3.1: RF magnetron sputtering conditions are tabulated for the silver depositions ordered according to the final surface roughness thickness.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Working pressure (mTorr)</th>
<th>Argon gas flow (sccm)</th>
<th>RF power (Watt)</th>
<th>Substrate temp. (°C)</th>
<th>Final surface roughness $d_s$ (Å)</th>
<th>Growth rate (Å/min)</th>
<th>Projected bulk thickness $d_b$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DS031 Subst. anneal</td>
<td>4</td>
<td>10</td>
<td>50</td>
<td>RT</td>
<td>4 ± 1</td>
<td>183 ± 5</td>
<td>2196 ± 60</td>
</tr>
<tr>
<td>DS005</td>
<td>4</td>
<td>10</td>
<td>50</td>
<td>RT (20)</td>
<td>6 ± 2</td>
<td>216 ± 8</td>
<td>3024 ± 112</td>
</tr>
<tr>
<td>DS009</td>
<td>4</td>
<td>10</td>
<td>50</td>
<td>RT</td>
<td>6 ± 2</td>
<td>190 ± 6</td>
<td>2850 ± 90</td>
</tr>
<tr>
<td>DS017</td>
<td>10</td>
<td>10</td>
<td>50</td>
<td>RT</td>
<td>10 ± 2</td>
<td>180 ± 5</td>
<td>2520 ± 70</td>
</tr>
<tr>
<td>DS019</td>
<td>4</td>
<td>10</td>
<td>100</td>
<td>RT</td>
<td>10 ± 3</td>
<td>374 ± 14</td>
<td>7400 ± 277</td>
</tr>
<tr>
<td>DS020</td>
<td>4</td>
<td>10</td>
<td>25</td>
<td>RT</td>
<td>12 ± 3</td>
<td>99 ± 3</td>
<td>1980 ± 60</td>
</tr>
<tr>
<td>DS016</td>
<td>4</td>
<td>10</td>
<td>50</td>
<td>RT</td>
<td>15 ± 3</td>
<td>187 ± 6</td>
<td>2618 ± 84</td>
</tr>
<tr>
<td>DS018</td>
<td>10</td>
<td>10</td>
<td>100</td>
<td>RT</td>
<td>16 ± 3</td>
<td>363 ± 12</td>
<td>5068 ± 168</td>
</tr>
<tr>
<td>DS011</td>
<td>4</td>
<td>10</td>
<td>50</td>
<td>30</td>
<td>21 ± 3</td>
<td>193 ± 6</td>
<td>2895 ± 90</td>
</tr>
<tr>
<td>DS012</td>
<td>4</td>
<td>10</td>
<td>50</td>
<td>30</td>
<td>27 ± 3</td>
<td>178 ± 5</td>
<td>2670 ± 75</td>
</tr>
<tr>
<td>DS013</td>
<td>4</td>
<td>10</td>
<td>50</td>
<td>50</td>
<td>28 ± 4</td>
<td>209 ± 7</td>
<td>3135 ± 105</td>
</tr>
<tr>
<td>DS010</td>
<td>4</td>
<td>10</td>
<td>50</td>
<td>50</td>
<td>31 ± 4</td>
<td>213 ± 8</td>
<td>3195 ± 120</td>
</tr>
<tr>
<td>DS021</td>
<td>4</td>
<td>10</td>
<td>50</td>
<td>87</td>
<td>55 ± 4</td>
<td>199 ± 6</td>
<td>3980 ± 120</td>
</tr>
<tr>
<td>DS030</td>
<td>7</td>
<td>30</td>
<td>50</td>
<td>170</td>
<td>100 ± 5</td>
<td>163 ± 4</td>
<td>3033 ± 74</td>
</tr>
<tr>
<td>DS028</td>
<td>7</td>
<td>30</td>
<td>50</td>
<td>190</td>
<td>105 ± 5</td>
<td>201 ± 7</td>
<td>3764 ± 131</td>
</tr>
</tbody>
</table>
From the table, two trends can be observed. First, the deposition rate of the films depends on the RF sputtering power. Second, the final surface roughness of Ag films increases linearly with the substrate temperature. In these depositions the Ar pressure and RF power were also changed, but these changes have a weaker influence on the final surface roughness. The observed trends are summarized in Figure 3.1.

Figure 3-1: The upper plot shows the dependence of the Ag surface roughness layer thickness on deposition temperature, as determined at the end of the deposition. The lower graph shows the dependence of the average bulk layer deposition rate on the RF power, obtained as a linear fit to the bulk layer thickness $d_b$. The procedures for obtaining these results are presented in Section 3.3.
3.2 Evolution of Ag Structure

The evolution of Ag thin film structure during growth can be studied by analyzing the real time spectroscopic ellipsometry (SE) data. First, the thickness of the SiO$_2$ layer on the oxidized silicon wafer substrate is determined at room temperature using least square regression analysis and standard reference dielectric functions for the c-Si and SiO$_2$ from the J.A. Woollam Co. software database. These reference data were also obtained at room temperature. Using the SiO$_2$ thickness and the room temperature dielectric function of SiO$_2$ from the database, the dielectric function of the crystalline silicon substrate is determined by exact numerical inversion of the raw SE data ($\psi$, $\Delta$). The input file of raw SE data for this inversion process is obtained at the first time point in the real time measurement. Thus, in this initial step, all the characteristics of the substrate are determined. For depositions at elevated temperature, this procedure neglects the temperature dependence of the SiO$_2$ dielectric function, which is a reasonable approximation, given its ~ 15 - 120 Å thickness. In addition, it is assumed that heating the substrate to the deposition temperature under vacuum does not lead to a change in oxide thickness.

In the second analysis step, the real time SE data collected during silver deposition are interpreted using the model in Figure 3.2. For a given deposition temperature, the correct Ag dielectric function, along with the bulk and surface roughness layer thicknesses $d_b$ and $d_s$, respectively, can be determined. These results are obtained at a selected time during silver deposition when $d_b$ lies within the thickness range of 700 - 1000 Å. The analysis to obtain these results applies a two-step sequence of exact inversion and least-squares regression embedded within an iteration program. The overall
process of deducing the dielectric function and the thickness evolution of the silver bulk and surface layers, as represented in the schematic of Fig. 3.2, can be described by a flow chart as shown in Figure 3.3.

Figure 3-2: The multilayer model shown here was used for the analysis of real time SE data collected for the silver depositions.
Figure 3-3: Flow chart is depicted for all steps applied in the analysis of real time SE data using the model presented in the schematic of Figure 3.2.

Examples of the final output of this analysis are given in Fig. 3.4 which shows the structural evolution of silver during growth for samples DS005 (p = 4 mTorr) and DS017 (p = 10 mTorr). Specifically, Fig. 3.4 provides the surface roughness and bulk layer thickness evolution for the two depositions, and Fig. 3.5 shows the nucleation and coalescence sequence for the two films superimposed over a limited time range. For both depositions, the initially nucleating film is in the form of a roughness layer modeled assuming a 0.5/0.5 volume fraction mixture of bulk Ag and void. This layer reaches a thickness of ~ 14 Å during pre-sputtering which implies that the shutter is not completely effective at blocking the pre-sputtered flux. Once the shutter is opened, the nucleation
continues to a thickness of 35 Å for the 4 mTorr deposition and 25 Å for the 10 mTorr deposition. During nucleation when the surface roughness layer increases in thickness, the best fit bulk layer thickness is zero. Near the maximum in the surface roughness layer thickness, however, the bulk layer thickness increases linearly above zero. The resulting behavior suggests that clusters form, increase in size, make contact, and coalesce, leading to roughness on the surface of the coalesced film on the order of a monolayer or less. The roughness layer thickness increases gradually with time after nuclei coalescence, reaching 6 Å and 10 Å at the end of deposition for samples DS005 and DS017, respectively.

In the later stages of growth, the bulk layer thickness cannot be determined as this layer becomes fully opaque over the entire spectral range of the measurement. A comparison of the two depositions in Figures 3.4 and 3.5 suggests that an increase in Ar pressure results in a decrease in Ag deposition rate, possibly due to gas phase scattering of sputtered Ag atoms away from the substrate. Also, the lowest pressure leads to a more stable surface with a constant roughness thickness versus time, possibly due to unscattered Ag atoms impinging at the film surface with sufficiently high energies to erode away surface asperities. Figure 3.6 shows similar structural evolution for a third Ag film, sample DS028, with a much larger final surface roughness thickness, 105 Å, deposited at the maximum substrate temperature of 190°C and an intermediate Ar pressure of p = 7 mTorr. For this deposition, the bulk and surface roughness layer thicknesses grow simultaneously upon opening the shutter. A smoothening effect is observed over the bulk layer thickness range of ~ 500-900 Å, before the resumption of roughening for bulk layer thicknesses greater than ~ 900 Å.
Figure 3-4: Structural evolution is presented for two Ag films deposited on SiO₂ covered c-Si wafers [sample numbers DS005 and DS017]. The films were sputtered onto room temperature substrates with a RF power level of 50 W and Ar pressures of 4 mTorr and 10 mTorr, respectively. The bulk layer thickness, the roughness layer thickness, and the quality of the fit are shown as functions of time. After a thickness of \( \sim 1000 \) Å, the silver film is essentially opaque over the entire spectral range and the bulk layer thickness cannot be determined. The left vertical line and the vertical line to the right of it show the times at which the plasma is started and the shutter is opened, respectively.
Figure 3-5: An expansion of the time scale is displayed in the neighborhood of nucleation and coalescence for the two films of Figure 3.4. The substrate temperature was room temperature and the RF power was 50 W for both depositions.
Figure 3-6: Structural evolution is presented for one of the roughest Ag films, that deposited at 190°C on a SiO\textsubscript{2} covered c-Si wafer (sample DS028). The Ar pressure was 7 mTorr and the RF power was 50 W. The bulk layer thickness, the roughness layer thickness, and the quality of fit are shown as functions of time. After a bulk layer thickness of ~ 1000 Å, the silver film is essentially opaque over the full spectral range and the bulk layer thickness cannot be determined.

As shown in Table 3.1 and in Figures 3.4 - 3.6, a variation of the substrate temperature over the range 20 ≤ T ≤ 190°C, yields Ag films with final surface roughness layer thicknesses, d\textsubscript{s}, over the range 4 ≤ d\textsubscript{s} ≤ 105 Å after bulk layer thicknesses of ~1500 Å.
Å. The roughness on the Ag surfaces is modeled by using the Bruggeman effective medium theory assuming a 0.5/0.5 volume fraction mixture of Ag and void. In previous studies, a 0.5 void volume fraction has been reported to work well for smooth Ag films. As the roughness of the Ag increases, however, the best fit void fraction was found to decrease to 0.3, implying roughness layers with a volume fraction mixture of 0.7/0.3 Ag/void (Dahal, 2013). In the present research, different behavior is likely since the quality of fit at the end of the deposition improves as the surface roughness layer thickness increases when using a model with a fixed volume fraction mixture of 0.5/0.5 Ag/void.

Considering the time evolution of the fitting quality in Figures 3.4 - 3.6, very poor fits are observed in the early stage of growth. This can be attributed to the dominance of small metal clusters on the substrate. Such a film structure is best modeled using a Maxwell-Garnett effective medium theory to simulate confined plasmon resonances within the clusters (Nguyen et al., 1993). The focus of this dissertation research is the ability of RTSE to determine the later stage roughness evolution and the final surface roughness layer thickness, and in this regime, the Bruggeman effective medium theory and a 0.5/0.5 volume fraction Ag/void composition is sufficient as indicated by the magnitude and behavior of fitting quality in Figures 3.4-3.6.

To validate the surface roughness layer thicknesses on Ag films as deduced from RTSE, atomic force microscopy (AFM) measurements have been performed. Figure 3.7 shows the roughness layer thickness of Ag films, as determined by RTSE at the end of the deposition, plotted against the root mean square (rms) roughness as measured by AFM (Dahal et al., 2011). The near unity slope and small intercept indicate that RTSE is
measuring a roughness thickness very close to the AFM rms value. The small intercept suggests that RTSE is measuring a component of the roughness that AFM is not. This may result for in-plane roughness scales much smaller than the AFM tip radius. In spite of this small difference, the results of Figure 3.7 corroborate RTSE as a probe of microscopic rms roughness.

Figure 3-7: Surface roughness layer thickness from RTSE for Ag depositions is correlated with the rms value from $5 \times 5 \, \mu m^2$ AFM images (Dahal et al., 2011).

The data of Figures 3.4 and 3.6 can be replotted to show the evolution of the surface roughness layer thickness with bulk layer thickness as depicted in Fig. 3.8. Three different behaviors are observed for low, intermediate, and high substrate temperatures. At the lowest substrate temperature of 20°C, nuclei grow to $\sim 20 \, \AA$ in height and coalesce to form a smooth, stable surface. At the intermediate elevated temperature of 87°C, nuclei grow to a larger thickness of 95 Å in height and coalesce, leading to a strong smoothening effect. The coalescence process leaves a 30 Å thick surface roughness layer
at $d_b = 200$ Å, however, and that roughness increases with thickness to a final value of 55 Å at $d_b \sim 3900$ Å. In this case, a longer diffusion length for Ag atoms on the SiO$_2$ surface may give rise to a lower nucleation density and a larger thickness at which nuclei make contact prior to coalescence. At such a low nucleation density, coalescence may be incomplete, and this leaves residual surface roughness that is enhanced with increasing bulk layer thickness. At the highest temperature, there is no clear nucleation and coalescence process in the initial growth stage. In this stage, the roughness layer and the bulk layer grow simultaneously; yielding $d_s = 100$ Å at $d_b = 350$ Å. There appears to be a later stage coalescence process in which the roughness decreases by 15 Å over the range of 500 to 900 Å.

Figure 3-8: Surface roughness evolution versus bulk layer thickness is shown for Ag films sputtered onto oxidized Si substrates at three temperatures, $T = 20$, 87, and 190°C.
3.4 Dielectric Functions of Ag

As described earlier in Section 3.3, the complex dielectric functions of the silver films are obtained in a two-step sequence of exact inversion and least-square regression analysis, both steps embedded within an iteration program. The model shown in Figure 3.2 is used, and the detailed analysis steps are shown in the flow chart of Figure 3.3. These inverted dielectric functions are very similar in nature and resemble an existing reference silver dielectric function (J.A. Woollam Company software database). In this section, the complex dielectric functions of Ag films fabricated and processed under different conditions, including high substrate temperature, as well as after an annealing step, are discussed. The resulting dielectric functions of the Ag films have been parameterized using oscillators, which enable us to study the intraband electronic transitions (free electrons, from a partially filled band) and interband electron transitions (bound electrons, from a completely filled band) for the various deposition and processing conditions.

Before presenting the dielectric functions, the details of the parameterization will be discussed. Parameterization involves describing each dielectric function using a single analytical function with photon-energy independent free parameters that are determined in least squares regression analysis of the dielectric function as obtained by inversion. The purpose of this is to extract physical parameters that may correlate with the processing conditions. In addition, if the parameterization provides a good fit, it can serve to mathematically smoothen the dielectric function, eliminating noise associated with the inversion. For the Ag samples, their complex dielectric functions are parameterized using a sum of a Drude component and a generalized critical point (CP)
oscillator. The Drude component of the complex dielectric function is described by the following equation:

\[
\varepsilon_D(E) = -\frac{A\Gamma}{E^2 + i\Gamma E},
\]

where \(A\) and \(\Gamma\) are the amplitude and the broadening parameter associated with the free electrons. From the Drude term parameters, the plasma energy can be determined as \(E_p = (A\Gamma)^{1/2}\). In the limit \(E_p >> \Gamma\), then the plasma energy is the energy at which the real part of the Drude term of Eq. (3.1) is minus unity. Similarly, the CP oscillator components are described collectively by the following pair of equations:

\[
\varepsilon_{CP}(E) = A e^{i\theta} \left( \frac{\Gamma}{2E_g - 2E - i\Gamma} \right)^{\mu}, \quad \mu = \pm 1/2;
\]

\[
\varepsilon_{CP}(E) = A e^{i\theta} \ln(2E_g - 2E - i\Gamma), \quad \mu = 0.
\]

Here \(\varepsilon(E)\) is the complex dielectric function component at energy \(E\), \(A\) is the amplitude, \(\Gamma\) is the broadening parameter, \(\theta\) is the phase projection factor, \(\mu\) is the exponent, and \(E_g\) is the bandgap energy. In Equation (3.2), if the exponent \(\mu\) has a value of \(+1/2\), the expression represents a one dimensional critical point (CP). The choices \(\mu = 0\) and \(\mu = -1/2\) are appropriate for two and three dimensional CP's, respectively (Aspnes, 1980). Finally, \(\mu = 1\) can be used to describe the critical point lineshape for discrete excitons (Collins and Ferlauto, 2005). Therefore, the overall dielectric function of Ag can be represented as:

\[
\varepsilon(E) = \varepsilon_{io} + \varepsilon_D(E) + \varepsilon_{CP}(E),
\]
where \( \varepsilon(E) \) is the total complex dielectric function of silver at energy \( E \), \( \varepsilon_{1o} \) is the photon energy independent contribution to the real part of the dielectric function, \( \varepsilon_D(E) \) is the Drude contribution, and \( \varepsilon_{CP}(E) \) is the CP contribution.

### 3.4.1 Room Temperature Deposition and Measurement

Figure 3.9 shows the inverted and best fit parameterized dielectric functions for two of the samples, namely DS005 and DS017, having final surface roughness layer thicknesses of 6 Å and 10 Å, respectively. The structural evolution was presented earlier for these samples. The best fit dielectric functions are obtained using a Drude term and a single CP oscillator term, along with a constant contribution to the real part of the dielectric function, designated \( \varepsilon_{1o} \), as described in Eq. (3.3). Both samples in Fig. 3.9 were deposited and measured at room temperature; however, sample DS005 was deposited at an Ar pressure of 4 mTorr whereas DS017 was deposited at 10 mTorr. Even at room temperature, variations of Ar pressure or RF power are expected to produce Ag films with different optical and electrical properties due to differences in the resulting grain structure of the polycrystalline films. A comparison of the best fit parameterized dielectric functions at room temperature is presented in Figure 3.10 for four Ag thin films deposited at room temperature. The sample designated DS031 was deposited on a room temperature oxidized Si wafer substrate that was annealed prior to Ag deposition. For this sample, the deposition conditions included an Ar pressure of 4 mTorr and an RF power level of 50 W.

From Figure 3.10, the effects of variations in the deposition conditions on the optical properties of silver thin films are clearly evident even for the set of films deposited at room temperature. The real parts of dielectric functions, \( \varepsilon_1 = n^2 - k^2 \), are...
dominated by the increasing k with decreasing photon energy. These spectra are similar for all four samples with minimum values in the range of of $\varepsilon_1 = -155$ to $-145$ at the lowest photon energy of 0.75 eV. The imaginary parts of dielectric functions $\varepsilon_2 = 2nk$ differ due to differences in the index of refraction. The $\varepsilon_2$ spectra for the films appear to be correlated with the surface roughness thickness. Two of the smooth samples, those labeled DS031 and DS005, having surface roughness layers with thicknesses $d_s$ of 4 Å and 6 Å, respectively, exhibit a higher magnitude $\varepsilon_2$ compared with the other two rougher samples, DS017 and DS020 with $d_s$ values of 10 Å and $d_s = 12$ Å, respectively.

For additional insights into the optical behavior for these four room temperature samples, Table 3.2 lists all the oscillator parameters along with the Drude plasma energy that describe the best fits to the dielectric functions obtained by inversion. The smoother samples, DS031 and DS005, have a smaller Drude amplitude and larger broadening (~1200 eV, ~0.07 eV) compared to the slightly rougher samples, DS017 and DS020 (~1800 eV, ~0.04 eV). The effects balance to give a similar plasma energy for all samples within confidence limits. In spite of the difference in the Drude parameters $A$ and $\Gamma$, the parameters that describe the CP oscillator show no similar clear trends.

It is of interest to contrast the deposition conditions for the two pairs of samples. Sample DS017 was deposited with higher Ar sputtering pressure of 10 mTorr, whereas all other samples were deposited at 4 mTorr. For sample DS020, the RF power applied to the target was reduced to 25 W from the 50 W level used for other samples. The reduced broadening parameters for samples DS017 and DS020 are an indication of a longer scattering time \( \tau \) for free electrons. A longer \( \tau \) in turn may imply a lower crystalline defect density or a larger average crystalline grain size. Thus, the results suggest that
either an increase in Ar pressure above the minimum value of 4 mTorr or a reduction in
the deposition rate can lead to an improvement in film quality. Evidently depositions at
low pressures lead to high bombardment energies and crystalline defects that become
trapped within the film when growth occurs at high rates. The longest scattering time
from among these samples is obtained for DS020 deposited at the lower power and, thus,
lowest deposition rate.

Figure 3-9: The dielectric functions of silver are presented for the two samples of Fig. 3.4
(DS005, top panels; and DS017, bottom panels) determined by two-step inversion and
least-square regression, followed by iteration for global minimization of the error
function (points). The solid lines represent the fits of the inverted dielectric functions
using an analytical formula combining an energy independent contribution to $\varepsilon_1$, a Drude
free electron term, and a CP oscillator.
Table 3.2: Drude and CP parameters are tabulated for Ag samples deposited at room temperature. The samples DS031 Ag and DS005 Ag have identical parameters within the confidence limits, but these parameters are different from those of samples DS017 and DS020, which are more closely similar to one another. The $\varepsilon_1$ offset $\varepsilon_{10}$ is a real constant added to $\varepsilon_1$ in the analytical expression for the dielectric function. A constant in excess of unity can account for optical transitions well above the energy range of analysis. This value was fixed to the numerical value of unity for all samples. Similarly, the exponent $\mu$ of the CP oscillator is fixed to the value of 0.309±0.006 for all samples deposited and measured at room temperature; the phase $\theta$ is fixed also to a value of 0.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Drude A (eV)</th>
<th>Drude $\Gamma$(eV)</th>
<th>Plasma Energy $E_p$(eV)</th>
<th>CP A</th>
<th>CP $E_g$(eV)</th>
<th>CP $\Gamma$(eV)</th>
<th>CP $\theta$(°)</th>
<th>CP $\mu$</th>
<th>$\varepsilon_{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DS031 Ag</td>
<td>1197.1±11.0</td>
<td>0.0714±0.0007</td>
<td>9.245±0.088</td>
<td>6.471±0.090</td>
<td>4.151±0.007</td>
<td>0.328±0.017</td>
<td>0 Fixed</td>
<td>0.309 Fixed</td>
<td>1 Fixed</td>
</tr>
<tr>
<td>DS005 Ag</td>
<td>1201.3±27.8</td>
<td>0.0716±0.0017</td>
<td>9.274±0.218</td>
<td>6.403±0.246</td>
<td>4.131±0.018</td>
<td>0.286±0.041</td>
<td>0 Fixed</td>
<td>0.309 Fixed</td>
<td>1 Fixed</td>
</tr>
<tr>
<td>DS017 Ag</td>
<td>1745.7±31.9</td>
<td>0.0475±0.0009</td>
<td>9.106±0.170</td>
<td>6.335±0.119</td>
<td>4.138±0.009</td>
<td>0.308±0.022</td>
<td>0 Fixed</td>
<td>0.309 Fixed</td>
<td>1 Fixed</td>
</tr>
<tr>
<td>DS020 Ag</td>
<td>1868.2±36.1</td>
<td>0.0438±0.0008</td>
<td>9.046±0.170</td>
<td>6.377±0.116</td>
<td>4.133±0.009</td>
<td>0.297±0.020</td>
<td>0 Fixed</td>
<td>0.309 Fixed</td>
<td>1 Fixed</td>
</tr>
</tbody>
</table>

Physical information about the Ag film can be extracted through further manipulations of the best fit Drude parameters used in the analytical expressions. The scattering time $\tau$ and dc resistivity $\rho_0 = 1/\sigma_0$ can be deduced by applying the relationship between the photon energy dependent ac conductivity and the dielectric function

$$
\sigma(E) = \frac{iE}{4\pi\hbar} [1 - \varepsilon(E)] = \frac{\sigma_0}{4\pi\varepsilon_0} \frac{1}{(1 - i\varepsilon_0 E \tau/\hbar)} ,
$$

where $\sigma_0$ is the dc conductivity, $\hbar = h/2\pi$ is Planck's constant, and $\varepsilon_0$ is the permittivity of free space. Substitution of Eq. (3.1) into Eq. (3.4) yields the following results
The plasma energy for the Ag, obtained from the plasma frequency by \( E_p = \hbar \omega_p \), is given simply by:

\[
E_p = (A \Gamma)^{1/2}, \tag{3.5c}
\]
as noted earlier. The carrier concentration can be determined according to

\[
N = \frac{m_0}{e^2 \tau \rho_0}, \tag{3.6}
\]
but only if the electron effective mass \( m_0 \) is known, where \( e \) is the charge of the electron. Finally, the carrier mobility is given by

\[
\mu_0 = \frac{e \tau}{m_0}, \tag{3.7}
\]
which also requires the effective mass. The effective mass can be estimated by solving Eq. (3.6) for \( m_0 \) and entering the carrier concentration deduced in a Hall effect measurement.

The results for \( E_p, \rho_0, \tau, N, \) and \( \mu_0 \) are presented in Table 3.3. In the determination of \( N \) and \( \mu_0 \), the effective mass for silver was taken as \( m_0 = 0.96 m_e \) (Johnson and Christy, 1972). The samples DS017 and DS020, which are deposited at room temperature with elevated Ar pressure or reduced plasma power, have lower resistivity and longer scattering time compared to samples DS005 and DS031 leading to lower energy dissipation. Applying the known crystal structure of Ag and a valence of unity, one calculates a carrier concentration of single crystal Ag of \( 5.86 \times 10^{22} \text{ cm}^{-3} \). In
fact, the average value of the four results in Table 3.3 is $5.85 \times 10^{22} \text{ cm}^{-3}$, very close to that predicted for single crystal Ag. The fact that the two samples DS031 and DS005 exhibit a carrier concentration higher than the single crystal prediction may arise from an inaccurate effective mass. In fact, a mass of $m_0 = 0.94 m_e - 0.95 m_e$ would yield agreement with the single crystal value of $N$ for these two samples. Another possibility is that Ag films sputter-deposited at low Ar pressure exhibit compressive strain and a higher atomic density than the single crystal, which would lead to a higher electron concentration. The lower values of $N$ in Table 3.3 for samples DS017 and DS020 may arise from a higher void fraction relative to the single crystal, but other effects such as tensile strain may contribute. The overall results suggest that the optical measurement and modeling are correctly determining the Drude free carrier absorption characteristic, and that there are no significant lower energy resonances contributing to this absorption.

The dc electrical resistivity of single crystal Ag near room temperature is known to follow the relationship

$$\rho = \rho_0 \left(\frac{T}{T_0}\right)^n$$

(3.8)

where $T_0 = 273 \text{ K}$, $\rho_0 = 1.46 \times 10^{-6} \Omega \text{ cm}$, and $n = 1.11$ (Kasap, 2006). At room temperature of $T = 295 \text{ K}$ where the measurements of Table 3.3 were obtained, the resulting resistivity is $1.59 \times 10^{-6} \Omega \text{ cm}$. The lowest resistivity among the samples of Table 3.3 is $3.98 \times 10^{-6} \Omega \text{ cm}$ (sample DS020), and the highest resistivity is $6.21 \times 10^{-6} \Omega \text{ cm}$ (sample DS031).

The difference between the single crystal and thin film results can be attributed to the polycrystalline nature of the thin films fabricated in this research. Mathiessen's rule
(Kasap, 2006) proposes that for independent scattering mechanism, in this case scattering by phonons and by grain boundaries, then \( \tau^{-1} = \tau_c^{-1} + \tau_g^{-1} \). Here \( \tau \) is the scattering time for the polycrystalline thin film, \( \tau_c \) is the scattering time for the single crystal, and \( \tau_g = \frac{R}{v_f} \) describes the effect of scattering by grain boundaries with \( R \) being the grain radius and \( v_f \) being the Fermi speed. Thus, a grain radius can be estimated based on this model as

\[
R = \frac{v_f \tau_c}{\tau_c - \tau}.
\] (3.9)

To take this model further, \( \tau_c \) is required. This value can be deduced from the Drude equation

\[
\tau_c = \frac{m_0}{N e^2 \rho_0},
\] (3.10)

where \( m_0 \) for single crystal Ag is given by \( m_0 = 0.96 \, m_e \). \( N \) calculated from the crystal structure assuming a valence of unity is \( 5.86 \times 10^{28} \, m^{-3} \), and \( \rho_0 = 1.59 \times 10^{-8} \, \Omega \cdot m \), as obtained from Eq. (3.8). Equation (3.10) yields \( \tau_c \) given by \( \tau_c = 36.6 \, \text{fs} \), and from the Fermi speed of \( 1.39 \times 10^6 \, \text{m/s} \), a grain size of \( R \approx 170 \, \text{Å} \) is found for sample DS005 and \( R \approx 355 \, \text{Å} \) for DS020. The other two samples lie within the range of 170-355 Å with DS031 near the lower limit and DS017 near the upper limit. An alternative interpretation of \( R \) is that it represents the mean free path of the electrons whereby the limiting scattering is from crystalline point and planar defects other than grain boundaries.
Figure 3-10: Analytical expressions are plotted that describe the real (upper) and imaginary (lower) parts dielectric functions of four silver thin films deposited at room temperature. These results are obtained in best fits to the dielectric functions from inversion using the expressions in Eqs. (3.1) and (3.2) with parameters given in Table 3.2.
Table 3.3: Drude parameters are tabulated for silver samples deposited at room temperature. The parameters $A$ and $\Gamma$ are determined from a fit to the inverted dielectric function over the complete spectral range of $0.75 - 5$ eV. The remaining parameters are determined from $A$ and $\Gamma$ using Equations (3.5)-(3.7). The carrier concentration $N$ and mobility $\mu$ require the effective mass $m_0$ which is assumed to be $m_0 = 0.96m_e$.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$0.75 - 5$ eV</th>
<th>Drude $A$ (eV)</th>
<th>Drude $\Gamma$ (eV)</th>
<th>Plasma Energy $E_p$ (eV)</th>
<th>Resistivity $\rho_0$ (Ω-cm)</th>
<th>Scattering Time $\tau$ (fs)</th>
<th>Carrier Concentration $N$ (cm$^{-3}$)</th>
<th>Carrier Mobility $\mu_0$ (cm$^2$V$^{-1}$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DS031</td>
<td>$d_s = 4$ Å</td>
<td>1197.1 ± 11.0</td>
<td>0.0714 ± 0.0007</td>
<td>9.245 ± 0.088</td>
<td>6.210 x10$^{-6}$ ± 0.057x10$^{-6}$</td>
<td>9.219 ± 0.087</td>
<td>5.951 x10$^{22}$ ± 0.003 x10$^{22}$</td>
<td>16.890 ± 0.156</td>
</tr>
<tr>
<td>DS005</td>
<td>$d_s = 6$ Å</td>
<td>1201.3 ± 27.8</td>
<td>0.0716 ± 0.0017</td>
<td>9.274 ± 0.218</td>
<td>6.191 x10$^{-6}$ ± 0.143x10$^{-6}$</td>
<td>9.194 ± 0.022</td>
<td>5.989 x10$^{22}$ ± 0.015 x10$^{22}$</td>
<td>16.843 ± 0.391</td>
</tr>
<tr>
<td>DS017</td>
<td>$d_s = 10$ Å</td>
<td>1745.7 ± 31.9</td>
<td>0.0475 ± 0.0009</td>
<td>9.106 ± 0.170</td>
<td>4.260 x10$^{-6}$ ± 0.078x10$^{-6}$</td>
<td>13.872 ± 0.257</td>
<td>5.768 x10$^{22}$ ± 0.003x10$^{22}$</td>
<td>25.413 ± 0.465</td>
</tr>
<tr>
<td>DS020</td>
<td>$d_s = 12$ Å</td>
<td>1868.2 ± 36.1</td>
<td>0.0438 ± 0.0008</td>
<td>9.046 ± 0.170</td>
<td>3.980 x10$^{-6}$ ± 0.077x10$^{-6}$</td>
<td>15.039 ± 0.294</td>
<td>5.694 x10$^{22}$ ± 0.003x10$^{22}$</td>
<td>27.552 ± 0.533</td>
</tr>
</tbody>
</table>

Table 3.4: Tabulation of Drude parameters $\varepsilon_{10}$, $A$, and $\Gamma$ deduced from fits to dielectric function of Ag deposited at room temperature. The inverted dielectric function in this case was modeled below 3.5 eV by using a Drude term and a variable constant contribution $\varepsilon_{10}$. The plasma energy $E_p$, the resistivity $\rho_0$, and the scattering time $\tau$ were determined from $A$ and $\Gamma$ via Eqs. (3.5).

<table>
<thead>
<tr>
<th>Samples</th>
<th>MSE</th>
<th>$\varepsilon_{10}$</th>
<th>Drude $A$ (eV)</th>
<th>Drude $\Gamma$ (eV)</th>
<th>Plasma Energy $E_p$ (eV)</th>
<th>Resistivity $\rho_0$ (Ω-cm)</th>
<th>Scattering Time $\tau$ (fs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DS031</td>
<td>0.247</td>
<td>4.263 ± 0.056</td>
<td>1203.6 ± 13.3</td>
<td>0.0715 ± 0.0008</td>
<td>9.28 ± 0.10</td>
<td>6.177x10$^{-6}$ ± 0.068x10$^{-6}$</td>
<td>9.201 ±0.101</td>
</tr>
<tr>
<td>DS005</td>
<td>0.599</td>
<td>4.136 ± 0.143</td>
<td>1209.7 ± 33.6</td>
<td>0.0716 ± 0.0020</td>
<td>9.31 ± 0.26</td>
<td>6.150x10$^{-6}$ ± 0.171x10$^{-6}$</td>
<td>9.197 ±0.254</td>
</tr>
<tr>
<td>DS017</td>
<td>0.338</td>
<td>4.119 ± 0.069</td>
<td>1748.9 ± 37.0</td>
<td>0.0477 ± 0.0010</td>
<td>9.13 ± 0.19</td>
<td>4.252x10$^{-6}$ ± 0.090x10$^{-6}$</td>
<td>13.805 ±0.293</td>
</tr>
<tr>
<td>DS020</td>
<td>0.305</td>
<td>4.101 ± 0.063</td>
<td>1870.1 ± 39.1</td>
<td>0.0440 ± 0.0009</td>
<td>9.07 ± 0.19</td>
<td>3.977x10$^{-6}$ ± 0.083x10$^{-6}$</td>
<td>14.955 ±0.313</td>
</tr>
</tbody>
</table>
Later in this dissertation in Chapters 5 and 6, the results of a study will be presented that focuses on the plasmons confined within protrusions at the interfaces between Ag and ZnO and between Ag and an aqueous etching solution that removes the ZnO. A simple equation for the resonance energy of this plasmon can be derived by substituting the Drude expression, including an \( \varepsilon_1 \) offset, into the Maxwell-Garnett effective medium approximation with the ambient medium as the host. Approximations lead to a Lorentz oscillator which accounts for the plasmon band and whose resonance energy depends on the Ag plasma energy, the \( \varepsilon_1 \) offset, the volume fraction of Ag, and the dielectric function of the ambient. The \( \varepsilon_1 \) offset \( \varepsilon_{1o} \) as well as the Drude parameters \( A \) and \( \Gamma \) were determined by modeling the dielectric functions of Ag below 3.5 eV. As a result of this spectral range restriction, the dielectric function expression that combines Eqs. (3.1) and (3.2) could be simplified by replacing the high energy interband critical point term by the variable constant contribution \( \varepsilon_{1o} \).

Table 3.4 shows that for this modeling approach the \( \varepsilon_{1o} \) values for all samples deposited at room temperature are within the range \( \sim 4.18 \pm 0.08 \), and the Ag plasma energy values deduced from \( A \) and \( \Gamma \) are within the range \( \sim 9.18 \pm 0.11 \) eV. Thus, the results in Table 3.4 provide values that can be used to determine the Lorentz oscillator energy and provide estimates of the confined plasmon resonance energies in Chapters 5 and 6. Table 3.4 also includes the derived parameters of \( \rho_0 \) and \( \tau \). A comparison of Tables 3.3 and 3.4 shows that the Drude parameters, \( A \), \( \Gamma \), \( \rho_0 \) and \( \tau \), do not change significantly when the photon energy range for fitting is reduced from 0.75 - 5 eV to 0.75 – 3.5 eV.
As the main focus of this dissertation research is the back-reflector used for the thin film Si:H solar cell, an understanding of the reflectance of these silver thin films is important. Figures 3.11 and 3.12 show the simulated normal-incidence reflectance spectra for four Ag samples deposited at room temperature. In these calculations, two different models of the surface are used. Figure 3-11 shows the simulated reflectance incorporating the complete model for each sample, which includes the opaque Ag inverted dielectric function and the surface roughness layer. Figure 3-12 shows the reflectance spectra for the smoothest sample (DS031) and roughest sample (DS020) among those prepared at room temperature. These results were generated with a model assuming no surface roughness layer, based on a calculation directly from the bulk layer dielectric function, and compared with those generated using the complete model as in Figure 3-11. Thus, the results in Figure 3-12 show the effect of the addition of roughness layers 4 Å and 12 Å in thickness on the reflectance spectra for samples DS031 and DS020, respectively.

As expected for these smooth Ag thin films deposited at room temperature, the spectra in all cases do not differ significantly on the largest reflectance scale shown (top panels). This may not be the case for silver films that are rougher, and this aspect will be discussed in detail later in this chapter. One observation from Figure 3-11 (expanded scale, lower panel) is that the reflectance for the samples DS017 and DS020 are slightly higher over the range of back-reflector operation than samples DS031 and DS005. This result is due to the longer scattering time for the former samples, which reduces the dissipation rate and the absorption losses. A second observation made from Figure 3-12
(expanded scale, lower panel) is that the reflectance decreases with the addition of roughness, but only at the higher energies above 1.5 eV.

Figure 3-11: Simulations of the normal incidence reflectance spectra are shown for smooth silver thin films deposited at room temperature. Both panels show the reflectance generated by considering the complete model of the Ag film, including the surface roughness layer. The bottom panel uses an expanded scale so that the sample trends can be identified.
Figure 3-12: Simulations of normal incidence reflectance spectra are shown for two silver thin films deposited at room temperature, DS031 and DS020, which exhibit 4 Å and 12 Å thick surface roughness (SR) layers, respectively. Both panels show the reflectance spectra generated by the bulk Ag components only, i.e. removing the surface roughness layers from the models, in comparison with the reflectance spectra for the sample structures including the surface roughness layers in the model.
3.4.2 Elevated Temperature Depositions and Measurement

3.4.2.1 Bruggeman EMA Model for the Surface Roughness Layer

Dielectric Function

The silver thin films deposited on c-Si substrates at elevated temperatures will be considered in this subsection. Figures 3-13, 3-14 and 3-15 (points) show the real and imaginary parts of dielectric functions obtained by inversion for the three Ag samples, DS013 (50°C), DS021 (87°C), and DS028 (190°C). The method of Fig. 3.3 has been used for the inversions, applying the Bruggeman EMA model for the dielectric function of the surface roughness layer in each case. The inverted dielectric functions of the films deposited at elevated temperatures exhibit low energy features in the range of 1.2 - 1.6 eV. Thus if the dielectric functions are to be closely fit for these samples, the analytical model requires not only the Drude term for the free electron characteristic and the generalized critical point oscillator for the interband absorption onset near 4 eV, but also a second low energy oscillator in the range of 1.2 - 1.6 eV.

Best fit results applying this model are shown as the solid lines in Figures 3-13 - 15. Figure 3-16 provides a comparison of the analytical functions that best fit the inverted dielectric functions for Ag samples deposited at increasing substrate temperatures from room temperature (DS031) to 190°C (DS028) for which the surface roughness on the films increases significantly. Table 3.5 provides the best fit parameters associated with the Drude and two generalized critical point oscillators, and Table 3.6 provides the derived parameters associated with the Drude term. Because the spectroscopic ellipsometry measurements were performed at the substrate temperature, which is different in each case, the best fit dielectric functions can be compared
quantitatively only if the intrinsic temperature dependence of the optical properties is taken into account. The qualitative discussion below focuses on differences that are either sufficiently large that they cannot be accounted for by the variation in measurement temperature, or trends that due to their nature cannot be attributed to measurement temperature.

In the comparison of Fig. 3-16, the real parts $\varepsilon_1$ of the dielectric function spectra are observed to be similar in shape for the samples deposited and measured at 87°C and below. For the sample deposited and measured at 190°C (DS028), however, $\varepsilon_1$ decreases more gradually with decreasing photon energy and, as a result, is significantly larger (less negative) at the lowest energy. The effect of deposition temperature is also clearly evident in the imaginary parts $\varepsilon_2$ of the dielectric function spectra. The spectra at low energies in general reflect the characteristics of the Drude term. When the substrate temperature is increased from 50°C to 87°C, Table 3.5 shows that the amplitude of the Drude term in the dielectric function increases and the broadening decreases. For the increase in substrate temperature from 87 °C to 190°C, however, the opposite behavior is observed. The resonance energy of the low energy oscillator is observed to red-shift over the range from 1.6 to 1.2 eV as the deposition temperature increases. In addition to the red-shift, this oscillator increases in amplitude and broadens monotonically with increasing substrate temperature.

If the bulk layer dielectric function truly arises from the sub-surface and does not include a roughness layer component, then one would not expect an oscillator feature in the range of 1.2 to 1.6 eV, i.e., below the interband transition near 4 eV. In fact, there are no band-to-band transitions in bulk Ag in the range identified for the low energy
oscillator of the rougher silver films of Figs. 3-13 to 15. One may consider that the low energy resonance in the bulk Ag layer is due to a bulk plasmonic effect. Electromagnetic waves being transverse in nature, however, cannot excite bulk plasmons. Furthermore, electromagnetic waves cannot excite propagating surface plasmons, unless macroscopic roughness exists that provides a momentum vector, as in the case of a grating coupler. Thus, it is more likely that the resonances are confined plasmons, not within the bulk layer, but within a surface roughness component. If the roughness layer itself is approaching opacity, the single-layer model used to analyze the ($\psi$, $\Delta$) spectra may force the roughness layer into two components – a near roughness surface layer and an underlying roughness layer. In this case, low energy resonance features having plasmon origins may be observed in the optical properties of both layers.

One should keep in mind that at higher deposition temperature the bulk dielectric function may change, but in addition, the optical properties of the roughness layer may require a modified model because of the increased roughness layer thickness. As described earlier in Section 3.3, which addressed the evolution of the Ag structure, the Bruggeman EMA has been used to model the surface roughness of silver samples deposited at both room temperature and elevated temperatures in order to extract the dielectric functions of Figures 3-13 to 15. In view of the low energy oscillator features observed in these bulk layer dielectric functions, one may consider using the Maxwell-Garnett effective medium theory (EMT) to determine the surface roughness layer dielectric function when the roughness layer increases in thickness. With such a new surface roughness model, the bulk layer dielectric function could then be obtained by numerical inversion to determine if the low energy features persist.
In following the procedure described in the previous paragraph, however, the least squares regression analyses performed using the Maxwell-Garnett EMT yield a much higher mean-squared error (MSE). Because of this, the surface roughness thickness and optical properties determined using the Bruggeman EMA are believed to present a more accurate representation of the roughness layer in spite of the appearance of the low energy features of the bulk layer dielectric function. Furthermore, in a comparison of the ellipsometry-derived surface roughness thickness with the AFM-derived root-mean-square (rms) surface roughness, the former value determined using the Bruggeman EMA yielded better agreement (see Fig. 3.7). It is interesting to note that the value of the surface roughness thickness determined using the Maxwell-Garnett effective medium theory is almost double that of the AFM rms roughness value (Dahal, 2013).
Figure 3-13: Real and imaginary parts of the dielectric functions are shown for Ag sample DS013 deposited at a substrate temperature of 50°C. The solid lines represent a fit of the inverted bulk layer dielectric function (points) using an analytical formula combining a Drude free electron term and two CP oscillators. The inversion was performed using a dielectric function for the 28 Å thick surface roughness layer defined using the Bruggeman EMA.
Figure 3-14: Real and imaginary parts of the dielectric functions are shown for Ag sample DS021 deposited at a substrate temperature of 87°C. The solid lines represent a fit of the inverted bulk layer dielectric function (points) using an analytical formula combining a Drude free electron term and two CP oscillators. The inversion was performed using a dielectric function for the 55 Å thick surface roughness layer defined using the Bruggeman EMA.
Figure 3-15: Real and imaginary parts of the dielectric functions are shown for Ag sample DS028 deposited at a substrate temperature of 190°C. The solid lines represent a fit of the inverted bulk layer dielectric function (points) using an analytical formula combining a Drude free electron term and two CP oscillators. The inversion was performed using a dielectric function for the 105 Å thick surface roughness layer defined using the Bruggeman EMA.
Figure 3-16: The real and imaginary parts of dielectric functions are shown for silver deposited at various substrate temperatures. Each pair of spectra in this figure represents an analytical expression with parameters found to generate a dielectric function that best fits the results obtained by numerical inversion. The expression includes a Drude term and a generalized critical point oscillator near 4.0 eV. A second oscillator with a resonance energy in the range of 1.2 - 1.6 eV was used for the three samples deposited at elevated temperatures, DS013, DS021, and DS028.
Table 3.5: Drude and critical point parameters for Ag samples deposited and measured at varying temperatures are shown: DS031 at room temperature, DS013 at 50°C, DS021 at 87°C, and DS028 at 190°C. For the higher temperature samples, a second CP oscillator is incorporated to model the inverted dielectric functions.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Drude A (eV)</th>
<th>Drude Γ(eV)</th>
<th>CP A</th>
<th>CP E(_p) (eV)</th>
<th>CP Γ(eV)</th>
<th>CP θ (°)</th>
<th>CP (\mu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DS031 T = RT</td>
<td>1197.1 ±11.0</td>
<td>0.0714 ±0.0007</td>
<td>6.471 ±0.090</td>
<td>4.151 ±0.007</td>
<td>0.328 ±0.017</td>
<td>0 Fixed</td>
<td>0.309 Fixed</td>
</tr>
<tr>
<td>DS013 T = 50°C</td>
<td>1422.4 ±24.2</td>
<td>0.0625 ±0.0011</td>
<td>6.649 ±0.130</td>
<td>4.153 ±0.012</td>
<td>0.377 ±0.029</td>
<td>0 Fixed</td>
<td>0.309 Fixed</td>
</tr>
<tr>
<td>2nd CP</td>
<td>0.964 ±0.115</td>
<td>1.618 ±0.058</td>
<td>0.966 ±0.143</td>
<td>0 Fixed</td>
<td>2.117 ±0.143</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DS021 T = 87°C</td>
<td>1703.4 ±59.7</td>
<td>0.0517 ±0.0018</td>
<td>7.291 ±0.153</td>
<td>4.152 ±0.012</td>
<td>0.379 ±0.031</td>
<td>0 Fixed</td>
<td>0.309 Fixed</td>
</tr>
<tr>
<td>2nd CP</td>
<td>4.409 ±0.122</td>
<td>1.474 ±0.015</td>
<td>1.209 ±0.062</td>
<td>0 Fixed</td>
<td>1.240 Fixed</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DS028 T = 190°C</td>
<td>655.9 ±34.0</td>
<td>0.0984 ±0.0056</td>
<td>8.584 ±0.227</td>
<td>4.115 ±0.031</td>
<td>1.027 ±0.090</td>
<td>0 Fixed</td>
<td>0.309 Fixed</td>
</tr>
<tr>
<td>2nd CP</td>
<td>17.430 ±0.394</td>
<td>1.186 ±0.020</td>
<td>1.886 ±0.052</td>
<td>0 Fixed</td>
<td>1.240 Fixed</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.6: Comparison are made for the free electron Drude parameters and associated derived results for Ag samples of Table 3.5 deposited and measured over a range of substrate temperatures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Drude A (eV)</th>
<th>Drude Γ(eV)</th>
<th>Plasma Energy (E_p) (eV)</th>
<th>Resistivity (\rho) (Ω-cm)</th>
<th>Scattering Time (\tau) (fs)</th>
<th>Carrier Concentration (N) (cm(^{-3}))</th>
<th>Carrier Mobility (\mu) (cm(^2)V(^{-1})s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>DS031 T = RT</td>
<td>1197.1 ±11.0</td>
<td>0.0714 ±0.0007</td>
<td>9.245 ±0.088</td>
<td>6.210 x 10(^{-6}) ± 0.057 x 10(^{-6})</td>
<td>9.219 ± 0.087</td>
<td>5.951 x 10(^{22}) ± 0.003 x 10(^{22})</td>
<td>16.890 ± 0.156</td>
</tr>
<tr>
<td>DS013 T = 50°C</td>
<td>1422.4 ±24.2</td>
<td>0.0625 ±0.0011</td>
<td>9.43 ± 0.16</td>
<td>5.227 x 10(^{-6}) ± 0.089 x 10(^{-6})</td>
<td>10.534 ± 0.185</td>
<td>6.189 x 10(^{22}) ± 0.003x10(^{22})</td>
<td>19.300 ± 0.329</td>
</tr>
<tr>
<td>DS021 T = 87°C</td>
<td>1703.4 ±59.7</td>
<td>0.0517 ±0.0018</td>
<td>9.38 ± 0.33</td>
<td>4.369 x 10(^{-6}) ± 0.153 x 10(^{-6})</td>
<td>12.746 ± 0.444</td>
<td>6.129 x 10(^{22}) ± 0.004x10(^{22})</td>
<td>23.335 ± 0.807</td>
</tr>
<tr>
<td>DS028 T = 190°C</td>
<td>655.9 ±34.0</td>
<td>0.0984 ±0.0056</td>
<td>8.03 ± 0.44</td>
<td>11.364 x 10(^{-6}) ± 0.589 x 10(^{-6})</td>
<td>6.710 ± 0.382</td>
<td>4.493 x 10(^{22}) ± 0.0131x10(^{22})</td>
<td>12.259 ± 0.507</td>
</tr>
</tbody>
</table>
3.4.2.2 Analytical Model for the Surface Roughness Layer Dielectric Function

It should be emphasized that as a metal film becomes increasingly rough, the ellipsometric spectra \((\psi, \Delta)\) are increasingly dominated by the surface roughness layer and less influenced by the bulk layer, especially at low photon energies where the absorption depth is so low. Because of this effect, the use of an effective medium theory (EMT) to describe the roughness layer dielectric function excessively constrains the data analysis. Because the EMT is an approximation, it is designed to correct for the effects of a thin roughness layer as a perturbation in determining the bulk layer dielectric function from \((\psi, \Delta)\). When the roughness layer becomes too thick and its dielectric function is over-simplified, the resulting artifacts are projected onto the bulk layer dielectric function obtained in the inversion. Based on such an argument, it is important to assess the possibility that the low energy features in the bulk layer dielectric functions [as seen in Figure 3-16] are artifacts of an inadequate surface layer dielectric function.

In an attempt to represent correctly the bulk layer dielectric functions of Ag thin films that were deposited at elevated substrate temperatures, the model applied to the three samples DS013, DS021, and DS028 was reconsidered. The schematic of the alternative model is shown in Figure 3-17.

The parameterized form of the Ag bulk layer dielectric function for the three samples deposited at elevated temperatures, consisting of a Drude and a CP oscillator, was adopted from sample DS031, the film deposited at room temperature that exhibits the smoothest surface. In this procedure, the Drude parameters for the three samples were fixed at the values obtained from sample DS031 for the appropriate measurement.
temperature, as deduced in the annealing experiment described in Sec. 3.4.3 (see Table 3.10). The CP oscillator parameters of the bulk layers of the three samples were handled in different ways as indicated in Table 3.8. The CP amplitudes were fixed as those from sample DS031, accounting for the appropriate variations in the measurement temperature (again, see Table 3.10); the resonance energies and widths were linked to the corresponding parameters of the surface roughness layer; and the phases and exponents were assigned the fixed values used throughout the analysis of sample DS031 in Section 3.4.3. In summary, this approach to represent the dielectric functions of the bulk components of the three Ag films with rougher surfaces deposited at elevated temperatures relies heavily on the analysis of the smoothest sample DS031 performed at elevated measurement temperatures as provided in Table 3.10.

The dielectric functions of the surface roughness layers for the three samples deposited at elevated temperatures were modeled using a Lorentz as well as a CP oscillator to account for plasmon related bands and the interband transitions in Ag, respectively. In the development of the dielectric function model for the roughness layer, the free electrons as described by the Drude term of the bulk layer were replaced by those of the plasmon band as described by the Lorentz oscillator term which is now unique to the roughness layer. The interband transition CP should be included in the surface layer dielectric function model, as well, and its amplitude and exponent were allowed to vary independently in the analysis. The other CP parameters of the surface layer dielectric function were either varied independently but linked to those of the bulk layer, or fixed at the same values as the bulk layer, as indicated in Table 3.9.
Figure 3-17: An alternative model is depicted that is used to analyze Ag films deposited at elevated substrate temperatures. The surface roughness layer was modeled with Lorentz and CP oscillators, assuming that all free electrons are associated with confined plasmons as modeled by the Lorentz oscillator. The Drude component of the bulk layer dielectric function was chosen as that from the smoothest room temperature deposited Ag sample (DS031), and the CP oscillator parameters associated with this dielectric function were varied as follows. The bulk layer CP amplitudes were fixed as those of sample DS031 for the appropriate measurement temperature, the CP energies and widths were linked with the corresponding values of the roughness layer, and the phases and exponents were fixed. For the surface layer, the CP amplitudes and exponents were varied independently, and the phases were fixed.

Applying the new model as shown in Figure 3-17, the surface roughness layer thicknesses are given in Table 3.7 for comparison with the thicknesses deduced from the Bruggeman EMA. The MSEs for the two models are also included in this Table. For the sample DS021 with deposition and measurement temperatures of $T = 87^\circ$C, the fitting quality using the new model shows a significant improvement; however, for the higher and lower temperature samples a less significant degradation of the fitting quality is observed. Degradation of the fitting quality in the analysis using the alternative model is possibly due to use of fixed dielectric function parameters for the bulk layer. Additionally, it may not be appropriate to eliminate the free electron contribution from the surface roughness layer in this alternative model. The only way to address such
issues is to increase the number of parameters in the model. This has been attempted but the result is a destabilization of the fitting process due to correlations of the additional parameters. As a positive outcome, however, the roughness layer thickness trends in Table 3.7 remain unchanged. This indicates that the roughness layer thickness is a robust parameter and its variation does not depend sensitively on the choice of model for the surface layer dielectric function. The analytical expressions combining the fixed and best fitting parameters are plotted in Figure 3-18 for the Ag bulk layer dielectric function and in Figure 3-19 for the surface roughness layer dielectric function. The resulting fixed and best fit parameters for the various oscillators in each of the analytical expressions are shown in Tables 3.8 and 3.9.

Table 3.7: The surface roughness layer thicknesses for three Ag samples fabricated at elevated temperatures are compared. These results were obtained from two models for the surface roughness layer dielectric function, an analytical oscillator model and the conventional Bruggeman EMA model. The MSEs for the two models are also compared in the right-most column.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bruggeman EMA: surface roughness thickness (Å)</th>
<th>Lorentz + CP model: surface roughness thickness (Å)</th>
<th>Reduction in roughness thickness for Lorentz + CP model (%)</th>
<th>Bruggeman EMA: MSE</th>
<th>Lorentz + CP model: MSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>DS013</td>
<td>28 ± 4</td>
<td>22.7±0.3</td>
<td>19</td>
<td>11.15</td>
<td>12.34</td>
</tr>
<tr>
<td>T = 50°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DS021</td>
<td>55 ± 4</td>
<td>45.9±0.6</td>
<td>17</td>
<td>26.21</td>
<td>17.86</td>
</tr>
<tr>
<td>T = 87°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DS028</td>
<td>105 ± 5</td>
<td>75.6±0.6</td>
<td>28</td>
<td>10.10</td>
<td>17.48</td>
</tr>
<tr>
<td>T = 190°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Ag bulk layer dielectric functions are shown as the best fit analytical expressions for films deposited and measured at elevated substrate temperatures. These results were obtained by fitting ($\psi$, $\Delta$) spectra. In these alternative analyses, the low energy (1.2 – 1.6 eV) second oscillator was removed from the analytical model for the bulk Ag dielectric function. The Drude and CP amplitude parameters of the bulk dielectric function were fixed in the analysis to the values obtained at the corresponding temperatures in the annealing experiment of sample DS031 presented in Section 3.4.3. The other bulk layer CP oscillator parameters were handled as follows. The energy and broadening were varied but linked to the corresponding parameters of the surface layer, and the phase and exponent were fixed at the values used for sample DS031. In this analysis, the surface roughness layers of all three rougher silver films were fitted by using Lorentz and CP oscillators. The Lorentz oscillator component was used for evaluation of the possibility of a confined plasmon band associated with the surface layer, thus eliminating the feature from the bulk layer. The resulting analytical expressions for the dielectric functions of the surface roughness layers are plotted in Figure 3-19, and the parameters of both layers are given in Tables 3.8 and 3.9.
Figure 3-19: Analytical expressions are shown that describe the surface roughness layer dielectric functions for rougher Ag films deposited at elevated substrate temperatures. The surface roughness layers of all three Ag films were fitted for the possible presence of confined plasmons by using a Lorentz oscillator. A CP oscillator was also added to the expression for the roughness layer dielectric function in order to model the interband transitions, however, the best fit amplitudes were very small and the oscillators are not clearly visible on this scale.
Table 3.8: The parameters of the Drude and the CP oscillator terms that describe the bulk layer dielectric functions of Figure 3-18 are tabulated for Ag samples deposited at varying substrate temperatures: DS031 at room temperature, DS013 at 50°C, DS021 at 87°C, and DS028 at 190°C. In this analysis, the Drude and CP amplitude parameters of the bulk layer dielectric functions are fixed to the values of sample DS031 as obtained at the corresponding temperatures in the annealing experiment described in Section 3.4.3. The CP parameters including the exponent \( \mu \), phase \( \theta \), as well as the offset \( \varepsilon_{10} \) were fixed at the following values: \( \mu = 0.309 \); \( \theta = 0^\circ \); and \( \varepsilon_{10} = 1 \). In contrast to the analysis results of Table 3.5 and 3.6, the dielectric function of the surface roughness layer was modeled in this analysis using an analytical model incorporating both Lorentz and CP oscillators.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bulk layer: Drude A (eV)</th>
<th>Bulk layer: Drude ( \Gamma ) (eV)</th>
<th>Drude ( \rho_o ) (( \Omega ) cm)</th>
<th>( \tau ) (fs)</th>
<th>Bulk layer: CP A</th>
<th>Bulk and roughness layer: CP ( E_g ) (eV) (linked)</th>
<th>Bulk and roughness layer: CP ( \Gamma ) (eV) (linked)</th>
<th>Bulk and roughness: CP ( \theta ) ((^\circ))</th>
<th>Bulk layer: CP ( \mu )</th>
</tr>
</thead>
<tbody>
<tr>
<td>DS031</td>
<td>1197.1 ± 11.0</td>
<td>0.0714 ± 0.0007</td>
<td>9.245 ± 0.088</td>
<td>6.21 x 10(^{-6}) ± 0.06 x 10(^{-6})</td>
<td>9.22 ± 0.09</td>
<td>6.471 ± 0.090</td>
<td>4.151 ± 0.007</td>
<td>0.328 ± 0.017</td>
<td>Fixed</td>
</tr>
<tr>
<td>T = RT</td>
<td>4 Å</td>
<td>Fixed</td>
<td>Fixed</td>
<td>Fixed</td>
<td>Fixed</td>
<td></td>
<td>Fixed</td>
<td>Fixed</td>
<td>0.309 Fixed</td>
</tr>
<tr>
<td>DS013</td>
<td>1299.5</td>
<td>0.0655 Fixed</td>
<td>9.22</td>
<td>5.72 x 10(^{-6})</td>
<td>10.0</td>
<td>6.376 Fixed</td>
<td>4.008 ± 0.005</td>
<td>0.226 ± 0.004</td>
<td>Fixed</td>
</tr>
<tr>
<td>T =50°C</td>
<td>28 Å</td>
<td>Fixed</td>
<td>Fixed</td>
<td>Fixed</td>
<td>Fixed</td>
<td></td>
<td>Fixed</td>
<td>Fixed</td>
<td>0.309 Fixed</td>
</tr>
<tr>
<td>DS021</td>
<td>1285.4</td>
<td>0.0648 Fixed</td>
<td>9.13</td>
<td>5.78 x 10(^{-6})</td>
<td>10.2</td>
<td>6.112 Fixed</td>
<td>3.878 ± 0.011</td>
<td>0.157 ± 0.007</td>
<td>Fixed</td>
</tr>
<tr>
<td>T =87°C</td>
<td>55 Å</td>
<td>Fixed</td>
<td>Fixed</td>
<td>Fixed</td>
<td>Fixed</td>
<td></td>
<td>Fixed</td>
<td>Fixed</td>
<td>0.309 Fixed</td>
</tr>
<tr>
<td>DS028</td>
<td>674.0</td>
<td>0.1143 Fixed</td>
<td>8.77</td>
<td>11.03 x 10(^{-6})</td>
<td>5.76</td>
<td>5.216 Fixed</td>
<td>4.180 ± 0.008</td>
<td>0.515 ± 0.012</td>
<td>Fixed</td>
</tr>
<tr>
<td>T =190</td>
<td>105 Å</td>
<td>Fixed</td>
<td>Fixed</td>
<td>Fixed</td>
<td>Fixed</td>
<td></td>
<td>Fixed</td>
<td>Fixed</td>
<td>0.309 Fixed</td>
</tr>
</tbody>
</table>
Table 3.9: The Lorentz and CP oscillator parameters along with the offset $\varepsilon_{1o}$ that describe the dielectric functions of the surface roughness layers are tabulated for three Ag samples deposited at elevated substrate temperature. The Lorentz oscillator energies $E_0$ are fixed to the values obtained for the second CP oscillator of the bulk layer used in the earlier model of Tables 3.5 and 3.6. The surface layer CP $E_g$ and $\Gamma$ values are linked to those of the bulk layer, and the CP phase was fixed to zero or $180^\circ$ (DS021) in order to avoid negative $\varepsilon_2$ values that resulted when it was varied. All other parameters in the model including the Lorentz oscillator amplitude and width, and the CP amplitude and exponent were varied independently.

<table>
<thead>
<tr>
<th>Sample</th>
<th>New Surface Roughness Layer Thickness (Å)</th>
<th>Lorentz A</th>
<th>$E_0$ (eV) (fixed from Table 3.4)</th>
<th>$\Gamma$ (eV)</th>
<th>CP A</th>
<th>$E_g$ (eV) (linked to that of the bulk layer)</th>
<th>$\Gamma$ (eV) (linked to that of the bulk layer)</th>
<th>$\mu$</th>
<th>$\varepsilon_{1o}$</th>
<th>MSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>DS013</td>
<td>28 Å</td>
<td>22.67 ±0.25</td>
<td>10.69 ±0.41</td>
<td>1.60</td>
<td>0.704 ±0.028</td>
<td>0.0935 ±0.0167</td>
<td>4.008 ±0.005</td>
<td>0.226 ±0.004</td>
<td>0.776 ±0.051</td>
<td>1 Fixed</td>
</tr>
<tr>
<td>DS021</td>
<td>55 Å</td>
<td>45.94 ±0.58</td>
<td>9.81 ±0.31</td>
<td>1.47</td>
<td>0.921 ±0.030</td>
<td>0.0604 ±0.0166</td>
<td>3.878 ±0.011</td>
<td>0.157 ±0.007</td>
<td>0.992 ±0.113</td>
<td>1 Fixed</td>
</tr>
<tr>
<td>DS028</td>
<td>105 Å</td>
<td>75.56 ±0.63</td>
<td>21.83 ±0.36</td>
<td>1.19</td>
<td>1.509 ±0.030/4</td>
<td>2.2537 ±0.0776</td>
<td>4.180 ±0.008</td>
<td>0.515 ±0.012</td>
<td>0.201 ±0.025</td>
<td>1 Fixed</td>
</tr>
</tbody>
</table>

When considering this complicated fitting procedure for the dielectric function parameters of both the bulk and surface layers for the set of Ag films deposited at elevated temperatures, the general outcome is consistent with the expectation that several parameters must be fixed in order to ensure convergence of the analysis program. For all samples, it is a challenge to determine the bulk and surface roughness layer dielectric function parameters independently, due to correlation of the parameters associated with the two layers.

As a result, the Drude parameters of the underlying bulk layer were fixed to the values obtained for sample DS031, which was deposited at room temperature and
exhibits the thinnest surface roughness layer (4 Å). This room temperature deposition result was used because there is no evidence of the low energy oscillator characteristic in its inverted bulk layer dielectric function, as shown in Figure 3-16. In addition, the parameters for this sample as a function of temperature in an annealing experiment are provided in Section 3.4.3. The CP amplitude, phase, and exponent of the bulk layer dielectric function for the samples deposited at elevated temperature were also selected as those of sample DS031. In addition, in the fitting procedure for the dielectric function parameters, the bulk and surface roughness interband energies and broadening parameters were linked for stability of the analysis. Other bulk layer CP parameters of phase and exponent were fixed at the values used in the analysis of Tables 3.5 and 3.6 which were also fixed for sample DS031.

For the samples with the thinner roughness layers in particular, it is a challenge to determine the resonance energy parameters of the surface roughness dielectric function. As a result, the Lorentz oscillator resonance energy for each sample was fixed at the bulk layer value obtained in the analysis of Tables 3.5 and 3.6, and the interband CP energy and broadening were linked in the fitting to the values of the bulk layer as noted in the previous paragraph. Thus, the roughness layer parameters that were free parameters and were determined in the analysis include the offset $\varepsilon_{1o}$, the Lorentz amplitude and broadening, and the interband CP amplitude and exponent. Reasonable trends for all variable parameters associated with the surface roughness layer have been obtained as shown in Table 3.9.

The free parameters for the bulk layer from Table 3.8 will be considered first, which include only $E_g$ and $\Gamma$ for the interband CP oscillator. For samples DS013 and
DS021 prepared at temperatures of 50°C and 87°C, respectively, both \( E_0 \) and \( \Gamma \) decrease considerably relative to the values for the reference sample prepared at room temperature. This behavior is observed in Figure 3-18, which shows variations in the interband CP behavior for samples DS013 and DS021 that are not observed in Figure 3-16. Thus, the resulting values are also lower than those obtained using the model of Tables 3.5 and 3.6. This is a surprising result considering that the primary difference between the two models lies in how the low energy Lorentz oscillator is handled, i.e. whether it is ascribed to the bulk layer or to the surface roughness layer as a component of the dielectric function. For the highest substrate temperature sample DS028, \( E_g \) and \( \Gamma \) return to values similar to those of the reference sample. The differences for the two pairs of samples may arise from fixing the CP amplitude of the bulk layer which may introduce instability in the fitting of the other parameters.

Insights into the behavior in Table 3.8 may also be gained by considering the results for the parameters that describe the surface layer dielectric function. These parameters vary consistently as a function of deposition temperature. The Lorentz oscillator parameters are the most critical in this analysis as these reflect the plasmon behavior of the surface layer. As the substrate temperature increases and the roughness layer thickness increases, the Lorentz oscillator amplitude tends to increase, at least for the highest temperature deposition, and the broadening increases as well. This behavior is attributed to a strengthening of the plasmon absorption, but with a wider distribution of local environments that may account for the greater plasmon band width. The red-shift, which arose from the fits using the Lorentz oscillator as a component of the bulk layer dielectric function, is attributed to an enhancement in the interactions between resonating
protrusions as the roughness thickness and the associated volume fraction of Ag surface protrusions increase together.

The simple Maxwell-Garnett effective medium theory approach given by Eq. (2.23) of Chapter 2 has been applied to predict the Ag volume fractions $Q_m$ in the surface layer based on the Lorentz oscillator resonance parameters of Table 3.9 with $\varepsilon_a = 1$. This analysis yields $Q_m$ values increasing from 0.6 to 0.9 for the Ag samples of Table 3.9 with roughness layer thicknesses increasing from 28 Å to 105 Å. These large volume fractions would seem to require that Ag serve as the host medium in the effective medium theory. The $Q_m$ values in turn enable the prediction of plasmon resonance energies via Eq. (2.24) substituting $\varepsilon_{1o} = 4.14$ and $E_p = 9.31$ eV for Ag from sample DS005. In this way resonance energies decreasing from 2.9 eV to 1.6 eV are predicted. Although the decreasing trend is consistent with experimental observations, the resonance energies are much higher than those in Table 3.9, which range from ~ 1.6 eV to 1.2 eV. This suggests that for the thicker roughness layers without screening ($\varepsilon_a = 1$), the simple Maxwell-Garnett model of Eqs. (2.23) and (2.24) does not adequately simulate the plasmon characteristics. The observed resonance energies in this case are more closely consistent with the maxima predicted by the Bruggeman EMA. Thus, as the volume fraction of resonating metal protrusions in the Ag surface layer increases, it is reasonable that the host dielectric function approaches the effective medium dielectric function in order to model and understand the observed resonance energies using the simple effective medium theories described in Chapter 2.
The interband amplitude is also observed to increase with increasing substrate temperature, however, these values are much smaller than the corresponding values for the bulk layer, which is also a surprising result.

The normal-incidence reflectance spectra for the three Ag samples deposited at elevated substrate temperatures, thus having larger surface roughness layer thicknesses, are shown in Figure 3-20. The upper panel shows the reflectance spectra incorporating the complete model for the sample, including the surface roughness layer. The lower panel shows the reflectance spectra generated assuming no surface roughness layer based on a calculation of reflectance directly from the bulk layer, given its known dielectric function. The upper panel shows that as the thickness of the surface roughness layer increases from 4 Å to ~ 100 Å, the reflectance decreases from 0.98-0.99 to ~ 0.8-0.9 in the near-infrared to visible region of the spectrum. The lower panel shows that upon analytical removal of the roughness layer from these samples, the reflectance spectra return to a level of 0.98-0.99 with the highest reflectance being obtained for sample DS013, deposited at 50°C. The significance of these results is that the two highest substrate temperature samples, DS021 and DS028, with the largest surface roughness layer thicknesses exhibit significant reflectance losses at low photon energies where the back-reflector operates due to the plasmon bands attributed to the surface roughness layer.
Figure 3-20: Simulations of normal incidence reflectance are shown for rougher silver films, deposited at elevated temperatures for comparison with a smooth film (sample DS031) deposited at room temperature. Here the simulated reflectance spectra in the upper panel are determined from the complete model of the Ag film structure, including the surface roughness layer. The simulated reflectance spectra in the lower panel are determined assuming a single interface between ambient air and the bulk Ag, using the dielectric function of the bulk layer, i.e. with the surface roughness layer removed.
3.4.3 Annealing of Ag Thin Films Deposited at Room Temperature

Thus far the optical properties of the Ag thin film samples have been discussed, focusing on the as-deposited films on crystalline silicon substrates. For some samples the deposition and measurement steps were performed at room temperature, whereas for others, elevated temperature was used for both steps. This section will focus on the optical and electrical properties of a Ag thin film sample that was deposited at room temperature and then step-wise annealed to a temperature exceeding the highest deposition temperature. It is possible to follow the free and bound electron behaviors for the bulk layer of the annealed samples as a function of annealing and measurement temperature and to characterize the changes in the surface roughness characteristics as has been described previously for the samples as-deposited at different temperatures.

For the Ag films deposited at elevated temperature with thicker surface roughness layers, the deduced bulk layer dielectric function, especially the imaginary part, differs depending on the optical model used for the surface roughness layer. The model for the dielectric function of the surface roughness layer incorporates either the Bruggeman EMA, which has been used previously when the roughness layer is very thin, or an analytical form which has been used when the roughness layer is thicker, the latter in an attempt to simulate the observed confined plasmon behavior attributed to the roughness layer.

When the Bruggeman EMA approach is used to characterize the dielectric function of thicker surface roughness layers on Ag films, one often needs a second oscillator at low energies to fit the inverted dielectric function of the underlying bulk film. Such a model, however, seems physically unrealistic unless the surface roughness
layer has reached opacity (and thus serves as the bulk layer) since the bulk layer by its definition does not support confined plasmons. As a result, all samples that require two oscillators in order to model the bulk layer dielectric function are instead re-analyzed using a physically realistic model with an analytical form for the dielectric function of the surface roughness layer that incorporates a confined plasmon band along with the interband CP oscillator. The analytical form for the confined plasmon is a Lorentz oscillator and, thus, the Bruggeman EMA is not applied in the alternative modeling approach. For samples as-deposited at elevated temperatures, the Lorentz oscillator is required at a deposition temperature as low as 50°C when the surface roughness thickness reaches 55 Å, whereas in the annealing studies of this section, such a second oscillator appears necessary for annealing temperatures above 100°C even when very thin roughness layers on the scale of a few monolayers are present.

The sample used for the purposes of annealing was DS031. The dielectric function of this sample was shown previously in Fig. 3.10, and the best fit oscillator parameters were given in Table 3.2. This sample was also used as a reference in Section 3.4.2 due to its smoothness and the availability of temperature dependent dielectric function data from the annealing studies of this section. This Ag film was deposited on a native oxide covered crystalline silicon substrate at room temperature. The fabrication process for this sample differed from the other samples in Table 3.1 to the extent that that the crystalline silicon substrate was heated to 200°C and then cooled to room temperature before depositing the silver film. The Ag film was fabricated by RF sputtering using deposition parameters including a RF plasma power of 50 W, an argon pressure of 4 mTorr, and an argon gas flow of 10 sccm, all held constant throughout the deposition.
The room temperature dielectric function of the Ag bulk layer for sample DS031 was extracted by using mathematical inversion based on the schematic model shown in Figure 3-21. The sample was then heated in steps of 20°C until the temperature reached 200°C, and at each such annealing step the sample was held for 40 minutes before collecting spectroscopic ellipsometry data. At each step up to and including 100°C, the dielectric function was inverted by using the same structural model shown in Figure 3-21, based on the assumption that no changes in film structure occurred over this temperature range. For annealing temperatures above 100°C, a model analogous to that of Figure 3-17 was used. For analysis using this model, two oscillators are incorporated into the analytical model that describes the dielectric function of the surface roughness layer. This appears necessary as a result the development of a more pronounced confined plasmon resonance in the surface roughness layer that requires an analytical form for its dielectric function, rather than the Bruggeman EMA.

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambient</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bruggeman EMA: (0.52 Ag-DS031)/(0.48 void)</td>
<td>4.3 Å</td>
<td></td>
</tr>
<tr>
<td>DS031: Ag from inversion</td>
<td>1888.8 Å</td>
<td></td>
</tr>
<tr>
<td>SiO₂ (native oxide)</td>
<td>18.2 Å</td>
<td></td>
</tr>
<tr>
<td>c-Si</td>
<td>1 mm</td>
<td></td>
</tr>
</tbody>
</table>

Figure 3-21: The schematic model is shown which was used to determine the dielectric function of Ag at room temperature via an inversion of (ψ, Δ) data. The same model was also used to determine the dielectric functions of annealed Ag thin films at 100°C and below, also via inversion. A model analogous to that shown in Figure 3-17 was used to determine the dielectric function of the sample when annealed above 100°C.
In this first analysis approach for determination of the annealing temperature dependent behavior of the Drude and CP parameters of the bulk layer, the best fit characteristics of the surface roughness, i.e., its thickness and composition, were fixed as shown in Figure 3-21 in order to enable \((\psi, \Delta)\) inversion that yields the bulk layer dielectric function. The starting (or trial) parameters in the analytical expression for this bulk layer dielectric function, including a Drude term and a single CP oscillator, were those obtained from the Ag sample at room temperature. In successive iterations, however, the parameters were allowed to vary in order to fit the inverted dielectric functions at each of the different annealing temperatures.

Table 3.10 presents the resulting best fitting parameters for sample DS031 annealed at various temperatures. These parameters describe the inverted dielectric functions assuming a constant surface roughness layer thickness and composition in accordance with the model shown in Figure 3-21. Best fit analytical expressions for the dielectric functions are shown in Figure 3-22 for selected annealing temperatures. As can be seen from Table 3.10, the MSE is acceptably low and nearly constant for temperatures of 100°C and below. This suggests that in this range the assumptions of the model are valid and the physical structure of the film is not changing. The MSE increases rapidly, however, for annealing temperatures above 100°C. It is unclear how much of this increase is due to a change in structure, e.g. roughness thickness or composition, invalidating the modeling assumptions, or to a change in dielectric function, e.g. the appearance of a confined plasmon band in the surface layer dielectric function, not accounted for by the assumed optical model which applies the Bruggeman EMA.
In order to better understand the origin of the increase in MSE in Table 3.10, a variation in the best fit analytical form for the bulk layer dielectric functions of Ag films was explored. Only a Drude term and a single CP oscillator for the bulk layer were used in the best fit for annealing temperatures up to and including 100°C, an approach supported by the low MSEs in Table 3.10. For temperatures above 100°C, however, the fit demands a second low energy oscillator which has been included in the bulk layer to simulate the appearance of a plasmon-related feature and to identify its energy position. By adding this second low energy oscillator to the model for the bulk layer dielectric function, the average MSE for the higher annealing temperatures (T > 100°C) can be reduced from an average of 0.565 as indicated in Table 3.10 to 0.112. As noted earlier, however, this second oscillator is believed to be associated not with the Ag bulk, but with confined plasmons that are sustained at the surface due to the presence of the roughness. Thus, the second oscillator must be incorporated instead into the dielectric function of the surface roughness layer in analogy to the model of Figure 3-17. As a result, this feature is assigned to the surface roughness layer in the subsequent analysis described in the next paragraphs.

For annealing temperatures above 100°C, the Bruggeman EMA model for the dielectric function of the surface layer has been replaced by an analytical model including Lorentz and CP oscillators. In the analysis at each annealing temperature, all three Lorentz oscillator parameters as well as the energy-independent contribution to the real part of the dielectric function were independently varied. The CP oscillator parameters of energy and broadening for the dielectric function of the much thinner surface layer were linked to the values associated with the bulk roughness layer. The CP amplitude and
exponent for the surface layer were independently varied, and the phase was fixed at zero. For the bulk layer, the Drude parameters were also allowed to vary. This was now possible also as a consequence of the much thinner roughness layers relative to the as-deposited samples of Sec. 3.4.2. The bulk layer CP parameters of amplitude, phase, and exponent were fixed as those at the highest annealing temperature, 100°C, for which reliable results are obtained without the presence of the confined plasmon. Finally, the single structural parameter, the surface roughness layer thickness, was varied, as well. The resulting dielectric functions for the surface roughness layer using this optical model are plotted in Figure 3-23. Presented in Table 3.11 are the Lorentz and CP oscillator parameters associated with the surface roughness layer, and in Table 3.12 are the Drude parameters associated with the bulk layer in this analysis of the measurements performed for temperatures above 100°C.
Table 3.10: The results of spectroscopic ellipsometry data analysis are tabulated for sample DS031 obtained during annealing. Dielectric functions were obtained for the bulk layer Ag by inversion and then fitted using a Drude term and one CP oscillator, keeping the surface roughness layer thickness fixed to 4.3 Å as in the model of Figure 3-21. This model applies the Bruggeman EMA for the dielectric function of the surface roughness. In this analysis, the bulk layer CP oscillator exponent $\mu$ and phase $\theta$, as well as $\varepsilon_{1o}$ were fixed at the following values: $\mu = 0.309; \theta = 0^\circ; \text{and } \varepsilon_{1o} = 1$. For annealing of the sample at 120°C and higher temperatures, a larger MSE results, which warrants a different modeling approach (see Table 3.11).

<table>
<thead>
<tr>
<th>Sample and Annealing T (0.75 - 5 eV data range)</th>
<th>MSE</th>
<th>Drude A (eV)</th>
<th>Drude $\Gamma$(eV)</th>
<th>Plasma Energy $E_p$ (eV)</th>
<th>CP A</th>
<th>CP $E_g$ (eV)</th>
<th>CP $\Gamma$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DS031 RT</td>
<td>0.205</td>
<td>1197.1 ±11.0</td>
<td>0.0714 ±0.0007</td>
<td>9.245 ± 0.088</td>
<td>6.471±0.090</td>
<td>4.151 ± 0.007</td>
<td>0.328 ± 0.017</td>
</tr>
<tr>
<td>DS031 40°C</td>
<td>0.196</td>
<td>1237.9 ±11.4</td>
<td>0.0688 ±0.0006</td>
<td>9.229 ± 0.083</td>
<td>6.415±0.086</td>
<td>4.150 ± 0.007</td>
<td>0.333 ± 0.017</td>
</tr>
<tr>
<td>DS031 60°C</td>
<td>0.199</td>
<td>1361.0 ±14.1</td>
<td>0.0622 ±0.0006</td>
<td>9.201 ± 0.092</td>
<td>6.336±0.086</td>
<td>4.147 ± 0.007</td>
<td>0.339 ± 0.018</td>
</tr>
<tr>
<td>DS031 80°C</td>
<td>0.200</td>
<td>1361.4 ±14.5</td>
<td>0.0615 ±0.0007</td>
<td>9.150 ± 0.100</td>
<td>6.208±0.086</td>
<td>4.141 ± 0.008</td>
<td>0.346 ± 0.018</td>
</tr>
<tr>
<td>DS031 100°C</td>
<td>0.276</td>
<td>1144.3 ±15.1</td>
<td>0.0710 ±0.0009</td>
<td>9.014 ± 0.117</td>
<td>5.935±0.120</td>
<td>4.132 ± 0.011</td>
<td>0.336 ± 0.026</td>
</tr>
<tr>
<td>DS031 120°C</td>
<td>0.439</td>
<td>923.9 ±16.6</td>
<td>0.0853 ±0.0015</td>
<td>8.877 ± 0.158</td>
<td>5.634±0.197</td>
<td>4.128 ± 0.018</td>
<td>0.317 ± 0.042</td>
</tr>
<tr>
<td>DS031 140°C</td>
<td>0.547</td>
<td>803.6 ±16.2</td>
<td>0.0965 ±0.0020</td>
<td>8.806 ± 0.180</td>
<td>5.449±0.249</td>
<td>4.128 ± 0.023</td>
<td>0.307 ± 0.053</td>
</tr>
<tr>
<td>DS031 160°C</td>
<td>0.602</td>
<td>730.5 ±15.1</td>
<td>0.1053 ±0.0022</td>
<td>8.770 ± 0.182</td>
<td>5.316±0.274</td>
<td>4.128 ± 0.026</td>
<td>0.307 ± 0.060</td>
</tr>
<tr>
<td>DS031 180°C</td>
<td>0.628</td>
<td>687.1 ±14.0</td>
<td>0.1118 ±0.0023</td>
<td>8.765 ± 0.179</td>
<td>5.237±0.283</td>
<td>4.131 ± 0.027</td>
<td>0.313 ± 0.064</td>
</tr>
<tr>
<td>DS031 200°C</td>
<td>0.611</td>
<td>660.8 ±12.5</td>
<td>0.1168 ±0.0022</td>
<td>8.785 ± 0.166</td>
<td>5.194±0.270</td>
<td>4.135 ± 0.027</td>
<td>0.326 ± 0.064</td>
</tr>
</tbody>
</table>
Figure 3-22: The analytical expressions that best fit the bulk layer dielectric functions are shown for a Ag film annealed and measured at different temperatures. The annealing and measurement temperatures were the same. The expressions used for all temperatures include a Drude term and a CP oscillator. The model used for this analysis is depicted in Figure 3-21, with a fixed surface roughness layer thickness whose dielectric function is determined from the Bruggeman EMA.
Figure 3-23: Analytical expressions that describe the dielectric functions of the surface roughness layer are shown for an annealed Ag sample. The annealing and measurement temperatures were the same. The expressions use a single Lorentz oscillator to model the confined plasmons and a CP oscillator, which is not visible on this scale, to model the interband transitions. This is the model selected for the dielectric functions of the roughness layers of samples annealed at temperatures greater than 100ºC. The deduced parameters in this analysis are given in Table 3.11. An analytical form for the bulk layer dielectric function was also used to define the model.
Table 3.11: Results of SE analysis of the annealed Ag sample DS031 are tabulated for annealing temperatures above 100°C. The results include the MSE in the fitting procedure, the surface roughness layer thickness, the energy-independent contribution to the real part of the dielectric function, and the three Lorentz and four CP oscillator parameters that characterize the surface roughness layer. In this analysis, the CP energy gap and broadening parameters were linked to those of bulk Ag layer. The Drude parameters of the bulk layer were also varied, but the remaining CP parameters of that layer were fixed to those of the same sample measured at the closest temperature of 100°C.

<table>
<thead>
<tr>
<th>Sample and temp. of anneal (0.75-5 eV)</th>
<th>MSE</th>
<th>Surface roughness thickness (Å)</th>
<th>ε₁₀</th>
<th>Lorentz A</th>
<th>Lorentz E₀ (eV)</th>
<th>Lorentz Γ(eV)</th>
<th>CP A</th>
<th>CP Eₜ (eV) (linked to bulk value)</th>
<th>CP Γ(eV) (linked to bulk value)</th>
<th>CP μ</th>
</tr>
</thead>
<tbody>
<tr>
<td>DS031 120°C</td>
<td>0.0091</td>
<td>4.3±0.3</td>
<td>1.15±0.07</td>
<td>24.78±2.72</td>
<td>1.83±0.02</td>
<td>0.364±0.026</td>
<td>0.0254±0.0087</td>
<td>4.059±0.003</td>
<td>0.256±0.004</td>
<td>3.00±0.18</td>
</tr>
<tr>
<td>DS031 140°C</td>
<td>0.0083</td>
<td>6.0±0.3</td>
<td>1.20±0.06</td>
<td>24.48±2.13</td>
<td>1.69±0.02</td>
<td>0.421±0.024</td>
<td>0.0251±0.0074</td>
<td>4.043±0.004</td>
<td>0.253±0.004</td>
<td>2.99±0.16</td>
</tr>
<tr>
<td>DS031 160°C</td>
<td>0.0075</td>
<td>7.7±0.4</td>
<td>1.17±0.05</td>
<td>23.10±1.71</td>
<td>1.60±0.02</td>
<td>0.462±0.021</td>
<td>0.0242±0.0059</td>
<td>4.022±0.004</td>
<td>0.249±0.004</td>
<td>2.90±0.14</td>
</tr>
<tr>
<td>DS031 180°C</td>
<td>0.007</td>
<td>9.0±0.4</td>
<td>1.15±0.04</td>
<td>22.53±1.47</td>
<td>1.54±0.02</td>
<td>0.487±0.019</td>
<td>0.0226±0.0049</td>
<td>4.007±0.004</td>
<td>0.249±0.004</td>
<td>2.97±0.13</td>
</tr>
<tr>
<td>DS031 200°C</td>
<td>0.0063</td>
<td>10.6±0.4</td>
<td>1.13±0.04</td>
<td>21.80±1.27</td>
<td>1.46±0.02</td>
<td>0.529±0.017</td>
<td>0.0209±0.0043</td>
<td>3.992±0.005</td>
<td>0.254±0.004</td>
<td>2.77±0.12</td>
</tr>
</tbody>
</table>
Table 3.12: The Drude parameters of $A$, $\Gamma$, and $E_p$ for the bulk Ag of the annealed sample DS031 are tabulated for annealing temperatures above 100°C. This analysis was performed using an analytical form for the dielectric function of the surface roughness layer.

<table>
<thead>
<tr>
<th>Sample and temp. of anneal (0.75-5 eV)</th>
<th>Drude A (eV)</th>
<th>Drude $\Gamma$(eV)</th>
<th>Plasma Energy $E_p$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DS031 120°C</td>
<td>1006.9 ±39.7</td>
<td>0.0809 ±0.0031</td>
<td>9.025 ±0.351</td>
</tr>
<tr>
<td>DS031 140°C</td>
<td>944.3 ±34.1</td>
<td>0.0866 ±0.0030</td>
<td>9.045 ±0.322</td>
</tr>
<tr>
<td>DS031 160°C</td>
<td>921.6 ±31.5</td>
<td>0.0895 ±0.0030</td>
<td>9.080 ±0.305</td>
</tr>
<tr>
<td>DS031 180°C</td>
<td>918.5 ±30.0</td>
<td>0.0906 ±0.0028</td>
<td>9.120 ±0.291</td>
</tr>
<tr>
<td>DS031 200°C</td>
<td>963.8 ±31.4</td>
<td>0.0875 ±0.0027</td>
<td>9.184 ±0.292</td>
</tr>
</tbody>
</table>

Table 3.11 suggests a steady but not significant increase in surface roughness upon annealing, an effect which may account for the development of an observable confined plasmon band as shown in Figure 3-23. The thickness increase is small, however, compared to the variations in roughness for films as-deposited at temperatures over the same range. There is no change in the energy-independent contribution to the real part of the dielectric function of the roughness layer upon annealing, at least within the confidence limits of ±0.04-0.07. The clear effect in Table 3.11 is that appearing in Figure 3-23, a red-shift in the photon energy and an increase in the broadening for the Lorentz oscillator band, attributed to the excitation of confined plasmon modes that span a wider range of energies with increased interactions between those modes due to the increase in surface roughness.
For the data of Fig. 3.7(a), the simple Maxwell-Garnett effective medium theory has been applied as in Section 3.4.2.2 to predict the Ag volume fractions $Q_m$ based on Eq. (2.23) and the plasmon resonance energies based on Eq. (2.24). This simple theory predicts $Q_m$ values increasing monotonically from 0.62 to 0.72 and resonance energies decreasing from 2.8 eV to 2.5 eV. The decreasing trend is consistent with experimental observations, but in this case as well, the predicted resonance energies are much higher than those in Table 3.11. This again suggests that the simple Maxwell-Garnett model of Eqs. (2.23) and (2.24) does not adequately simulate the plasmon characteristics for thicker roughness layers on Ag without screening ($\varepsilon_a = 1$), and that the observed resonance energies are more closely consistent with the maxima predicted by the Bruggeman EMA. Results presented in Chapter 5 will show that the simple Maxwell-Garnett approach of Eqs. (2.23) and (2.24) appears adequate for describing the plasmon resonance at Ag/ZnO interfaces fabricated starting from smooth Ag surfaces. For such interfaces $Q_m$ is small and the screening is large so the interaction between neighboring protrusions is significantly reduced. The simple Maxwell-Garnett approach may also be applicable for describing plasmons associated with inhomogeneous doping in ZnO:Al films as described in Chapter 4.

The amplitude of the interband CP oscillator associated with the surface roughness layer is very weak, and the resonance is not visible on the scale of Figure 3-23. In addition, the energy of this CP oscillator, which is obtained by linking the corresponding parameters of the bulk and surface roughness layers, shows a red-shift relative to the corresponding results of Table 3.10 using the Bruggeman EMA analysis approach. These two surprising features have been observed in the analysis of the
previous section and may be a characteristic of models that constrain the fit through linking of parameters associated with surface roughness and bulk layers. In addition, the use of a variable CP exponent for the surface layer may also impact the results of the analysis. A deeper understanding of these surprising features must await further modeling and is reserved for future study.

Table 3.12 shows an increase in the bulk layer Drude broadening parameter over the range of 120-180°C. This effect can be attributed to an increase in crystalline defects or the introduction of contaminants through diffusion with increasing temperature. The temperature dependence of the scattering time according to $\tau \propto T^{-1}$ may also contribute to this trend. The increase in plasma energy is followed by an apparent decrease above 180°C; however, this decrease is smaller than the range of the confidence limits from the analysis. The apparent increase in plasma energy with annealing temperature, although monotonic, is also within the range of the confidence limits.

The CP resonance energy from the bulk layer dielectric function, representing the interband absorption onset of Ag, is plotted versus the annealing/measurement temperature in Figure 3-24. The results in the upper panel are obtained by applying the dielectric function model of the surface roughness layer that applies the Bruggeman EMA. The CP energy is obtained as one of the parameters that define the best fit analytical dielectric function of the bulk layer from the analysis in Table 3.10. In the fit, all CP parameters were varied except the phase $\theta$ which was fixed at zero, and the exponent $\mu$ which was fixed at the room temperature value of 0.309. The lower panel in Figure 3-24 includes results for the annealing temperature dependence of the interband CP energy obtained using the analytical model for the surface roughness layer. In this
case, the CP energy and broadening parameter for the surface layer were linked to those of the bulk layer. For the two temperatures ranges of the upper and lower panels, the CP energy was fit to linear functions, as this is the expectation for the measurement temperature variation of the interband energy above the Debye temperature. The best fit linear temperature coefficients for the lower and upper temperature ranges that use the two different surface roughness models are $-2.3 \times 10^{-4}$ eV/K and $-8.6 \times 10^{-4}$ eV/K, respectively, which together bracket the value of $-6.5 \times 10^{-4}$ eV/K reported previously by Winsemius et al. [1976] as the measurement temperature dependence of the interband energy. An apparent change in the bandgap variation occurs for temperatures of 140ºC and above, resulting in an increased temperature coefficient magnitude as shown in the lower panel. The change in slope cannot be interpreted solely as a measurement temperature effect due to the annealing that occurs simultaneously.
Figure 3-24: The critical point resonance energy is plotted versus temperature for the Ag film DS031 measured during annealing. The results plotted in the upper panel are those from Table 3.10 in which case the Bruggeman EMA model is used to describe the dielectric function of the surface roughness. In the best fit to the dielectric function, the phase \( \theta \) is fixed at zero, and the exponent \( \mu \) is fixed to the value \( \mu = 0.309 \). The solid line is a best fit linear function to the data over the range of 20-120°C. The results plotted in the lower panel are those from Table 3.11 in which case an analytical model is used to describe the roughness layer dielectric function. The solid line is a linear fit over the range of 120-200°C.
The complication in evaluating the results in Figure 3-24 and making literature comparisons arise from the two types of changes in the Ag optical properties that occur simultaneously during the spectroscopic ellipsometry experiments performed with step-wise increases in the sample temperature. The annealing effect changes the sample structure and dielectric function irreversibly due to changes in grain size, defect concentration, etc., whereas the measurement temperature effect on the dielectric function is reversible (assuming no change in the material structure) and is caused predominantly by changes in the phonon population. For example, if the weak bandgap variation for temperatures below 140ºC is due to a competing annealing effect, then this effect will distort determination of the measured temperature coefficient due to measurement temperature alone, leading to a weaker coefficient. This may account for the difference between the results reported here and the literature results of Winsemius et al. Although the fits in the analyses at low temperatures in Table 3.10 are very good, as indicated by the MSE, an annealing effect may still occur as long as that effect can be characterized within the framework of the existing optical model. For example, if the annealing effect does not change the sample structure but changes the Drude parameters then the model of Figure 3-21 can capture that effect producing a low MSE.

The overall results of this section suggest an improved, two-cycle experimental approach for annealing experiments, which will be applied to ZnO in Chapter 4. In the first cycle, the sample is heated to a specific annealing temperature and then cooled to room temperature. Measurements at room temperature before and after this first heating cycle provide the effect of annealing on the sample structure. In a second heating cycle to the same temperature, it can be assumed that the structure of the film doesn’t change
and measurements at fixed temperature steps upon heating and cooling provide the measurement temperature dependence of the dielectric function.

In some cases, however, a known measurement temperature dependent contribution can be separated from the unknown irreversible contribution caused by annealing. For example, this separation can be performed for the free carrier characteristics of Ag, as represented by the Drude term in the bulk layer dielectric function. Considering this term, the reversible measurement temperature dependences of the two Drude parameters of Ag derive from the well-known temperature dependence of the resistivity which in turn derives from the temperature dependence of the scattering time. In contrast, the plasma energy, electron concentration and the effective mass, determined by the atomic valence, crystal structure, and band structure are not expected to be temperature dependent. With this in mind, the temperature dependence of the Drude parameters are easily derived from the following equations

\[
A = \frac{\hbar}{\varepsilon_0 \rho_0},
\]

\[
\Gamma = \frac{\hbar}{\tau} = \frac{N e^2 h \rho_0}{m_0}.
\]  \hspace{1cm} (3.11)

According to the simple theory of the dc resistivity of polycrystalline films that applies the Debye approximation, \( \rho_0 = \rho_\text{ex} + \rho_\text{in} = \rho_\text{ex} + bT \), where \( \rho_\text{in} \) is the intrinsic resistivity associated with the defect-free single crystal having the temperature dependence \( \rho_\text{in} \sim bT \), with \( b \) as a constant, and \( \rho_\text{ex} \) is a temperature independent extrinsic contribution generated due to grain boundary and defect scattering. Alternatively, an empirical expression can be used for \( \rho_\text{in} \) from Eq. (3.8), namely \( \rho_\text{in} (\Omega\text{-cm}) = \rho_\text{in}(273 \text{ K}) \)
For the former expression, the amplitude $A$ should be inversely proportional to the term linear in temperature, i.e., decreasing according to $(a + bT)^{-1}$, and the broadening $\Gamma$ should be directly proportional to this same term, such that the square root of the product, which is the plasma energy $E_{p} = [\Lambda \Gamma]^{1/2}$, is independent of temperature.

Depicted in Figure 3-25 are the dependences of $A$ and $\Gamma$ from Table 3.10 for $T < 120^\circ$C and from the analysis of Table 3.12 for higher temperatures. These plots reveal inverse behavior such that the square root of the product, the plasma energy $E_p$, plotted in Figure 3-26, shows a much weaker variation with temperature. The weak variation in $E_p$ yields a weak variation in electron concentration which will be discussed shortly. Also plotted in Figure 3-25 are the trend lines expected if the Drude parameters $A$ and $\Gamma$ at the highest temperature of 200ºC define the value of $\rho_{ex}$, and the change with measurement temperature occurs in accordance with the empirical expression for the resistivity given in Eq. (3.8). The fact that $\Gamma$ initially decreases with temperature $T$ for $20^\circ$C $\leq T \leq 80^\circ$C suggests that in the low temperature range, the effect of annealing is to increase the grain size or decrease the defect density, thus increasing the scattering time. The correlation of this behavior with the weak $T$ dependence of the CP resonance energy suggests that this energy increases as the grain size increases or the defect density decreases. This may suggest that the deduced interband onset energy is influenced by a broadening effect due to grain boundaries and defects.

For $80^\circ$C $< T < 140^\circ$C in Figure 3-25, the Drude amplitude decreases more rapidly and the broadening increases more rapidly than the theoretical result for the effect of measurement temperature alone, suggesting that an effect of annealing in this
temperature range is to increase the defect density. It seems unlikely that the defects are thermally generated, however, one possible explanation is that as the temperature increases, vacuum residual impurity atoms are incorporated by diffusion into the Ag film. For temperatures above 140°C in Figure 3-25, the Drude parameters tend to parallel the theoretically predicted trend, possibly due to the saturation of the annealing effects that occur at the lower temperatures.

Plotted in Figure 3-27 are the resistivity $\rho$ and the scattering time $\tau$, deduced from the best fit values of $A$ and $\Gamma$. In fact, $\rho$ and $\tau$ are inversely related to $A$ and $\Gamma$, with proportionality constants of $\hbar/\epsilon_0$ and $\hbar$, respectively. Predictions for the measurement temperature dependence can be added to these plots as well, based on the empirical expression for the power law temperature dependence of $\rho_{\text{in}}$ of Eq. (3.8). In Figure 3-27 (top panel), the resistivity trend is also shown for single crystal Ag with $\rho(273 \text{ K}) = 1.46 \times 10^{-6} \ \Omega \ \text{cm}$, which is significantly lower than the experimental result due to the polycrystalline nature of the thin film. From this difference, selecting data for the highest temperature of 200°C, a value of $\rho_{\text{ex}} = 5.03 \times 10^{-6} \ \Omega \ \text{cm}$ is obtained. The polycrystallinity of the film leads to a shorter scattering time of electrons due to grain boundaries or a higher defect density within the grains. The trends with temperature in the measured resistivity as well as that for the scattering time are consistent with the proposed decrease in the concentration of scattering centers upon annealing between room temperature and 80°C, and a subsequent increase above 80°C, approaching the measurement temperature dependence above 140°C. Such behavior is expected based on the results for $A$ and $\Gamma$ in Figure 3-25, and the simple relationships between the two pairs of parameters. Finally, in Figure 3-28, the carrier concentration is plotted along with the constant value predicted.
assuming a single crystal structure and a valence of unity. The Drude parameters, including derived results, are shown as a function of annealing/measurement temperature in Table 3.13.

The weak reduction in the electron concentration over the temperature range up to ~ 80°C is interesting. This behavior suggests that the role of low temperature annealing is a relaxation of compressive stress built into the film due to the deposition at low temperature and Ar pressure. Stress relaxation could lead to an increase in grain size and to void development in grain boundary regions, accounting for a reduction in atomic concentration, and thus, electron concentration. In order for this relaxation to occur, however, the film thickness must increase slightly, an effect that cannot be detected optically due to the opacity of the film. Relaxation of stress that reduces the scattering center concentration is also consistent with the effects on A and Γ as well as ρ and τ over the lower range of annealing temperature. The overall results suggest that some improvement in the quality of the Ag film as a reflector is possible through annealing the sample to ~ 80°C which may relax the stress, but with little improvement beyond. The reversal and increase in electron concentration above 80°C may occur due to a densification of the film especially since the behavior appears to reach the single crystal concentration at 200°C annealing temperature. Such behavior, however, is not expected to lead to the observed increase in resistivity and decrease in scattering time in Figure 3-27. For this reason, the latter effects have been proposed to result from impurity incorporation.
Table 3.13: The Drude parameters, including derived results, are tabulated for the bulk Ag layer of the annealed sample DS031. For annealing/measurement temperatures up to and including 100°C, the model uses an EMA surface roughness layer, and the Drude parameters A and Γ were extracted from Table 3.10. For higher annealing temperatures (120°C and above), an analytical form for the roughness layer was used in the model with parameters A and Γ taken from Table 3.12. The other Drude parameters in the table were derived from these two parameters (A and Γ) for each annealing temperature. The effective mass $m_o = 0.96m_e$ was assumed for silver in the calculation of N and μ.

<table>
<thead>
<tr>
<th>Sample and temp. of anneal (0.75-5 eV)</th>
<th>Drude A (eV)</th>
<th>Drude Γ(eV)</th>
<th>Plasma Energy $E_p$ (eV)</th>
<th>Resistivity $\rho$ (Ω-cm)</th>
<th>Scattering Time $\tau$ (fs)</th>
<th>Carrier Concentration N (cm$^{-3}$)</th>
<th>Carrier Mobility $\mu$(cm$^2$V$^{-1}$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DS031 RT</td>
<td>1197.1 ±11.0</td>
<td>0.0714 ±0.0007</td>
<td>9.245 ± 0.088</td>
<td>6.210 x 10$^{-6}$ ± 0.057 x 10$^{-6}$</td>
<td>9.219 ± 0.087</td>
<td>5.951 x10$^{22}$ ± 0.003 x 10$^{22}$</td>
<td>16.89 ± 0.16</td>
</tr>
<tr>
<td>DS031 40°C</td>
<td>1237.9 ±11.4</td>
<td>0.0688 ±0.0006</td>
<td>9.229 ± 0.083</td>
<td>6.005 x 10$^{-6}$ ± 0.055 x 10$^{-6}$</td>
<td>9.570 ± 0.090</td>
<td>5.929 x10$^{22}$ ± 0.003 x 10$^{22}$</td>
<td>17.53 ± 0.16</td>
</tr>
<tr>
<td>DS031 60°C</td>
<td>1361.0 ±14.1</td>
<td>0.0622 ±0.0006</td>
<td>9.201 ± 0.092</td>
<td>5.462 x 10$^{-6}$ ± 0.056 x 10$^{-6}$</td>
<td>10.576 ± 0.111</td>
<td>5.898 x10$^{22}$ ± 0.004 x 10$^{22}$</td>
<td>19.38 ± 0.20</td>
</tr>
<tr>
<td>DS031 80°C</td>
<td>1361.4 ±14.5</td>
<td>0.0615 ±0.0007</td>
<td>9.150 ± 0.100</td>
<td>5.460 x 10$^{-6}$ ± 0.058 x 10$^{-6}$</td>
<td>10.696 ± 0.116</td>
<td>5.833 x10$^{22}$ ± 0.003 x 10$^{22}$</td>
<td>19.60 ± 0.21</td>
</tr>
<tr>
<td>DS031 100°C</td>
<td>1144.3 ±15.1</td>
<td>0.0710 ±0.0009</td>
<td>9.014 ± 0.117</td>
<td>6.496 x 10$^{-6}$ ± 0.085 x 10$^{-6}$</td>
<td>9.273 ± 0.125</td>
<td>5.656 x10$^{22}$ ± 0.003 x 10$^{22}$</td>
<td>16.99 ± 0.22</td>
</tr>
<tr>
<td>DS031 120°C</td>
<td>1006.9 ±39.7</td>
<td>0.0809 ±0.0031</td>
<td>9.025 ± 0.351</td>
<td>7.382 x 10$^{-6}$ ± 0.059 x 10$^{-6}$</td>
<td>8.136 ± 0.056</td>
<td>5.672 x10$^{22}$ ± 0.012 x 10$^{22}$</td>
<td>14.91 ± 0.58</td>
</tr>
<tr>
<td>DS031 140°C</td>
<td>944.3 ±34.1</td>
<td>0.0866 ±0.0030</td>
<td>9.045 ± 0.322</td>
<td>7.872 x 10$^{-6}$ ± 0.069 x 10$^{-6}$</td>
<td>7.597 ± 0.057</td>
<td>5.697 x10$^{22}$ ± 0.012 x 10$^{22}$</td>
<td>13.93 ± 0.49</td>
</tr>
<tr>
<td>DS031 160°C</td>
<td>921.6 ±31.5</td>
<td>0.0895 ±0.0030</td>
<td>9.080 ± 0.305</td>
<td>8.066 x 10$^{-6}$ ± 0.075 x 10$^{-6}$</td>
<td>7.356 ± 0.058</td>
<td>5.742 x10$^{22}$ ± 0.013 x 10$^{22}$</td>
<td>13.49 ± 0.45</td>
</tr>
<tr>
<td>DS031 180°C</td>
<td>918.5 ±30.0</td>
<td>0.0906 ±0.0028</td>
<td>9.120 ± 0.291</td>
<td>8.093 x 10$^{-6}$ ± 0.076 x 10$^{-6}$</td>
<td>7.267 ± 0.058</td>
<td>5.793 x10$^{22}$ ± 0.014 x 10$^{22}$</td>
<td>13.32 ± 0.42</td>
</tr>
<tr>
<td>DS031 200°C</td>
<td>963.8 ±31.4</td>
<td>0.0875 ±0.0027</td>
<td>9.184 ± 0.292</td>
<td>7.713 x 10$^{-6}$ ± 0.068 x 10$^{-6}$</td>
<td>7.521 ± 0.056</td>
<td>5.873 x10$^{22}$ ± 0.015 x 10$^{22}$</td>
<td>13.79 ± 0.43</td>
</tr>
</tbody>
</table>
This chapter concludes with a brief presentation and discussion of reflectance data obtained at different annealing/measurement temperatures for the sample of Figs. 3-25 to 3-28. Figure 3-29 shows the predicted normal incidence reflectance for the annealed Ag samples, first considering the model for the sample that includes the surface roughness layer (upper panel), and then considering the bulk Ag with the surface roughness layer removed (lower panel). Both data sets show similar behavior for photon energies less than 1 eV and greater than 2.5 eV, suggesting that within these ranges the dominant effect of annealing on the reflectance is not the increase in roughness layer, but rather the change in the bulk layer dielectric function. The increase in bulk layer scattering time for annealing temperatures between 20°C and 80°C leads to an optimum reflectance at 80°C due to the minimum in dissipation. In the range from 1.0 to 2.5 eV, the roughness layer with its plasmon band observed for temperatures above 100°C leads to reductions in the reflectance by ~ 0.02 in broad bands centered near 1.7 eV for 140°C and near 1.5 eV for 200°C. These effects can be observed more clearly from the same set of results but on an expanded scale in Figure 3-30.
Figure 3-25: The Drude parameters of amplitude and broadening for the Ag bulk layer are shown as functions of annealing temperature. The measurements were performed in situ at the annealing temperatures. In describing the dielectric function of the surface roughness layer in the analysis, the Bruggeman EMA was applied for $T \leq 100^\circ C$ and an analytical form was applied for $T > 100^\circ C$. The solid lines represent a prediction of the parameters based on an empirical expression for the measurement temperature dependence of the resistivity of single crystal Ag assuming that there are no structural changes in the material upon annealing. The empirical expression is shifted such that it passes through the data points at $T = 200^\circ C$ to account for the increased resistivity of the polycrystalline material.
Figure 3-26: The plasma energy, which is the square root of the product of the Drude amplitude and broadening, is shown for the Ag bulk layer as a function of the annealing temperature. Here, the data are combined from two different methods of analysis applied to lower and higher temperature ranges of annealing. Data from the analysis method of Table 3.10 are used for T ≤ 100°C, and data from the method of Table 3.12 are used for T > 100°C.
Figure 3-27: The Drude parameters of resistivity and scattering time are shown as functions of annealing temperature. The measurements were performed in situ at the annealing temperature. Data from the analysis methods of Tables 3.10 and 3.11 are used for $T \leq 100^\circ C$ and for $T > 100^\circ C$, respectively. The triangles show the resistivity as a function of measurement temperature for single crystal Ag based on an empirical expression. The solid lines represent a prediction of the parameters, assuming that there are no structural changes in the material upon annealing. These lines are shifted such that they pass through the data points at $T = 200^\circ C$ to account for the increased resistivity of the polycrystalline material.
Figure 3-28: The carrier concentration is plotted versus the annealing temperature, applying a constant effective mass of $m_o = 0.96 \, m_e$. These results are obtained from the Drude parameters of Figure 3-27. Thus, data from the analysis methods of Tables 3.10 and 3.11 are used for $T \leq 100\,^\circ C$ and for $T > 100\,^\circ C$, respectively. The theoretical prediction is shown as the horizontal solid line based on a calculation for single crystal Ag assuming a valence/atom of unity.
Figure 3-29: Normal incidence reflectance simulations are shown for the as-deposited Ag films of Figs. 3-25-3-28 and for three annealing/measurement temperatures. Two different models for the film are used to generate the data in the two panels. The reflectance in the upper panel reflectance is derived from the complete model of the Ag film, including the surface roughness layer. The reflectance in the bottom panel is derived assuming a single interface between Ag and the ambient medium, whereby the bulk layer dielectric function is used for the Ag. In addition, the simulations are combined from two different methods of data analysis applied to lower and higher temperature ranges of annealing. Data from the analysis method of Table 3.10 are used for $T \leq 100^\circ C$, and data from the analysis method of Table 3.11 are used for $T > 100^\circ C$. 
Figure 3-30: Normal incidence reflectance simulations are shown for the as-deposited Ag films of Figs. 3-25-3-28 and for three annealing temperatures. These results are the same as those of Figure 3-29 but plotted on an expanded reflectance scale.
Chapter 4

Dielectric Functions of Undoped and Doped ZnO

4.1 Introduction

This chapter is devoted to presentation and discussion of the optical properties of ZnO and aluminum doped zinc oxide (ZnO:Al; AZO) thin films deposited at room temperature and measured by spectroscopic ellipsometry. Moreover, the effect of annealing on the optical and electrical properties of these thin films is treated in detail.

Zinc oxide is a direct and wide bandgap II-VI semiconductor with a bandgap of ~3.3 eV. In fact, literature reports on ZnO provide bandgap values ranging from 3.1 to 3.4 eV (Jin et al., 1988; Srikant and Clarke, 1998). ZnO exhibits the hexagonal wurtzite crystalline structure, and its thin film growth typically exhibits a preferred (001) orientation (Xing et al., 2008). Because of the hexagonal crystal structure, ZnO is optically anisotropic with uniaxial symmetry. This implies two sets of optical properties, ordinary and extraordinary for fields perpendicular and parallel to the unique c-axis of the crystal, respectively. The anisotropy is very weak, however, with only small differences between the ordinary and extraordinary properties. The refractive indices of ZnO below the band edge at a wavelength of 600 nm are 1.997 for the ordinary wave and 2.015 for the extraordinary wave, resulting in a difference of 0.018. The direct-bandgap energy for
the ordinary wave is reported as 3.372 eV whereas for the extraordinary wave, it is reported as 3.405 eV (Jellison and Boatner, 1998). For ellipsometry measurements of thin films, anisotropic effects may be suppressed further still by a distribution of grain orientations, even for preferentially-oriented films, due to the large angle of incidence.

Because of its favorable optical and electrical properties, ZnO is a very attractive material for wide variety of applications, such as transparent conducting oxide (TCO) films, thin film solar cell contacts and window layers, thin film gas sensors, ultraviolet (UV) lasers, acoustic wave devices, among others (Kang et al., 2004). Furthermore, ZnO is non-toxic, relatively abundant, and thus, a low-cost material. By n-type doping with aluminum, ZnO can be made sufficiently conductive to be used as a TCO material with the capability of replacing the widely used tin-doped indium oxide (In$_2$O$_3$:Sn; ITO). This is desirable due to the relatively low abundance of In, which can lead to high material costs in ITO fabrication for large area electronic displays and photovoltaics. Compared to undoped ZnO, aluminum doped ZnO exhibits lower resistivity, higher transmittance in the ultraviolet due to the effects of degenerate doping, and better stability, while having similar crystallographic and structural properties ( Li et. al., 2009; Yang et. al., 2009).

4.2 Dielectric Functions of Undoped ZnO

In this section, the dielectric functions of undoped zinc oxide for different substrates and for various deposition conditions will be compared. In fact throughout the present chapter, the dielectric function of ZnO used primarily as a reference in the Chapter 5 study of ZnO deposition on Ag will be compared with other samples of ZnO. This particular sample was deposited specifically for the Ag/ZnO studies using an oxidized Si wafer as the substrate and is denoted "PVIC" in these dielectric function
comparisons. Table 4.1 shows the available deposition conditions for seven samples from different sources including sample "PVIC". In Table 4.1, two samples are missing deposition parameters, as indicated by "NA" (not available). These samples were prepared in industry R&D laboratories, and details could not be disclosed. It is known that these samples, labeled "USIA" (US industry A) and "USIB" (US industry B), were both prepared by sputtering, but on different substrates, c-Si (Ferreira, 2004) and flexible stainless steel, respectively.

Table 4.1: The deposition conditions of ZnO samples are tabulated. The gas flow in the case of sample DS-LD-009 was unique in that it included 1 sccm of a mixture of 5 vol.% O₂ in Ar in addition to 10 sccm of pure Ar.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Substrate</th>
<th>Subst. Temp.</th>
<th>Power (W)</th>
<th>Pressure (mTorr)</th>
<th>Gas flow (sccm)</th>
<th>Bulk (dₖ) and surface roughness (dₛ) thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>DS-LD-009</td>
<td>Borosilicate glass</td>
<td>RT</td>
<td>100</td>
<td>5</td>
<td>10 (Ar) 1 (Ar + 5 vol.% O₂)</td>
<td>dₖ = 1511 Å  dₛ = 129 Å</td>
</tr>
<tr>
<td>DS-LD-009</td>
<td>Borosilicate glass</td>
<td>RT</td>
<td>100</td>
<td>5</td>
<td>10 (Ar) 1 (Ar + 5 vol.% O₂)</td>
<td>dₖ = 1536 Å  dₛ = 111 Å</td>
</tr>
<tr>
<td>After Annealing</td>
<td>Borosilicate glass</td>
<td>RT</td>
<td>100</td>
<td>5</td>
<td>10 (Ar) 1 (Ar + 5 vol.% O₂)</td>
<td>dₖ = 1536 Å  dₛ = 111 Å</td>
</tr>
<tr>
<td>DA-CL-006</td>
<td>c-Si, thermal oxide; dₒₓ=412 Å</td>
<td>RT</td>
<td>50</td>
<td>10</td>
<td>10 (Ar)</td>
<td>dₖ = 2128 Å  dₛ = 43 Å</td>
</tr>
<tr>
<td>LD-MV-409c</td>
<td>c-Si</td>
<td>RT</td>
<td>100</td>
<td>5</td>
<td>10 (Ar)</td>
<td>dₖ = 3171 Å  dₛ = 128 Å</td>
</tr>
<tr>
<td>USIA</td>
<td>c-Si</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>dₖ = 771 Å</td>
</tr>
<tr>
<td>USIB</td>
<td>Stainless steel</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>dₖ = 6368 Å  dₛ = 484 Å</td>
</tr>
<tr>
<td>PVIC</td>
<td>c-Si, native oxide; dₒₓ=17Å</td>
<td>RT</td>
<td>50</td>
<td>4</td>
<td>10 (Ar)</td>
<td>dₖ = 1860 Å  dₛ = 38 Å</td>
</tr>
</tbody>
</table>

In order to perform an initial comparison of the real and imaginary parts of the dielectric functions of the seven different ZnO samples of Table 4.1, the results as obtained from the original sources (typically as analytical functions or spline-smoothed inverted spectra)
were parameterized by using two generalized critical point (CP) oscillators. The CP oscillator expression was given as Equation (3.2) in Chapter 3. The results of this initial fitting procedure yield the best fit dielectric functions shown in Fig. 4.1.

All ZnO samples of Table 4.1 exhibit similarly shaped dielectric functions with a peak in $\varepsilon_1$ and a step in $\varepsilon_2$ at the band gap near 3.3 - 3.4 eV as shown in Fig. 4.1. The amplitudes of the ($\varepsilon_1$, $\varepsilon_2$) spectra vary in magnitude and systematic variations also occur in the sharpness of the band gap exciton resonance feature which appears correlated with its energy position. Among all the ZnO samples, the one deposited on a glass substrate and annealed (sample "DS-LD-009 After Annealing") shows the highest values of $\varepsilon_1$ at the lowest photon energies below the 3.3 eV band gap, which suggests it has the highest density microstructure. On this basis, one may also conclude that sample USIA deposited on a c-Si substrate has the lowest density microstructure. Among this subset of ZnO samples deposited on crystalline silicon (c-Si) substrates, the one deposited at a pressure of 10 mTorr and an RF power of 50 W, namely DA-CL-006, exhibits the highest values of $\varepsilon_1$ below the ZnO band gap. Because of the combination of a relatively low Ar pressure (i.e. the mean free path of the sputtered species is longer than the target to substrate spacing) and a low power density plasma, the deposited thin film is likely to be denser compared with other samples deposited on c-Si substrates. Among these samples, the ZnO deposited on glass has the sharpest critical point structure due to the exciton, and this may be caused by the lowest doping level by native defects and also the largest grain size and crystalline quality. In contrast, the ZnO sample USIB has the broadest critical point structure, indicating highest doping level by native defects from among the seven samples compared.
As a next analysis step, possible variations in the void fraction of the samples were incorporated as a component of quantitative analysis. Thus, considering the dielectric functions of the seven samples of Fig. 4.1, a reference sample was chosen as the one with the highest amplitude of $\varepsilon_1$ well below the band gap. In fact, the sample selected was "DS-LD-009 After Annealing" as noted in the previous paragraph. The void volume percentages of the other six samples were determined by fitting using the Bruggeman effective medium approximation as a mixture of the assumed densest material and void. The results of this analysis are shown in Table 4.2. It is interesting to note that the industry-supplied sample USIA has the highest void content of 11.73 ± 0.09 vol.%, as expected from the comparison of the amplitudes in Fig. 4.1.

In a third analysis step, the deduced void volume percentage was removed analytically via inversion, yielding dense phase dielectric functions for each of the samples of Table 4.1. In a fourth and final step, the dense phase dielectric functions were parameterized using different oscillator combinations in an approach similar to the initial analysis step that led to the results in Fig. 4.1. The purpose of this fourth step is to evaluate the number and type of oscillators needed to fit the full set of dielectric function data for the dense phase materials. The results for the different trial attempts are shown in Table 4.2 and a plot of the MSE using the different models is shown in Fig. 4.2. For the reference sample "DS-LD-009 After Annealing", the fit was performed on the original inverted dielectric function, and this accounts for the higher MSE for this sample in Fig. 4.2. The lowest sum of the mean-squared errors (MSE) was obtained for an 11 parameter 2-CP model, and any attempt at reduction in the number of parameters by fixing parameters or applying simpler oscillators with fewer parameters led to a reduction
in the overall fit quality. The sequence of analysis steps is summarized in Table 4.4 and the resulting best fit parameters using the 11 parameter 2-CP model are given in Table 4.5.

The first half of Table 4.5 shows the CP oscillator with its resonance in the range of ~ 3.3-3.4 eV, which fits the excitonic feature at the band gap and thus the step in $\varepsilon_2$ and the peak in $\varepsilon_1$ (see Fig. 4.2). These are the most obvious features of the ZnO dielectric function. The resonance energy of the second CP oscillator lies above that of the first oscillator, but varies considerably. This second oscillator appears to simulate the weakly varying $\varepsilon_2$ spectra above the band gap of ZnO, serving as above-band-gap background absorption, i.e. absorption not due to a critical point in the band structure. From the energy parameters of the first CP ($E_g$-1) oscillator, one can see that most ZnO samples have band gaps of ~ 3.30 eV, a value which matches the published value by Srikant and Clarke (1998). There exists a range of values from 3.29 to 3.39 eV, however. This widest band gap may arise due to its highest level of doping by native defects, which is also reflected in the largest broadening parameter. The bandgap shift is likely to occur through the Burstein-Moss effect for degenerately-doped semiconductors.
Figure 4-1: The real and imaginary parts of the dielectric functions are shown for ZnO deposited under various conditions on different substrates. These dielectric functions are the results of initial analytical fits using two CP oscillators to evaluate the relative amplitudes and shapes of the dielectric functions.

The series of plots including Figs. 4.3 to 4.7 have been generated on the basis of the 11-parameter model of Table 4.3 using the parameters of Table 4.5. In Figs. 4.3 and 4.4, the best fits of dielectric functions are shown as the sum of the contributions of the two CP oscillators as well as that of the photon energy independent contribution $\varepsilon_{10}$. Then in Figs. 4.5-4.7, the various parameters are correlated in scatter plots with the void volume percentage and the energy gap of the first CP oscillator given as the abscissa values. The goal of these plots is to determine if correlations exist in the parameters. If
correlations can be identified, simplifications in the optical model may be possible by reduction in the number of free parameters.

Table 4.2: This table provides the void volume percentage of six samples of Table 4.1 measured relative to the reference sample "DS-LD-009 After Annealing".

<table>
<thead>
<tr>
<th>Sample name</th>
<th>CP-1 $E_g$ (eV)</th>
<th>Void volume %</th>
<th>MSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>DS-LD-009 After Annealing</td>
<td>3.2987 ± 0.0021</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>DS-LD-009</td>
<td>3.3012 ± 0.0001</td>
<td>0.40 ± 0.09</td>
<td>0.0085</td>
</tr>
<tr>
<td>DA-CL-006</td>
<td>3.2925 ± 0.0002</td>
<td>0.48 ± 0.06</td>
<td>0.0059</td>
</tr>
<tr>
<td>USIB</td>
<td>3.3943 ± 0.0001</td>
<td>2.41 ± 0.15</td>
<td>0.0150</td>
</tr>
<tr>
<td>LD-MV-409c</td>
<td>3.3375 ± 0.0001</td>
<td>4.55 ± 0.08</td>
<td>0.0086</td>
</tr>
<tr>
<td>PVIC</td>
<td>3.3133 ± 0.0001</td>
<td>7.57 ± 0.12</td>
<td>0.0123</td>
</tr>
<tr>
<td>USIA</td>
<td>3.3548 ± 0.0001</td>
<td>11.73 ± 0.09</td>
<td>0.0097</td>
</tr>
</tbody>
</table>

Table 4.3: The models, numbers of parameters varied, and the sum of the mean-squared error (MSE) are tabulated from analyses of the dielectric functions of the seven samples presented in Table 4.1. Different oscillator models were applied after extracting the voids from the samples analytically (with the exception of the reference sample, which has 0 vol.% void by definition). As can be seen, the 11 parameter 2-CP model exhibits the lowest sum of the MSEs.

<table>
<thead>
<tr>
<th>Models</th>
<th>Number of parameters</th>
<th>Sum of MSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 Parameter CP-TL</td>
<td>1 CP (5 parameters: $A$, $E_0$, $\Gamma$, $\mu$, $\varphi$)</td>
<td>0.1968</td>
</tr>
<tr>
<td></td>
<td>1 TL (1 parameter: $A$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 Sellmeier (2 parameters: $A$, $\varepsilon_{10}$)</td>
<td></td>
</tr>
<tr>
<td>10 Parameter CP-TL</td>
<td>1 CP (5 parameters: $A$, $E_0$, $\Gamma$, $\mu$, $\varphi$)</td>
<td>0.1557</td>
</tr>
<tr>
<td></td>
<td>1 TL (3 parameters: $A$, $E_n$, $\Gamma$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 Sellmeier (2 parameters: $A$, $\varepsilon_{10}$)</td>
<td></td>
</tr>
<tr>
<td>8-10 Parameter 2-CP</td>
<td>2 CP (8 or 9 parameters: $A$, $E_0$, $\Gamma$, $\mu$, $\varphi$; for some samples $\varphi$ is fixed)</td>
<td>0.0997</td>
</tr>
<tr>
<td></td>
<td>1 $\varepsilon_{10}$ (for some samples, $\varepsilon_{10}$ is fixed)</td>
<td></td>
</tr>
<tr>
<td>11 Parameter 2-CP</td>
<td>2 CP (2 x 5 parameters: $A$, $E_0$, $\Gamma$, $\mu$, $\varphi$)</td>
<td>0.0456</td>
</tr>
<tr>
<td></td>
<td>1 $\varepsilon_{10}$</td>
<td></td>
</tr>
</tbody>
</table>
Figure 4-2: The MSEs are shown for individual samples obtained using various oscillator models, as presented in Table 4.3. For clarity, the sample designations are abbreviated by removing the code numbers.
Table 4.4: A tabulation is presented for the sequence of analysis steps used to obtain the dielectric function parameters of Table 4.5 and the resulting dielectric functions plotted in Figs. 4.3 and 4.4.

<table>
<thead>
<tr>
<th>Analysis Step</th>
<th>Procedure</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Least squares regression analysis with a 2-CP dielectric function model</td>
<td>Identification of variations in the dielectric function amplitudes for assessment of the relative void volume percentages in the materials</td>
</tr>
<tr>
<td>2</td>
<td>Least squares regression analysis with the void volume percentage as a single parameter</td>
<td>Determination of void volume percentage on a scale relative to the lowest void percentage material</td>
</tr>
<tr>
<td>3</td>
<td>Mathematical inversion</td>
<td>Extraction of the volume percentage of voids determined in Step 2, yielding the dense phase dielectric function for each sample</td>
</tr>
<tr>
<td>4</td>
<td>Least squares regression with 2-CP optical model</td>
<td>Identification of the appropriate model needed for parameterization of the dense phase dielectric functions and interpretation of the resulting parameters</td>
</tr>
</tbody>
</table>
Table 4.5: The following tabulation provides the oscillator parameters for the ZnO dielectric functions obtained according to the series of analysis steps in Table 4.4. The sample "DS-LD-009 After Annealing" of the first column is taken as a reference sample, and void percentages were determined for the other six samples with respect to this sample. For the remaining six samples, the columns provide the best fit parameters obtained for the dense phase dielectric functions after the voids were removed. The first set of the rows shows the first CP (CP-1) oscillator parameters used to determine the characteristics of the lowest optical band gap, and the second set of rows shows the best fit parameters for the second CP (CP-2) oscillator which serves to model background absorption.

<table>
<thead>
<tr>
<th></th>
<th>DS-LD-009 After Annealing 0.73-5 eV</th>
<th>DS-LD-009 0.73-5 eV</th>
<th>DA-CL-006 0.76-5eV</th>
<th>LD-MV-409c 0.74-5.1eV</th>
<th>USIA 1.5-4.95eV</th>
<th>USIB 0.8-5 eV</th>
<th>PVIC 0.74-5 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSE</td>
<td>0.04054</td>
<td>0.00041</td>
<td>0.00255</td>
<td>0.00021</td>
<td>0.00021</td>
<td>0.00024</td>
<td>0.00123</td>
</tr>
<tr>
<td>ε_10</td>
<td>2.763 ± 0.094</td>
<td>1.863 ± 0.001</td>
<td>2.252 ± 0.012</td>
<td>0.995 ± 0.007</td>
<td>1.278 ± 0.001</td>
<td>2.217 ± 0.001</td>
<td>−4.907 ± 0.557</td>
</tr>
<tr>
<td>CP-1 A</td>
<td>2.949 ± 0.145</td>
<td>4.538 ± 0.002</td>
<td>2.978 ± 0.015</td>
<td>3.535 ± 0.002</td>
<td>4.812 ± 0.001</td>
<td>2.400 ± 0.004</td>
<td>3.021 ± 0.011</td>
</tr>
<tr>
<td>CP-1 E_g (eV)</td>
<td>3.2987 ± 0.0021</td>
<td>3.3012 ± 0.0001</td>
<td>3.2925 ± 0.0002</td>
<td>3.3375 ± 0.0002</td>
<td>3.3548 ± 0.0001</td>
<td>3.3943 ± 0.0001</td>
<td>3.3133 ± 0.0001</td>
</tr>
<tr>
<td>CP-2 Γ (eV)</td>
<td>0.1238 ± 0.0102</td>
<td>0.1044 ± 0.0001</td>
<td>0.1846 ± 0.0011</td>
<td>0.1577 ± 0.0001</td>
<td>0.1750 ± 0.0001</td>
<td>0.3615 ± 0.0003</td>
<td>0.2322 ± 0.0007</td>
</tr>
<tr>
<td>CP-2 θ (°)</td>
<td>−17.705 ± 3.098</td>
<td>2.394 ± 0.006</td>
<td>−23.289 ± 0.274</td>
<td>−10.290 ± 0.020</td>
<td>−0.017 ± 0.003</td>
<td>−33.423 ± 0.078</td>
<td>−26.469 ± 0.182</td>
</tr>
<tr>
<td>CP-2 μ</td>
<td>0.4113 ± 0.0361</td>
<td>0.2327 ± 0.0001</td>
<td>0.3888 ± 0.0032</td>
<td>0.2955 ± 0.0002</td>
<td>0.2038 ± 0.0001</td>
<td>0.4574 ± 0.0001</td>
<td>0.4004 ± 0.0022</td>
</tr>
<tr>
<td>CP-2 A</td>
<td>2.050 ± 0.478</td>
<td>0.332 ± 0.001</td>
<td>1.318 ± 0.007</td>
<td>1.926 ± 0.007</td>
<td>0.345 ± 0.001</td>
<td>1.351 ± 0.003</td>
<td>8.087 ± 0.560</td>
</tr>
<tr>
<td>CP-2 E_g (eV)</td>
<td>6.443 ± 0.547</td>
<td>4.861 ± 0.005</td>
<td>5.931 ± 0.065</td>
<td>5.986 ± 0.006</td>
<td>4.177 ± 0.001</td>
<td>4.395 ± 0.003</td>
<td>4.456 ± 0.030</td>
</tr>
<tr>
<td>CP-2 Γ (eV)</td>
<td>2.597 ± 0.823</td>
<td>4.169 ± 0.020</td>
<td>4.769 ± 0.077</td>
<td>3.695 ± 0.010</td>
<td>1.848 ± 0.002</td>
<td>3.794 ± 0.007</td>
<td>4.416 ± 0.040</td>
</tr>
<tr>
<td>CP-2 θ (°)</td>
<td>12.084 ± 9.599</td>
<td>169.840 ± 0.754</td>
<td>7.765 ± 0.726</td>
<td>3.683 ± 0.036</td>
<td>168.420 ± 0.257</td>
<td>9.977 ± 0.070</td>
<td>0.622 ± 0.055</td>
</tr>
<tr>
<td>CP-2 μ</td>
<td>1.136 ± 0.254</td>
<td>2.607 ± 0.013</td>
<td>0.675 ± 0.015</td>
<td>0.274 ± 0.002</td>
<td>1.987 ± 0.002</td>
<td>0.472 ± 0.001</td>
<td>0.069 ± 0.005</td>
</tr>
</tbody>
</table>
Figure 4-3: Contributions of the 2-CP oscillator best fits to the dielectric functions are shown for four samples, with the results for the remaining three samples shown in Fig. 4.4. Here, the input data are plotted, representing the dielectric function with the void volume percentage analytically removed (open squares), along with the output best fit to this dielectric function (solid line), and the contributions of the two CP oscillators, including that of ε₁₀ (open circles and triangles, respectively). The sum of these contributions is the best fit to the input dielectric functions (solid line).
Figure 4-4: Contributions of the 2-CP oscillator fits to the dielectric functions are shown as in Fig. 4.3, but for the remaining three samples: USIA, USIB, and DA-CL-006.
Figure 4-5: Scatter plots are shown for the first and second CP oscillator amplitudes and broadening parameters (CP-1 and CP-2) plotted on the same scales as functions of the void volume percentage. The lowest panel shows the results for the CP-1 broadening parameter on an expanded scale.
Figure 4-6: The four parameters of the first CP oscillator (CP-1) are shown including the amplitude, broadening, exponent, and phase; as well as $\varepsilon_{10}$. These results are plotted as functions of the CP-1 energy gap ($E_g$). The possibility of a relationship between the broadening and the energy gap is explored here. The solid line shows the best linear relationship between the two parameters.
Figure 4-7: All five parameters including the amplitude, broadening, energy, exponent, and phase are plotted for the second CP oscillator (CP-2) as functions of the CP-1 energy gap (E_g).

An inspection of Figs. 4.3 through 4.7 show instabilities in the fitting parameters, likely due to correlations. Although the 11 parameter model with two CPs provides the best overall MSE sum, the resulting parameters show considerable scatter and suggest that specific parameters for some samples must be fixed. For example, \( \varepsilon_{10} \) for all samples lies within the reasonable range from 1 to 3 with the exception of the sample labeled "PVIC". In this case, very little dispersion appears for CP-2, resulting in a correlation between its amplitude and \( \varepsilon_{10} \) for this sample. This problem also appears in Figs. 4.5 and 4.7 which show the amplitude of CP-2 as an outlier point. Such a correlation likely leads
to smaller scale scatter in $\varepsilon_{10}$ and the CP-2 amplitude for the other samples, as well. In general, it must be concluded that there are no clear trends between parameters and any reduction in the number of parameters must occur only on a sample-by-sample basis. Future efforts should focus more intensively on addressing this problem.

4.3  Effect of Thermal Annealing on the Optical Properties of ZnO

In this section, the effect of thermal annealing on the zinc oxide structure and optical properties will be discussed for sample DS-LD-009 deposited on a borosilicate glass substrate. The deposition conditions for this sample were provided in Table 4.1. For annealing of the ZnO and studies of the temperature dependence of the substrate and the ZnO optical properties, the heating stage was maintained under vacuum at a pressure on the order of $10^{-8}$ Torr.

The ellipsometry parameters ($\psi$, $\Delta$) at room temperature before and after annealing to 700 K are shown in Figure 4.8. The solid black line represents the data before annealing commences. The data given by the solid red squares and open circles were taken at room temperature after one cycle of annealing (heating to 700 K and back), and after two cycles of annealing, respectively. During the first annealing cycle, the film structure is changing (for example, the bulk layer defect density, grain size, surface roughness), and simultaneously the optical and electrical properties of the films are also changing. In order to study the temperature dependence of optical properties, as caused by a change in lattice parameters and phonon population, however, the material structure should not change as the temperature is varied. For this reason, the sample was measured at room temperature and during the second annealing cycle at every 50 K up to 650 K.
It should be emphasized that upon annealing during the first cycle, there is an irreversible change in $\psi$ at the higher energies. In contrast, the room temperature data after the second annealing cycle coincides with those of the film after the first annealing cycle, which confirms that the film properties are reversible during the second annealing cycle. It should be noted that near and below the band edge, all the data in Fig. 4.8 coincide. Later, in Section 4.5 it will be interesting to find that an aluminum doped zinc oxide (AZO) film shows behavior different from that of sample DS-LD-009. In fact, after a single annealing cycle the room temperature optical properties of the AZO throughout the measured photon energy range are very different from those obtained before annealing.

The resistivity of ZnO at room temperature was also measured before and after the first annealing cycle to 700 K by using a four point probe (Model 2400, Keithley Instruments). The instrument basically determines the sheet resistance $R_s$, which when multiplied by the effective thickness of the film $d_{\text{eff}}$, gives the electrical resistivity ($\rho_o$):

$$\rho_o = R_s \cdot d_{\text{eff}} = \frac{m^*/N}{e^2 \tau} = \frac{1}{N \mu_e \tau}$$

where $e$, $m^*$, $N$, $\tau$, and $\mu$ represent the charge, resistivity effective mass, concentration, scattering time, and mobility, respectively, for the dominant charge carrier which is the electron in ZnO (Hook and Hall, 1991). Here, the effective thickness is defined as the volume/area of the ZnO film, which can be determined as the ZnO volume fraction in a layer multiplied by the layer thickness, and summed over all layers that include a ZnO component. The third equality in Eq. (4.1) derives from the relationship between the mean free time $\tau$ and the mobility $\mu$ according to

$$\mu = \frac{e \tau}{m^*}$$
Thus, for a given material, there is a direct relation between the mobility and the scattering time provided that the effective carrier mass is known.

In order for a thin film material with a given effective mass to exhibit lower resistivity, the charge carrier concentration must be increased at fixed scattering time. Alternatively the scattering time or mobility must be increased at fixed electron concentration. Of course, the greatest benefit in reducing the resistivity is to increase both $N$ and $\tau$ or $\mu$ simultaneously. The resistivity of the sample DS-LD-009 before heating was $1.73 \times 10^4 \ \Omega$-cm. The first annealing cycle, i.e. heating the sample to 700 K and then cooling it to room temperature, however, significantly reduced the resistivity to 67.8 $\Omega$-cm. One possible reason for this effect may be a reduction in defect density in the crystallites and an increase in the crystallite size. In both cases, electron scattering time is likely to be increased, in one case by elimination of the defects themselves and in the second case by a reduction in volume associated with grain boundary regions. Another possible effect is a reduction in p-type compensating defects by annealing which can in turn increase $N$. The native n-type defect that leads to the relatively low resistivity for such a wide band gap material is believed to be the Zn interstitial which can donate two electrons to the conduction band. Thus, even unintentionally doped ZnO is an n-type transparent conducting oxide. The annealing effects in the case of Al doped ZnO will be presented later in the chapter.

The measured ellipsometry spectra at room temperature before and after the first annealing cycle were fit using two CP oscillators. Each parameter was varied with the exception of the phases, which were fixed at the values obtained before annealing. Varying the phases in this study can result in unphysical negative excursions for the
imaginary part of the dielectric function $\varepsilon_2$. The best fit parameters are provided in Table 4.6. It can be seen from the table that the effective thickness appears to increase by 16 Å upon annealing. The effect could result from small spatial thickness non-uniformities of the sample, coupled with measurement of slightly different sample spots before and after annealing. The table also shows that the lowest CP energy, i.e. the optical band gap, has increased only slightly upon annealing. The amplitude and exponent of the lowest energy critical point show no change within the confidence limits.

Figure 4-8: Ellipsometry spectra ($\psi$, $\Delta$) at room temperature are shown for the ZnO thin film sample DS-LD-009 deposited on borosilicate glass as measured before annealing the sample and after one and two annealing cycles.
Table 4.6: The best fit CP oscillator parameters are shown for dielectric functions measured at room temperature for the ZnO sample DS-LD-009 deposited on borosilicate glass before and after the first annealing cycle from room temperature to 700 K and back. Here the notations 'CP-1' and 'CP-2' designate the parameters for the first and second CP oscillators.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>RT Before Annealing</th>
<th>RT After Annealing</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSE</td>
<td>0.00697</td>
<td>0.00856</td>
</tr>
<tr>
<td>ZnO Bulk Thickness (Å)</td>
<td>1511.1±1.3</td>
<td>1536.0±2.3</td>
</tr>
<tr>
<td>ZnO Surface Roughness (Å)</td>
<td>129.0±0.7</td>
<td>110.8±1.2</td>
</tr>
<tr>
<td>Effective Thickness (Å)</td>
<td>1575.6±1.7</td>
<td>1591.4±2.9</td>
</tr>
<tr>
<td>$\varepsilon_{1o}$</td>
<td>1.438±0.093</td>
<td>1.645±0.135</td>
</tr>
<tr>
<td>CP-1 A</td>
<td>5.097±0.089</td>
<td>4.947±0.132</td>
</tr>
<tr>
<td>CP-1 $E_g$ (eV)</td>
<td>3.293±0.002</td>
<td>3.300±0.002</td>
</tr>
<tr>
<td>CP-1 $\Gamma$ (eV)</td>
<td>0.075±0.003</td>
<td>0.058±0.003</td>
</tr>
<tr>
<td>CP-1 $\mu$</td>
<td>0.197±0.006</td>
<td>0.199±0.010</td>
</tr>
<tr>
<td>CP-1 θ (°)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CP-2 A</td>
<td>0.766±0.096</td>
<td>2.274±2.100</td>
</tr>
<tr>
<td>CP-2 $E_g$ (eV)</td>
<td>5.395±0.101</td>
<td>5.446±0.271</td>
</tr>
<tr>
<td>CP-2 $\Gamma$ (eV)</td>
<td>0.692±0.139</td>
<td>0.541±0.114</td>
</tr>
<tr>
<td>CP-2 $\mu$</td>
<td>1.587±0.496</td>
<td>1.594±0.547</td>
</tr>
<tr>
<td>CP-2 θ (°)</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

The parameter that appears to change in a readily interpretable manner is the broadening parameter of the first CP. The clear reduction in $\Gamma$ for CP-1 by $0.0171±0.0057$ eV coupled with the slight increase in bandgap by $0.007±0.004$ eV can be attributed to a reduction in the density of defects that scatter excited electrons. The increase in band gap suggests an increase in carrier concentration via the Burstein-Moss effect, suggesting that the defects being annealed away are compensating defects that lead to an increase not only in electron mobility but also in electron concentration, as also indicated by the decrease in resistivity. It should be noted that these defects may exist at grain boundaries in which case the observed effect could be due to an increase in grain size. Another effect is an apparent increase in the $\varepsilon_{1o}$ upon annealing, and an increase in the amplitude of the second CP. Although these effects would appear to be attributed to an increase in
ZnO bulk layer density upon annealing, it is best to evaluate the density on the basis of inspection of the dielectric functions and application of the Bruggeman effective medium approximation. This has been done in Table 4.2 where it is shown that the void fraction before annealing is \(~0.40\pm0.09\) vol.% higher than that after annealing.

The room temperature dielectric functions of zinc oxide before and after annealing are shown in Fig. 4.1 (left panel), and compared with the reference dielectric function of the sample PVIC that consists of ZnO deposited on c-Si. This comparison emphasizes the sharper CP-1 structure for the ZnO on glass which is clearly enhanced upon annealing. Moreover, the enhanced, more abrupt absorption increase seen after \(~4.5\) eV for the sample after annealing is the primary reason for the higher amplitude and lower broadening observed in the second CP oscillator in the Table 4.6, rather than an effect of a density increase. Because the resonance energy of this oscillator is outside the spectral range, the confidence limits are large.

Next the temperature dependence of the optical properties of ZnO will be explored by studying how the oscillator parameters change as the temperature increases during the second annealing step. The sample was held for forty minutes at each \(+50\) K temperature step before collecting spectroscopic ellipsometry data. Figure 4.9 shows the optical model used to analyze the ellipsometry data as the temperature of the sample is varied. Since borosilicate glass was the substrate, the temperature dependence of the dielectric functions of this glass sample must be extracted first using the same heat stage where ZnO has been studied during annealing. This helps to ensure that the temperatures at which the substrate is measured are the same as those at which the ZnO on the substrate is measured.
The dielectric functions of borosilicate glass derived from spectroscopic ellipsometry data for the different temperatures are shown in Figure 4.10. Once the dielectric function of the glass substrate is known, one can analyze the data to find the dielectric function of ZnO by using the model shown in Figure 4.9. Again, two CP oscillators were used to model the dielectric functions of ZnO at the different temperatures. For the room temperature data, all CP oscillator parameters, including the thickness of the bulk ZnO as well as of surface roughness, were varied. The total number of parameters including $\varepsilon_{10}$ is 13. The resulting fit to the spectroscopic ellipsometry data collected from the sample at room temperature is shown in Fig. 4.11. Then after several trial fits, the parameters that are insensitive or less sensitive to temperature, or varying randomly are fixed. Table 4.7 represents the summary of variable and fixed parameters for the analysis of data collected versus measurement temperature during the second annealing step of the ZnO sample.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc oxide surface roughness layer</td>
<td>110.8 ± 1.2 Å</td>
</tr>
<tr>
<td>Zinc oxide bulk layer (2 CP Oscillators)</td>
<td>1536.0 ± 2.3 Å</td>
</tr>
<tr>
<td>Borosilicate glass substrate</td>
<td>1 mm</td>
</tr>
</tbody>
</table>

Figure 4-9: The model depicted here was used to study the temperature dependence of the ZnO dielectric function. The thicknesses were deduced from analysis of the room temperature spectroscopic ellipsometry data and were then fixed in the analysis.
Figure 4-10: The real (upper) and imaginary (lower) parts of the dielectric function of borosilicate glass are plotted for different measurement temperatures. These dielectric functions are used to characterize the substrate and analyze the temperature dependence of the ZnO dielectric function measured during the second annealing step. The borosilicate glass dielectric functions were obtained by assuming a Sellmeier oscillator when fitting the $(\psi, \Delta)$ spectra.
Figure 4-11: The experimental (ψ, Δ) spectra are shown for the ZnO sample DS-LD-009 as obtained at room temperature during the second annealing step when the structure is stable versus temperature (open circles). The model of Fig. 4.9 has been used to determine the ellipsometry spectra (ψ, Δ) (solid lines) that best fit the room temperature data.
Table 4.7: The fixed and variable fitting parameters for ZnO sample DS-LD-009 are shown for the analysis of the temperature dependence of the ZnO dielectric function from 300 K to 650 K. The energy range used for fitting is 0.75 - 5 eV.

<table>
<thead>
<tr>
<th>Fixed parameters in the best fit</th>
<th>Variable parameters in the best fit</th>
</tr>
</thead>
<tbody>
<tr>
<td>(room temperature values)</td>
<td>1st CP Oscillator:</td>
</tr>
<tr>
<td></td>
<td>A</td>
</tr>
<tr>
<td>ZnO Bulk = 1536.02 Å</td>
<td>Eg (eV)</td>
</tr>
<tr>
<td>Surface Roughness = 110.81 Å</td>
<td>Γ(eV)</td>
</tr>
<tr>
<td>1st CP Oscillator:</td>
<td></td>
</tr>
<tr>
<td>μ = 0.199</td>
<td></td>
</tr>
<tr>
<td>θ = 0°</td>
<td></td>
</tr>
<tr>
<td>2nd CP Oscillator:</td>
<td></td>
</tr>
<tr>
<td>Eg = 5.446 eV</td>
<td></td>
</tr>
<tr>
<td>Γ = 0.541 eV</td>
<td></td>
</tr>
<tr>
<td>θ = 0°</td>
<td></td>
</tr>
</tbody>
</table>

For the parameters that were varied in the analysis, as listed on the right side of Table 4.7, the temperature dependences are plotted in Figs. 4.12 - 4.14 along with the best fit equations. Figure 4.12 shows the temperature dependence of the energy gap of the first CP oscillator. These results show that the optical band gap of ZnO is red-shifted linearly with a temperature coefficient of $-2.57 \times 10^{-4}$ eV/K as the measurement temperature is increased. Thus, for a temperature increase from room temperature to 650 K, the band gap energy decreases by 90 meV. A linearly decreasing trend is also observed in Fig. 4.13 (upper panel) for the amplitude of this first CP oscillator. In contrast, as shown in Fig. 4.13, the broadening parameter (lower panel) increases with increasing temperature. For the second CP oscillator, which provides background absorption above the bandgap with a resonance energy outside the spectral range, only the amplitude and exponent of the oscillator were varied, the latter controlling the shape of the background. Both the resonance energy and the width were fixed versus
temperature; otherwise they would be highly correlated with one another, and with the other second CP parameters. Both the amplitude and exponent show a linearly decreasing trend with increasing temperature. Based on these analyses, the dielectric functions of ZnO at different measurement temperatures can be plotted as shown in Figure 4.15. For clarity, the dielectric functions for only selected temperatures are shown.

\[ E_g (\text{eV}) = 3.377 \text{ eV} - (2.569 \times 10^{-4} \text{ eV K}^{-1}) T (\text{K}) \]

![Graph showing the temperature dependence of the band gap of ZnO](image)

Figure 4-12: The temperature dependence of the band gap of ZnO is plotted, determined as the resonance energy of the CP-1 oscillator. The linear red-shift of the band gap is also shown in the equation obtained from a best fit to the results.
Figure 4-13: These plots show that with increasing measurement temperature the first critical point amplitude decreases but the broadening parameter increases. The best fit linear equations are also shown in the plots.
Figure 4-14: The exponent $\mu_2$ and amplitude $A_2$ of the second CP oscillator are plotted versus measurement temperature along with the best fit linear equations.
Figure 4-15: The real parts (upper panel) and imaginary parts (lower panel) of the dielectric functions of ZnO are plotted for different measurement temperatures. These are obtained from the best fit analytical functions using a complex expression that includes two CP oscillators and a constant contribution to $\varepsilon_1$. The peak heights in $\varepsilon_1$ and $\varepsilon_2$ decrease monotonically as the temperature is increased. The dielectric functions for some of the measurement temperatures are not shown for clarity.

Because the lower energy critical point of intrinsic ZnO describes the direct bandgap, then the results of Fig. 4.12 show the temperature behavior of the band gap.
This is an important quantity for a semiconductor as it impacts the temperature characteristics of electronic devices such as diodes, transistors, and solar cells. The reduction in the band gap of a semiconductor with increasing temperature is due to two effects. The dominant effect is thermal expansion of the lattice, and the secondary effect is enhanced electron-phonon interactions. Various mathematical expressions have been developed, generally semi-empirical in form, that describe $E_g(T)$, including one by Varshni (1967) and more recently one by Pässler (2001). All such forms suggest that the bandgap should decrease linearly with temperature in the limit of high temperature, i.e., at temperatures above the Debye temperature where all phonon modes are excited. Because the Debye temperature for ZnO is reported to be 370 K (Robie and Edwards, 1966), the temperature range of 300 K - 650 K in Fig. 4.12 does not meet the qualifications for expected linearity. In the lower T range in Fig. 4.12, however, one does not observe the expected weakening of the temperature coefficient that would be due to freezing out of the highest energy optical phonon modes from the process. Thus, the temperature dependence of the band gap has been fit to linear behavior for the entire range of $300 \ K < T < 650 \ K$. These results along with a literature survey of the temperature coefficient of the band gap of ZnO using other methods, including index of refraction, absorption coefficient, and photoluminescence are provided in Table 4.8. The results in this dissertation are deemed most accurate due to the use of spectroscopic ellipsometry and the theoretically supported critical point expression to define the band gap. Differences in the results from different laboratories may arise due to the differences in the structural properties of the ZnO which may influence electron-phonon interactions.
The temperature coefficient of ZnO is compared with those of other group II-VI semiconductors in Table 4.9.

Table 4.8: The temperature coefficient of the band gap of ZnO is tabulated.

<table>
<thead>
<tr>
<th>Experimental technique</th>
<th>Temperature coefficient (eV/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectroscopic ellipsometry (this study)</td>
<td>((2.57 \times 10^{-4}) \pm (0.06 \times 10^{-4}))</td>
</tr>
<tr>
<td>Reflection measurement (Jensen, 1974)</td>
<td>(3.65 \times 10^{-4})</td>
</tr>
<tr>
<td>Photoluminescence measurement (Boemare et al., 2001)</td>
<td>(2.50 \times 10^{-4})</td>
</tr>
<tr>
<td>Transmittance measurement (Rai et al., 2012)</td>
<td>((2.00 \times 10^{-4}) \pm (0.20 \times 10^{-4}))</td>
</tr>
</tbody>
</table>

Table 4.9: Temperature coefficient of the bandgap for group II-VI semiconductors are tabulated (Pässler, 2001).

<table>
<thead>
<tr>
<th>Semiconductor</th>
<th>Temperature coefficient (eV/K)</th>
<th>Semiconductor</th>
<th>Temperature coefficient (eV/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>(2.57 \times 10^{-4})</td>
<td>CdO</td>
<td>NA</td>
</tr>
<tr>
<td>ZnS</td>
<td>(5.49 \times 10^{-4})</td>
<td>CdS</td>
<td>(4.09 \times 10^{-4})</td>
</tr>
<tr>
<td>ZnSe</td>
<td>(5.00 \times 10^{-4})</td>
<td>CdSe</td>
<td>(4.10 \times 10^{-4})</td>
</tr>
<tr>
<td>ZnTe</td>
<td>(4.68 \times 10^{-4})</td>
<td>CdTe</td>
<td>(3.09 \times 10^{-4})</td>
</tr>
</tbody>
</table>

The results show that with the exception of the ZnO of this work and CdS, the temperature coefficient decreases with increasing cation and anion atomic weight. There
are two possible differences in this work. First, the dissertation results were obtained on a polycrystalline film; second, and more fundamentally, the oxides may show different behavior due to the higher electronegativity and so more ionic character.

A reasonably good fit to linear behavior is also expected at high temperatures, i.e. above the Debye temperature, for the first critical point (CP-1) or bandgap broadening parameter $\Gamma_1$. The reason is that for independent excited carrier scattering mechanisms in a degenerate semiconductor the broadening parameter can be expressed as:

$$\Gamma(T) = \frac{\hbar}{\tau_d} + \frac{\hbar}{\tau_{ph}(T)},$$

where $\tau_d$ represents the excited state lifetime, an accumulation of temperature-independent effects, including scattering from defects and grain boundaries. In contrast, $\tau_{ph}(T)$ represents phonon scattering processes that limit the lifetime. For a degenerate semiconductor, Fermi-Dirac statistics apply as the Fermi level is located within a high density of states, and above the Debye temperature, $\tau_{ph}(T) = C/T$, where $C$ is a constant. Table 4.10 shows a comparison of the linear temperature coefficient of $\tau$ from this work for ZnO, and for other II-VI polycrystalline semiconductors from the work of Li (2010).

Table 4.10: Temperature coefficient of the bandgap broadening parameter for polycrystalline group II-VI semiconductors are tabulated.

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature coefficient of bandgap broadening parameter (eV/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS (Li, 2010)</td>
<td>$1.99 \times 10^{-4}$</td>
</tr>
<tr>
<td>CdTe (Li, 2010)</td>
<td>$1.22 \times 10^{-4}$</td>
</tr>
<tr>
<td>ZnO (this work)</td>
<td>$0.43 \times 10^{-4}$</td>
</tr>
</tbody>
</table>
A variation of the amplitude of the band gap critical point with temperature may be expected if the broadening increases, whereas the concentration of electrons participating in the band-to-band transition is unchanged. The decreasing amplitude observed is a consequence of the rather complex CP equation that is designed to identify the energy and broadening parameters of a critical point, but does not have a clearly defined relationship to the electron concentration, as compared to a Lorentz oscillator, for example. Similarly difficult to interpret are the temperature dependences of the amplitude and exponent for the second critical point. Since these are used in order to achieve a good fit to the magnitude and shape of the onset of absorption for a CP that is outside the spectral range, the temperature dependence of these parameters do not provide useful physical information as would, for example, a CP energy.

4.4 Dielectric Functions of Doped ZnO

In this section the discussion focuses on the optical and electrical properties of aluminum doped zinc oxide thin films (ZnO:Al; AZO) deposited on various substrates and measured using two spectroscopic ellipsometers, which together span a range from the mid-infrared to the ultraviolet. In the first part, the dielectric functions over the wide range of photon energy are discussed for AZO samples deposited on soda line glass substrates. In the second part, the dielectric functions focusing on the narrower near-infrared to ultraviolet range of photon energy are discussed for AZO layers deposited on a variety of substrates and for gallium doped zinc oxide (ZnO:Ga; GZO) as reported in the literature.
4.4.1 Optical Properties of AZO on Soda Lime Glass from the Infrared to the Ultraviolet (0.08 - 5 eV)

Four different AZO samples deposited on soda lime glass (SLG) substrates were explored over the wide spectral range from the mid-infrared to the ultraviolet. All AZO thin films were deposited at room temperature using a target consisting of 2 wt.% Al$_2$O$_3$ and 98 wt.% ZnO. The pressure and rf sputtering power settings are in the 2-3 mTorr and the 150-250 W ranges, respectively. The first two samples, DS40143 and DS40144, were deposited under identical conditions including a pressure of 2 mTorr and a sputtering power of 150 W. Sample DS40143 was the second deposition in a series after opening the deposition chamber, and sample DS40144 was the third deposition after chamber opening. Generally, the opening of the deposition chamber of a thin film fabrication system, e.g., for cleaning (as opposed to the standard procedure of simply opening the load-lock) can introduce contaminants that decrease in concentration for the sequence of standard procedure depositions thereafter. The substrate/film for these two depositions, namely DS40143 and DS40144, was not rotated during the AZO film fabrication. The other two AZO samples, DS40139 and DS40132, were deposited under conditions different than the first two, including 3 mTorr and 175 W power for DS40139 and 2 mTorr and 250 W power for DS40132. In each case the substrate/film was rotated during the deposition. As a result, these two samples should exhibit more uniform AZO films on the substrate surface. The AZO thicknesses of the first three samples were intended to be $\sim$ 3000 Å, whereas sample DS40132 was deposited to an intended thickness double that of the other samples by using an elevated rf power level.
Spectroscopic ellipsometers purchased from J.A. Woollam Co., Inc were used in the characterization of these samples. Spectra were collected throughout the mid-infrared range (IR) (0.08 - 0.7 eV) and over the range from the near-infrared (NIR) to the ultraviolet (UV) (0.7 - 5.0 eV). The IR and NIR-UV SE data were analyzed simultaneously using the WVASE data analysis software, which was provided with these instruments. The dielectric function of the bulk AZO layer in the model for the IR data was coupled to that of the respective layer in the model for the NIR-UV data. In other words, the same mathematical expression was used for this dielectric function with the same parameter values in the least-squares regression analysis, which was applied to both sets of data simultaneously. In contrast, the bulk AZO thickness was allowed to vary independently in the IR and NIR-UV models in order to account for different measurement spots and possible thickness non-uniformity over the substrate area; however, the AZO surface roughness and interface thicknesses (the latter between the glass and bulk AZO layer) were coupled in both models used in the fitting procedure. The two models for the IR and NIR-to-UV SE data are shown in Figure 4.16.

Considering the optical properties of surface roughness and interface layers, the dielectric function of the AZO component of the surface layer, which was also varied in the analysis, was assumed to be the same as that of the bulk AZO. Thus, when the AZO dielectric function changes so does that of the surface layer -- in accordance with the Bruggeman effective medium approximation. In contrast, because the interface layer may be optically different than the bulk AZO layer, the value of the photon energy independent offset in $\varepsilon_1$ was allowed to vary for the interface layer, whereas the corresponding offset for the bulk layer AZO was fixed to unity. This variability of the
offset implies that the interface and bulk layer dielectric functions will differ by a photon energy independent constant. Any further complexity introduced into the interface optical properties would be difficult to identify given the thinness of the interface layer. The dielectric function of the bulk AZO was fitted using a Drude term, two Lorentz oscillators, and a CP oscillator; the best fit parameters and their confidence limits for the four samples are shown in Table 4.11.

**NIR-UV SE Model**

<table>
<thead>
<tr>
<th>Surface (EMA of AZO/Void)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk AZO (Drude term, 2 Lorentz oscillators, and 1 CP oscillator)</td>
</tr>
<tr>
<td>Interface (Bulk AZO with a variable ( \varepsilon_{10} ) value)</td>
</tr>
<tr>
<td>Soda Lime Glass (SLG)</td>
</tr>
</tbody>
</table>

**IR SE Model**

<table>
<thead>
<tr>
<th>Surface (EMA Coupled to NIR-UV Surface)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZO (Coupled to NIR-UV AZO)</td>
</tr>
<tr>
<td>Interface (Coupled to NIR-UV Interface)</td>
</tr>
<tr>
<td>Soda Lime Glass (SLG) (Coupled to NIR-UV SLG)</td>
</tr>
</tbody>
</table>

Figure 4-16: The dielectric functions of AZO deposited on soda lime glass for a wide photon energy range (0.08 to 5 eV) were found by fitting both IR and NIR-UV data simultaneously using these models. The upper model was used to fit the NIR-UV data, whereas the lower model was used to fit the IR data. The dielectric function of each layer of the IR model was coupled to that of the respective layer in the NIR-UV model. The surface and interface layer thicknesses were also coupled; however, the bulk layer thickness was independently varied.
Table 4.11: The resulting best fit parameters based on the models shown in Fig. 4.16 for samples of (Soda Lime Glass)/AZO are provided for the energy range of 0.08 - 5 eV. The AZO layers of all samples were deposited at room temperature using a target consisting of 2 wt.% Al$_2$O$_3$ and 98 wt.% ZnO. The phase ($\theta$) of the CP oscillator was fixed to zero for these best fits.

<table>
<thead>
<tr>
<th></th>
<th>DS40143 SLG/AZO 150 W, 2 mTorr Substrate not rotated</th>
<th>DS40144 SLG/AZO 150 W, 2 mTorr Substrate not rotated</th>
<th>DS40139 SLG/AZO 175 W, 3 mTorr Substrate rotated</th>
<th>DS40132 SLG/AZO 250 W, 2 mTorr Substrate rotated</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSE</td>
<td>0.0097</td>
<td>0.0089</td>
<td>0.0078</td>
<td>0.0099</td>
</tr>
<tr>
<td>Deposition time (min)</td>
<td>90</td>
<td>90</td>
<td>80</td>
<td>90</td>
</tr>
<tr>
<td>AZO Thickness from NIR-UV SE (Å)</td>
<td>2808.7 ± 61.2</td>
<td>2727.4 ± 51.5</td>
<td>2779.9 ± 50.3</td>
<td>5891.7 ± 19.3</td>
</tr>
<tr>
<td>AZO Thickness from IR SE (Å)</td>
<td>2870.9 ± 77.6</td>
<td>2827.8 ± 65.7</td>
<td>2879.8 ± 64.4</td>
<td>4914.0 ± 75.6</td>
</tr>
<tr>
<td>Interface Thickness (Å)</td>
<td>399.7 ± 74.4</td>
<td>451.0 ± 61.6</td>
<td>348.2 ± 62.5</td>
<td>141.8 ± 29.4</td>
</tr>
<tr>
<td>Interface $\varepsilon_{10}$</td>
<td>1.27 ± 0.06</td>
<td>1.23 ± 0.04</td>
<td>1.28 ± 0.06</td>
<td>2.76 ± 0.38</td>
</tr>
<tr>
<td>Surface Roughness Thickness (Å)</td>
<td>125.0 ± 1.8</td>
<td>84.0 ± 1.8</td>
<td>114.3 ± 3.7</td>
<td>138.1 ± 5.9</td>
</tr>
<tr>
<td>Surface Roughness Void Content (vol.%)</td>
<td>47± 2</td>
<td>50± 4</td>
<td>32± 1</td>
<td>18± 1</td>
</tr>
<tr>
<td>Drude A (eV)</td>
<td>3.138 ± 0.041</td>
<td>3.894 ± 0.050</td>
<td>4.873 ± 0.057</td>
<td>5.703 ± 0.125</td>
</tr>
<tr>
<td>Drude $\Gamma$ (eV)</td>
<td>0.1140 ± 0.0038</td>
<td>0.1182 ± 0.0043</td>
<td>0.1270 ± 0.0045</td>
<td>0.0933 ± 0.0080</td>
</tr>
<tr>
<td>Lorentz A</td>
<td>0.8401 ± 0.0263</td>
<td>0.8413 ± 0.0241</td>
<td>0.5740 ± 0.0197</td>
<td>0.8733 ± 0.0096</td>
</tr>
<tr>
<td>Lorentz $E_n$ (eV)</td>
<td>0.7438 ± 0.0016</td>
<td>0.7623 ± 0.0015</td>
<td>0.7718 ± 0.0018</td>
<td>0.7718 ± 0.0018</td>
</tr>
<tr>
<td>Lorentz $\Gamma$ (eV)</td>
<td>0.1007 ± 0.0044</td>
<td>0.1007 ± 0.0040</td>
<td>0.1016 ± 0.0048</td>
<td>0.1016 ± 0.0048</td>
</tr>
<tr>
<td>Lorentz A</td>
<td>13.76 ± 0.19</td>
<td>13.12 ± 0.28</td>
<td>14.39 ± 0.34</td>
<td>9.82 ± 1.22</td>
</tr>
<tr>
<td>Lorentz $E_n$ (eV)</td>
<td>0.2048 ± 0.0009</td>
<td>0.2000 ± 0.0012</td>
<td>0.1955 ± 0.0009</td>
<td>0.1713 ± 0.0065</td>
</tr>
<tr>
<td>Lorentz $\Gamma$ (eV)</td>
<td>0.2382 ± 0.0016</td>
<td>0.2483 ± 0.0018</td>
<td>0.2163 ± 0.0021</td>
<td>0.3147 ± 0.0054</td>
</tr>
<tr>
<td>CP A</td>
<td>4.492 ± 0.021</td>
<td>4.518 ± 0.020</td>
<td>4.473 ± 0.018</td>
<td>4.864 ± 0.029</td>
</tr>
<tr>
<td>CP $E_g$ (eV)</td>
<td>3.659 ± 0.0042</td>
<td>3.666 ± 0.0038</td>
<td>3.689 ± 0.0036</td>
<td>3.652 ± 0.0035</td>
</tr>
<tr>
<td>CP $\Gamma$ (eV)</td>
<td>0.2690 ± 0.0088</td>
<td>0.2785 ± 0.0087</td>
<td>0.3036 ± 0.0060</td>
<td>0.2546 ± 0.0047</td>
</tr>
<tr>
<td>CP $\mu$</td>
<td>0.2009 ± 0.0023</td>
<td>0.2014 ± 0.0019</td>
<td>0.2031 ± 0.0018</td>
<td>0.2133 ± 0.0012</td>
</tr>
</tbody>
</table>
The measured ellipsometric spectra $\psi$ and $\Delta$ for one of the four samples, namely DS40139, are shown in Figures 4-17, 4-18, and 4-19 for the NIR-UV and IR spectral ranges, respectively. The low energy results within the IR range are shown on an expanded scale in Figure 4-19. Also shown are the best fit simulated spectra resulting from the models of Figure 4.16 with the parameters tabulated in Table 4.11. As shown in Table 4.11, the sample DS40139 of Figures 4.17 and 4.18 was fabricated before chamber opening using 175 W power and 3 mTorr Ar pressure. The experimental data and model fit are in good agreement, and the confidence limits on all parameters are relatively narrow, supporting the validity of the model.

The existence of an interface layer of different dielectric function than the bulk layer is also supported in the analysis. Evidence for the existence of such an interface for AZO deposited on glass was also provided by researchers elsewhere (Ehrmann and Reineke-Koch, 2010). It can be observed in Table 4.11 that the photon energy independent $\varepsilon_{10}$ for the interface layer is greater than unity, implying that the interface is optically denser than the bulk AZO. The origin of the interface layer is unclear; however, two related explanations may account for the higher density. First, in the initial stages of film growth, the film structure may consist of much smaller grains, essentially characterized by a nanocrystalline structure, as opposed to the larger grain polycrystalline structure of the bulk layer. This layer may result from a high density of crystallite nucleation sites and represents a region of crystallite competition for available space at the growing film surface. Second, or in addition, voids may develop in the bulk layer as a response to the build-up of film strain in the early stages of growth, possibly as a result of the fine grained structure.
Next the critical point resonance energy, or fundamental optical band gap, from Table 4.11 will be considered. The optical band gap or absorption onset of a thin film depends on the deposition conditions, and in particular for ZnO, on the doping level which arises from the Al in the sputtering target. For the AZO samples listed in Table 4.11, the optical bandgap range is relatively narrow, from 3.65 to 3.69 eV, as determined from the resonance energy \( (E_g) \) of the CP oscillator. This is expected since the target which is the source of the dopant atoms is the same for all depositions. This energy range lies within that reported by Ma et al., 2007 (3.58 - 3.74 eV). It does not, however, overlap the ranges reported by Kim et al., 1997 (3.46 - 3.54 eV), suggesting a lower doping level in their samples, and by Yang et al., 2009 (3.75 - 3.86 eV), suggesting a higher doping level in their samples. Comparing these values to intrinsic ZnO, which exhibits an optical band gap of 3.30 eV, the reported ranges represent large blue-shifts in the observed gap, as would be expected for a degenerately-doped wide bandgap semiconductor according to the Burstein-Moss (BM) effect. Because of this effect, the fundamental absorption onset of a degenerately-doped semiconductor shifts to higher energy as the carrier concentration increases (Burstein, 1954; Moss, 1954).

In the BM effect, as the carrier concentration increases, the Fermi level increases in energy into the conduction band, thereby widening the optical bandgap, due to the filling of the lower energy states in the conduction band by electrons. The Fermi level shift provides the band gap shift relative to the undoped ZnO according to (Suchea et al., 2007):

\[
\Delta E_g = \left( \frac{\hbar^2}{2m^*} \right) \left( 3\pi^2 N \right)^{2/3}, \tag{4.2}
\]
where $\Delta E_g$ is the band gap shift, $m^*$ is the density of states effective mass of the electron, $\hbar$ is Planck's constant, and $N$ is the electron concentration. The BM effect arises in a degenerately-doped semiconductor when the carrier concentration exceeds a critical value of $N_c = 2(2\pi m^* k_b T)^{3/2}/\hbar^3$, where $k_b$ and $\hbar$ are the Boltzmann constant and Planck's constant. This is the density of states within $kT$ of the conduction band minimum. In the case of ZnO, $N_c = 3.68 \times 10^{18} \text{ cm}^{-3}$ (Singh et al., 2010). All the AZO samples in Table 4.7 exhibit an electron concentration above this limit.

Interesting features appear in the experimental data of Figures 4.17, 4.18, and 4.19 at photon energies below the band gap in the NIR and IR regions. First, a feature appears at $\sim 0.75$ eV, modeled as a Lorentz oscillator in the first three samples having AZO thickness of $\sim 3000$ Å. Because this feature is missing in sample DS40132 of thickness $\sim 5900$ Å, the feature may be extrinsic in nature, originating for example from contamination by water vapor introduced either during or after deposition. Alternatively, dopant clustering may occur under specific deposition conditions, and this clustering may lead to a plasmon associated absorption band. The second feature, also modeled as a Lorentz oscillator, appearing at $\sim 0.20$ eV is seen in all samples without exception. This suggests an origin intrinsic to the ZnO, for example, an absorption band associated with the vibrational modes of the Zn-O bonds.

The Drude component deduced from the IR and NIR-UV spectroscopic ellipsometry study can be validated through a free carrier analysis based on the deduced parameters. Listed in Table 4.12 are the Drude parameters of amplitude, broadening, and plasma energy, the latter deduced from the two former parameters simply by $E_p = (A \Gamma)^{1/2}$. The electrical properties also deduced from $A$ and $\Gamma$ and the corresponding
results obtained directly from dc measurements are included as well. In deriving the dc resistivity and scattering time from IR and NIR-UV SE as in Table 4.12, the Drude parameters can be used without additional assumptions. In deriving the carrier concentration and mobility in this table, an electron resistivity effective mass $m_e^*$ must be assumed. Here, $m_e^* = 0.4 m_0$ is assumed where $m_0$ is free-electron mass (Ehrmann & Reineke-Koch, 2010). In the table, it is clearly seen that the resistivity derived from IR and NIR-UV SE is in reasonably good agreement with the dc resistivity directly measured from a four point probe instrument (Keithley Instruments, Model 2400). Of interest is the fact that the thicker AZO sample exhibits a longer scattering time and, as a result, a higher electron mobility, although the carrier concentration is within the range of those for the thinner samples. This may be due to the larger grain size that evolves in a thicker film based on the concept that the mean free path is limited by scattering at grain boundaries. Although the target material, deposition process, and the parameters that characterize the process dictate the ultimate properties of thin films, we find that the electrical property parameters listed in Table 4.12 (i.e., $\rho_o$, $\tau$, $N$, and $\mu$) closely match values reported by Galca et al., 2010 for a similar composition target ($\text{Al}_2\text{O}_3$ content of 2 wt.%) and film thickness.
Table 4.12: IR and NIR-UV SE derived Drude parameters and four-point probe measurements of resistivity are shown for all four samples of AZO (0.08 - 5 eV) analyzed in this study. The basic deposition conditions of the samples are given in the heading row; all samples were deposited at room temperature on soda lime glass substrates using a sputtering target consisting of 2 wt.% Al$_2$O$_3$ and 98 wt.% ZnO.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Drude A (eV)</th>
<th>Drude Γ(eV)</th>
<th>Plasma Energy (eV)</th>
<th>Resistivity $\rho_o$ (Ω·cm)</th>
<th>Four Point Probe Resistivity</th>
<th>Scattering Time $\tau$ (fs)</th>
<th>Carrier Concentration N (cm$^{-3}$)</th>
<th>Carrier Mobility $\mu$ (cm$^2$V$^{-1}$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DS40143 AZO/SLG</td>
<td>3.14 ± 0.04</td>
<td>0.1140 ± 0.0038</td>
<td>0.5981 ± 0.0139</td>
<td>0.00238 ± 0.00003</td>
<td>0.00234</td>
<td>5.718 ± 0.187</td>
<td>1.043x10$^{20}$ ± 0.024x10$^{20}$</td>
<td>25.2 ± 0.8</td>
</tr>
<tr>
<td>DS40144 AZO/SLG</td>
<td>3.89 ± 0.05</td>
<td>0.1182 ± 0.0043</td>
<td>0.6784 ± 0.0167</td>
<td>0.00191 ± 0.00002</td>
<td>0.00181</td>
<td>5.570 ± 0.197</td>
<td>1.335x10$^{20}$ ± 0.035x10$^{20}$</td>
<td>24.5 ± 0.9</td>
</tr>
<tr>
<td>DS40139 SLG/AZO</td>
<td>4.87 ± 0.06</td>
<td>0.1270 ± 0.0045</td>
<td>0.7867 ± 0.0186</td>
<td>0.00153 ± 0.00002</td>
<td>0.00133</td>
<td>5.184 ± 0.179</td>
<td>1.795x10$^{20}$ ± 0.047x10$^{20}$</td>
<td>22.8 ± 0.8</td>
</tr>
<tr>
<td>DS40132 SLG/AZO</td>
<td>5.70 ± 0.13</td>
<td>0.0933 ± 0.0079</td>
<td>0.7294 ± 0.0393</td>
<td>0.00130 ± 0.00003</td>
<td>0.00154</td>
<td>7.057 ± 0.589</td>
<td>1.543x10$^{20}$ ± 0.103x10$^{20}$</td>
<td>31.0 ± 2.6</td>
</tr>
</tbody>
</table>
Table 4.13: The predicted electron concentration from Eq. (4.2) is tabulated in comparison with that from the Drude term given in Table 4.13. In the analysis of N from the Drude term, the resistivity effective mass $m^* = 0.4m_e$ is used, whereas the table shows that the density of states effective mass of $m^* = 0.29m_e$ gives better agreement of the electron concentration for the two different methods of calculation.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Sample ID</th>
<th>Power (W)</th>
<th>Pressure (mTorr)</th>
<th>Drude Term (N/cm$^3$)</th>
<th>Eq. (4.2) with $m^* = 0.4m_e$</th>
<th>Eq. (4.2) with $m^* = 0.29m_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZO/SLG</td>
<td>DS40143</td>
<td>150</td>
<td>2</td>
<td>0.367</td>
<td>1.043 x 10$^{20}$ ± 0.024 x 10$^{20}$</td>
<td>2.56 x 10$^{20}$</td>
</tr>
<tr>
<td></td>
<td>DS40144</td>
<td></td>
<td></td>
<td>0.374</td>
<td>1.335 x 10$^{20}$ ± 0.035 x 10$^{20}$</td>
<td>2.63 x 10$^{20}$</td>
</tr>
<tr>
<td>SLG/AZO</td>
<td>DS40139</td>
<td>175</td>
<td>3</td>
<td>0.397</td>
<td>1.795 x 10$^{20}$ ± 0.047 x 10$^{20}$</td>
<td>2.87 x 10$^{20}$</td>
</tr>
<tr>
<td></td>
<td>DS40132</td>
<td>250</td>
<td>2</td>
<td>0.360</td>
<td>1.543 x 10$^{20}$ ± 0.103 x 10$^{20}$</td>
<td>2.48 x 10$^{20}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Sample ID</th>
<th>Power (W)</th>
<th>Pressure (mTorr)</th>
<th>Drude Term (N/cm$^3$)</th>
<th>Eq. (4.2) with $m^* = 0.4m_e$</th>
<th>Eq. (4.2) with $m^* = 0.29m_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| ∆$E_g$ (eV) | 0.367 | 0.374 | 0.397 | 0.360 |
| Electron Concentration N (cm$^3$) from the Drude term | 1.043 x 10$^{20}$ ± 0.024 x 10$^{20}$ | 1.335 x 10$^{20}$ ± 0.035 x 10$^{20}$ | 1.795 x 10$^{20}$ ± 0.047 x 10$^{20}$ | 1.543 x 10$^{20}$ ± 0.103 x 10$^{20}$ |
| Electron Concentration N (cm$^3$) Calculated from Eq. (4.2) with $m^* = 0.4m_e$ | 2.56 x 10$^{20}$ | 2.63 x 10$^{20}$ | 2.87 x 10$^{20}$ | 2.48 x 10$^{20}$ |
| Electron Concentration N (cm$^3$) Calculated from Eq. (4.2) with $m^* = 0.29m_e$ | 1.58 x 10$^{20}$ | 1.63 x 10$^{20}$ | 1.78 x 10$^{20}$ | 1.54 x 10$^{20}$ |
Figure 4-17: The data (points) and best fit (line) are shown for AZO sample DS40139, obtained by NIR-UV SE. The model used for SE analysis is shown in Figure 4.16 and the best fit parameters are given in Table 4.11. The sample was deposited at room temperature on a soda lime glass substrate using a sputtering target consisting of 2 wt.% Al$_2$O$_3$ and 98 wt.% ZnO, a 175 W target power, and a 3 mTorr Ar pressure. The substrate was rotated during deposition.
The data (points) and best fit (line) are shown for AZO sample DS40139, obtained by IR SE. The model used for SE analysis is shown in Figure 4.16 and the best fit parameters are given in Table 4.11. The sample was deposited at room temperature on a soda lime glass substrate using a sputtering target consisting of 2 wt.% Al₂O₃ and 98 wt.% ZnO, a 175 W target power, and a 3 mTorr Ar pressure. The substrate was rotated during deposition.
Figure 4-19: Spectroscopic ellipsometry data (points) and best fit (line) are shown over an expanded scale of 0.08 to 0.2 eV within the IR range from Figure 4-18. The sample was deposited at room temperature on a soda lime glass substrate using a sputtering target consisting of 2 wt.% Al₂O₃ and 98 wt.% ZnO, a 175 W target power, and a 3 mTorr Ar pressure.

Equation 4.2 can be applied to estimate the electron concentration in these AZO samples based on the shift in the band gap. These results are presented in Table 4.13 for comparison with the electron concentration deduced from the Drude term. In the calculation of Eq. 4.2, the lowest bandgap of \( E_{g0} = 3.293 \) eV, observed for the undoped
ZnO from Table 4.2, is selected for the determination of the band gap shift. If the calculation is performed using the resistivity effective mass of \( m^* = 0.4m_e \), then the agreement is poor between the two electron concentration estimates. The agreement improves considerably when the proper density of states effective mass of \( m^* = 0.29m_e \) is used as shown in Table 4.13.

The real and imaginary parts of the dielectric functions of AZO for all four samples deduced from the model of Fig. 4.16 and the parameters of Table 4.11 are compared over the range from 0.08 to 5 eV in Figure 4-20. As the photon energy range shown in Figure 4-20 is very large, the real and imaginary part of the dielectric functions are shown separately on expanded scales in Figures 4-21 and 4-22, respectively. For the thickest sample (DS40132), the free electron behavior or metallic character of the dielectric function is more pronounced. The characteristics of free electron absorption include the rapid downward negative trend in the real part \( \varepsilon_1 \) and the upward positive trend in the imaginary part \( \varepsilon_2 \) with decreasing photon energy. The difference in behavior for the thicker sample may have two origins as indicated in the parameter differences in Table 4.11. First, the scattering time is longer which may account for the sharper free electron characteristic. It should be noted that the Drude term generates an absorption half-band at zero energy (not strictly a damped oscillator, however, due to the lack of a restoring force), and the half-width of that band is inversely proportional to the scattering time. Second, the lowest energy feature described by the Lorentz oscillator near 0.2 eV for the thickest sample (DS40132) is weaker (lower amplitude, A), broader (larger broadening parameter \( \Gamma \)), and shifted to lower energy (lower \( E_0 \)) relative to the other
samples, and suppression of this feature may also account for the observed dominance of the free electron behavior.

Figure 4-20: Dielectric functions from 0.08 to 5 eV are shown for the four AZO samples. These results are obtained from the analytical expressions into which the best fit parameters of Table 4.11 have been substituted. All four samples were deposited on soda lime glass substrates from a target consisting of 2 wt.% Al$_2$O$_3$ and 98 wt.% ZnO using the conditions shown in the heading of Table 4.11.
Figure 4-21: Real parts of the dielectric functions are shown on an expanded energy scale for the AZO samples of Figure 4-20. The upper panel shows the results in the IR region of photon energy, whereas the bottom panel shows results in the NIR-UV region. These results are obtained from the analytical expressions into which the best fit parameters of Table 4.11 have been substituted.
Figure 4-22: Imaginary parts of dielectric functions are shown on expanded energy scales for the AZO samples of Figure 4-20. These results are obtained from the analytical expressions into which the best fit parameters of Table 4.11 have been substituted.

The goal in the fabrication of TCOs for photovoltaics when used as a top contact such as in CIGS solar cells is to achieve the largest transmittance $T$ possible and thus the lowest reflectance $R$ and absorbance $A$ possible, typically for the spectral range of $\sim 1 – 3$ eV. It should be emphasized, however, that the optical data of $R$, $T$, and $A$ for the TCO depend on its thickness and the solar cell structure in which it is integrated. This section will conclude with a discussion of spectra in the reflectance $R$ and transmittance $T$, as well as that in the absorbance $A = 1 – R – T$ for the set of samples of Table 4.11. Such results are shown in Figure 4-23 for samples DS40144 and DS40139; similar behavior is
observed for the third thinner sample (DS40143). The results for these three samples can be compared due to their similar thicknesses, whereas DS40132 is significantly thicker which leads to much greater absorbance in the film.

Without an anti-reflection coating, the reflectance losses from ZnO and AZO will typically lie within the range of 7-14% due to indices of refraction of these materials in the range of 1.7-2.2. Thin film interference will modulate this reflectance level as shown in Figure 4-23, yielding reflectances as large as ~ 20% at the higher photon energies where the index of refraction is highest. The transmittance decreases with increasing photon energy at high energies due to the onset of absorption at the optical gap; it decreases with decreasing photon energy at low energies due to free electron absorption. An increase in carrier concentration is expected to shift the optical gap to higher energies, increasing the transmittance near 3 eV and above, whereas such an increase reduces the transmittance near 1 eV due to free carrier absorption. For a given carrier concentration, an increase in the scattering time for free electrons is expected to increase the transmittance near 1 eV due to a reduction in the rate of dissipation. These characteristics are more clearly observed in the absorbance spectra in Figure 4-23 which shows differences between the spectra for the two samples. The lower absorbance for DS40144 is attributed to a lower electron concentration and a longer scattering time which reduces dissipation. The reduced absorption occurs at the expense of a higher resistivity and possibly increased series resistance in the solar cell structure.

As noted just above, for the sample with the thickest AZO (DS40132), it is difficult to make meaningful comparisons with the thinner films with respect to the effect of scattering time since the transmittance drops rapidly with increasing thickness, and this
is expected to be a dominant effect. For films whose thicknesses are significantly different, a comparison of the dielectric functions themselves for all four samples as described previously in this section is more informative.

Figure 4-23: Transmittance (T) and reflectance (R) spectra (upper panel) as well as absorbance spectra (lower panel) are shown for AZO samples DS40144 and DS40139 deposited on soda lime glass substrates. A sputtering target consisting of 2 wt.% Al₂O₃ and 98 wt.% ZnO was used for both samples, and (plasma power level, Ar pressure) values of (150 W, 2 mTorr) and (175 W, 3 mTorr) were used for samples DS40144 and DS40139, respectively. The results for the third sample (DS40143) are not shown since similar behavior is observed.
4.4.2 Dielectric Functions in the NIR-UV Range (~ 0.7 - 5 eV) for AZO

Deposited on Different Substrates

In this sub-section, the dielectric functions of aluminum doped zinc oxide (AZO) deposited on a variety of substrates using various process conditions will be compared for the photon energy range of ~ 0.7 to 5 eV. The dielectric functions of gallium doped zinc oxide (GZO) will also be compared to the results for AZO. Professor Hiroyuki Fujiwara provided the dielectric functions for GZO, which were obtained from in-depth spectroscopic ellipsometry studies (Fujiwara and Kondo, 2005).

Before presenting these results, a brief description of the deposition conditions of the samples of Figs. 4-24 - 4-27 will be presented. The first five samples in the figures are aluminum doped ZnO from a target with an Al₂O₃ content of 2 wt.% deposited on glass substrates. Of the five samples, four AZO samples (namely DS40143, DS40144, DS40139, and DS40132) were deposited on soda lime glass (SLG) substrates, and their deposition conditions have been described earlier in Section 4.4.1 (see Table 4.11). A fifth sample, designated DS40162, was deposited on a borosilicate glass (BSG) substrate at room temperature. For this latter deposition, the substrate was rotated during sputtering, and the conditions during this process include 150 Watt RF power and 2 mTorr chamber Ar pressure. In fact, these are the same conditions as were used for the deposition of sample DS40144, but with the exception of the substrate rotation. Also DS40144 was the third sample deposited in a sequence after opening the deposition chamber. The bulk layer thickness of the AZO of sample DS40162 is 2697 Å, which is the also same as that of sample DS40144 within the confidence limits.
The samples designated MV022, MV211, and MV070 were deposited in a cluster tool deposition system with interconnected chambers that enable preparation of multiple layers of a complete solar cell without exposure to laboratory air between the layers (Dahal, 2013). Dr. Lila Dahal is acknowledged for depositing these samples and providing the dielectric function data. These three AZO samples were deposited from a target with Al$_2$O$_3$ content of 2 wt.% on room temperature substrates with 150 Watt RF sputtering power and with 5 mTorr chamber Ar pressure to a bulk layer thickness of ~2900 Å. The AZO film of the first sample, MV022, was deposited on a thermally oxidized crystalline silicon substrate, whereas the AZO film of the second sample, MV211, was deposited on top of a crystalline silicon substrate which was previously coated by an opaque Ag film. For the AZO of the third sample, MV070, the substrate was polyethylene naphthalate (PEN) polymer also coated with opaque Ag. For the latter sample, during the deposition of the Ag and AZO films, the polymer substrate was moving at a speed of 0.0077 cm/s, which was standard for the roll-to-roll coating process (Dahal, 2013).

The last three samples of gallium (Ga) doped ZnO (GZO) were deposited on thermally oxidized crystalline silicon substrates at deposition temperatures ranging from 25 to 240 °C. All three GZO samples, labeled HF-2, HF-3, and HF-4, were deposited by DC sputtering using a target power of 200 Watt and a chamber Ar pressure of 1 mTorr. The ZnO targets used in the GZO fabrication have different Ga$_2$O$_3$ contents in a range from 0.5 to 5.7 wt.%, yielding the samples with differing gallium doping level. The first sample HF-2 exhibits an electron concentration of $N=1.1\times10^{20}$ cm$^{-3}$ as measured by the Hall effect; HF-3 exhibits $N = 4.8\times10^{20}$ cm$^{-3}$; and HF-4 exhibits $N = 6.5\times10^{20}$ cm$^{-3}$. 
Moreover, HF-4 was deposited at an elevated substrate temperature of 240°C from a ZnO target incorporating 5.7 wt. % of Ga₂O₃. The thicknesses of all three samples were ~700 Å.

Figures 4-24 and 4-25 (upper panels) show examples of the experimentally determined real and imaginary parts of the dielectric functions for this set of samples, one from each group (points), including DS40132 which is from the series deposited on SLG, MV070 which is the sample deposited on Ag coated polymer, and HF-4 which is the GZO sample deposited at elevated temperature. Such dielectric functions of all 11 samples were parameterized over the range of 0.7-5 eV using a Drude term, as well as one critical point (CP) oscillator and one Lorentz oscillator. In this study, the Lorentz oscillator was used to model an absorption band at the lower limit of the spectral range, as described in the previous subsection. In contrast to the study of undoped ZnO in Sec. 4.1, a single CP can provide a good fit above the band gap. The reason is that upon doping, the optical gap CP becomes broader and smoother and no additional background oscillator is required. The best fit parameters from this dielectric function model are provided in Tables 4.14, 4.15, and 4.16, respectively. The derived parameters of resistivity, scattering time, carrier concentration and mobility are shown in Table 4.17. Only the AZO samples deposited on glass, with the exception of the thickest sample, require the low energy Lorentz oscillator. For all the AZO deposited on c-Si or Ag coated substrates, including the GZO, only the Drude term and the single CP oscillator are required in the fit.

Figures 4-24 and 4-25 (upper panels) shows the best fits to the real and imaginary parts of the dielectric functions for the samples, DS40132, MV070, and HF-4, selected as
examples. Because the results from many samples are compared here (11 in total), for clarity the analytical expressions for the real and imaginary parts of the dielectric functions obtained using the parameters of Tables 4.14-4.16 are plotted separately, and each part of these dielectric functions is further grouped according to substrate or dopant. The analytical forms of the real parts of the dielectric functions of the complete set of samples are shown in Figure 4-24 (lower panel) for comparison. Three groups of samples can be distinguished and compared separately. The first group consists of AZO films deposited on glass substrates whose dielectric functions were analyzed in the previous section. The second group includes AZO on substrates other than glass, including crystalline silicon, Ag coated crystalline silicon, and Ag coated polymer substrates. A third group includes the GZO materials deposited on crystalline silicon in an evaluation of the data provided by Fujiwara (Fujiwara and Kondo, 2005). The real parts of the dielectric functions of these three distinct groups of doped ZnO are plotted separately in Figure 4-26. Similarly, the analytical forms of the imaginary parts of the dielectric functions are plotted for all samples in Figure 4-25 (lower panel), and the same data are also shown in Figure 4-27 separated into the three groups. Next, the discussion will focus on parameters in Tables 4.14-4.17, as deduced from the best fits, considering each group of samples individually.

The AZO thin films deposited on soda lime glass (SLG) substrates have a narrow optical band gap range of ~ 3.65-3.70 eV, as determined from the resonance energy ($E_g$) of the CP oscillator in each case. The corresponding value for the AZO on borosilicate glass is somewhat higher, 3.72 eV. For the samples on SLG, the Lorentz oscillator resonance, again only seen in the thin layers, appears in the range ~ 0.75-0.77 eV. For
the AZO film on the borosilicate glass substrate, the low energy Lorentz oscillator is observed, but with a slightly higher energy position of 0.81 eV. This result suggests that the low energy band appearing for the thinner AZO on the glass substrate is not specific to the type of glass. Thus, it seems unlikely that the band is caused by Na or other alkali metal contaminants that diffuse from the glass side, as BSG does not contain such elements and in fact is more stable than SLG.

The AZO sample MV022 deposited on bare crystalline silicon exhibits an optical gap of 3.73 eV, whereas the other two AZO films on top of Ag have wider optical gaps of 3.76 and 3.85 eV. These results suggest possible diffusion of Ag atoms into the AZO, leading to additional doping and a widening of the optical band gap. For the GZO samples, one can clearly observe that the optical band gap shifts to higher energy according to the Burstein-Moss effect as the free electron concentration increases. An optical band gap of 3.55 eV is observed for the electron concentration of \( N = 1.1 \times 10^{20} \) cm\(^{-3} \), and the gap increases to 3.99 eV for \( N = 6.5 \times 10^{20} \) cm\(^{-3} \).
Figure 4-24: The real parts of the dielectric functions are compared for three groups of AZO and GZO samples. The upper panel shows example results for three samples, one from each group, including both the data (points) and the best fit analytical function (lines). The bottom panels show the best fit analytical functions for all eleven samples from the three groups. The first group of five consists of AZO samples deposited on glass substrates; the second group includes three samples of AZO deposited on crystalline silicon or on silver coated substrates; and the third group includes three gallium doped zinc oxide samples deposited on crystalline silicon substrates.
Figure 4-25: The imaginary parts of the dielectric functions are compared for three groups of AZO and GZO samples. The upper panel shows example results for three samples, one from each group, including both the data (points) and the best fit analytical function (lines) in each case. The bottom panels shows the best fit analytical functions for all eleven samples from the three groups. The first group of five consists of AZO samples deposited on glass substrates; the second group includes three samples of AZO deposited on crystalline silicon or on silver coated substrates; and the third group includes three gallium doped zinc oxide samples deposited on crystalline silicon substrates.
Table 4.14: Best fit Drude parameters are tabulated for the doped ZnO samples of Figs. 4-24 - 4-25.

<table>
<thead>
<tr>
<th>Samples</th>
<th>MSE</th>
<th>Drude A (eV)</th>
<th>Drude Γ (eV)</th>
<th>E_p (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DS40143 SLG/AZO (0.7 - 5eV)</td>
<td>0.04165</td>
<td>13.15±4.17</td>
<td>0.0779±0.0260</td>
<td>1.01 ± 0.33</td>
</tr>
<tr>
<td>DS40144 SLG/AZO (0.7 - 5eV)</td>
<td>0.04913</td>
<td>16.10±6.29</td>
<td>0.0679±0.0275</td>
<td>1.04 ± 0.42</td>
</tr>
<tr>
<td>DS40139 SLG/AZO (0.7 - 5eV)</td>
<td>0.05314</td>
<td>11.31±2.15</td>
<td>0.1137±0.0229</td>
<td>1.13 ± 0.22</td>
</tr>
<tr>
<td>DS40132 SLG/AZO (0.7 - 5eV)</td>
<td>0.03860</td>
<td>6.71±0.35</td>
<td>0.1738±0.0090</td>
<td>1.08 ± 0.06</td>
</tr>
<tr>
<td>DS40162 BSG/AZO (0.7 - 5eV)</td>
<td>0.04737</td>
<td>9.76±1.04</td>
<td>0.1439±0.0161</td>
<td>1.18 ± 0.12</td>
</tr>
<tr>
<td>MV022 c-Si/AZO (0.75 - 5eV)</td>
<td>0.01008</td>
<td>8.60 ± 0.12</td>
<td>0.1680 ± 0.0023</td>
<td>1.20 ± 0.02</td>
</tr>
<tr>
<td>MV211 c-Si/Ag/AZO (0.73 - 5eV)</td>
<td>0.00070</td>
<td>13.07±0.01</td>
<td>0.1470 ± 0.0001</td>
<td>1.39 ± 0.01</td>
</tr>
<tr>
<td>MV070 polymer/Ag/AZO (0.73 - 5eV)</td>
<td>0.03879</td>
<td>8.48±0.42</td>
<td>0.1736 ± 0.0085</td>
<td>1.21 ± 0.06</td>
</tr>
<tr>
<td>HF-2 c-Si/GZO (0.73 - 4.7 eV)</td>
<td>0.03962</td>
<td>2.60 ± 0.18</td>
<td>0.2713 ± 0.0188</td>
<td>0.84 ± 0.06</td>
</tr>
<tr>
<td>HF-3 c-Si/GZO (0.73 - 4.7 eV)</td>
<td>0.04019</td>
<td>10.54 ± 0.45</td>
<td>0.1628 ± 0.0069</td>
<td>1.31 ± 0.06</td>
</tr>
<tr>
<td>HF-4 c-Si/GZO (0.73 - 4.7 eV)</td>
<td>0.03922</td>
<td>16.34 ± 0.52</td>
<td>0.1495 ± 0.0047</td>
<td>1.56 ± 0.05</td>
</tr>
</tbody>
</table>
Table 4.15: Best fit CP oscillator parameters are tabulated for the doped ZnO samples of Figs. 4-24 - 4-25.

<table>
<thead>
<tr>
<th>Samples</th>
<th>CP A</th>
<th>CP $E_g$ (eV)</th>
<th>CP $\Gamma$(eV)</th>
<th>CP $\mu$</th>
<th>CP $\theta$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DS40143 SLG/AZO (0.7 - 5eV)</td>
<td>4.360 ±0.016</td>
<td>3.684 ±0.004</td>
<td>0.4083 ±0.0124</td>
<td>0.2155 ±0.0021</td>
<td>−0.835 ±0.209</td>
</tr>
<tr>
<td>DS40144 SLG/AZO (0.7 - 5eV)</td>
<td>4.436 ±0.019</td>
<td>3.688 ±0.004</td>
<td>0.4144 ±0.0143</td>
<td>0.2197 ±0.0025</td>
<td>−0.859 ±0.241</td>
</tr>
<tr>
<td>DS40139 SLG/AZO (0.7 - 5eV)</td>
<td>4.407 ±0.021</td>
<td>3.702 ±0.005</td>
<td>0.3965 ±0.0154</td>
<td>0.2119 ±0.0026</td>
<td>−0.808 ±0.254</td>
</tr>
<tr>
<td>DS40132 SLG/AZO (0.7 - 5eV)</td>
<td>4.643 ±0.016</td>
<td>3.648 ±0.003</td>
<td>0.3490 ±0.0093</td>
<td>0.2131 ±0.0017</td>
<td>−0.832 ±0.159</td>
</tr>
<tr>
<td>DS40162 BSG/AZO (0.7 - 5eV)</td>
<td>4.520 ±0.019</td>
<td>3.722 ±0.004</td>
<td>0.3675 ±0.0122</td>
<td>0.2183 ±0.0022</td>
<td>−0.836 ±0.214</td>
</tr>
<tr>
<td>MV022 c-Si/AZO (0.75 - 5eV)</td>
<td>4.394 ±0.004</td>
<td>3.729 ±0.001</td>
<td>0.3493 ±0.0029</td>
<td>0.1882 ±0.0004</td>
<td>−1.445 ±0.042</td>
</tr>
<tr>
<td>MV211 c-Si/Ag/AZO (0.73 - 5eV)</td>
<td>4.563 ±0.003</td>
<td>3.846 ±0.001</td>
<td>0.2475 ±0.0002</td>
<td>0.1941 ±0.0001</td>
<td>−0.708 ±0.006</td>
</tr>
<tr>
<td>MV070 polymer/Ag/AZO (0.73 - 5eV)</td>
<td>4.565 ±0.017</td>
<td>3.758 ±0.003</td>
<td>0.3264 ±0.0090</td>
<td>0.2142 ±0.0017</td>
<td>−2.139 ±0.162</td>
</tr>
<tr>
<td>HF-2 c-Si/GZO (0.73-4.7 eV)</td>
<td>4.327 ±0.019</td>
<td>3.554 ±0.004</td>
<td>0.4370 ±0.0130</td>
<td>0.2094 ±0.0023</td>
<td>−2.011 ±0.189</td>
</tr>
<tr>
<td>HF-3 c-Si/GZO (0.73 -4.7 eV)</td>
<td>4.292 ±0.015</td>
<td>3.824 ±0.004</td>
<td>0.4315 ±0.013</td>
<td>0.2059 ±0.0022</td>
<td>−1.962 ±0.178</td>
</tr>
<tr>
<td>HF-4 c-Si/GZO (0.73 -4.7 eV)</td>
<td>4.228 ±0.014</td>
<td>3.988 ±0.004</td>
<td>0.4563 ±0.0132</td>
<td>0.2058 ±0.0023</td>
<td>−1.903 ±0.172</td>
</tr>
</tbody>
</table>
Table 4.16: Best fit Lorentz oscillator parameters are tabulated for different samples of doped ZnO from Figs. 4-24 - 4-25 deposited on glass substrates. Sample DS40132 listed here with the thicker ZnO layer, as well as samples deposited on substrates other than glass, did not show the absorption band near 0.7 eV and so did not require this oscillator in the dielectric function model. It should be noted that the range of energy used to fit the data in this comparison study (0.7 - 5 eV) is different from that used in the fits shown in Section 4.4.1 (0.08 - 5 eV).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Lorentz A</th>
<th>Lorentz $E_0$ (eV)</th>
<th>Lorentz $\Gamma$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DS40143 SLG/AZO (0.7 - 5eV)</td>
<td>1.019±0.056</td>
<td>0.746±0.003</td>
<td>0.136±0.014</td>
</tr>
<tr>
<td>DS40144 SLG/AZO (0.7 - 5eV)</td>
<td>1.061±0.057</td>
<td>0.761±0.003</td>
<td>0.139±0.015</td>
</tr>
<tr>
<td>DS40139 SLG/AZO (0.7 - 5eV)</td>
<td>0.683±0.055</td>
<td>0.772±0.004</td>
<td>0.126±0.021</td>
</tr>
<tr>
<td>DS40132 SLG/AZO (0.7 - 5eV)</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>DS40162 BSG/AZO (0.7 - 5eV)</td>
<td>0.512±0.043</td>
<td>0.806±0.005</td>
<td>0.113±0.020</td>
</tr>
</tbody>
</table>
Table 4.17: The resistivity, scattering time, carrier concentration, and mobility are tabulated as obtained from the amplitude and broadening parameters of the Drude term listed in Table 4.14 for the 11 doped ZnO samples from that table. The resistivity effective mass used to derive the latter two parameters is also listed; for the GZO HF series, the effective mass deduced by Fujiwara is included. This value was obtained using the reported Hall carrier concentration.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Effective mass</th>
<th>Resistivity $\rho_o$ (Ω·cm)</th>
<th>Scattering Time $\tau$ (fs)</th>
<th>Carrier Concentration $N$ (cm$^{-3}$)</th>
<th>Carrier Mobility $\mu$/(cm$^2$·V$^{-1}$·s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DS40143 SLG/AZO (0.7 - 5eV)</td>
<td>0.40</td>
<td>$6.28 \times 10^{-4}$</td>
<td>9.51 $\pm$ 3.17</td>
<td>$2.974 \times 10^{20}$ $\pm 0.038 \times 10^{20}$</td>
<td>37.14 $\pm$ 8.37</td>
</tr>
<tr>
<td>DS40144 SLG/AZO (0.7 - 5eV)</td>
<td>0.40</td>
<td>$5.45 \times 10^{-4}$</td>
<td>11.59 $\pm$ 4.69</td>
<td>$3.169 \times 10^{20}$ $\pm 0.035 \times 10^{20}$</td>
<td>42.65 $\pm$ 12.99</td>
</tr>
<tr>
<td>DS40139 SLG/AZO (0.7 - 5eV)</td>
<td>0.40</td>
<td>$6.82 \times 10^{-4}$</td>
<td>6.03 $\pm$ 1.22</td>
<td>$3.730 \times 10^{20}$ $\pm 0.035 \times 10^{20}$</td>
<td>25.45 $\pm$ 3.98</td>
</tr>
<tr>
<td>DS40132 SLG/AZO (0.7 - 5eV)</td>
<td>0.40</td>
<td>$11.10 \times 10^{-4}$</td>
<td>3.79 $\pm$ 0.21</td>
<td>$3.384 \times 10^{20}$ $\pm 0.017 \times 10^{20}$</td>
<td>16.65 $\pm$ 0.86</td>
</tr>
<tr>
<td>DS40162 BSG/AZO (0.7 - 5eV)</td>
<td>0.40</td>
<td>$7.62 \times 10^{-4}$</td>
<td>4.57 $\pm$ 0.53</td>
<td>$4.074 \times 10^{20}$ $\pm 0.024 \times 10^{20}$</td>
<td>20.11 $\pm$ 1.97</td>
</tr>
<tr>
<td>MV022 c-Si/AZO (0.75 - 5eV)</td>
<td>0.40</td>
<td>$8.65 \times 10^{-4}$</td>
<td>3.92 $\pm$ 0.06</td>
<td>$4.191 \times 10^{20}$ $\pm 0.010 \times 10^{20}$</td>
<td>17.22 $\pm$ 0.23</td>
</tr>
<tr>
<td>MV211 c-Si/Ag/AZO (0.73 - 5eV)</td>
<td>0.40</td>
<td>$5.69 \times 10^{-4}$</td>
<td>4.48 $\pm$ 0.01</td>
<td>$5.577 \times 10^{20}$ $\pm 0.022 \times 10^{20}$</td>
<td>19.68 $\pm$ 0.02</td>
</tr>
<tr>
<td>MV070 polymer/Ag/AZO (0.73 - 5eV)</td>
<td>0.40</td>
<td>$8.76 \times 10^{-4}$</td>
<td>3.79 $\pm$ 0.20</td>
<td>$4.273 \times 10^{20}$ $\pm 0.013 \times 10^{20}$</td>
<td>16.67 $\pm$ 0.82</td>
</tr>
<tr>
<td>HF-2 c-Si/GZO (0.73-4.7 eV)</td>
<td>0.22</td>
<td>$28.50 \times 10^{-4}$</td>
<td>2.43 $\pm$ 0.18</td>
<td>$1.128 \times 10^{20}$ $\pm 0.011 \times 10^{20}$</td>
<td>19.39 $\pm$ 1.33</td>
</tr>
<tr>
<td>HF-3 c-Si/GZO (0.73 -4.7 eV)</td>
<td>0.38</td>
<td>$7.05 \times 10^{-4}$</td>
<td>4.04 $\pm$ 0.18</td>
<td>$4.756 \times 10^{20}$ $\pm 0.033 \times 10^{20}$</td>
<td>18.61 $\pm$ 0.79</td>
</tr>
<tr>
<td>HF-4 c-Si/GZO (0.73 -4.7 eV)</td>
<td>0.37</td>
<td>$4.55 \times 10^{-4}$</td>
<td>4.40 $\pm$ 0.14</td>
<td>$6.487 \times 10^{20}$ $\pm 0.060 \times 10^{20}$</td>
<td>21.15 $\pm$ 0.66</td>
</tr>
</tbody>
</table>
Table 4.18: The predicted electron concentration from Eq. (4.2) is tabulated for AZO in comparison with that from the Drude term given in Table 4.17. For the GZO, the comparison is between N from Eq. (4.2) and N from Hall effect. In the determination of N from Eq. (4.2), the density of states effective mass of $m^* = 0.29m_e$ is used, whereas in the determination of N from the Drude term for the AZO, the resistivity effective mass $m^* = 0.4m_e$ is used in the absence of Hall effect measurements.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Resistivity /Density of States Effective Masses</th>
<th>$\Delta E_g = E_g - 3.293$ (eV)</th>
<th>Carrier Concentration N from Eq. (4.2) (cm$^{-3}$)</th>
<th>Carrier Concentration N from Eq. (4.1) or from Hall effect (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DS40143 SLG/AZO (0.7 - 5eV)</td>
<td>0.40/0.29</td>
<td>0.393 ± 0.004</td>
<td>1.75 x 10$^{20}$ ± 0.03 x 10$^{20}$</td>
<td>2.974 x 10$^{20}$ ±0.038 x 10$^{20}$</td>
</tr>
<tr>
<td>DS40144 SLG/AZO (0.7 - 5eV)</td>
<td>0.40/0.29</td>
<td>0.395 ± 0.004</td>
<td>1.76 x 10$^{20}$ ± 0.03 x 10$^{20}$</td>
<td>3.169 x 10$^{20}$ ±0.035 x 10$^{20}$</td>
</tr>
<tr>
<td>DS40139 SLG/AZO (0.7 - 5eV)</td>
<td>0.40/0.29</td>
<td>0.409 ± 0.005</td>
<td>1.86 x 10$^{20}$ ± 0.03 x 10$^{20}$</td>
<td>3.730 x 10$^{20}$ ±0.035 x 10$^{20}$</td>
</tr>
<tr>
<td>DS40132 SLG/AZO (0.7 - 5eV)</td>
<td>0.40/0.29</td>
<td>0.355 ± 0.003</td>
<td>1.50 x 10$^{20}$ ± 0.02 x 10$^{20}$</td>
<td>3.384 x 10$^{20}$ ±0.017 x 10$^{20}$</td>
</tr>
<tr>
<td>DS40162 BSG/AZO (0.7 - 5eV)</td>
<td>0.40/0.29</td>
<td>0.429 ± 0.004</td>
<td>1.99 x 10$^{20}$ ± 0.03 x 10$^{20}$</td>
<td>4.074 x 10$^{20}$ ±0.024 x 10$^{20}$</td>
</tr>
<tr>
<td>MV022 c-Si/AZO (0.75 - 5eV)</td>
<td>0.40/0.29</td>
<td>0.436± 0.001</td>
<td>2.04 x 10$^{20}$ ± 0.007 x 10$^{20}$</td>
<td>4.191 x 10$^{20}$ ±0.010 x 10$^{20}$</td>
</tr>
<tr>
<td>MV211 c-Si/Ag/AZO (0.73 - 5eV)</td>
<td>0.40/0.29</td>
<td>0.553 ± 0.001</td>
<td>2.91 x 10$^{20}$ ± 0.008 x 10$^{20}$</td>
<td>5.577 x 10$^{20}$ ±0.022 x 10$^{20}$</td>
</tr>
<tr>
<td>MV070 polymer/Ag/AZO (0.73 - 5eV)</td>
<td>0.40/0.29</td>
<td>0.465 ± 0.003</td>
<td>2.25 x 10$^{20}$ ± 0.02 x 10$^{20}$</td>
<td>4.273 x 10$^{20}$ ±0.013 x 10$^{20}$</td>
</tr>
<tr>
<td>HF-2 c-Si/GZO (0.73-4.7 eV)</td>
<td>0.22/0.29</td>
<td>0.261 ± 0.004</td>
<td>0.95 x 10$^{20}$ ± 0.02 x 10$^{20}$</td>
<td>1.128 x 10$^{20}$ ±0.011 x 10$^{20}$</td>
</tr>
<tr>
<td>HF-3 c-Si/GZO (0.73 -4.7 eV)</td>
<td>0.38/0.29</td>
<td>0.531 ± 0.004</td>
<td>2.74 x 10$^{20}$ ± 0.03 x 10$^{20}$</td>
<td>4.756 x 10$^{20}$ ±0.033 x 10$^{20}$</td>
</tr>
<tr>
<td>HF-4 c-Si/GZO (0.73 -4.7 eV)</td>
<td>0.37/0.29</td>
<td>0.695 ± 0.004</td>
<td>4.11 x 10$^{20}$ ± 0.04 x 10$^{20}$</td>
<td>6.487 x 10$^{20}$ ±0.060 x 10$^{20}$</td>
</tr>
</tbody>
</table>
Figure 4-26: The real parts of the best fit analytical expressions are shown separately for the dielectric functions of three distinct groups of samples. The first group of five (upper left) consists of AZO samples deposited on glass substrates; the second group (upper right) includes three samples of AZO deposited on crystalline silicon or on silver coated substrates; and the third group (lower) includes three gallium doped zinc oxide samples.
Figure 4-27: The imaginary parts of the best fit analytical expressions are shown separately for the dielectric functions of three distinct groups of samples. The first group of five (upper left) consists of AZO samples deposited on glass substrates; the second group (upper right) includes three samples of AZO deposited on crystalline silicon or on silver coated substrates; and the third group (lower) includes three gallium doped zinc oxide samples.

In Table 4.18, the carrier concentrations deduced from Eq. (4.2) are compared with those from Eq. (4.1) for the AZO samples fabricated in this study. For the GZO samples fabricated by Fujiwara, the comparison is made between the carrier concentration from Eq. (4.2) and that from Hall effect measurements. In the comparison for the AZO samples fabricated in this study, the Eq. (4.2) estimate is smaller by a factor of approximately two. This difference arises in part because SE analysis over the narrower spectral range of 0.7 – 5.0 eV yields a larger value of the electron concentration.
compared with the wider range of 0.08 - 5.0 eV, the latter result being more definitive. The problem for some samples may be due in part to the distortion of the Drude characteristic by the Lorentz oscillator near the lower limit of the photon energy range. The comparison in Table 4.18 for the GZO samples enables an estimate of the density of states effective mass based on the assumption that the Hall effect measurement of the carrier concentration is valid. The results are 0.33m_e, 0.42m_e, and 0.39m_e for HF-2, HF-3, and HF-4, respectively, which suggests similar behavior for the density of states and resistivity effective masses (Fujiwara and Kondo, 2005). Specifically, both masses appear to increase with increasing carrier concentration, possibly due to the deviation of the conduction band density of states from a square-root function of energy which in turn may derive from the non-parabolicity of the conduction band $E(k)$ diagram. It should also be noted that at the lowest GZO electron concentration, the density of states effective mass of $m^* = 0.33m_e$ is close to the literature result of $m^* = 0.29m_e$ that yields reasonable agreement between the electron concentrations from Eqs. (4.1) and (4.2) for the AZO deposited on glass substrates as described in Section 4.4.1.

Additional study of the dielectric functions of Figs. 4-24 - 4-27 involves an attempt to estimate the relative void volume percentage for the 11 samples. The reference sample in this case was chosen as the doped ZnO sample with the highest $\varepsilon_1$ amplitude below the bandgap. The sample meeting this requirement was HF-2 c-Si/GZO, which also exhibits the smallest CP bandgap and electron concentration, as listed in Table 4.14. Relative to HF-2, the void volume percentage for the other 10 samples was estimated from their dielectric functions using a single parameter analysis with the Bruggeman effective medium approximation, yielding the results shown in Table 4.19.

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It can be seen from the table that the deduced void volume fraction follows closely the CP bandgap. This behavior suggests that the shift in the bandgap to higher energies generates a reduction in the index of refraction over a large part of the photon energy range which is then incorrectly interpreted as an increase in void volume percentage. Thus, for this set of doped ZnO samples, such an analysis of the void fraction can only be valid for samples with similar CP band gaps. The corresponding analysis of Section 4.2, Table 4.3 appears valid since the lowest CP bandgap range is relatively narrow, with all gaps within a range of ~ 0.1 eV, and no clear correlation is observed between void volume percentage and bandgap for these samples. One of the few possible conclusions that can be made based on the results of Table 4.19 is that sample MV022, AZO deposited on c-Si, exhibits a lower void percentage than samples DS40139 and DS40162, AZO samples deposited on SLG and BSG, respectively. In fact, sample MV022 is the only one whose void percentage deviates from the correlation with band gap.
Table 4.19: Attempts to determine the void volume percentage relative to that of sample HF-2 c-Si/GZO are summarized for the 10 doped ZnO samples. The reference sample HF-2 exhibits the highest amplitude of $\varepsilon_1$ below the band gap. The samples are ordered according to band gap, demonstrating that the trend in void percentage appears to reflect the change in band gap rather than the presence of voids in the material.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Critical point energy (eV)</th>
<th>Void volume %</th>
<th>Confidence limit</th>
<th>MSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF-2 c-Si/GZO</td>
<td>3.554±0.004</td>
<td>0.00</td>
<td>NA</td>
<td>0</td>
</tr>
<tr>
<td>DS40132 SLG/AZO</td>
<td>3.648±0.003</td>
<td>9.29</td>
<td>0.43</td>
<td>0.044</td>
</tr>
<tr>
<td>DS40144 SLG/AZO</td>
<td>3.688±0.004</td>
<td>13.33</td>
<td>0.75</td>
<td>0.079</td>
</tr>
<tr>
<td>DS40143 SLG/AZO</td>
<td>3.684±0.004</td>
<td>13.38</td>
<td>0.68</td>
<td>0.073</td>
</tr>
<tr>
<td>DS40139 SLG/AZO</td>
<td>3.702±0.005</td>
<td>15.63</td>
<td>0.78</td>
<td>0.084</td>
</tr>
<tr>
<td>DS40162 BSG/AZO</td>
<td>3.722±0.004</td>
<td>17.19</td>
<td>0.80</td>
<td>0.089</td>
</tr>
<tr>
<td>MV022 c-Si/AZO</td>
<td>3.729±0.001</td>
<td>15.61</td>
<td>0.71</td>
<td>0.077</td>
</tr>
<tr>
<td>MV070 polymer/Ag/AZO</td>
<td>3.758±0.003</td>
<td>19.53</td>
<td>0.84</td>
<td>0.095</td>
</tr>
<tr>
<td>HF-3 c-Si/GZO</td>
<td>3.824±0.004</td>
<td>23.14</td>
<td>1.15</td>
<td>0.134</td>
</tr>
<tr>
<td>MV211 c-Si/Ag/AZO</td>
<td>3.846±0.001</td>
<td>27.39</td>
<td>1.37</td>
<td>0.167</td>
</tr>
<tr>
<td>HF-4 c-Si/GZO</td>
<td>3.988±0.004</td>
<td>32.79</td>
<td>1.86</td>
<td>0.239</td>
</tr>
</tbody>
</table>

Correlations have been explored between the CP oscillator parameters and the Drude term parameters of Tables 4.15, 4.17, and 4.19. The series of scatter plots in Fig. 4-28 – 4-31 depict a selection of these correlations. Based on an inspection of these figures, one can conclude that the only clear trend appears in the correlation between the bandgap of the CP oscillator and the electron concentration. Such a relationship between
these parameters is expected based on Eq. (4.2), and an individual correlation plot including a fit using that equation is shown in Figure 4-29.

In this figure, the CP energy gap versus $N^{2/3}$ is plotted, where $N$ is the electron concentration. The intercept gives the band gap of the undoped material which is found to be $E_g = 3.264$ eV, relatively close to the minimum band gap which is $E_g = 3.293$ eV in the studies of undoped ZnO. The latter wider band gap may indicate the presence of intrinsic defects such as Zn interstitials which account for the conductive nature of the undoped material.

The best fit slope in Figure 4-29 gives the density of states effective mass of $m^* = 0.42m_e$, which is higher than the value of $m^* = 0.29m_e$ identified in the previous section for the set of AZO samples on glass substrates. The difference is likely to be due to the inclusion of a larger set of samples that span a wider range of electron concentration, coupled with the fact that the effective mass may depend on carrier concentration as shown by Fujiwara and Kondo (2005). In fact, the value from Figure 4-29 is closer to the conductivity effective mass of $m^* = 0.40m_e$ which is used in the previous section, and it is also consistent with the high electron concentration values of the conductivity effective mass obtained by Fujiwara ($m^* = 0.42m_e$, and $0.39m_e$). For the correlation in Figure 4-29, the deduced density of states effective mass appears to decrease with increasing electron concentration from a high of $\sim 0.7m_e$ for electron concentrations up to $3.5 \times 10^{20}$ cm$^{-3}$ to a low of $\sim 0.3m_e$ for carrier concentrations up to $7 \times 10^{20}$ cm$^{-3}$. Thus, the behavior appears opposite to that of the conductivity effective mass reported by Fujiwara and Kondo (2005).
Figure 4-28: The band gap energy and broadening parameter of the CP oscillator and the scattering time from the Drude term are plotted versus the electron concentration for the 11 doped ZnO samples of this section. The scattering time for samples DS40139, DS40143, and DS40144 were obtained from Table 4.12 due to the large confidence limits for the results in Table 4.17. A clear trend is observed for the CP bandgap versus electron concentration, as would be expected from Eq. (4.2).
Figure 4-29: The CP energy gap $E_g$ is plotted versus $N^{2/3}$, where $N$ is the free electron concentration, according to the Burstein-Moss gap shift described by Equation 4.2. The best fit to the full set of data gives a density of states effective mass of $m^* = 0.42 m_e$ and an energy gap for undoped ZnO of 3.264 eV. The broken lines shows fits at low and high electron concentrations suggesting that there may be a variation in the effective mass from $m^* = 0.7m_e$ at low $N$ to $m^* = 0.3m_e$ at high $N$. 

\[
E_g (eV) = 3.264 \text{ eV} + (0.086 \text{ eV } 10^{-13} \text{ cm}^2) N^{2/3} (10^{13} \text{ cm}^{-2})
\]
Figure 4-30: The bandgap and broadening parameter of the CP oscillator are plotted versus the scattering time from the Drude term for the 11 doped ZnO samples of Table 4.15 and 4.17. The scattering time for samples DS40139, DS40143, and DS40144 were obtained from Table 4.12 due to the large confidence limits for the results in Table 4.17.
Figure 4-31: The broadening parameter, phase, and exponent of the CP oscillator are plotted versus the CP bandgap for the 11 doped ZnO samples of Table 4.15.

4.5 Effect of Annealing and Measurement Temperatures on the Properties of AZO

In this section, the effect of annealing on the optical and electrical properties of aluminum doped zinc oxide will be discussed. The primary interest is to observe the effect of annealing on the free electron behavior of an AZO film fabricated in a standard process at the University of Toledo. The sample annealed in this study was DS40162, an AZO sample deposited on borosilicate glass. Because the undoped ZnO described in Section 4.3 was also deposited on borosilicate glass substrate, a comparison of doped and undoped samples can be made.
In this study of AZO, the sample was heated to 700 K and then cooled as described in Section 4.3 where the annealing results for undoped ZnO were presented. As a result, during the cooling cycle and in a subsequent heating cycle, there is no change in the crystalline structure of AZO. Then, for every 50 K increment of temperature during the second heating cycle, the ellipsometry spectra were recorded. First, the room temperature data before and after annealing, i.e., the first heating cycle, will be discussed. Then detail will be presented on how the various best fit oscillator parameters change during the second heating cycles as the temperature is increased every 50 K from room temperature to 650 K. These latter changes describe how the optical properties of AZO vary with the measurement temperature.

**4.5.1 Comparison of Room Temperature Data Before and After Annealing**

The as-deposited AZO sample DS40162 was measured ex-situ by spectroscopic ellipsometry at room temperature. The sample was then heated directly to 700 K, over the period of one hour, annealed at that temperature for 8 hours, then cooled to room temperature, and again measured in situ by spectroscopic ellipsometry. In situ SE implies that the sample was mounted within the cryostat/heater system that provides optical access to the sample. In this system, the sample is maintained under vacuum to avoid contamination and associated reactions during heating and cooling. The differences in spectroscopic ellipsometry data $\psi$ and $\Delta$ can be observed in Figure 4-32. Throughout the measured photon energy range (0.7 - 5 eV), it is clear that the AZO structure and/or optical properties have been modified in the annealing process. In contrast, in the case of undoped ZnO, changes upon annealing were observed only over the higher energy range of the spectra above the band gap.
Both sets of room temperature data in Figure 4-32, before and after annealing, were modeled using a Drude term as well as Lorentz and CP oscillators, and the best fit parameters are shown in Tables 4.20 and 4.21. The best fit analytical forms of the real and imaginary parts of the dielectric functions before and after annealing are shown in Figure 4-33. It should be emphasized that all the parameter determinations and dielectric functions in each case were obtained at room temperature before and after annealing, so there is no issue associated with the measurement temperature dependence of the dielectric function.

First, the changes in the structure of the AZO layer upon annealing will be addressed. The AZO bulk layer thickness decreases by ~ 90 Å upon annealing, and the total thickness and the effective thickness change by similar amounts (in the range of 80-90 Å). The total thickness is the sum of the interface, bulk, and surface layer thicknesses, and the effective thickness in this case is that obtained by starting from the total thickness and subtracting out the volume/area associated with the surface roughness voids. In addition to the bulk layer thickness change, the distribution of material between the bulk, interface, and surface roughness layers has changed upon annealing. The surface roughness layer has become thicker and more optically dense, indicated by the increase in the photon energy independent $\varepsilon_1$ value. The interface layer has become thinner but also more optically dense, as well. The magnitude of $\varepsilon_2$ above the optical band gap has also increased significantly, and this is an indication of an increase in density of the bulk layer. In general, the results suggest that the film has become more compact, and given that there is a fixed amount of AZO material (assuming no evaporation of material upon annealing), this may account for the thickness decrease upon annealing.
Based on previous literature studies, the annealing of AZO thin films is expected to enhance grain growth, to narrow the grain boundary regions, and also to promote diffusion of the Al atoms from the grain boundary regions into the crystalline lattice (Ikhmayies et al., 2010). The net results of these effects are to increase the density, as indicated in the previous paragraph, to increase the free electron concentration, and to decrease the resistivity. The expected behavior of the electrical properties is clearly observed in this work as well, based on the entries of Table 4.21. Although the electron concentration increases upon annealing, the scattering time and mobility decreases. This may indicate that the source of the reduction in scattering time is an increase in ionized impurities, resulting from more efficient doping. Furthermore, the shift in optical band gap, modeled using the CP oscillator, is also consistent with the increase in electron concentration. In particular, the observed increase in gap from 3.72 eV to 3.85 eV is likely due to the B-M effect. Table 4.22 shows the predicted electron concentrations from Eq. (4.2) for AZO before and after annealing in comparison with those from the Drude term given in Table 4.21. Thus, the results for the CP bandgap shift support the conclusion of an increase in carrier concentration, drawn on the basis of the Drude parameters, as a result of annealing. The broadening parameter of the band gap critical point is not observed to change within the confidence limits, which suggests that the electrons excited in interband transitions are not affected by the increase in the free electron concentration.

One interesting result from Table 4.20 is the blue shift upon annealing for the low energy band, modeled as a Lorentz oscillator. In fact, the oscillator resonance energy increases significantly from 0.80 eV to 1.26 eV upon annealing. As noted earlier, this
absorption band is observed only in thin AZO layers deposited on glass substrates, irrespective of the composition of the glass. A continuous shift in such a well-defined band appears inconsistent with vibrational modes due to contaminants, a possible model that was suggested in Section 4.4.1. An alternative possibility more likely to explain the low energy feature is a plasmon-related band due to inhomogeneous doping. Inclusions of more heavily doped material may be surrounded by a host of lightly doped or undoped material. It is unclear, however, why this segregation would occur only for thin layers and glass substrates and not for thick layers and other substrates, such as crystalline Si and Ag coated crystalline silicon.

Simple calculations can be made based on the concept of inhomogeneous doping. For inclusions of AZO in ZnO, the plasmon mode is predicted to appear at:

\[ E_0 \sim E_p \left\{ \varepsilon_{1o} + \left[ (2 + Q_m)/(1 - Q_m) \right] \varepsilon_a \right\}^{-1/2}, \tag{4.3} \]

where \( E_p \) is the plasma energy and \( \varepsilon_{1o} \) is the constant contribution in the Drude equation for the dielectric function of the AZO inclusions, \( Q_m \) is the volume fraction of AZO inclusions, and \( \varepsilon_a \) is the dielectric function of the ZnO host medium at the plasmon energy (Collins and Ferlauto, 2005). This result can be derived by substituting the Drude equation for the dielectric function of the AZO into the Maxwell-Garnett effective medium theory as shown in Section 2.2 of Chapter 2. According to Equation 2.23, the volume fraction of the metal (or Drude) component can be estimated as

\[ Q_m = \frac{B^2}{3\varepsilon_a E_0^2 + B^2}, \tag{4.3a} \]

where \( B^2 \) is the amplitude of the plasmon represented by a Lorentz oscillator defined in Eq. 2.22 and \( E_0 \) is its resonance energy.
Applying $B^2 = E_0 \Gamma A$ in Eq. (4.3a), where the values of resonance energy $E_0$, broadening $\Gamma$, and unitless amplitude $A$ are given in Table 4.20, and approximating $\varepsilon_a$ as 3.5, then the values of $Q_m$ are found from Eq. (4.3a) to be 0.0072 for AZO before annealing and 0.0075 after annealing. Before applying Eq. (4.3), the dielectric functions of the AZO before and after annealing must be fit with a single Drude term along with the constant contribution in order to obtain the required relevant parameters of $\varepsilon_{1o}$ and $E_p$. This procedure yields $E_p = 1.34$ eV and $\varepsilon_{1o} = 3.94$ for AZO before annealing and $E_p = 1.52$ eV and $\varepsilon_{1o} = 3.85$ for AZO after annealing. Substituting these values along with $Q_m = 0.0072$ before annealing and 0.0075 and after annealing, as well as $\varepsilon_a = 3.5$ all into Eq. (4.3), plasmon bands at 0.40 eV and 0.46 eV are predicted for AZO before and after annealing, respectively. These resonance energies are much lower than those observed experimentally; however, it is likely that the doped regions have higher plasma energies than the $E_p$ values given in Table 4.21. In fact, plasma energies of $E_p \sim 2.7$ eV and 4.2 eV for the doped regions would be necessary to generate the observed resonance features at 0.80 and 1.26 eV, given the values of $Q_m = 0.0072$ and 0.0075 before and after annealing, respectively. The proportionality between $E_p^2$ and carrier concentration $N$ would then suggest that the more heavily doped regions exhibit higher carrier concentrations by factors of 4 before annealing and 7.5 after annealing, relative to the surrounding AZO. Thus, applying the results of Table 4.21, the carrier concentration values in the heavily doped regions would be $1.6 \times 10^{21}$ cm$^{-3}$ before annealing and $4.4 \times 10^{21}$ cm$^{-3}$ after annealing. Given that the volume fractions in both cases are $\sim 0.0073$, accumulations of only 3-5% of the dopants from the host material would be needed to form these heavily doped regions.
Figure 4-32: Room temperature (RT) ellipsometry spectra in $\psi$ and $\Delta$ are compared for the AZO sample DS40162 measured before and after annealing. The circles represent the experimental spectra collected on the as-deposited sample before annealing, and the triangles represent spectra collected after the sample was first heated to 700 K then cooled back to RT. The solid and dashed lines are the respective best fits to the experimental spectra obtained before and after annealing.
Figure 4-33: The best fit analytical expressions for the real (top) and imaginary (bottom) parts of the dielectric function are shown for AZO sample DS40162 measured at room temperature before and after annealing.
Table 4.20: The best fit structural and dielectric function parameters are shown for the AZO sample DS40162 measured at room temperature before and after annealing. In this analysis the photon energy independent contributions to $\varepsilon_1$ for the bulk AZO layer are fixed at unity, and the phases of the CPs are fixed at zero. The energy range used for the fitting was 0.7 - 5 eV.

<table>
<thead>
<tr>
<th></th>
<th>RT Before Annealing (Same Day of Deposition)</th>
<th>RT After Annealing to 700 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSE</td>
<td>0.00775</td>
<td>0.0131</td>
</tr>
<tr>
<td>AZO Surface Roughness Thickness (Å)</td>
<td>94.1 ± 5.1</td>
<td>257.7 ± 10.0</td>
</tr>
<tr>
<td>Surface Roughness Void vol.%</td>
<td>31.4 ± 2.2</td>
<td>10.1 ± 0.3</td>
</tr>
<tr>
<td>AZO Bulk Thickness (Å)</td>
<td>2696.7 ± 29.3</td>
<td>2606.6 ± 18.1</td>
</tr>
<tr>
<td>AZO Interface Thickness (Å)</td>
<td>252.0 ± 41.1</td>
<td>92.8 ± 21.7</td>
</tr>
<tr>
<td>$\varepsilon_{10}$ for AZO Interface</td>
<td>1.490 ± 0.095</td>
<td>3.792 ± 0.641</td>
</tr>
<tr>
<td>Drude A (eV)</td>
<td>11.65 ± 0.57</td>
<td>15.68 ± 0.54</td>
</tr>
<tr>
<td>Drude $\Gamma$(eV)</td>
<td>0.1179 ± 0.0059</td>
<td>0.1294 ± 0.0042</td>
</tr>
<tr>
<td>Lorentz A</td>
<td>0.513 ± 0.019</td>
<td>0.480 ± 0.031</td>
</tr>
<tr>
<td>Lorentz $E_0$ (eV)</td>
<td>0.7974 ± 0.0022</td>
<td>1.2556 ± 0.0072</td>
</tr>
<tr>
<td>Lorentz $\Gamma$(eV)</td>
<td>0.1173 ± 0.0086</td>
<td>0.2087 ± 0.0211</td>
</tr>
<tr>
<td>CP A</td>
<td>4.672 ± 0.023</td>
<td>5.064 ± 0.053</td>
</tr>
<tr>
<td>CP $E_g$ (eV)</td>
<td>3.725 ± 0.003</td>
<td>3.855 ± 0.006</td>
</tr>
<tr>
<td>CP $\Gamma$ (eV)</td>
<td>0.2809 ± 0.0040</td>
<td>0.2783 ± 0.0093</td>
</tr>
<tr>
<td>CP $\mu$</td>
<td>0.2079 ± 0.0015</td>
<td>0.2379 ± 0.0023</td>
</tr>
</tbody>
</table>

Table 4.21: The Drude or free electron parameters are shown for sample DS40162 obtained from SE analyses of data collected at RT before and after annealing. The resistivity effective mass of electrons in AZO is assumed to be given by $m_e^* = 0.4 \, m_e$, where $m_e$ is the true electron mass.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Drude A (eV)</th>
<th>Drude $\Gamma$(eV)</th>
<th>Plasma Energy (eV)</th>
<th>Resistivity $\rho_0$ (Ω-cm)</th>
<th>Scattering Time $\tau$ (fs)</th>
<th>Carrier Concentration N (cm$^{-3}$)</th>
<th>Carrier Mobility $\mu$ (cm$^2$V$^{-1}$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT Before Annealing</td>
<td>11.65 ± 0.57</td>
<td>0.1179 ± 0.0058</td>
<td>1.172 ± 0.057</td>
<td>0.000638 ± 0.000037</td>
<td>5.585 ± 0.338</td>
<td>3.984x10$^{20}$ ± 0.024x10$^{20}$</td>
<td>24.55 ± 1.22</td>
</tr>
<tr>
<td>RT After Annealing to 700 K</td>
<td>15.68 ± 0.54</td>
<td>0.1294 ± 0.0042</td>
<td>1.424 ± 0.048</td>
<td>0.000474 ± 0.000018</td>
<td>5.088 ± 0.187</td>
<td>5.885 x10$^{20}$ ± 0.030x10$^{20}$</td>
<td>22.37 ± 0.69</td>
</tr>
</tbody>
</table>
Table 4.22: The predicted electron concentration from Eq. (4.2) is tabulated for AZO before and after annealing in comparison with that from the Drude term given in Table 4.21. In the determination of N from Eq. (4.2), the density of states effective mass of $m^* = 0.29m_e$ is used, whereas in the determination of N from the Drude term for the AZO, the resistivity effective mass $m^* = 0.4m_e$ is used.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density of States Effective Mass (in units of $m_e$)</th>
<th>$E_g$ (eV)</th>
<th>$\Delta E_g = E_g - 3.293$ (eV)</th>
<th>Carrier Concentration N from Eq. (4.2) (cm$^{-3}$)</th>
<th>Carrier Concentration N from Eq. (4.1) (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT Before Annealing</td>
<td>0.29</td>
<td>3.725 ± 0.003</td>
<td>0.432 ± 0.003</td>
<td>3.06 x 10$^{20}$ ± 0.03 x 10$^{20}$</td>
<td>3.98 x 10$^{20}$ ± 0.02 x 10$^{20}$</td>
</tr>
<tr>
<td>RT After Annealing to 700 K</td>
<td>0.29</td>
<td>3.855 ± 0.006</td>
<td>0.562 ± 0.006</td>
<td>3.98 x 10$^{20}$ ± 0.06 x 10$^{20}$</td>
<td>5.89 x 10$^{20}$ ± 0.03 x 10$^{20}$</td>
</tr>
</tbody>
</table>

The sample of Table 4.17, DS40162 (BSG/AZO), was also directly measured by the four-point probe method to deduce its dc resistivity $\rho_o$. The result before heating the sample was $9.60 \times 10^{-4}$ Ω-cm whereas the SE analysis given in Table 4.17 yielded $6.38 \times 10^{-4}$ Ω-cm. The result after heating the sample was $8.01 \times 10^{-4}$ Ω-cm by four-point probe in comparison with the value of $4.74 \times 10^{-4}$ Ω-cm from SE. In this annealing study, which involves SE analysis over the NIR-UV range of 0.7 – 5 eV, there is a relatively large discrepancy in resistivity between the values measured by four-point probe and those derived from the SE analysis. Such was not the case in previous analyses of SE data over the IR-UV range of 0.08 - 5 eV. Thus, in order to obtain a reliable measure of the free electron behavior, SE data should extend as far as possible into the IR range. One may suggest that the optical-electrical discrepancy is the greatest for samples that exhibit a low energy band, modeled as a Lorentz oscillator. This would lead to a greater challenge in deconvolving the free electron absorption and the NIR band absorption.
Similar discrepancies in the measurement of resistivity between the optical and electrical measurements were reported by Volintiru et al., 2008, who used SE spectra over photon energy range of 0.72 - 4.13 eV. The extent of the photon energy range of the data into the IR will not affect the determination of CP parameters, including the optical band gap, as the resonance of the CP is confined within the spectral range of analysis. Thus, one may conclude that the estimate of the increase in carrier concentration upon annealing from Eq. (4.2) is more accurate than that from Eq. (4.1), assuming that the effective masses used in these estimates are correct.

4.5.2 Temperature Dependence of the AZO Dielectric Function

The annealed AZO sample DS40162 was heated in a second cycle to 650 K in steps of 50 K using the same cryostat/heating system as was used for AZO annealing (which was the first heating cycle). The goal of this second heating cycle is to determine the measurement temperature dependence of the optical properties of the AZO by stepwise collection of the ellipsometry spectra at increasing temperatures. At the beginning of the measurement process, starting at room temperature, the base pressure within the heating system was 1.1x10^{-7} Torr; however, during step-wise heating, the pressure decreased to the 10^{-8} - 10^{-9} Torr range. For each temperature step, the temperature was allowed to stabilize for 40 minutes before collecting spectroscopic ellipsometry data.

Shown in Figure 4-34 are the spectra in the ellipsometry parameters ψ and Δ for AZO sample DS40162 collected at room temperature before and after annealing and those collected at 650 K during the second cycle of heating. From the spectra collected during this second cycle, the temperature dependence of the dielectric function is the final
outcome. In Figure 4-34, one can observe that the interference fringes have become sharper and their amplitudes have become higher after annealing due to an increase in the optical contrast between AZO and each of the bounding media. In addition, the optical band gap has been blue-shifted as a result of the increase in carrier concentration through the BM effect. Upon heating during the second cycle to 650 K, the optical band gaps measured at the elevated temperatures red-shift as expected due to the effects of lattice expansion and increased electron-phonon interaction. In order to model the spectroscopic ellipsometry data and extract the optical parameters and the electrical parameters derived from them, the model of Table 4.23 is used.

Table 4.23: This structural/optical model is used in the study of the temperature dependence of the dielectric function for AZO sample DS40162.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZO Surface Roughness Layer [EMA of (Bulk AZO)/Void: 89.9/10.1 vol.%]</td>
<td>257.7 Å</td>
</tr>
<tr>
<td>AZO Bulk Layer [Dielectric function coupled to interface layer]</td>
<td>2606.6 Å</td>
</tr>
<tr>
<td>AZO Interface Layer [Dielectric function coupled to bulk layer]</td>
<td>92.8 Å</td>
</tr>
<tr>
<td>Borosilicate Glass Substrate</td>
<td></td>
</tr>
</tbody>
</table>

As a general procedure for modeling the dielectric function, first all the parameters are varied, including the bulk layer thickness, in order to fit the spectroscopic ellipsometry data acquired at different temperatures. Then the parameters are identified that are insensitive or less sensitive to temperature, and the fit is repeated using fixed values for those parameters. After several iterations of the analysis steps, one can decide which parameters to fix and which ones to vary in order to extract the dielectric function and derived electrical properties of the sample under consideration. For the particular analysis of AZO sample DS40162, six trial fits were performed and the resulting model
indicating the variable and fixed parameters is elaborated in Table 4.24. In the procedure, it was found that the parameters fixed during the fitting of the data collected versus temperature could be assigned the values that were obtained at room temperature for the annealed sample.

Figure 4-34: Spectra in the ellipsometry parameters $\psi$ and $\Delta$ acquired at room temperature before annealing (solid line) and after annealing (square data points connected by a line) for AZO sample DS40162 are compared with the corresponding data acquired at 650 K during a second heating cycle (circular data points connected by a line). Thus, room temperature (RT) data were acquired twice, once before annealing and a second time after annealing to 700 K and subsequent cooling. The 650 K data were taken in a second heating cycle in order to characterize the optical properties of the AZO as a function of temperature.
Table 4.24: The fixed and variable fitting parameters are shown for analysis of the SE data acquired on AZO sample DS40162 during the second heating cycle for the purpose of measuring the temperature dependence of the optical properties spanning the range from 300 K to 650 K. The energy range used for fitting the SE data was 0.7 - 5 eV.

<table>
<thead>
<tr>
<th>Fixed Parameters in the Best Fit Model (Fixed to room temperature values)</th>
<th>Variable Parameters in the Best Fit Model</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Layer Thicknesses:</strong></td>
<td><strong>Dielectric Function Parameters</strong></td>
</tr>
<tr>
<td>Surface Roughness: d_s = 257.7 Å</td>
<td>Drude Term:</td>
</tr>
<tr>
<td>AZO Bulk: d_b = 2606.6 Å</td>
<td>A (eV)</td>
</tr>
<tr>
<td>AZO Interface: d_i = 92.8 Å</td>
<td>Γ (eV)</td>
</tr>
<tr>
<td>Void in Surface Layer: f_vs = 10.1 vol.%</td>
<td>Lorentz Oscillator:</td>
</tr>
<tr>
<td>Dielectric Function Parameters:</td>
<td>Γ (eV)</td>
</tr>
<tr>
<td>ε_1 Offset for Bulk Layer: ε_{1o} = 1.0</td>
<td>CP Oscillator:</td>
</tr>
<tr>
<td>Lorentz Oscillator: A = 0.4797</td>
<td>A</td>
</tr>
<tr>
<td>E_g = 1.2556 eV</td>
<td>E_g (eV)</td>
</tr>
<tr>
<td>CP Oscillator: θ = 0°</td>
<td>Γ (eV)</td>
</tr>
<tr>
<td>μ = 0.2379</td>
<td>ε_{1o} for Interface Layer</td>
</tr>
</tbody>
</table>

The fixed structural parameter for this model derive from the model developed for the annealed AZO sample DS40162, assuming that the structure of the film does not change during the second heating cycle. The surface roughness was modeled as an EMA layer using a mixture of bulk AZO/void (air), as a 90/10 vol.% mixture, respectively. Moreover, the dielectric functions of the bulk AZO layer and the interface layer were coupled so that as the bulk AZO layer changes so does the interface layer. The optical properties of the two layers are not identical, however, since the photon energy independent value of ε_{1o} for the bulk AZO layer was fixed to unity whereas that of the interface was allowed to vary to account for a density difference.

The temperature dependence of the Drude parameters will be presented and discussed first. Figure 4-35 shows that as the temperature increases, the Drude amplitude
decreases and the broadening parameter increases with similar slopes. Figure 4-36 shows the temperature dependence of the parameters derived from the Drude amplitude and the broadening parameter. The resistivity and scattering time can be derived without assuming an effective mass. The resistivity is observed to increase linearly whereas the scattering time decreases linearly. Such behavior is expected for metals and degenerate semiconductors in which the Fermi level resides within a high density of states and the electrons obey Fermi-Dirac statistics, considering the temperature regime near and above the Debye temperature.

Determination of the free electron concentration and the carrier mobility from the Drude parameters requires the electron effective mass which is taken to be $m_e^* = 0.4m_e$. Although the electron concentration is modeled in terms of a decrease with increasing temperature using a polynomial of order two, the effect is negligible ~1% compared with the changes of 10-20% in resistivity and scattering time. The mobility decreases linearly with temperature as expected, reflecting the decrease in scattering time. Similar trends in resistivity, mobility, and carrier concentration have been reported by Lee et al., 2005 and Yang et al., 2010.
Figure 4-35: The Drude parameters are plotted as functions of the measurement temperature for the annealed AZO sample DS40162. The best fit linear equations are also shown above each plot.

\[ A (\text{eV}) = 17.637 \text{ eV} - (6.440 \times 10^{-3} \text{ eV K}^{-1}) T(\text{K}) \]

\[ \Gamma (\text{eV}) = 0.112 \text{ eV} + (5.735 \times 10^{-6} \text{ eV K}^{-1}) T(\text{K}) \]
Figure 4-36: Electronic characteristics deduced from the Drude parameters of AZO sample DS40162 are plotted as functions of the measurement temperature. The best fit linear and parabolic equations are shown above each plot.

For the low energy band modeled as a Lorentz oscillator, only the broadening parameter is varied in the analysis. The amplitude and resonance energy are fixed at the values given in Table 4.24. The constant contribution to the interface layer dielectric function $\varepsilon_{1o}$ is also varied in the analysis, whereas the corresponding parameter for the bulk layer dielectric function is fixed at unity. The two variable parameters of Lorentz broadening and interface layer $\varepsilon_{1o}$ are shown in Figure 4-37. The low energy band, which is seen only in thinner AZO layers deposited on glass substrates, exhibits a broadening parameter that decreases with increasing measurement temperature. The origin of such
behavior is unclear in a free electron system following Fermi-Dirac statistics. On the other hand, for a collection of free electrons following Boltzmann statistics, as in a non-degenerate semiconductor, a reduction in broadening with increasing temperature is consistent with the characteristics of ionized impurity scattering. The constant contribution to the real part of the dielectric function $\varepsilon_1$ for the interface layer increases linearly with increasing measurement temperature. This behavior is difficult to interpret due to the complexity of the optical properties of the interface layer, as the other contributions to the dielectric function of the interface layer are linked to those of the bulk layer.
Figure 4-37: Results as functions of measurement temperature are provided for the best fit parameters including the Lorentz broadening for the low energy band and the photon energy independent contribution to $\varepsilon_1$ for the interface layer. These parameters are used as variables in the analysis of SE data for AZO sample DS40162.

A parameter of major interest for the AZO sample is the optical band gap which is represented by the resonance energy of the CP oscillator and plotted as a function of
temperature in Figure 4-38. As expected for temperatures near and above the Debye temperature, the energy gap is found to red-shift linearly with increasing temperature. For the AZO sample, the red shift is ~ 104 meV when sample is annealed from 300 K to 650 K, yielding a temperature coefficient of $-2.975 \times 10^{-4}$ eV/K.

The other variable parameters for the CP oscillator are shown as functions of temperature in Figure 4-39. Here, it can be observed that the broadening parameter increases linearly with increasing temperature, whereas the amplitude decreases weakly at the lower temperatures and more rapidly as the temperature increases, consistent with a parabolic trend versus temperature. The behavior for the broadening parameter parallels that of the Drude broadening parameter, but with a somewhat higher temperature coefficient. Again this behavior is expected over the temperature range of these measurements. Finally, the real and imaginary parts of the final AZO dielectric functions are shown in Figure 4-40 for the annealed AZO sample at five selected measurement temperatures.

In concluding, Table 4.25 is presented, which provides a comparison of the amplitudes, bandgaps, broadening parameters, and temperature coefficients associated with the lowest energy CP for undoped and aluminum doped ZnO. These measurements were performed during the second heating cycle after annealing the samples at 700 K and cooling to room temperature prior to the measurements. The amplitude of the CP measured at room temperature is similar for both doped and undoped samples, and the small difference may be related to the fact that the dielectric function of the undoped sample is modeled using two CPs whereas that for the doped sample is modeled using a single CP. Although the signs of the temperature coefficients of the amplitude are the
same for both samples, the difference in the magnitude of the coefficients may have a similar origin as the difference in the amplitude itself.

Although the bandgap is much larger for the doped ZnO due to the B-M effect as described earlier, the temperature coefficients of the bandgaps for the two samples are similar in magnitude with that of the doped sample being somewhat larger. Similarly, the bandgap broadening parameter is much larger for the doped sample, possibly due to the presence of charged defects in the doped material which reduce the excited state lifetime associated with the bandgap excitation. Alternatively, the grain size in the doped ZnO is reduced; however, such an effect is unlikely to explain the very large increase in broadening upon doping. The temperature coefficient of the broadening parameter for the doped ZnO is also much larger than that of undoped ZnO, meaning that as the sample temperature increases the difference between the broadening parameters for the two samples increases.
Figure 4-38: The measurement temperature dependence of the CP resonance energy, representing the optical band gap, is shown for AZO sample DS40162.
Figure 4-39: The measurement temperature dependences of the CP oscillator parameters, amplitude and broadening, are plotted for AZO sample DS40162.
Figure 4-40: Analytical expressions for the real and imaginary parts of the dielectric functions are plotted for AZO sample DS40162 at different measurement temperatures. For clarity, not all temperatures are shown.
Table 4.25: The amplitudes, bandgaps, and broadening parameters associated with the lowest energy CP are compared for undoped and aluminum doped ZnO. Also compared are the temperature coefficients of these three parameters. In order to measure the temperature dependence of the dielectric function properly between 300 K and 650 K, the two samples were annealed at 700 K and cooled to room temperature prior to the measurements.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$A$ (300 K)</th>
<th>$dA/dT$ (K$^{-1}$)</th>
<th>$E_g$ (300 K) (eV)</th>
<th>$dE_g/dT$ (eV K$^{-1}$)</th>
<th>$\Gamma$ (300 K) (eV)</th>
<th>$d\Gamma/dT$ (eV K$^{-1}$)</th>
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<tbody>
<tr>
<td>Annealed Undoped ZnO DS-LD-009</td>
<td>4.948</td>
<td>$-6.369 \times 10^{-4}$</td>
<td>3.300</td>
<td>$-2.569 \times 10^{-4}$</td>
<td>0.058</td>
<td>$+4.334 \times 10^{-5}$</td>
</tr>
<tr>
<td>Annealed AZO DS40162</td>
<td>5.060</td>
<td>$-1.578 \times 10^{-4}$ *</td>
<td>3.855</td>
<td>$-2.975 \times 10^{-4}$</td>
<td>0.278</td>
<td>$+7.836 \times 10^{-5}$</td>
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* Linear coefficient determined over the narrower temperature range of 300 K to 550 K.
Chapter 5

Analysis of Ag/ZnO Interfaces in Solar Cell Back-Reflectors

5.1 Introduction

As described in earlier chapters, the back-reflector (BR) is a very important component of thin film Si:H solar cells. In the case of the hydrogenated silicon (Si:H) n-i-p solar cell configuration, the BR consists of a substrate-supported opaque layer of Ag or Al, followed by a ~3000 Å thick layer of ZnO. In this configuration, both metal and ZnO layers are sputtered onto a low-cost flexible substrate such as stainless steel or polymer foil. In this thesis study, the back-reflector was deposited on an oxidized c-Si substrate and monitored in real time by spectroscopic ellipsometry. A schematic representation of the different layers of the substrate/back-reflector of this study is shown in Fig. 5.1.

Figure 5-1: Schematic representation is shown for the different layers that comprise the substrate/back-reflector configuration studied in this thesis.
The interface layer between Ag and ZnO in Fig. 5.1 was found to be necessary in the optical model, and details of its formation and evolution will be discussed in the next section. Then the remainder of the chapter will focus on the optical analysis of the optical behavior of the Ag/ZnO interface layer for Ag layers deposited with differing thicknesses of surface roughness.

The main purpose of a back-reflector in the thin film Si:H solar cell is to reflect near-infrared wavelengths (650 to 1000 nm; 1.2 to 1.8 eV) back into the cell for possible absorption during additional passes as the thin film Si:H absorption is weak in that spectral range (Banerjee and Guha, 1991). In addition, the Ag/ZnO interface is designed to be macroscopically rough in order to enhance the optical path length of reflected light rays via non-specular scattering. Before discussing the details of the interface study by spectroscopic ellipsometry, it is helpful to consider the various possible optical processes at Ag/ZnO interfaces, which are depicted in Fig. 5.2.

Figure 5-2: Various possible optical processes at Ag/ZnO interfaces are depicted: (1) specular reflectance, (2) direct non-specular scattering, (3) dissipation by interband and intraband electronic excitations, (4) confined plasmon excitation followed by either (5) dissipation or (6) re-emission, (7) propagating surface plasmon excitation, followed by either (8) dissipation or (9) re-emission (Dahal, 2013).

The surface optical processes depicted in Fig. 5.2 include specular reflection [labeled (1)], plasmon excitation [labeled (4), (7)], non-specular scattering [labeled (2),
(6), (9)], and dissipation [labeled (3), (5), (8)]. The primary optical process at the interface is specular reflection (labeled 1) which is described in accordance with the complex Fresnel equations, based on macroscopically smooth multilayer models. Other important phenomena include the coupling of incident light either to confined plasmons (labeled 4), which can be described collectively as an oscillator in the optical properties of a distinct surface layer and handled through Fresnel's equations, or to propagating surface plasmons (labeled 7) which cannot be described through Fresnel’s equations. Coupling to propagating surface plasmons in this optical configuration occurs only through a grating effect which requires macroscopic surface roughness. Direct scattering (labeled 2) by macroscopically rough surfaces as well as scattering mediated through confined plasmons (labeled 6) or propagating surface plasmons (labeled 9) are also potentially important optical processes at the interface. Furthermore, dissipation is associated with all processes including specular reflection (labeled 3) and confined plasmon excitation (labeled 5), both describable by Fresnel's equations, as well as propagating surface plasmons (labeled 8).

5.2 Evolution of ZnO Structure from Real Time Spectroscopic Ellipsometry

The ZnO thin film fabrications were carried out using an RF sputter deposition chamber in an argon atmosphere under similar conditions as those used for the Ag thin films as described in Chapter 3. A back-reflector for the Si:H n-i-p solar cell is formed by depositing a ZnO layer on top of an underlying Ag film. For analysis of the real time spectroscopic ellipsometry data obtained during the deposition of ZnO on Ag, the dielectric functions of both the ZnO and Ag films are required. Thus, an initial deposition of ZnO was carried out using the same conditions as for back-reflector deposition but
with an oxide covered crystalline silicon (c-Si) substrate for the purpose of determining the dielectric function in a less complicated sample structure. Thus, the dielectric functions of the ZnO thin films as well as their structural evolution were determined from real time spectroscopic ellipsometry data collected during this initial deposition.

The analysis of the data collected during the ZnO deposition on native-oxide-covered c-Si was performed assuming a model consisting of a bulk layer and surface roughness layer of ZnO both on top of the substrate. A short time range was identified during the deposition of ZnO, selected such that the optical properties of the material are not expected to vary over the range. For this particular analysis, the time range during deposition was selected as 13.2 to 14.5 min with the inversion point fixed near the center of the range at 13.8 min. Trial values of the two layer thicknesses are selected at this time point, which enables inversion to extract a dielectric function subsequently used to analyze the data set over the 1.3 min time range. The accumulated MSE over this range was used as a criterion for identifying the correct thicknesses, which were 303 Å and 22 Å for the bulk and surface roughness layer thicknesses, respectively. Over the time range from 13.2 to 14.5 min, the bulk thickness values were found to increase from 275 Å to 332 Å, and the surface roughness thickness values were found to decrease from 25 Å to 18 Å. The resulting ZnO dielectric function obtained by inversion in this analysis was fit using a parameterized model consisting of two oscillators described by band structure critical-points based on the assumption of parabolic valence and conduction bands and a photon energy independent momentum matrix element.

The results of the analysis to determine the room temperature dielectric function of the ZnO film deposited on c-Si are described next. Figure 5.3 shows these results as
obtained by inversion together with the best fit using the parameterized model. The
parameterized model serves to smoothen the noise in the data, and generate $\varepsilon_2 = 0$ below
the band gap of the ZnO. Figure 5.4 shows the parameterized dielectric function of
Figure 5.3 for comparison with that of a reference ZnO sample obtained in an ex situ
measurement of a film deposited on c-Si as supplied by Energy Conversion Devices, Inc.
The two dielectric functions appear similar, but the one determined in this study exhibits
a higher amplitude, most likely due to a higher density film microstructure. In addition,
the dielectric function of this study has broader critical point structures in $\varepsilon_1$ and $\varepsilon_2$,
indicating a higher defect density or smaller crystalline grain size.
Figure 5-3: Real ($\varepsilon_1$, upper) and imaginary ($\varepsilon_2$, lower) parts of the dielectric function are shown for ZnO deposited at room temperature on a crystalline silicon substrate. The experimentally determined result obtained by exact inversion (circles) is plotted together with the result derived from the best fit analytical model (solid line).

Subsequent ZnO depositions were performed on previously deposited Ag films, which in turn were deposited on c-Si substrates to evaluate the back-reflector properties. The same iterative two-step procedure described previously in Chapter 3 was applied to deduce the structural evolution and dielectric functions of the Ag films (see Chapter 3, Figs. 3.4 and 3.10). With the dielectric functions of component layers of the structure
now available, in particular those of the Ag and ZnO layers of the back reflector, one can progress to determine the evolution of the thicknesses of the semi-transparent deposited bulk layers as well as the layers that may form at the interfaces between the overlying and underlying layers. As a first approximation the surface roughness on the ZnO films will be neglected since the optical contrast between the ZnO and air is not very large, whereas the optical contrast between Ag and ZnO is extremely large, especially in the near infrared. Specifically, over the spectral range of Fig. 5.4, the ambient medium is non-absorbing and the ZnO is essentially non-absorbing below the band gap and weakly absorbing above. In contrast, Ag is strongly absorbing below the band gap of ZnO. Because the Ag is grown to opacity in this study, any film structure beneath the Ag layer need not be incorporated into the optical model; (i.e., Ag is considered as a semi-infinite slab in the optical model). Thus, the model for ZnO deposition on relatively smooth Ag appears as shown in Fig. 5.5.
Figure 5-4: The analytical expression serving as the best-fit to the inverted dielectric function of ZnO obtained by real time SE (solid line) is shown for a sample fabricated under standard conditions on a crystalline silicon wafer substrate (labeled “Univ. of Toledo”). This dielectric function is relevant for a measurement temperature of 25°C and is used in most real time spectroscopic ellipsometry analyses of back reflectors in this dissertation research. The dielectric function shown as the broken line was obtained in an analysis of ex situ SE data for a ZnO film supplied through an industry collaboration (Energy Conversion Devices; labeled “ECD”).

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<tr>
<td>Ambient</td>
<td>Ambient</td>
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<tr>
<td>ZnO</td>
<td>(experimentally determined: reference deposition)</td>
</tr>
<tr>
<td>Interface layer</td>
<td></td>
</tr>
<tr>
<td>Ag (determined by inversion: same deposition)</td>
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Figure 5-5: The model used for the analysis of the ZnO depositions on opaque Ag is depicted.
In implementing this model in the analysis of the data, least squares regression is applied. The best fit, as evaluated by the error function \( \sigma \), in least-square regression is the result of a numerical algorithm that minimizes the differences between the spectra obtained experimentally and that simulated based on the model. The specific quantity minimized is the square of the unbiased estimator of the mean square deviation, denoted as \( \sigma^2 \) and defined as

\[
\sigma^2 = \frac{1}{NM - p - 1} \sum_{j=1}^{M} \sum_{i=1}^{N} [g_{j,\text{exp}}(E_i) - g_{j,\text{cal}}(E_i, x)]^2 ,
\]

(5.1)

where \( N \) is the number of spectral points, \( M \) is the number of data sets, \( p \) is the number of free parameters, the functions \( g_{j,\text{exp}}(E_i) \) and \( g_{j,\text{cal}}(E_i, x) \) are the experimental and calculated quantities at photon energy \( E_i \) for the \( j^{th} \) data set, and \( x \) is a vector with \( p \) components which are free parameters (Jellison, 1998). In ellipsometry, two experimental spectra \([\psi(E), \Delta(E)]\) are measured simultaneously; thus \( M=2 \). For the rotating compensator spectroscopic ellipsometer used in this thesis study, the real and imaginary parts of the complex amplitude reflection ratio \( \rho \) are chosen as their deviations do not depend as strongly on the instrument configuration as other common error functions. Thus, Equation 5.1 can be rewritten as (Podraza, 2008)

\[
\sigma^2 = \frac{1}{2N - p - 1} \sum_{i=1}^{N} \left\{ \left[ \text{Re} \rho_{\text{exp}}(E_i) - \text{Re} \rho_{\text{cal}}(E_i, x) \right]^2 + \left[ \text{Im} \rho_{\text{exp}}(E_i) - \text{Im} \rho_{\text{cal}}(E_i, x) \right]^2 \right\} .
\]

(5.2)

The initial approach used in the analysis of RTSE data for the deposition of ZnO on Ag was to neglect the interface layer, as shown in Fig. 5.6 (solid lines) for sample DS013 having an initial Ag surface roughness layer thickness of 28 Å. In this case, the quality of fit achieved in simulating the experimental spectra by the best fit calculated
spectra is observed to be poor when considered as a function of time over the range of ~10 to 15 min. This corresponds to the ZnO bulk layer thickness range of 200 - 600 Å. Over this thickness range, the sensitivity to the Ag/ZnO interface appears to be the highest. In fact, at t = 12.5 min, when the ZnO thickness is 400 Å, the error function σ reaches its maximum of σ = 0.4, which is ~ 8 times higher than the ZnO baseline value obtained at the endpoint ZnO thickness of 1300 Å. In addition to the poor fitting quality, an unphysical oscillation in the deposition rate of the ZnO is observed over the range of 250 - 500 Å.

The second step in an attempt to improve the quality of the fit versus time was to incorporate an interface mixing layer whose optical properties were determined by the Bruggeman effective medium approximation as a simple 50/50 volume percent mixture of Ag/ZnO. This layer could serve to simulate either interface roughness or a chemically mixed region. Addition of the interface layer yielded a significant improvement in the fit quality as shown in Fig. 5.6 (open circles) and an elimination of the observed deposition rate artifact; however, in this case an apparently unphysical oscillation appeared in the time evolution of the interface layer thickness, suggesting further improvement in the model is possible. The oscillation in the interface layer thickness appears to be unphysical as it occurs after the interface layer is covered by 300 Å of ZnO bulk layer. After being completely covered in this way, one would expect that the interface properties would stabilize, or possibly show a monotonic trend versus time, rather than an oscillation.
Figure 5-6: The ZnO bulk layer thickness (top panel, solid line) and the quality of the fit $\sigma$ (bottom panel, solid line) are plotted versus the deposition time as obtained in an analysis of real time spectroscopic ellipsometry data for deposition DS013 assuming an abrupt Ag/ZnO interface. Also shown are corresponding results (top and bottom panels, data points) assuming an interface layer between the Ag and ZnO whose dielectric function is determined by the Bruggeman EMA assuming 50/50 volume % Ag/ZnO with a thickness determined in the analysis (center panel). Incorporation of an interface layer significantly improves the quality of fit although the time evolution of the interface thickness shows an apparently unphysical oscillation.

A third step toward improving the time averaged fit quality was to perform an overall optimization procedure for the interface layer composition used in the effective medium approximation. The final results are shown in Fig. 5.7, which reveals a minimum
in the average quality of fit parameter for $f_i = 0.28$. Here $f_i$ is the volume fraction of ZnO in the (Ag + ZnO) effective medium mixture that describes the interface layer.

![Graph showing time average of quality of fit parameter as a function of ZnO volume fraction.]

Figure 5-7: The time average of the quality of fit parameter is plotted as a function of the ZnO volume fraction in the EMA mixture consisting of Ag and ZnO. An effort is made to identify the ZnO content in the EMA by minimizing the time average of $\sigma$.

Thus, the choice of 72/28 vol.% Ag/ZnO for the composition of the interface layer in the effective medium approximation yields a dielectric function that appears to better simulate the interface layer properties. As shown in Fig. 5.7, however, the unphysical oscillation in the interface layer thickness versus time becomes even more pronounced with the new interface optical properties. In Fig. 5.8 the results of this new analysis are shown in comparison with the results obtained by assuming no interface layer and an interface layer with a 50/50 vol. % Ag/ZnO composition.
Figure 5-8: The ZnO bulk layer thicknesses (top panel) are shown for three different models of the Ag/ZnO interface layer used in the analysis of real time spectroscopic ellipsometry data for the deposition DS013. The models include no interface layer (solid line) and interface layers whose dielectric functions are determined by the effective medium approximation as 50/50 (circles) and 72/28 (squares) vol.% mixtures of Ag/ZnO. Also shown are the Ag/ZnO interface layer thicknesses (center panel) for the latter two models and the quality of the fit $\sigma$ (bottom panel) versus the deposition time for all three models. The time averaged value of $\sigma$ indicates an improvement in the overall fit with the addition of an interface layer; additional improvement is possible by optimization of the interface layer composition in the EMA.
Subsequently, a fourth modeling approach was applied which involved extracting the dielectric function of the interface layer directly, illustrated here for the same sample DS013 whose results have been presented in Figs. 5.6 - 5.8. For this sample, the interface dielectric function was determined by exact mathematical inversion of \((\psi, \Delta)\) spectra collected by RTSE at a time of \(t = 11.09\) min for a selected combination of trial bulk layer and interface layer thicknesses \((d_b, d_i)\). The analysis used the dielectric functions of Ag and ZnO that had been determined previously. After the interface layer dielectric function was found by inversion using the selected pair of \((d_b, d_i)\), the real time ellipsometry spectra over the time range from 10.24 to 11.95 min were fitted using this dielectric function. This time range of analysis corresponds to the \(d_b\) range of 273 to 357 Å, an estimate based on the results from the third modeling approach. This multi-time analysis generates a time averaged quality of fit, which is stored in 2D matrix of \((d_b, d_i)\) values. This procedure is repeated for a grid of trial \((d_b, d_i)\) values and the lowest average \(\sigma\) identifies the best fit pair of thicknesses and the correct interface dielectric function. The interface dielectric function obtained from this approach for sample DS013 with best fit \(d_b\) and \(d_i\) values of 251 and 90 Å, respectively, is shown in Fig 5.9.

Superimposed on the inverted dielectric function in Fig. 5.9 is a simulated result obtained by fitting using an analytical dielectric function incorporating different oscillators. Clearly the imaginary part of dielectric function, \(\varepsilon_2\), of the interface layer shows a strong resonance at \(\sim 2.8\) eV that is present neither in the bulk Ag dielectric function (broken lines) nor in the ZnO dielectric function (triangles). This resonance can be fitted reasonably well with a single Lorentz oscillator; however, in order to describe the dielectric function throughout the photon energy range a Drude term and a CP
oscillator are required. The increase in $\varepsilon_2$ with increasing photon energy at $\sim 4$ eV derives directly from the interband transitions of electrons in the Ag component (see broken lines) of the interface layer. The absorption onset of the ZnO component (see triangles) may also contribute; however, if this is the case, the ZnO band gap has shifted to higher energies in the interface layer relative to the bulk ZnO layer. The rapid decrease at low photon energies in the real part of the dielectric function, $\varepsilon_1$, is also attributed to the dielectric function of the Ag component of the layer, namely to the intraband transitions of free electrons.
Figure 5-9: Real (upper) and imaginary (lower) parts of the dielectric function of the Ag/ZnO interface layer for sample DS013 (circles), obtained by exact inversion of ellipsometric spectra at a deposition time of 11.09 min. Also shown is a fit using an optical model including a Lorentz oscillator at ~ 2.8 eV, an interband transition resonance at ~ 4 eV, and a Drude free electron contribution that accounts for the decrease in $\varepsilon_1$ at low energies (lines). The broken lines and triangles represent the dielectric functions of the underlying Ag and the overlying ZnO, respectively, that serve to confine the interface region.
By using the dielectric function of the interface layer obtained by exact inversion, one can significantly reduce the unphysical interface thickness oscillations observed when using the EMA dielectric function that minimizes the average fitting error. Figure 5.10 shows the time evolution of the bulk layer thickness, the interface layer thickness, and the quality of fit for sample DS013, comparing three cases. These cases include an interface layer having a dielectric function obtained as (i) a Bruggeman EMA mixture of 72/28 vol.% Ag/ZnO, (ii) an inversion at a deposition time of 11.09 min with $d_b$ and $d_i$ values of 251 and 90 Å, and (iii) an analytical model that best fits the inversion result (ii). In case (iii) then, the inverted dielectric function of the interface layer was smoothed using an oscillator model. Additional details of the model will be provided in the next section. Here the focus is on the structure of the film, i.e. the evolution of the bulk and interface layer thicknesses, and the quality of the fit.

Although the average fitting error increases slightly when using the inverted dielectric function in place of the best EMA dielectric function, the behavior as a function of time for the interface thickness becomes more physically realistic. Specifically rather than showing a strong oscillation and a later decay versus time, the interface thickness for case (ii) shows a rise of 75 Å and stability versus time later in the growth process. When the analytically smoothed dielectric function of case (iii) is used, the average quality of fit improves considerably again, and the behavior for the interface thickness is also quite reasonable and similar to the results for case (ii). Although the unphysical oscillation in the time evolution of the interface layer thickness is suppressed for cases (ii) and (iii), features appear at 16 min in these cases. When the inverted dielectric function of case (ii) is used, the feature consists of a decrease in interface thickness from 60 Å to a
minimum of 35 Å before this thickness returns to the stable value of 75 Å. When the analytically smoothed dielectric function of case (iii) is used, the feature consists of an interface thickness increase from 60 Å to 100 Å before it returns to the stable value of 75 Å. These features are likely caused by small errors in the interface dielectric function in conjunction a high sensitivity to the interface characteristics at a bulk layer thickness of ~ 500 Å, meaning that even small errors in the dielectric function lead to large errors in interface thickness. It should be noted that an average of the interface thickness results from cases (ii) and (iii) eliminate the features. Thus for sample DS013 having an initial Ag surface roughness layer thickness of 28 Å, we can conclude that the interface thickness is 75 ± 8 Å and forms completely within 9 to 10 minutes of deposition. The bulk thickness is approximately 300 Å when the interface thickness stabilizes, which occurs after 12 minutes.

From the dielectric function obtained by inversion as shown in Fig. 5.9 for case (ii), one can clearly see three characteristics of the interface layer dielectric function: free electrons following a Drude characteristic, bound electrons associated with a confined plasmon resonance, and bound electrons associated with interband transitions. In fact the dielectric function deduced using the 0.72/0.28 EMA mixture of Ag/ZnO is a reasonable, but far from perfect approximation to the inverted dielectric function, as shown by the comparison in Fig. 5.11 between the EMA and analytically smoothed dielectric functions. Among the differences in the EMA dielectric function include (i) a non-Lorentzian lineshape for the plasmon resonance with broader structure and weaker maximum amplitude, (ii) a weaker interband absorption amplitude near 4 eV, and (iii) stronger dissipation associated with the free electron component apparently due to a shorter
relaxation time. These differences that arise due to the use of the EMA dielectric function are apparently significant with respect to the deduced structural evolution and give rise to the unphysical interface layer oscillations.

Figure 5-10: The bulk layer thickness (top panel), interface layer thickness (center panel), and quality of fit (bottom panel) are shown as a function of deposition time. Three different determinations of the interface layer dielectric functions are applied, including an EMA mixture of 72 vol.% Ag and 28 vol.% ZnO (squares), exact inversion of the (ψ, Δ) data at a time of 11.09 min (inverted triangles), and an analytical form (solid line) that best fits the inversion.
Figure 5-11: Real (upper) and imaginary (lower) parts of the dielectric functions of the Ag/ZnO interface layer for sample DS013 deduced by considering an EMA of 72/28 vol.% Ag/ZnO (circles) and an analytical dielectric function obtained as a best fit to an inverted result (sold line).
5.3 Dependence of the Structure and Dielectric Function of Ag/ZnO Interfaces on the Ag Roughness Thickness as Obtained by RTSE

In the previous section, we have described how the inclusion of an interface layer between the bulk Ag and ZnO layers significantly improves the fit to the full real time spectroscopic data set collected during the evolution of ZnO on an opaque Ag film. Moreover, the optical properties of Ag/ZnO interface show features that are observed neither in Ag nor in ZnO. In this section, the results of studies of the dielectric functions of the interface layer are presented for a wider set of thin film samples. An interesting physical property of the Ag/ZnO interface observed in these studies is observed in Fig. 5.12 where the average interface layer thickness $d_i$ is plotted as a function of the initial Ag surface roughness thickness $d_s$. The average is performed versus elapsed time of ZnO deposition after the saturation thickness in $d_i$ has been reached. The average interface thickness calculated in this way is found to correlate with the starting microscopic roughness on the Ag surface with extrema values of Ag/ZnO $d_i = (40, 233)$ Å for Ag $d_s = (6, 105)$ Å. It is interesting that the $d_i$ intercept at $d_s = 0$ for the best fit line is 25 Å. This suggests that when the Ag is atomically smooth, an interface layer is generated nonetheless. This interface layer component may arise due to the damage of the incident high energy ions that serve as the precursors of the ZnO film and impact the Ag surface during deposition. The resulting chemically mixed layer, however, is unlikely to exhibit strong plasmon behavior due to the suppression of free electron characteristics in such a layer.
Figure 5-12: Ag/ZnO interface layer thickness ($d_i$) is plotted here as a function of initial Ag surface roughness thickness ($d_s$). The interface thickness is obtained as an average versus time during ZnO deposition after the saturation thickness in $d_i$ has been reached. The broken line depicts the best fit linear trend.

As described in the previous section (Section 5.2), the effort to represent the dielectric function of the Ag/ZnO interface layer with the Bruggeman EMA produced an unphysical oscillation in the interface layer thickness. That problem was resolved by determining the interface layer dielectric function by numerical inversion in the same analysis procedure that provided the ZnO bulk and Ag/ZnO interface layer thicknesses. The details of this procedure have been described in Section 5.2. The results of the exact inversion to determine the interface dielectric functions are shown in Fig. 5.13 for four samples with initial surface roughness layer thicknesses for the Ag that range from 12 Å to 105 Å, including the $d_s = 28$ Å result for sample DS013 from Section 5.2.
Figure 5-13: The experimentally determined dielectric functions of the Ag/ZnO interface layer as obtained by exact inversion are shown for four samples, including sample DS013 from Section 5.2. The sample number and the surface roughness thicknesses $d_s$ on the initial Ag film are given in the legend. Also indicated in the legend are the resulting Ag/ZnO interface roughness thicknesses $d_i$.

For all four samples, the imaginary part of the dielectric function, $\varepsilon_2$, shows a resonance near 2.8 eV that is present neither in the Ag nor the ZnO dielectric functions.

To characterize and understand the optical properties of the Ag/ZnO interface layer, the
inverted dielectric functions were fit using an oscillator model. Figures 5.14 and 5.15 show the real and imaginary parts of the dielectric functions of the interface layers in a comparison of samples with initial Ag surface roughness thicknesses of 28 Å and 12 Å, respectively. The results for the sample with initial Ag surface roughness thickness of 28 Å are from Section 5.2. In the figures, the inverted dielectric functions are represented by open circles and the best fit results using an oscillator model are shown as the lines. Figure 5.15 also shows the deconvolution of the optical model used in the fit in terms of individual oscillator and Drude component terms.
Figure 5-14: Real (upper) and imaginary (lower) parts of the dielectric function of the Ag/ZnO interface layer for the sample DS013 with an initial Ag surface roughness layer thickness of $d_s = 28 \text{ Å}$, obtained by exact inversion of ($\psi$, $\Delta$) spectra (circles); a fit using an oscillator model is also shown (lines).
Figure 5-15: (Left) Real (upper) and imaginary (lower) parts of the dielectric function of the Ag/ZnO interface layer are shown for the sample with initial Ag surface roughness layer thickness of $d_s = 12$ Å, obtained by exact inversion of $(\psi, \Delta)$ spectra (circles); a fit using an oscillator model is also shown (lines). (Right) A decomposition is shown for the optical model, which consists of Drude, Lorentz, and critical point (CP) oscillators.

The features in the data and the simulation exhibit similar characteristics and as a result support the validity of the real time SE data analysis. The interface layer analysis includes (i) a free electron component modeled using the Drude expression, (ii) a plasmon band modeled as a Lorentz oscillator, and (iii) a bound electron absorption feature modeled assuming transitions between parabolic bands near a band structure critical point (Collins and Ferlauto, 2005). The Lorentz oscillator parameters of the plasmon band (ii), which has also been suggested in earlier studies of the Ag/ZnO interface (Springer et al., 2004), are plotted versus the $d_s$ value describing the roughness on the starting Ag surface in Fig. 5.16. Although the confidence limits achieved in the
analytical fits are relatively narrow, there is significant scatter in the data well outside the confidence limits. This is likely due to small errors in the bulk ZnO and Ag/ZnO interface layer thicknesses that have a relatively large effect on the interface layer dielectric function via the inversion analysis.

The top panel does shows a trend indicating that the energy of the plasmon band decreases as the Ag $d_\parallel$ value increases. For the range of $d_\parallel$ investigated here, this shift is $\sim$0.2 eV. For a plasmon propagating at the surface of a metal with an ambient dielectric function of $\varepsilon_a$, the plasmon peak is predicted to occur at a photon energy of $E_0 \sim E_p (1 + \varepsilon_a)^{-1/2}$. The values $E_p = 8.8$ eV for the bulk free-electron plasmon energy of Ag from the literature and $\varepsilon_a = 4.0$ for ZnO at the photon energy of the observed $E_0$ value of 2.85 eV together yield $E_0 = 3.9$ eV for Ag/ZnO, significantly higher than the experimental value. Furthermore, unless significant macroscopic roughness exists at the interface that enables the incident wave to couple to propagating surface plasmons, then such excitations will not occur. Thus, the resonances in Figs. 5.14 and 5.15 are not attributed to propagating plasmons, but instead to localized plasmon (or plasmon-polariton) modes that exist due to protrusions on the Ag surface.

For simple spherically-shaped protrusions, these modes are predicted to appear with a resonance energy of:

$$E_0 \sim E_p \left\{ \varepsilon_{lo} + [(2 + Q_m)/(1 - Q_m)] \varepsilon_a \right\}^{-1/2},$$  \hspace{1cm} (5.3)

a result that was derived in Section 2.2 of Chapter 2 by substituting the Drude equation for the dielectric function of the guest material into the Maxwell-Garnett effective medium theory. In Eq. 5.3, $\varepsilon_{lo}$ is the constant contribution in the Drude equation for the
Ag dielectric function and $Q_m$ is the volume fraction of metal protrusions in the surface layer (Collins and Ferlauto, 2005).

Substituting the Lorentz oscillator parameter values from Fig. 5.16 into Eq. (4.3a) (Chapter 4) yields the range $Q_m = 0.05$ to 0.13 for the volume fraction associated with the metal protrusions in the Ag/ZnO interface layers with plasmon resonance energies ranging from 2.94 eV to 2.76 eV. Taking $E_p = 9.20$ eV and $\varepsilon_{10} = 4.15$, which are averages from Table 3.4, and also $\varepsilon_a = 4.0$, then Eq. 5.3 gives $E_0 = 2.57$ eV for $Q_m = 0.05$ and $E_0 = 2.46$ eV for $Q_m = 0.13$. Thus, electronic resonances within surface protrusions can reasonably account for the plasmon energy of Fig. 5.16. An increase in the volume fraction associated with the protrusions can account for the energy decrease with increasing Ag $d_s$ over the range observed in Figure 5.16. The higher energies for the experimental result cannot be attributed to incorrect values of $Q_m$ since even the minimum of $Q_m = 0$, which generates the maximum possible $E_0$, yields a predicted range from $E_0 = 2.63$ eV to 2.51 eV, still lower than the observations. The observed higher resonance energies may derive from reduced screening of the plasmons by the ZnO at the interface, which may exhibit a different $\varepsilon_a$ value relative to bulk ZnO, possibly due to interface voids or a higher doping level at the interface. For example, if $\varepsilon_a = 2.6$, rather than 4.0, then $Q_m$ is found to range from 0.07 to 0.19, and $E_0$ is predicted to range from 2.92 eV to 2.75 eV, which matches both the observed magnitude and shift in the plasmon band observed in Fig. 5.16.

In Table 5.1(a), the resonance energy of the confined plasmon band at the Ag/ZnO interface is compared with results from other forms of nanoparticle Ag. This comparison includes the corresponding values for confined plasmon bands in colloidal Ag.
nanoparticles as reported by Aryal (P. Aryal, 2014) and nucleating sputtered Ag thin films as reported by Little (S. A. Little, 2012). The results from the latter study suggest that in the application of Eq. (5.3) to describe the plasmon resonance energy, the low energy plasmon resonances predict volume fraction of Ag nanoparticles (fourth column) that are unphysically high, in fact as high as 0.9.

This may suggest that as the volume fraction of protrusions increases, the resonance energy decreases more rapidly than predicted by Eq. 5.3. Such an effect may be explained in two ways. First, within the framework of the simple Maxwell-Garnett effective medium theory with a well-defined host, one may need to introduce interactions between particles not included in the simple theory in order to model the physical situation. Alternatively, as the volume fraction of protrusions increases, a better choice may be the Bruggeman effective medium theory, which assigns the effective dielectric function as the host dielectric function. With the Bruggeman theory and assuming an ambient medium of air or vacuum, the prediction for the Ag volume fraction is $Q_m = 0.09$ to 0.23 assuming a maximum in $\varepsilon_2$ starting from 3 eV and decreasing to 1.4 eV, as shown in Fig. 2.8.

For an evaluation of the plasmon resonances for the Ag/ZnO interface on the other hand, the Maxwell-Garnett approach appears suitable and leads to two suggestions, namely, that the protrusions are widely spaced as indicated in Table 5.1 and that screening is much lower, possibly due to a low $\varepsilon_a$ for the ZnO near the interface.

The center panel in Fig. 5.16 shows the width of the plasmon band versus Ag $d_s$. A value of $\Gamma = 0.7 \pm 0.25$ eV characterizes the results for all samples. By applying the expressions $\tau = h/\Gamma$ with $L = v_F\tau$ for the relaxation time and mean free path, respectively,
where $\hbar = 6.58 \times 10^{-16}$ eV s is Planck’s constant and $v_F = 1.39 \times 10^6$ m/s is the Fermi velocity for electrons in Ag, then ranges of $\tau = (1.1 \pm 0.4) \times 10^{-16}$ s and $L = 15 \pm 6$ Å are obtained. A strong broadening effect (consequently short relaxation time and mean free path) relative to that of bulk Ag (with $\Gamma \sim 0.054$ eV, $\tau = 1.23 \times 10^{-14}$ s, and $L = 370$ Å; see Table 5.1), can be attributed to surface scattering due to the small size of the structures; disorder of the Ag at the interface may also play a role.

In Table 5.1(b), the broadening energy, relaxation time, and mean free path of free electrons associated with the confined plasmon band at the Ag/ZnO interface are compared with results from other forms of Ag. This comparison includes the corresponding values for confined plasmon bands in colloidal Ag nanoparticles as reported by Aryal (Aryal, P., 2014), nucleating sputtered Ag thin films as reported by Little (Little, S. A., 2012), and for free electrons in sputtered Ag thin films as reported by Dahal (Dahal, 2013). The results show that the relaxation time and mean free path for the confined plasmon band associated with the Ag/ZnO interface is similar to that of Ag nanoparticles but longer than that associated with sputtered Ag clusters in the initial nucleation stage. This comparison suggests that the in-plane scale of the protrusions are larger than in the case of the nuclei in sputtered thin films, but similar to that of the nanoparticles which is known to be $\sim 60$ Å.

Finally, in the bottom panel of Fig. 5.16 the amplitude of the plasmon band is observed to be relatively constant in the range of $9 \pm 2$ eV for Ag roughness thickness in the range $d_s > 20$ Å. For thinner roughness layers, the spread is $6 \pm 2$ eV. The amplitude of the transition for a given width is expected to scale with the concentration of electrons participating in the plasmon resonance and thus the volume fraction of metal as indicated
by Eq. (4.3a). The lower amplitudes for thinner Ag surface roughness layers suggest that the volume fraction of metal that sustains the plasmon resonances in these thin layers is reduced. The 25 Å thick component of $d_i$ in the form of the chemically-mixed layer is likely to exert a dominant effect for samples fabricated with low Ag roughness thicknesses and to contribute to the reduction in plasmon amplitude observed in the bottom panel of Fig. 5.16.

Figure 5-16: Resonance energy ($E_0$), broadening ($\Gamma$), and amplitude ($A$) of the plasmon band associated with the Ag/ZnO interface layer plotted as functions of initial Ag surface roughness thickness, $d_s$. To obtain this information, the plasmon band has been modeled as a single Lorentz oscillator.
Table 5.1: (a) The resonance energy ($E_0$) range for electrons associated with the confined plasmon band is shown, as determined in this work, in comparison with the ranges of values for colloidal Ag nanoparticles reported in Aryal, P., 2014 (indicated as Ref. 1) and sputtered Ag thin films reported in Little, S. A., 2012 (indicated as Ref. 2). The range in the values of $Q_m$ consistent with Eq. (5.3) or the Bruggeman theory of Fig. 2.8 are given. (b) The broadening energy ($\Gamma$), relaxation time ($\tau$), and mean free path ($L$) of electrons associated with the confined plasmons are shown, as determined in this work, in comparison with those values for colloidal Ag nanoparticles reported in Aryal, P., 2014 (indicated as Ref. 1), sputtered Ag thin films reported in Little, S. A., 2012 (indicated as Ref. 2), and in Dahal, 2013 (indicated as Ref. 3). In the last two columns, $\hbar = 6.58 \times 10^{-16}$ eV s is Planck’s constant and $v_F = 1.39 \times 10^6$ m/s is the Fermi velocity for electrons in Ag.

(a)

<table>
<thead>
<tr>
<th>Material</th>
<th>Ambient medium with $\varepsilon_a$</th>
<th>Confined plasmon energy range $\tau = h/\Gamma$ (s)</th>
<th>Range in $Q_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag/ZnO interface confined plasmon (this work)</td>
<td>ZnO ($\varepsilon_a \sim 4.0$)</td>
<td>2.7 - 2.9 eV</td>
<td>Eq. 5.3: ~0</td>
</tr>
<tr>
<td>Colloidal Ag nanoparticle; confined plasmon (Ref. 1)</td>
<td>Alkanethiol ($\varepsilon_a \sim 2.3$)</td>
<td>2.37 - 2.43 eV</td>
<td>Eq. 5.3: 0.48 - 0.45</td>
</tr>
<tr>
<td>Sputtered Ag during nucleation; confined plasmon (Ref. 2)</td>
<td>Vacuum ($\varepsilon_a = 1$)</td>
<td>1.4 - 3.0 eV</td>
<td>Eq. 5.3: 0.9-0.5 EMA Fig. 2.8: 0.23 – 0.09</td>
</tr>
</tbody>
</table>

(b)

<table>
<thead>
<tr>
<th>Material</th>
<th>Broadening $\Gamma$ (eV)</th>
<th>Relaxation time, $\tau = h/\Gamma$ (s)</th>
<th>Mean free path, $L = v_F \tau$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag/ZnO interface confined plasmon (this work)</td>
<td>0.70 ± 0.25</td>
<td>(1.1 ± 0.4) $\times 10^{-15}$</td>
<td>15 ± 6</td>
</tr>
<tr>
<td>Colloidal Ag nanoparticle; confined plasmon (Ref. 1)</td>
<td>0.75</td>
<td>0.88 $\times 10^{-15}$</td>
<td>12.2</td>
</tr>
<tr>
<td>~ 1000 Å thick smooth sputtered Ag (Ref. 3)</td>
<td>0.054</td>
<td>12.29 $\times 10^{-15}$</td>
<td>171</td>
</tr>
<tr>
<td>Sputtered Ag during nucleation; confined plasmon (Ref. 2)</td>
<td>1.65</td>
<td>$\sim 0.4 \times 10^{-15}$</td>
<td>5.6</td>
</tr>
<tr>
<td>Sputtered Ag immediately after coalescence (Ref. 2)</td>
<td>0.11</td>
<td>$\sim 6 \times 10^{-15}$</td>
<td>83</td>
</tr>
</tbody>
</table>
5.4 Ex-Situ SE Analysis of a Textured Back-Reflector

A further increase in the initial surface roughness of Ag into the macroscopic range (as in the highest efficiency solar cell structures) may cause a red shift of the plasmon band into a region where it will impact solar cell quantum efficiency. For example when $Q_m$ is 0.5 in Eq. (5.3), $E_0$ is predicted to be $\sim 1.9$ eV which, when coupled with a plasmon band width of 0.7 eV, is expected to yield significant absorption within the critical region of back reflector operation. For such a large $Q_m$, interactions between protrusions or a change in the appropriate effective medium theory as described in the previous section may lead to an even greater red shift, in fact further into the region of back-reflector operation.

In this section, the results of ex-situ SE analysis of an industry-prepared back-reflector will be presented, and these results will be compared with those obtained for back-reflectors fabricated and studied by RTSE at University of Toledo. The back-reflector in this study was prepared at the Energy Conversion Devices, Inc. (ECD) on a flexible stainless steel substrate; no other fabrication conditions were available. Since this industry standard back-reflector exhibits a thicker interface layer than those prepared and studied by RTSE, it is of interest to compare the interface layer’s optical properties to those obtained in this dissertation research for laboratory-deposited back-reflectors.

Ex-situ analysis of this structure is a more challenging problem with greater uncertainty, first because of the thicker interface layer and second because no reference dielectric functions for Ag and ZnO specific to the industry-prepared device structure were available for this study. Here the interface dielectric function for the ECD Ag/ZnO structure will be presented, and the discussion will focus on the details of how it was
obtained. Additional details on the ECD back-reflector can be found in the research of J. Stoke (Stoke, 2008).

For the ECD back-reflector, a single scan of \((\psi, \Delta)\) was performed using the same spectroscopic ellipsometer (J.A. Woollam Co., Model M2000-DI) as was used to obtain the real time results for Ag and ZnO thin films shown in Sections 5.2 and 5.3. Using standard software (J.A. Woollam Co., WVASE) which employs a least-squares regression analysis procedure, the single pair of \((\psi, \Delta)\) spectra was analyzed assuming a multilayer model. The initial study of this structure was performed by J. Stoke (2008), and the best fit model along with the parameters obtained using the model are shown along with the ellipsometric spectra in Fig. 5.17. Since dielectric functions of Ag and ZnO of ECD back-reflector were not available, the reference dielectric functions for those materials used in the analysis were obtained at the University of Toledo. The dielectric function of the room temperature deposited sample DS005 was used for the Ag and the dielectric function presented in Fig. 5.3 was used for the ZnO. With the exception of the opaque silver layer in the model, all the layers – interface, bulk, and surface roughness – were modeled by Stoke as composites using the Bruggeman EMA. In fact, the Ag/ZnO interface layer was modeled as a two layer structure; in this model, the bottom layer is Ag-rich whereas the top layer is ZnO rich. This two-layer attempt to represent a graded interface was found to produce a much better fit than a single layer. The fit is still not perfect, however, and further improvement is needed.

In the RTSE studies of Sections 5.2 and 5.3, it was found that Ag/ZnO interface layer dielectric functions obtained by inversion provided a better understanding of the structural evolution of the layer. Furthermore, an analytical form of the interface
dielectric function obtained in a best fit to the inverted result also led to a much better fit in an analysis of the structural evolution of the layer. Based on these findings, the dielectric function of the interface layer for the industry-prepared back-reflector was modeled using an oscillator expression consisting of two Lorentz and a Tauc-Lorentz oscillator. The approach is similar to that developed to model the corresponding dielectric function in the analysis of smoother back-reflector samples prepared at University of Toledo. Parameters in this oscillator model were used as free parameters in addition to thicknesses in the analysis of the \((\psi, \Delta)\) spectra. The new analysis results are shown in Fig. 5.18.

![Figure 5-17](image)

Figure 5-17: (Left) The model used to fit the experimental data for the ECD back-reflector is depicted, including semi-infinite Ag as a substrate, two layers representing the roughness between Ag and ZnO, a bulk ZnO layer with a density deficit relative to the reference material whose dielectric function was used in the analysis, and a surface roughness layer on the ZnO. (Right) Ellipsometric spectra are shown for a textured ECD Ag/ZnO back-reflector deposited on flexible stainless steel (points). The solid lines represent the results of a best fit model shown at the left (Stoke, 2008).
Figure 5.18 shows an excellent fit to experimental ellipsometric parameters ($\psi, \Delta$) with a model for the dielectric function of the Ag/ZnO interface region that incorporates multiple oscillators (Sainju et al., 2007). When this new dielectric function is used, changes in the structural parameters occur relative to those in Fig. 5.17, including a reduction in the total thickness of the interface layer from 335 Å to 250 Å and a reduction in the ZnO surface roughness thickness from 300 Å to 175 Å. The thick interface layer obtained using either model is a consequence of the fact that the starting Ag surface exhibits macroscopic roughness, meaning that the in-plane scale of the roughness is larger than the wavelength and as a result there exists a significant scattered light component. The extracted interface dielectric function is shown in Fig. 5.19 and will be compared in the next paragraph (see Fig. 5.20) with two interface dielectric functions obtained in laboratory-prepared Ag/ZnO structures with thinner Ag/ZnO interface layers. The most obvious new feature is that the new interface dielectric function for the industry back-reflector shows evidence of a lower energy absorption feature, consistent with larger isolated Ag structures.
Figure 5-18: (Left) The model used to fit the experimental data for the ECD back reflector is depicted, now modified from that shown in Fig. 5.17. The new model includes a single layer at the Ag/ZnO interface with a dielectric function expressed using an oscillator model, rather than the Bruggeman EMA. (Right) Ellipsometric spectra are shown for the textured ECD Ag/ZnO back reflector deposited on flexible stainless steel (open circles). The solid lines represent the results of the best fit model shown at left.
Figure 5-19: Real (upper) and imaginary (lower) parts of the dielectric function of the interface layer (d_i = 250 Å) for an ECD Ag/ZnO sample prepared with macroscopic roughness at the Ag/ZnO interface. This dielectric function derives from a best fit oscillator model deduced in an analysis of ex situ SE data.

Figure 5.20 depicts the interface layer dielectric functions deduced by real time spectroscopic ellipsometry for two samples prepared with different initial Ag surface roughness layer thicknesses, 12 and 105 Å. Also depicted in Fig. 5.20 are the results of
the ex situ SE study in which $\varepsilon_1$ and $\varepsilon_2$ for the Ag/ZnO interface have been extracted for the textured back reflector structure fabricated by Energy Conversion Devices, Inc. (ECD). Samples with greater Ag surface roughness exhibit increased low energy absorption losses, as can be seen from the $\varepsilon_2$ spectra in Fig. 5.20. For the ECD back-reflector, dielectric function features are nearly equally spaced in photon energy, appearing at 3.7, 2.7, and 1.6 eV. Presumably it is the increased scale of the initial surface roughness on the Ag associated with the texturing (or macroscopic roughness development) for the ECD back reflector structure that yields a Ag/ZnO interface dielectric function with a low energy plasmon resonance as indicated by its $\varepsilon_2$ spectrum. In fact, the associated reflectance predictions to be presented in Sec. 5.5 indicate a significant reduction in reflectance over the near-infrared spectral range where high back-reflector performance is desired for enhanced light collection in the solar cell.

Figure 5.20 suggests a number of trends, which provide insights into the optical nature of the Ag/ZnO interface layer as a function of its thickness, and possible future directions for improvement of the analysis. First as the interface layer thickness increases, the separation between the plasmon and the interband transitions becomes less distinct due to the overlap of their absorption tails. This may indicate that for the thick interface layers, the ZnO component exhibits a wider range of absorption onsets, due to a wider range of doping levels, which then overlap to broaden the high energy absorption onset. The broadening of the interband transitions due to a shorter excited state lifetime of electrons in the Ag component is also possible, but this cannot explain the apparent energy shifts that also occur for this high energy band in Fig. 5.20.
Figure 5.20 shows a shift in the 2.9 eV plasmon band to lower energy with increasing interface thickness, an effect suggested by Fig. 5.16 and interpreted in terms of an increase in Ag volume fraction in the interface layer as it increases in thickness. This effect can be understood through a substitution of the Drude expression into the Maxwell-Garnett effective medium theory yielding an equation for the resonance energy given by Eq. (5.3). Finally, with increasing Ag/ZnO interface thickness, there is a clear trend toward increasing $\varepsilon_1$ at low energies associated with the Drude component in Fig. 5.20 and the ultimate development of a low energy band from this component as indicated in $\varepsilon_2$. This suggests that the plasmon band is developing a broader distribution of modes associated with both microscopic roughness (modes at higher energies) and macroscopic roughness (modes at lower energies). In this range, the Maxwell-Garnett theory may also fail due to the large volume fraction of metal. Interactions between resonating protrusions may also exert a dominant influence. When macroscopic roughness is present, it appears that the Drude free electron component no longer contributes significantly to the interface dielectric function, as indicated by the result for the ECD back-reflector.
Figure 5-20: Real and imaginary parts of the best fit dielectric functions for the Ag/ZnO interface layer are shown for two samples prepared at University of Toledo using two initial Ag surface with different microscopic roughness layer thicknesses. Also shown are corresponding results for a Ag/ZnO back-reflector prepared at Energy Conversion Devices, Inc. in such a way as to yield macroscopic roughness (or texture) at the interface.
5.5 Reflectance Study of Ag/ZnO Back-Reflector

The dielectric functions deduced by RTSE reveal coupling of the electromagnetic wave to plasmons localized within Ag protrusions of the interface layer between the Ag and ZnO. Considering the operation of the Ag/ZnO structure as a back-reflector, it is important to understand how the plasmonic effect is manifested in the normal incidence reflectance spectra. As a result, ex situ normal incidence reflectance measurements have been performed on the Ag/ZnO structures. The first goal is to evaluate the optical models developed by RTSE. It is important to note that the observed reflectance spectra cannot be modeled successfully without including an interface layer of approximately the same thickness as that deduced by RTSE. Thickness differences between the best fits to the RTSE data and to the reflectance spectra may result because the probe beam may be reflected from different spots on the sample, and laboratory-prepared samples exhibit thickness non-uniformity over the surface area. The normal incidence experimental reflectance spectra for three samples with different values of the Ag/ZnO interface layer thickness are shown in Fig. 5.21.
Figure 5-21: Normal incidence specular reflectance spectra are shown for three Ag/ZnO structures with different interface layer thicknesses. The sample with the highest reflectance at low energies (DS013) exhibits the lowest Ag/ZnO interface roughness thickness of 78 Å with a ZnO thickness of 1500 Å; the sample with the intermediate reflectance at low energies (DS028) exhibits a 233 Å thick Ag/ZnO interface roughness layer and a 1250 Å thick ZnO bulk layer. The sample with the lowest reflectance was prepared at Energy Conversion Devices, Inc. (ECD) using a starting textured Ag surface yielding a 250 Å Ag/ZnO interface layer. The thickness of the ZnO bulk layer for the ECD sample is ~ 3200 Å.

The normal incidence specular reflectance data for the laboratory-prepared samples have been modeled using the dielectric functions as obtained from the analysis of RTSE data for the Ag bulk layer of the specific sample under study and for the ZnO bulk layer of the single reference sample, both fabricated on c-Si substrates. The dielectric function of the Ag/ZnO interface obtained for the specific sample was also used.
in this analysis. The reflectance data for the industry-prepared sample have been modeled using the dielectric functions of individual Ag and ZnO reference materials prepared in the laboratory at University of Toledo. The dielectric function of the Ag/ZnO interface was also used, as obtained by ex situ SE for the specific ECD sample.

Both data and simulations are plotted in Fig. 5.22 including the measured reflectance for ZnO prepared on Ag with $d_s = 28$ Å and with Ag/ZnO $d_i = 78$ Å (open circles). In fact, the measured reflectance is reasonably consistent with an optical model (dotted line) that includes the same 78 Å interface layer as deduced in the RTSE analysis. Figure 5.22 (a) reveals a strong minimum in the measured and simulated reflectance, which corresponds to an expected maximum in the absorbance at the plasmon resonance energy of 2.6 eV. In contrast, the simulation without the interface layer predicts a very high reflectance with no absorbance feature. In addition, the absorbance appears to be enhanced by interference within the ZnO layer with a fringe minimum at a photon energy matching the plasmon resonance, leading to an interesting effect of interference-enhanced excitation of confined interface plasmons.

From Fig. 5.22 (a), one can conclude that resonant enhancement of losses due to the Ag/ZnO interface layer of this sample occurs for photon energies within a 0.6 eV wide band centered at 2.6 eV. The strong minimum in Fig. 5.22 (a) at 2.6 eV occurs when an interference minimum in R overlaps the plasmon energy, which leads to a strong coupling of the energy from the optical field into the plasmon modes. In spite of this effect, occurring in the visible region of the spectrum for this sample, no significant losses are observed in the near-infrared below ~ 1.7 eV. Thus, the interference enhanced plasmon absorption is of marginal importance as a loss mechanism in a solar cell that
uses this particular back-reflector structure (i.e., for the observed $d_i$ range and associated dielectric function).

Figure 5.22 (b) shows reflectance simulations assuming a thicker ZnO layer ($d_b = 3000 \, \text{Å}$), demonstrating that the dominant losses in the spectral range of interest for solar cell back-reflectors (1.2 to 1.8 eV) are independent of $d_i$ for this relatively thin, smooth Ag/ZnO interface. In this situation, the existing small losses in the 1.2 to 1.8 eV range must be due to intrinsic absorption in the Ag, again enhanced by interference [noting the minimum at 1.6 eV in Fig. 5.22 (b)], since the losses do not depend on the interface thickness. Figure 5.22 (b) clearly shows the effect of interference enhanced plasmon excitation as the spectral region that is affected by the interface layer thickness ranges from 2.0 to 3.2 eV and is strongly modulated by an interference pattern generated by multiple reflections within the 3000 Å thick ZnO layer. The strongest reduction in reflectance relative to the $d_i = 0 \, \text{Å}$ spectrum occurs for the interference minima closest to the center of the plasmon band at 2.6 eV.
Figure 5-22: (a) Spectroscopic reflectance data (points) and simulations (lines) are shown for Ag/ZnO structures with a ZnO thickness of $d_b = 1500 \text{ Å}$ and Ag/ZnO interface layer thicknesses of $d_i = 0 \text{ Å}$ (solid line) and $d_i = 78 \text{ Å}$ (broken line). (b) Reflectance simulations are presented with $d_b = 3000 \text{ Å}$ and different $d_i$ values from 0 Å (solid line) to 100 Å (broken line), whereby the interface $\varepsilon$ is determined from the data for the sample with initial Ag $d_s = 28 \text{ Å}$ and Ag/ZnO interface $d_i = 78 \text{ Å}$.

A different interface type, resulting from a thicker initial Ag surface roughness layer, and thus a thicker Ag/ZnO interface layer, strongly affects the reflectance spectrum. In order to illustrate this effect, Fig. 5.23 (a) shows the measured reflectance
for ZnO prepared on Ag with $d_s = 105 \, \text{Å}$ (open circles) as well as the simulated reflectance assuming a specular structure with a $233 \, \text{Å}$ thick Ag/ZnO interface layer, which is the thickness deduced in the real time SE analysis (applying the interface layer dielectric function obtained in the same analysis). The large differences between the simulated and measured reflectance spectra in this situation may be attributed to the increased level of light scattering for the rougher initial Ag surface, as the macroscopic roughness regime is entered. Alternatively, due to the macroscopic roughness, light may be coupled into the film and excite propagating surface plasmons, an effect that is not included in the simulation and so may additionally account for the reflectance deficit. The difference between the simulated and measured reflectance spectra vanishes at 2.7 eV, which is near the center of the plasmon band. This is also an interesting effect, observed for this particular sample, and appears to suggest that light at the plasmon energy is not directly scattered nor does it excite propagating surface plasmons, but instead excites confined plasmons that can subsequently dissipate the energy or radiate it in the form of scattering. Such processes are shown in Figure 5.1, and further information can be deduced in the light scattering experiments described in Section 5.6.

Figure 5.23 (b) represents a series of simulations of different Ag/ZnO structures for which the ZnO bulk layer thickness is fixed at 3000 Å, whereas the interface layer thickness is varied within the range $0 \leq d_i \leq 300 \, \text{Å}$. With the dielectric function for this interface and a 3000 Å bulk ZnO layer, significant optical losses occur in the region of 1.2-1.8 eV due in part to absorption in the bulk Ag (since they are observed for $d_i = 0 \, \text{Å}$). More importantly, the reflectance losses increase steadily in this region with increasing interface layer thickness.
Interesting effects are observed in Fig 5.23 in comparison with the results in Fig.
5.22. First the reflectance in the simulations of Fig. 5.23 (a) decreases with decreasing
photon energy below 2 eV, an effect that is not observed the simulations in Fig. 5.22 (a).
This difference must be due to the greater dissipation associated with the bulk dielectric
function of the Ag layer having thicker surface roughness. For the simulation with 3000
Å thick ZnO, the dissipation in the bulk layer is enhanced by interference, which leads to
a minimum in the reflectance at 1.6 eV for the simulation with d_i = 0 Å. This minimum
is further enhanced upon incorporation of the interface layer which leads to additional
dissipation at the interference minimum.
Figure 5-23: (a) Reflectance spectra (points) and simulations (lines) are shown for Ag/ZnO structures with a ZnO thickness of $d_b = 1250$ Å and Ag/ZnO interface layer thicknesses of $d_i = 0$ Å (solid line) and $d_i = 233$ Å (broken line). (b) Reflectance simulations are presented with $d_b = 3000$ Å and different $d_i$ values from 0 Å (solid line) to 300 Å (broken line). The interface $\varepsilon$ is determined from the RTSE data collected on the Ag/ZnO structure with $d_s = 105$ Å for the starting Ag surface and $d_i = 233$ Å for the Ag/ZnO interface thickness.
The effect of macroscopic Ag surface roughness, i.e., roughness with an in-plane scale on the order of the wavelength of light, is also clearly observed in a normal incidence reflectance study. The reflectance of the ECD back-reflector at normal incidence has been compared with two laboratory-prepared back-reflector samples in Fig. 5.21. In this figure a decreased reflectance with an interference pattern due to the thicker ZnO layer is observed for the textured ECD back-reflector. In Fig. 5.24, the experimental normal incidence reflectance is compared with the simulated reflectance so that the scattering due to surface roughness can be quantified. In contrast to the result for the structure with the \( d_i = 233 \ \text{Å} \) thick Ag/ZnO interface layer in Fig. 5.23, the reflectance deficit minima in Fig. 5.24 are not aligned with the plasmon resonances. The difference may result from the fact that the sample with macroscopic roughness may exhibit greater direct scattering as well as enhanced excitation of propagating surface plasmons. Compared to the smoother structures, the simulated reflectance deduced from the model established by ex-situ SE shows considerable losses due to absorption even in the low energy range. These losses can be ascribed to the absorption feature shown in the dielectric function of Fig. 5.19, compounded by interference.
Figure 5-24: (Top) measured normal incidence reflectance spectra (points) and simulated reflectance spectra (lines) are shown for the ECD back-reflector with a Ag/ZnO interface thickness of 250 Å. (Bottom) The deficit between the predicted reflectance from an ex situ SE analysis and the experimental reflectance for the ECD back-reflector is also shown. The reflectance deficit can be attributed to effects that are not included in the modeling of the structure via the Fresnel equations for transmission and reflection from specular interfaces. These effects include direct scattering and coupling to propagating surface plasmons via macroscopic roughness.
5.6 Scattering Study of Ag/ZnO Back-Reflectors

5.6.1 Scattering Study of Ag/ZnO Back-Reflectors: Introduction

Returning to the specular reflectance results for the Ag/ZnO back-reflector of Fig. 5.22, the apparent absorbance associated with the excitation of confined plasmons, observed in both experimental and simulated spectra, is very strong ~0.75; however, this absorbance does not necessarily lead to dissipative losses. Some fraction of the energy absorbed by the plasmons in fact may be re-radiated, whereas the remainder may be dissipated to heat. To evaluate this energy partitioning, one must also measure scattering, as will be described in this section. Detailed scattering studies for the various Ag/ZnO back reflectors as well as Al/ZnO back-reflectors can be found in the dissertation of Dahal (Dahal, 2013) and in collaborative publications (Dahal et al., 2008 and Dahal et al., 2009). Here the first sample to be discussed is DS013, a sample that has been investigated extensively throughout this dissertation research. Then, a comparison of scattering, absorbance, and re-radiation for this sample will be made to those of samples having much smoother and rougher surfaces. Sample DS013 exhibited a starting Ag surface roughness of 28 Å and over-deposition of ZnO led to a ZnO/Ag interface thickness of 78 Å.
Figure 5-25: Schematics of the instrumentation used for the specular reflectance measurement (top) and the diffuse reflectance or scattering measurement (bottom) are shown. This instrumentation is used to quantify the optical properties of Ag/ZnO back-reflectors (Dahal, 2013).

5.6.2 Scattering Study of Ag/ZnO Back-Reflectors: Instrumentation

The schematic diagrams in Fig. 5.25 depict the apparatus used for measuring the normal incidence specular reflectance and the diffuse reflectance or scattering. The spectrophotometer used here was manufactured by Shimadzu and provides spectral range from 1.4 to 4.25 eV. The reference used for the specular reflectance was a single crystal
silicon wafer, whereas that used for the scattering measurement was a substrate coated with BaSO$_4$ powder. Since diffuse reflectance or scattering does not obey the Fresnel Laws of reflection and refraction for planar interfaces, scattered light can appear in any direction on the ambient side of the Ag/ZnO structure, and to quantify scattering, the light must be collected using an integrating sphere. An integrating sphere is a hollow cavity whose interior is coated with BaSO$_4$ or Teflon for highly diffuse reflectivity so that the surface luminance is isotropic. For the scattering apparatus, since the incident light impinges on the sample perpendicularly, the specularly reflected light returns through the same entrance hole and only the scattered light is collected.

5.6.3 Results and Discussion

Scattering Study of Ag/ZnO Back-Reflector with $d_i = 78 \, \text{Å}$

Next, the possible origins of light scattering in terms of re-radiation by plasmons will be assessed. Toward this goal, spectra in the reflectance deficit $\Delta R = R_c - R_e$ and calculated absorbance $A_c$ have been correlated with spectra in the scattered irradiance $S$ for Ag/ZnO structures having interface layers with a wide range of thickness from smooth to textured. The reflectance deficit here is defined by the difference between the reflectance spectrum at normal incidence $R_c$ calculated by the RTSE-deduced model and that measured experimentally $R_e$. Because the transmittance is zero, the calculated normal incidence absorbance is given simply by $A_c = 1 - R_c$, where $R_c$ is the calculated normal incidence reflectance. The correlations with scattering are challenging since the calculated reflectance and absorbance are indirectly determined quantities based on analysis of RTSE data collected at the end of the deposition, and furthermore the measured reflectance $R_e$ is difficult to obtain with high accuracy.
Fig. 5.26 shows a comparison of measured scattering integrated over all ambient-
side solid angles with the calculated reflectance deficit and absorbance for the back-
reflector with initial Ag surface roughness of \( d_s = 28 \text{ Å} \) and final Ag/ZnO interface
thickness of \( d_i = 78 \text{ Å} \). In these studies, several key observations can be made and are
discussed below by considering the behavior at different wavelengths.

(a) \textit{Interband Photon Energy Region}

Considering the data at high energies > 3 \text{ eV} first, single-reflection direct
scattering by macroscopic roughness on the same scale as the wavelength is likely to be
the greatest here due to the short wavelength. The scattering \( S \) is relatively small,
however, and decreasing for photon energies decreasing from 4.2 to 3.3 \text{ eV} (\( S \sim 0.03 \rightarrow
0.015 \)). A small step increase to \( S = 0.05 \) occurs below the band gap of the ZnO at 3.3 \text{ eV},
suggesting that single-reflection direct scattering is greater for the Ag/ZnO interface than
for the ZnO/ambient interface. Due to the absorption by the overlying ZnO layer, it can
be concluded that propagating plasmons cannot be excited at energies > 3.3 \text{ eV}. Even for
thin ZnO, in which case light may reach the Ag/ZnO interface, any plasmon excitation
would be suppressed by the presence of Ag and ZnO interband excitations of the same
energy; in fact, \( \varepsilon_2 \) is significantly greater than zero for both interface components above 4
\text{ eV}. These observations are consistent with the small reflectance deficit \( \Delta R \) which reflects
the processes of direct scattering (which occurs only weakly for this sample) and
coupling to propagating surface plasmons (which does not occur for photon energies >
3.3 \text{ eV}, above the ZnO interband onset energy).
(b) *Plasmon Band Absorbance Maximum*

At the strong confined plasmon absorbance maximum of $A_c \sim 0.75$ near 2.6 eV, the reflectance deficit $\Delta R$ vanishes, meaning that the predicted and measured reflectances are in agreement, suggesting that all light that is not reflected is absorbed and excites confined plasmons. The scattering, however, is not zero, but rather is near $S = 0.10$. This would imply that light absorbed into the confined plasmon band is re-radiated as scattered light. The re-radiation efficiency $\eta_r$ can be estimated as $\eta_r = (S - \Delta R)/A_c \sim 12\%$ at the absorbance maximum at 2.6 eV. The maximum in the scattering occurs near 2.35 eV (vertical line in Fig. 5.26) and derives primarily from the increase in reflectance deficit which indicates either direct scattering or propagating plasmon excitation. Due to this rapid increase in reflectance deficit, mitigated by the decrease in absorbance due to the plasmon band, the re-radiation efficiency $\eta_r$ decreases to $\eta_r = (S - \Delta R)/A_c \sim 5\%$ at the scattering maximum at 2.35 eV. This factor of two reduction in efficiency parallels the reduction in plasmon absorbance.

(c) *Reflectance Deficit Maximum*

At the reflectance deficit maximum of $\Delta R = 0.13$ at 2.25 eV, the loss in reflectance via direct single-reflection scattering appears to be unlikely based on the discussions of (a). At this maximum, however, the absorbance is significantly reduced implying that the light can undergo multiple passes within the ZnO film. This can enhance direct scattering and contribute to the scattering maximum, even though the single-reflection scattering is $< 0.05$. Thus, as the plasmon absorbance drops, the possibility of multiple passes increases and direct scattering contributes most to the observed scattering maximum. Another possible contribution to the reflectance loss is by
propagating surface plasmons generated through weak surface corrugations, since the absorbances in this range for both components of the interface are very weak (with $\varepsilon_2 \sim 0$) and propagating plasmons may be sustainable. Thus, the scattering level of 0.08 may arise from three sources, direct scattering, re-radiation by confined plasmons at low efficiency (< 5%), and re-radiation by propagating plasmons. The fact that significant plasmonic emission activity is occurring in the range of 2.2 – 2.5 eV is likely to be due to the lowest value of $\varepsilon_2$ for both bulk ZnO and Ag in this range, meaning that the dissipation rate of energy carried by plasmons is lowest.

(d) *Below the Plasmon Band*

Finally the situation at 1.6 eV is considered. In this case, the reflectance deficit is small implying that wavelengths are sufficiently long such that direct scattering is suppressed. The weak scattering collected in this case $S \sim 0.03$ may continue to arise from the multiple sources as described in (c), keeping in mind the uncertainties associated with the reflectance deficit.

**Scattering Study of Ag/ZnO Back-Reflectors with $d_i = 18$ Å and 250 Å**

The above discussion focuses on normal incidence reflectance, absorbance, and scattering processes at different photon energies for the Ag/ZnO sample with the 78 Å thick Ag/ZnO interface layer as shown in Fig. 5.26. Next, insights will be presented and discussed through a comparison of the sample of Fig. 5.26 with samples starting from much thinner (Figure 5.27) and thicker (Figure 5.28) Ag/ZnO interface layers. In fact, similar observations result by considering the much smoother sample and the textured interface sample as shown in Figures 5.27 and 5.28, respectively. These observations can be described in a parallel format as follows.
(a) **Interband Photon Energy Region**

Considering the results at high photon energies, as the Ag/ZnO interface becomes thinner relative to the sample with $d_i = 78$ Å, the reflectance remains similarly small and the scattering decreases as well -- by a factor of two from $S \sim 0.015$ to $\sim 0.0075$ at 4 eV. For the ECD back-reflector with $d_i = 250$ Å, the scattering and reflectance deficit are both higher and overlap at 0.09 at 4 eV. In this region, plasmonic excitation is negligible due to the large value of $\varepsilon_2$; thus, direct scattering dominates. For the two samples with the thinner interface layers, the light not absorbed is predominantly specularly reflected, considering the interband photon energy range. For the sample with the thick interface layer, the specular reflectance is negligible and the light that is not absorbed is scattered.

(b) Considering the sample with $d_i = 18$ Å, the mid-range absorbance shows a weak onset near 2.2 eV, reaching a plateau at 2.6 eV and merging with the ZnO interband absorption onset at higher energies. The weak onset near 2.2 eV is attributed to plasmonic absorption. Similar to the behavior for the sample with $d_i = 78$ Å, the reflectance deficit vanishes near the center of the absorbance plateau, once again suggesting that all light not reflected is absorbed through plasmon excitation. The scattering is not zero; however, but is $S = 0.01$ with a maximum centered on the absorption plateau. This suggests that re-radiation occurs with an efficiency of $\eta_r = 7\%$ at the center of the plasmon resonance and the efficiency decreases away from this energy. For the back-reflector with $d_i = 250$ Å, the re-radiation effects are more pronounced in the visible range, occurring where plasmon absorbances are at their maxima and the reflectance deficits are relatively low $< 0.1$. Estimated efficiencies of re-radiation increase weakly over the range $\sim 38$-42\% for energies decreasing from 3 eV to
2.3 eV. Because of the near constant re-radiation efficiency, the variation in scattering reflects variations in absorption into the plasmon band.

(c) For the sample with the thinnest interface layer, the reflectance deficit maximum at 2.25 eV is much lower, near 0.03. This is near the accuracy of the experimental reflectance measurement and so does not warrant further discussion beyond that of the previous sub-section. For the back-reflector with $d_i = 250 \, \text{Å}$, however, the maxima in the reflectance deficit are relatively large and tend to occur at the minima in the absorbance, throughout the photon energy range from 1.7 to 3.2 eV. In this case, direct scattering is likely to occur; in fact, the reflectance deficit peak near 2 eV of $\Delta R \sim 0.26$ is only slightly lower in amplitude than the scattering at this energy $S \sim 0.3$. This behavior does not rule out possible coupling to propagating surface plasmons; however, it is likely that confined plasmons in the thick layer of surface protrusions dominate.

(d) The behavior near 1.6 eV for the sample with $d_i = 18 \, \text{Å}$ is similar to that for the sample with $d_i = 78 \, \text{Å}$. The reflectance deficit vanishes within experimental error, and the absorbance is very weak and can be attributed to the Drude free electrons. The very weak scattering is within the uncertainty of the reflectance deficit and so no definitive conclusions can be made about its origin. For the sample with $d_i = 250 \, \text{Å}$, the absorbance reaches a maximum at low energies where the reflectance deficit is low and the absorbance is strong. This suggests continued high efficiency ($\eta_r \sim 65\%$) re-radiation by confined plasmons contribute to the performance of the back-reflectors in solar cells.

Through these variations, it can be concluded that as the interface thickness increases the direct scattering and re-radiation of energy absorbed by confined plasmons increases. Thus, the mechanism for optimization of back-reflectors used by industry
appears to be interference-enhanced localized plasmon excitation in protrusions, which can lead to efficient re-radiation observed to be as high as 65% for properly designed microstructures.
Figure 5-26: (Top) A comparison of the normal incidence reflectance deficit with the measured scattering is shown for a Ag/ZnO back-reflector with a starting Ag roughness layer thickness of $d_s = 28$ Å and a final Ag/ZnO interface layer thickness of $d_i = 78$ Å. (Bottom) A comparison of predicted absorbance with measured scattering is also presented (Dahal et al., 2008).
Figure 5-27: (Top) A comparison of the normal incidence reflectance deficit with the measured scattering is shown for a Ag/ZnO back-reflector with a starting Ag roughness layer thickness of $d_s = 4$ Å and a final Ag/ZnO interface layer thickness of $d_i = 18$ Å. (Bottom) A comparison of predicted absorbance with measured scattering is also presented (Dahal et al., 2008).
Figure 5-28: (Top) A comparison of the normal incidence reflectance deficit with the measured scattering is shown for a Ag/ZnO back-reflector fabricated by industry with a final Ag/ZnO interface layer thickness of $d_i = 250 \, \text{Å}$. (Bottom) A comparison of predicted absorbance with measured scattering is also presented (Dahal et al., 2008).
5.7 Solar Cell Optical Performance Simulations

Polarization analysis of specular and textured thin film amorphous silicon (a-Si:H) based solar cell structures, applying spectroscopic ellipsometry (SE) measurements, demonstrates that microscopic surface and interface roughness is ubiquitous and exerts considerable influence on the specular reflectance and hence the quantum efficiency of the solar cells [Collins et al., 2000; Drevillon, 1993]. In addition to microscopic surface and interface roughness, chemically and optically modified interface regions can occur in the solar cell structures, and these can have a significant influence on the reflectance, absorbance, and quantum efficiency, as well.

Very little research has been performed to assess the nature of such layers and their impact on solar cell performance. In this section, simulations of the optical quantum efficiency (QE) of a-Si:H based solar cells in the substrate/BR/n-i-p configuration have explored the effects of a modified Ag/ZnO interface layer in the Ag/ZnO back reflector (Parikh et al., 2007). This interface layer is significant because of the absorption losses that it generates upon reflection of near-infrared wavelengths back into the cell. Although introducing macroscopic roughness in addition to the microscopic roughness at the Ag/ZnO interface leads to scattering of the near-infrared light upon back-reflection, thereby increasing the optical path length and hence the QE, this roughness also can have an offsetting detrimental effect in that it enhances absorption losses at the Ag/ZnO interface. It should be kept in mind, however, that processes described by the Fresnel equations as absorption and dissipation through confined plasmons may provide a subsequent pathway for energy return to the thin film structure through re-radiation that
is not included in the simulations. Such re-radiation has been evaluated in the previous section where evidence for efficiencies as high as ~65% have been presented.

Figure 5.29 summarizes the basic optical model used for computing the characteristics of the a-Si:H triple junction solar cell. The thicknesses of the i-layers in Figure 5.29 are chosen for current matching in the triple junction device with a current density of 7.3 mA/cm² under a global air mass 1.5 solar spectrum. The model used here is based on normal-incidence specular reflection and transmission at interfaces using standard Fresnel coefficients, and the multiply-reflected beams within all solar cell layers are assumed to add coherently. It should be noted that non-specular scattering -- which is an important aspect of light trapping -- has yet to be incorporated into the modeling procedure due to the general lack of experimentally-verifiable inputs.

Three different Ag/ZnO back-reflector structures were modeled, including (i) the structure with an initial Ag surface roughness layer thickness of $d_s = 28 \text{ Å}$ yielding $d_i = 78 \text{ Å}$ (DS013), (ii) the structure with $d_s = 105 \text{ Å}$ yielding $d_i = 233 \text{ Å}$ (DS028), and (iii) a structure prepared at Energy Conversion Devices (ECD) used as a standard. Although the initial Ag surface roughness layer thickness for the ECD back-reflector is unknown, the Ag/ZnO interface thickness is $d_i = 250 \text{ Å}$, thicker than that of sample DS028. The back-reflector structures with greater initial Ag surface roughness and thus a thicker Ag/ZnO interface layer (including the sample with $d_s = 105 \text{ Å}$, and the ECD back-reflector, as well) have revealed significantly different interface layer dielectric functions compared to the sample with lower initial roughness ($d_s = 28 \text{ Å}$), as shown in Figures 5.14 and 5.20. The interface layer dielectric functions for all three structures were
obtained using oscillator models deduced in analyses of RTSE or ex situ SE data as described in Sections 5.2 and 5.3.

Figure 5-29: Schematic multilayer optical structure of a triple-junction a-Si:H based solar cell is shown in the substrate/BR/n-i-p configuration, where BR indicates the back-reflector. The intent of such modeling is to assess the role of the interface layer between the Ag and ZnO of the back-reflector. Other non-idealities throughout the structure, including microscopic surface and interface roughness layers, are neglected since the goal of the study is to isolate the role of the Ag/ZnO interface layer in the solar cell.

The upper panel of Fig. 5.30 shows the predicted optical absorbance within six different Ag/ZnO interface layers for the solar cell structure of Fig. 5.29. The plot compares two interface thicknesses of 100 Å and 400 Å for each one of the three
interface dielectric functions deduced from the three different structures described in the previous paragraph. The onset of absorption in all cases occurs at a wavelength of ~ 600 nm, showing that all incident irradiance below that wavelength is absorbed by the overlying structure. Enhanced absorbance with increasing wavelengths above 600 nm can be attributed to the fact that increased irradiance reaches the back-reflector interface. The model predicts significant absorption in the interface layer of the ECD and $d_s = 105$ Å back-reflectors in the spectral region of 700-1000 nm for both interface thicknesses. It should be emphasized that some fraction of this light is re-radiated by excited plasmons and contribute to scattering and useful collection, as is the goal of introducing the texturing, in fact. The model incorporating initial Ag surface roughness of $d_s = 28$ Å shows minor interface layer absorption losses and thus stronger reflected irradiance (lower panel of Fig. 5.30) that potentially could be collected for wavelengths below the band gap of the bottom cell with proper multilayer design incorporating light trapping without scattering.

The key point of the results of Fig. 5.30 is that the Ag/ZnO interface layers generated when the initial surface roughness layer on the Ag is relatively thick absorb more strongly even for a given thickness of the interface layer. Without a detailed experimental study of integrated scattering from the structure such as that of Sec. 5.6 for the Ag/ZnO structure, however, it is unclear how much of this absorption represents a dissipative loss for the solar cell. For the absorption that leads to true dissipation, there is less reflected irradiance available for capture in a second pass (or more) through the cell. In particular, the ECD back-reflector which incorporates macroscopic roughness as well as microscopic roughness leads to the largest absorbance, presumably due to the largest
initial roughness on the Ag. The similarity of the results for the \(d_s=105 \text{ Å}\) and the ECD back-reflector structures suggests that the former structure also incorporates macroscopic roughness. This can be assessed by directly measuring the scattering as well as by comparing the reflectance deficit, i.e., the difference between the reflectance predicted from complete polarization analysis of the multilayer structure (which is not influenced by scattering losses from the specular beam) and the measured reflectance as was done in Sec. 5.6.

![Figure 5-30: Predicted spectra are plotted for the absorbance (upper panel) within the Ag/ZnO interface layer of a triple-junction a-Si:H based solar cell (Fig. 5.29), using three different dielectric functions obtained from analyses of the interface structures with \(d_s(\text{Ag}) = 28 \text{ Å}, 105 \text{ Å}\), and a textured back reflector supplied by ECD. Also shown are the corresponding predicted reflectance spectra (lower panel) for the entire solar cell multilayer structure. The three different interface layers, characterized by their dielectric functions, were each modeled assuming two different interface layer thicknesses, \(d_i = 100\) and 400 Å.](image)
Figure 5.31 (a) shows the potential gain in $J_{sc}$ that could be achieved if all absorbance losses in the Ag/ZnO interface could be eliminated and converted to useful current through absorption in the i-layers in one or more passes through the solar cell. This current gain is obtained by integrating the product of the optical absorbance in the interface layer and the AM 1.5 spectral photon flux over the spectral range from 305 to 1033 nm. The interface absorbance is predicted to strongly affect the performance of the solar cell when a model is assumed having an interface dielectric function based on analysis of the ECD sample. The absorbance does not significantly impact cell performance when the model uses the dielectric function deduced from the sample with initial Ag surface roughness of $d_s = 28$ Å. In particular, it can be seen that for low initial Ag surface roughness, the cell performance is predicted to only weakly depend on the interface thickness. Again, it must be emphasized that plasmon absorbance does not necessarily represent a loss, and as the interface structures increase in size, their radiative efficiency increases.

The potential gain simulations in Figure 5.31(a) are unrealistic since not all the light recovered by eliminating absorption in the interface can be collected in the active layers of the solar cell, which are the three i-layers. In particular, for light in the range of 890-1033 nm, below the band gap of the bottom cell, it is impossible to recover light that would otherwise be absorbed by the interface. A better estimate of the recoverable current is given in Figure 5.31(c), which shows the summed integrated current from all three active layers over the same spectral range, from 305 to 1033 nm, as a function of the interface layer thickness. For perfect current matching, the triple junction solar cell
current would be one third of this total current, or ~ 7.65 mA/cm² without an interface layer.

In general, this summed current is predicted to decrease with increasing interface thickness. The change in this current is attributed to the change in quantum efficiency of the bottom cell i-layer with the lowest band gap of $E_g = 1.4$ eV. This means that infrared photons absorbed in interface layer and thus not reflected back from the Ag otherwise could have been absorbed in the lowest band gap active layer. The current through the highest bandgap active layer, $E_g = 1.8$ eV, remains nearly unchanged with interface layer thickness, whereas the middle band gap active layer, $E_g = 1.6$ eV, exhibits a relatively small variation. Such behavior is to be expected since the role of the back-reflector is to enhance absorbance in the bottom cell. Thus, any loss by absorption in the interface layer leads to a loss in potential current generated by the bottom i-layer. It can also be seen that if interface absorption losses could be eliminated, a gain of a maximum of ~ 0.9 mA/cm² of total current would be possible for an interface layer thickness of 250 Å based on this more realistic calculation. Thus, the current through the triple junction solar cell under perfect current-matched conditions could be increased by ~ 0.3 mA/cm².
Figure 5-31: Included in this figure are panels depicting (a) loss which occurs by absorption in the Ag/ZnO interface layer, (b) reflectance which is available for collection in improved back-reflector designs, and (c) current which is generated by absorption in the three i-layers, assuming that all electron-hole pairs generated by absorption in the i-layers are separated and contribute to the current. These results are plotted as functions of interface layer thickness for each type of interface layer dielectric function extracted from the real time and ex situ spectroscopic ellipsometry studies of this chapter.
Chapter 6

Etching Studies of Ag/ZnO Structures

6.1 Introduction

As presented in Chapter 5, we have observed that the resonance energy of the plasmon band at the interface in the Ag/ZnO back-reflector structure appears to red-shift as the surface roughness thickness on the initial Ag film increases. One of the methods for mitigating plasmon absorption and dissipation in such structures is to blue-shift the dominant plasmon mode. In order to blue-shift the plasmon energies, the screening effect of ZnO can be reduced through a reduction in $\varepsilon_a$ in the expression for the plasmon band energy presented in Chapter 5. This expression is reproduced here:

$$E_0 \sim E_p \left\{ \varepsilon_{1o} + \left[ \frac{2 + Q_m}{1 - Q_m} \right] \varepsilon_a \right\}^{-1/2}, \quad (6.1)$$

where $E_p$ is the bulk plasmon energy of Ag, and $\varepsilon_{1o}$ is the photon energy independent offset added to the real part of the Drude component of the dielectric function of Ag. The parameters $E_p$ and $\varepsilon_{1o}$ are fixed characteristics of the bulk Ag that cannot be readily controlled. Table 6.1 summarizes the values of $\varepsilon_{1o}$ offset and other Drude parameters derived from SE analysis below 3.5 eV for the Ag thin films of this study. This analysis employs an analytical form for the dielectric function that includes only $\varepsilon_{1o}$ and the
Drude term. The resulting average offset and the plasma energy from Table 6.1 are given by $\varepsilon_{1o} = 4.01$ and $E_p = 9.44$ eV, respectively, values that will be used for the three samples investigated in this chapter.

The parameters that can be more readily controlled to blue-shift the plasmon energies based on Eq. (6.1) include the metal volume fraction $Q_m$ within which the plasmon oscillations occur and the dielectric function of the ambient medium, which is $\varepsilon_a \sim 4$ for bulk density ZnO associated with the plasmon band identified in Chapter 5. In this expression, if random macroscopic roughness with $Q_m \sim 0.5$ is assumed in a layer sufficiently thick to scatter light for optical trapping, there is limited adjustability in the volume fraction parameter. If one assumes that the adjustability exists to decrease $Q_m$ from 0.6 to 0.4, then the peak plasmon energy can be shifted from 1.72 eV to 2.11 eV. The real part of the dielectric function of the ZnO at the plasmon band energy $\varepsilon_a$ can also be tuned to a greater extent by using the methods described in the next paragraph. When the index of refraction of the ZnO is reduced from $n = 2$ to $n = 1.5$, which is reasonably well attainable using the methods to be described, with $Q_m = 0.4$, then the plasmon band can be shifted by $\sim 0.5$ eV from 2.11 eV to 2.62 eV. It should be noted that a Ag surface with $Q_m = 0.4$ in an ambient medium of laboratory air gives a plasmon band of energy 3.34 eV, which is well outside the operational range of the back-reflector and even approaches the low energy tail in $\varepsilon_2$ associated with the interband absorption onset. As this occurs, the plasmons are not sustainable due to dissipation in the Ag via interband excitations.
Table 6.1: The best fit energy independent contribution to the real part of the dielectric function $\varepsilon_{1o}$ and the Drude parameters of plasma energy $E_p$, resistivity $\rho_o$, and scattering time $\tau$ are shown for various Ag thin film samples. For the industry sample provided by ECD, an uncoated Ag thin film was not available. As a result, the parameters were obtained from the etched back-reflector sample after the ZnO was removed. Thus, the data for the ECD sample were obtained with the sample immersed in a water ambient. For the DS-designated samples, the measurement was performed under vacuum. For all Ag samples, the resulting dielectric functions were fitted below 3.5 eV using only $\varepsilon_{1o}$ and the Drude term.

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<th>Samples</th>
<th>MSE</th>
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<th>Plasma energy $E_p$ (eV)</th>
<th>Resistivity $\rho_o$ (Ω-cm)</th>
<th>Scattering Time $\tau$ (fs)</th>
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<td>Ag DS005</td>
<td>0.599</td>
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<td>9.31 ± 0.26</td>
<td>(6.15±0.17) x $10^{-6}$</td>
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</tr>
<tr>
<td>Ag Etched ECD</td>
<td>1.518</td>
<td>3.44±0.01</td>
<td>10.42 ± 0.09</td>
<td>(4.89±0.04) x $10^{-6}$</td>
<td>9.21±0.08</td>
</tr>
<tr>
<td>(1.4-3.5 eV)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

There are two methods for reducing the real part of the dielectric function for ZnO below its bandgap. First the $\varepsilon_{1o}$ component (material density) can be reduced, and second the Drude component (carrier concentration) can be increased. The first method relies on the inverse relationship between the void volume fraction and index of refraction below the bandgap of a material. Thus, ZnO films with low $\varepsilon_a$ can be prepared by introducing voids during the deposition. In applying the second method, the...
relaxation time of the free carriers in the ZnO must be sufficiently long that the increase in the Drude component does not lead to significant free carrier absorption in the ZnO.

One possible approach for making a porous ZnO film is to sputter deposit the film at a high Ar pressure in the chamber. The high pressure leads to thermalization of the incident film precursors before they reach the substrate, which in turn suppresses bombardment-induced compaction of the film structure during the deposition process. A second way of depositing a porous ZnO thin film is by grazing angle deposition using either evaporation or low pressure collimated sputtering processes (Podraza et al., 2005). Thin film deposition processes are initiated through nucleation, and the nuclei subsequently coalesce to form the film. By depositing at grazing incidence, however, the peaks of the nuclei intercept incoming grazing flux whereas the valleys between nuclei are fully shadowed from the flux by neighboring nuclei. As a result, coalescence is hindered and as long as surface diffusion of precursors is limited, the film grows as vertical columns with intervening voids. One of the disadvantages of porous ZnO films in the back-reflector is their potential environmental instability due the adsorption of atmospheric species such as water vapor onto the internal surfaces of such films.

For previously deposited Ag/ZnO back-reflectors, we can explore the effect of the dielectric function of the ambient medium by etching away the ZnO in an aqueous medium and observing possible plasmon peak energy shifts. In this chapter, an etching study of three such back-reflector samples is discussed in detail. Two samples have been prepared at the University of Toledo, one deposited at room temperature with a starting Ag surface roughness layer thickness of $d_s = 12 \, \text{Å}$ and a Ag/ZnO interface layer of $d_i = 53 \, \text{Å}$ (sample DS020) and another deposited at $190^\circ\text{C}$ with $d_s = 105 \, \text{Å}$ and $d_i = 233 \, \text{Å}$.
A third sample was the industry standard back-reflector prepared at ECD with \( d_i = 250 \, \text{Å} \). Each Ag/ZnO back-reflector sample was immersed in 300 mL of deionized water at room temperature in a pyrex cell that provides optical access to the sample surface, and 0.2 mL of hydrochloric acid (HCl) was added to form an aqueous solution with a 1:1500 HCl:H\(_2\)O volume ratio. The entire etching process was monitored in real time using the same spectroscopic ellipsometer as that applied for monitoring the Ag/ZnO back-reflector depositions. Since the HCl:H\(_2\)O solution does not etch Ag, the etching process naturally terminates when the ZnO is removed and the uncoated Ag is in contact with the solution. This etching endpoint is early identified by real time spectroscopy ellipsometry.

6.2 Dielectric Functions Before and After Etching

The smoothest back reflector structure, sample DS020, exhibits a starting Ag surface roughness layer thickness of 12 Å, an average Ag/ZnO interface layer thickness of 53 Å, and a ZnO bulk layer thickness of 607 Å, as deduced from the RTSE analysis. The sample was etched for 120 minutes while being monitored in real time by spectroscopic ellipsometry. The measurements analyzed in this sub-section represent the etching endpoint after the ZnO was completely removed and were performed while the sample was immersed in the etching solution.

The resulting data were modeled as shown in Fig. 6.1. The dielectric function of the bulk Ag layer in this model was obtained by inversion from real time spectroscopic ellipsometry studies of the deposition process for the same sample (DS020). As described in Chapter 3, this deposition showed no evidence of plasmon behavior in the bulk layer dielectric function, suggesting that the 12 Å thick surface roughness layer was
adequately modeled by the EMA. Because the deposition was performed at room temperature, the Ag bulk layer dielectric function deduced in the real time analysis of the deposition process is also relevant for the measurements of the etched samples which were also performed at room temperature. Because of the thinness of the surface roughness layer for this sample, the analytical model for this layer used only the offset term $\varepsilon_{1o}$, a Drude term, and a Lorentz oscillator. The interband critical point oscillator was neglected as its parameters could not be determined for such a thin roughness layer. The fit to the $(\psi, \Delta)$ spectra applying this structural and optical model is shown in Fig. 6.2.

<table>
<thead>
<tr>
<th>Ambient: Deionized Water</th>
<th>22.8 ± 0.4 Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>General Oscillator Model (Drude and Lorentz)</td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>(semi-infinite)</td>
</tr>
</tbody>
</table>

Figure 6-1: A schematic model is shown for the etched sample DS020 having an initial Ag surface roughness layer 12 Å thick, as determined by real time spectroscopic ellipsometry measurements before fabrication of the ZnO layer. The model depicted here was used to determine the thickness and dielectric function of the surface layer on the Ag sample that remains after etching the ZnO away in a solution of 1:1500 HCl:H₂O. The data analyzed using this model were acquired with the sample immersed in the etching solution. The best fit Ag surface layer thickness is shown in the model, and the dielectric function of this layer was simulated using $\varepsilon_{1o}$, a Drude term, and a Lorentz oscillator. The surface layer dielectric function thus obtained is compared in Fig. 6.7 with the ZnO/Ag interface layer dielectric function obtained before etching.
Figure 6-2: Experimental ellipsometry parameters $\psi$ and $\Delta$ (points) are shown along with the best fit simulation (lines) based on the model of Fig 6.1 for the back-reflector sample DS020. The initial Ag surface roughness layer thickness for this sample was 12 Å, as determined by real time spectroscopic ellipsometry measurements before fabrication of the ZnO layer. The data depicted here were acquired from the Ag sample immersed in etching solution after complete removal of the ZnO in 120 minutes of etching.

For sample DS028 with a starting Ag surface roughness thickness of 105 Å measured before the deposition of ZnO, an average Ag/ZnO interface layer thickness of 233 Å and a bulk ZnO layer thickness of 1250 Å were deduced using RTSE. The sample was etched for 169 minutes and monitored in real time again by SE. The Ag sample structure remaining after completion of the etching process was modeled as shown in Fig.
6.3. In contrast to the modeling approach of Fig. 6.1, the bulk layer dielectric function of this sample (DS028) obtained before the deposition of ZnO could not be used in the model of Fig. 6.3 because a room temperature measurement is not available. In addition, because of the thick initial roughness layer on the Ag surface, the dielectric function of the surface layer was better modeled using an analytical function. This in turn generates challenges in extracting the true dielectric function of the bulk layer beneath the surface layer. As a result of these issues, the Ag bulk layer dielectric function for the room temperature deposition DS020 is used for this analysis. Using the model of Fig. 6.3, the resulting best fit simulation for the etched Ag sample immersed in the etching solution is shown in Fig. 6.4.

Figure 6-3: A schematic model is shown for the etched sample DS028 having an initial Ag surface roughness layer 105 Å thick, as determined by real time spectroscopic ellipsometry measurements before fabrication of the ZnO layer. The model depicted here was used to determine the thickness and dielectric function of the surface layer on the Ag sample that remains after etching the ZnO away in a solution of 1:1500 HCl:H₂O. The data analyzed using this model were acquired with the sample immersed in the etching solution. The best fit Ag surface layer thickness is shown, and the dielectric function of this layer was simulated using ε₁₀, a Drude term, and Lorentz and critical point (CP) oscillators. The Ag surface layer dielectric function thus obtained is compared in Fig. 6.7 with the Ag/ZnO interface layer dielectric function obtained before etching.
Figure 6-4: Experimental ellipsometry parameters $\psi$ and $\Delta$ (points) along with the best fit simulation (lines) based on the model shown in Fig 6.3 for the back-reflector sample with an initial Ag surface roughness layer thickness of 105 Å, as determined by real time spectroscopic ellipsometry measurements before fabrication of the ZnO layer. The data depicted here were acquired from the Ag sample immersed in etching solution after complete removal of the ZnO in 169 minutes of etching.

For the industry standard back-reflector sample fabricated by Energy Conversion Devices (ECD), the starting Ag surface roughness layer thickness is unknown; however, ex-situ spectroscopic ellipsometric analysis revealed that the sample exhibits a Ag/ZnO interface layer thickness of 250 Å and a ZnO bulk layer thickness of 3164 Å. In this case, the sample was etched for 269 minutes and during etching real time spectroscopic
ellipsometry was performed. The data obtained on the structure in the etching solution after completion of etching was modeled as shown in Fig. 6.5. Again, due to the lack of information on the Ag dielectric function before ZnO deposition, the Ag bulk layer dielectric function in the model of Fig. 6.5 was taken to be that of sample D020 as obtained by RTSE at room temperature before ZnO deposition. Thus, the analysis of all three samples of this subsection were performed consistently using the dielectric function of the bulk layer as that of sample D020. Using the model of Fig. 6.5, the resulting best fit simulation for the ECD back-reflector immersed in the etching solution after complete removal of ZnO is shown in Fig. 6.6.

### Ambient: Deionized Water

| General Oscillator Model (Drude, Lorentz, and CP) | 78.3 ± 0.9 Å |
| Ag (semi-infinite) | |

Figure 6-5: A schematic model is shown for the back-reflector sample fabricated at ECD after the etching experiment. The model depicted here was used to determine the thickness and dielectric function of the surface layer on the Ag sample that remains after etching the ZnO away in a solution of 1:1500 HCl:H₂O. The data analyzed using this model were acquired with the sample immersed in the etching solution. The best fit Ag surface layer thickness is shown, and the dielectric function of this layer was simulated using ε₁₀, a Drude term, and Lorentz and critical point (CP) oscillators. The Ag surface dielectric function thus obtained is compared in Fig. 6.7 with the Ag/ZnO interface layer dielectric function obtained before etching.
Figure 6-6: Experimental ellipsometry parameters $\psi$ and $\Delta$ (points) along with the best fit simulation (lines) based on the model shown in Fig 6.5 for the back-reflector sample fabricated at ECD and found to exhibit a 250 Å Ag/ZnO interface layer by ex situ spectroscopic ellipsometry. The data depicted here were acquired from the Ag sample immersed in etching solution after complete removal of the ZnO in 269 minutes of etching.

Summarized in Table 6.2 are the thicknesses of the surface layers on the three samples from Figures 6.1, 6.3, and 6.5, obtained after etching while the sample remains immersed in the etching solution. The thicknesses of the surface layers of the Ag samples with initial roughness values of 12 Å and 105 Å before ZnO deposition return to surface layer thicknesses that are 11-12 Å thicker upon removal of the ZnO. Thus, the surface
layer thickness after ZnO etching for samples DS020 and DS028, 23 Å and 117 Å, are much thinner than the Ag/ZnO interface layers determined before etching, 53 Å and 233 Å, respectively. The origin of the transition from the thick interface to the much thinner surface layer upon etching is unclear; however, these results also suggest that the reverse behavior occurs upon deposition of the ZnO. Thus, the observations appear reversible, a conclusion that should be verified in future experiments with a subsequent ZnO deposition on the etched Ag surface. It seems possible that upon deposition of the ZnO, the screening effect of that material is strong and such an effect influences not only the interface layer optical properties but also its deduced thickness.

For the ECD back-reflector, the observed 250 Å Ag/ZnO interface layer would be expected to result from a 124 Å initial surface roughness layer on the Ag before ZnO deposition, according to the correlation in Fig. 5.12. The significant reduction in the surface layer thickness by 46 Å, from the proposed value of 124 Å to the result of 78 Å after etching (as opposed to the 11-12 Å increase for samples DS020 and DS028), however, may demonstrate a smoothening process associated with the etching that is unique to the industry sample. Alternatively, the correlation of Fig. 5.12 may not be relevant for this sample and the 124 Å thickness may not be a valid estimate.

Table 6.2 provides the best fit parameters of the analytical model that describes the dielectric functions of the surface roughness layers on the three samples of Figs. 6.1-6.6. It should be emphasized that the data analyzed for this table were obtained after etch removal of the ZnO while the sample remained immersed in the 1:1500 HCl:H₂O etching solution. In Fig. 6.7, the dielectric functions of the Ag/ZnO interface layers for all three samples (left) are compared with the dielectric functions of the surface layer on Ag after
complete removal of the ZnO in the etching solution (right). Because the determination of these surface layer dielectric functions is a challenge, especially when the layers are thin, it is helpful to inspect the pseudo-dielectric functions of these samples using the model shown in Figure 6.8. The pseudo-dielectric function results from a re-expression of the ellipsometry angles ($\psi, \Delta$) using the conversion equations based on a single interface. Thus, no data fitting is required to generate the pseudo-dielectric function. These results, given in Figures 6.9-6.11, will be discussed later in this chapter and will be found to support the identification of the plasmon resonances in the surface layers as shown in Fig. 6.7.

As can be observed in Fig. 6.7 and verified in Table 6.2, the plasmon bands modeled as Lorentz oscillators appear at different energy positions after etching. The sample with initial $d_s = 12$ Å shows the strongest resonance and thus provides the most accurate peak energy of 3.32 eV. This represents a blue-shift by 0.43 eV from the value for the Ag/ZnO interface when ZnO is replaced by water in the etching process.

Applying the best fit resonance parameters for sample DS020 as obtained before etching, along with $\varepsilon_a = 4.0$ in Eq. (4.3a), yields $Q_m = 0.09$ for the volume fraction of metal protrusions. Next applying this value of $Q_m$, the average values of $E_p = 9.44$ eV and $\varepsilon_{10} = 4.01$, and the screening value $\varepsilon_a = 4.0$, the plasmon resonance energy of 2.60 eV is predicted for the Ag/ZnO interface. This resonance energy is lower than the observed value of 2.89 eV, and the difference is consistent with reduced screening as described in Section 5.3. Selecting a value for the ZnO ambient of $\varepsilon_a \sim 2.75$ ($n \sim 1.66$), one can find $Q_m = 0.126$ and $E_0 = 2.89$ eV, a prediction that matches the observed resonance energy. This agreement suggests that the screening is reduced relative to the
expected value of $\varepsilon_a \sim 4$ ($n \sim 2$), possibly due to voids on the ZnO side of the Ag/ZnO interface, and that the interface layer resonances tend to be spatially separated (low $Q_m$) with weak interactions between the resonating protrusions.

The increase in resonance energy upon etching from 2.89 to 3.32 eV for sample DS020 appears understandable qualitatively in terms of the replacement of a higher index of refraction screening material by a lower index one (e.g. ZnO with $n = 1.66$ by water with $n = 1.34$). Because of the relatively low accuracy with which the oscillator parameters are obtained after etching, it is assumed that the volume fraction of metal within surface layer of the etched Ag film is the same as that before etching, which is 0.126 for sample DS020. Next, applying this value of $Q_m$, along with $E_p = 9.44$ eV, $\varepsilon_{1o} = 4.01$, and $\varepsilon_a = 1.8$, a predicted resonance energy of 3.26 eV is obtained. This predicted value is close enough to the observed result of 3.32 eV to support the assumptions made. The observed result could be matched by simply reducing $Q_m$ to 0.09. Finally, it should be noted that in the limit of $Q_m = 0$ and $\varepsilon_a = 1$, i.e. an uncoated Ag sample, the plasmon resonance would be predicted at 3.85 eV, which is within the tail of the interband absorption onset at $E_g = 4.13$ eV and which has a width of $\Gamma = 0.3$ eV (see Table 3.2). When the imaginary part of the dielectric function becomes appreciable as is the case here, the plasmon resonance is suppressed. Suppressions that occur as the plasmon band shifts to higher energies may contribute to the inability of the resonance amplitude parameters to provide reliable values for $Q_m$ (as is the case here) as the resonance energy shifts above 3 eV. For sample DS028 with the thicker roughness layer of $d_s = 105$ Å, the increase in plasmon energy upon removal of the ZnO and replacement by water is not observed. In fact, for sample DS028, there appears to be no shift at all, and the plasmon
resonance energy is 2.76 eV for both ambients. This behavior can be understood qualitatively by a densification of the interface that reverses the effect of reduced screening as will be discussed in the following paragraph. First, applying the best fit resonance parameters of relevance to sample DS028 as obtained before etching, along with $\varepsilon_a = 4.0$ in Eq. (4.3a), $Q_m = 0.13$ is obtained for the volume fraction of metal protrusions. Next applying this value of $Q_m$, $E_p = 9.44$ eV, $\varepsilon_{1o} = 4.01$, and $\varepsilon_a = 4.0$, the plasmon resonance energy of 2.54 eV is predicted for the Ag/ZnO interface. This resonance energy is lower than the observed value of 2.76 eV, and the difference is again consistent with reduced screening as described in Section 5.3. Selecting a value for the ZnO ambient of $\varepsilon_a \sim 2.9$ ($n \sim 1.70$), one can find $Q_m = 0.175$ and $E_0 = 2.76$ eV, in consistency with the observed resonance.

Taking the same approach for sample DS028 after etching with $Q_m = 0.175$ and $\varepsilon_a = 1.8$, a plasmon band at 3.19 eV is predicted. In order to understand the observed lower plasmon energy, densification of the interface in the transition from the ZnO to water ambient medium is the most likely explanation. In fact, an increase in $Q_m$ from 0.175 to 0.43 leads to a downward shift in the predicted plasmon band from 3.19 eV to the observed value of 2.76 eV. An additional contributor to the lower energy plasmon after etching may be increased screening relative to a water ambient medium. This effect may occur if not all the ZnO is etched away or if higher index of refraction etching products remained trapped at the interface. Next for the ECD sample, it is reasonable to assume that it is the higher energy plasmon band at 2.75 eV that increases in energy upon etching and gives rise to the Lorentz oscillator centered at 3.09 eV in the completely etched sample. Starting with the ECD sample before etching and using the Lorentz oscillator
parameters in Eqs. (4.3a) and (6.1), the values of $Q_m = 0.09$ and $E_0 = 2.60$ eV are obtained for the ambient of ZnO with $\varepsilon_a = 4$ before etching away the ZnO. Lower screening of $\varepsilon_a = 3.3$ with $Q = 0.110$ is needed to reach the observed resonance energy of 2.75 eV. After etching away the ZnO, the reduction of $\varepsilon_a$ to 1.8 yields a predicted value of $E_0 = 3.28$ eV based on the assumption that $Q_m$ remains 0.110. This resonance energy again is larger than observed and suggests densification of the interface/surface region upon etching, as in the case of sample DS028. In fact, an increase in $Q_m$ to 0.24 yields a predicted resonance of 3.09 eV in agreement with the experiment.

The proposed increases in surface metallic volume fraction $Q_m$ for the two rougher samples after etching are required in order to understand the lack of a shift or a weaker shift to high energy for the plasmon band. This behavior may be attributed to additional roughening upon etching which enhances the plasmonic behavior as observed in Chapter 5. An alternative possibility is that for these samples, etching by-products with a higher index of refraction remain at the interface to limit the expected reduction in screening. In contrast, for the smoothest sample the plasmon band amplitude shifts in a manner expected according to a reduction in screening from $\varepsilon_a = 2.75$ to $\varepsilon_a = 1.8$. 
Table 6.2: The parameters in the analytical expression for the dielectric function of the surface roughness layer are tabulated for samples DS020, DS028, and the industry standard back-reflector sample. These results were obtained in fits to data collected with the sample immersed in the etching solution after removal of the ZnO.

<table>
<thead>
<tr>
<th>Sample (substrate temperature, $d_s$)</th>
<th>DS020 (RT; 12 Å)</th>
<th>DS028 (190°C, 105 Å)</th>
<th>ECD (unknown)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSE</td>
<td>0.00396</td>
<td>0.00125</td>
<td>0.00373</td>
</tr>
<tr>
<td>$d_s$ (Å)</td>
<td>22.8±0.4</td>
<td>116.6±0.6</td>
<td>78.3±0.9</td>
</tr>
<tr>
<td>$\varepsilon_{10}$</td>
<td>2.536±0.030</td>
<td>2.235±0.004</td>
<td>2.168±0.103</td>
</tr>
<tr>
<td>Lorentz A</td>
<td>7.490±0.083</td>
<td>0.630±0.007</td>
<td>0.508±0.043</td>
</tr>
<tr>
<td>Lorentz $E_n$ (eV)</td>
<td>3.315±0.006</td>
<td>2.761±0.003</td>
<td>3.092±0.008</td>
</tr>
<tr>
<td>Lorentz $\Gamma$ (eV)</td>
<td>0.834±0.011</td>
<td>0.731±0.012</td>
<td>0.243±0.038</td>
</tr>
<tr>
<td>Drude A (eV)</td>
<td>$1.057 \times 10^4 \pm 2.930 \times 10^6$</td>
<td>$2.119 \pm 0.010$</td>
<td>$2.123 \pm 0.044$</td>
</tr>
<tr>
<td>Drude $\Gamma$ (eV)</td>
<td>$1.6 \times 10^{-4} \pm 4.3 \times 10^{-2}$</td>
<td>$5.2 \pm 0.2$</td>
<td>10.0±8.3</td>
</tr>
<tr>
<td>$E_p$ (eV)</td>
<td>1.29±276.11</td>
<td>3.319±0.072</td>
<td>4.608±2.728</td>
</tr>
<tr>
<td>CP A</td>
<td>1.042±0.009</td>
<td>1.450±0.119</td>
<td></td>
</tr>
<tr>
<td>CP $E_g$ (eV)</td>
<td>3.989±0.004</td>
<td>3.797±0.015</td>
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</tr>
<tr>
<td>CP $\Gamma$ (eV)</td>
<td>0.666±0.017</td>
<td>1.250±0.158</td>
<td></td>
</tr>
<tr>
<td>CP $\theta$ (°)</td>
<td>$-13.51\pm2.44$</td>
<td>$-5.71\pm14.51$</td>
<td></td>
</tr>
<tr>
<td>CP $\mu$</td>
<td>0.982±0.021</td>
<td>1.113±0.178</td>
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</table>
Figure 6-7: A comparison of interface and surface layer dielectric functions is presented on the same plotting scales. The panels on the left depict the dielectric functions of the Ag/ZnO interface layers each formed upon deposition of the ZnO film on top of the underlying Ag film. The panels on the right depict the dielectric functions of the surface layers remaining on the Ag after etching away the ZnO film in a solution of 1:1500 HCl:H₂O. These latter results were obtained from fits to data acquired with the sample immersed in the etching solution.

From the fully etched samples with initial Ag surface roughness layer thicknesses of \( d_s = 12 \, \text{Å} \) and 105 Å, the pseudo-dielectric functions were extracted and compared with the corresponding results for the Ag film obtained before over-deposition of the ZnO to form the back-reflector. The simple equation for a single interface is used to determine the pseudo-dielectric function from the ellipsometry spectra in \((\psi, \Delta)\). This equation is based on the model for the sample after complete etching shown in Fig. 6.8. Thus, the pseudo-dielectric function of Ag is determined by analytical conversion of the ellipsometric parameters \( \psi \) and \( \Delta \) with the ambient being deionized water.
The resulting two pseudo-dielectric functions before ZnO growth and after ZnO etching are compared in Fig. 6.9 and Fig. 6.10 for samples DS020 with $d_s = 12$ Å and DS028 with $d_s = 105$ Å, respectively. It is of interest to investigate these pseudo-dielectric functions since the roughness layer thicknesses before ZnO deposition and after ZnO etching are quite close. As noted earlier, the roughness is 11-12 Å thicker after the etching process for both DS020 and DS028 samples. These differences are small compared to those between the thicknesses of the Ag/ZnO interface layer and the etched Ag surface layer. With similar roughness values before ZnO deposition and after etching, the pseudo-dielectric functions can be compared, and direct evidence of plasmon behavior to support the results in Table 6.2 can be identified in the two pseudo-dielectric functions.

Figure 6-8: This model for a single interface between Ag and vacuum or deionized water was used to calculate the pseudo-dielectric function of the Ag film before ZnO deposition or after complete ZnO etching, respectively. The pseudo-dielectric function is obtained from $(\psi, \Delta)$ via an analytical expression derived from the Fresnel equations for a single interface.

For the smoother sample with starting Ag surface roughness of 12 Å (DS020), Fig. 6.9 shows that the real parts of the pseudo-dielectric functions ($\varepsilon_1$) for the samples before ZnO deposition and after complete etching are quite close relative to the scale of the spectral variations. The difference can be attributed to the 11 Å difference in the
thickness of the surface layer. There is a clear difference in the imaginary parts of the
dielectric function $\varepsilon_2$, however, as indicated by a well-defined band at $\sim 3.3$ eV for the
etched result which is not observed in the original Ag pseudo-dielectric function measured before ZnO deposition. This plasmon energy has also been identified more accurately as $3.32$ eV by fitting the surface layer dielectric function. It is important to emphasize that the plasmon band deduced in the fitting of the surface layer dielectric function is observed directly in the converted $(\psi, \Delta)$ data. This supports the validity of the fitting result of Table 6.2. Thus, it is clear that this is the plasmon band, having been red-shifted from higher energies (where plasmonic behavior cannot be sustained due to the larger $\varepsilon_2$), as a result of the replacement of ambient laboratory air before ZnO deposition by water after ZnO etching. As noted previously, the resonance energy of $\sim 3.32$ eV was associated with $\varepsilon_a = (1.34)^2 = 1.8$ and $Q_m \sim 0.09$. If $\varepsilon_a = 1$, and the same value of $Q_m = 0.09$ is used, then the plasmon band would be shifted to $E_0 = 3.76$ eV, in which case the plasmon would occur in the tail of the interband transitions and would be suppressed. It is for this reason that the Bruggeman effective medium approximation appears to provide a suitable description of the dielectric function of thin roughness layers on Ag, because with $\varepsilon_a = 1$ and with the low $Q_m$ for this layer, a well-defined plasmon band is not observed. It should be further noted that the value of $Q_m$ in Eq. 6.1 represents the volume fraction of resonating protrusions which can be lower than the volume fraction of the metallic component itself. Finally, Eqs. 4.3a and 6.1 derive from a relatively simple theoretical approach that provides a guide as to how the different characteristics of the surface and interface layers influence the plasmon band; thus, a precise analysis is not to be expected using this approach.
Figure 6-9: A comparison of pseudo-dielectric functions is provided for the same sample of Ag (DS020) obtained initially before deposition of ZnO and then after complete removal of the ZnO layer by etching in a 1:1500 HCl:H₂O solution. The starting Ag surface roughness thickness for this sample is 12 Å, and the surface layer thickness after etching is 23 Å. The pseudo-dielectric function is calculated directly from the $(\psi, \Delta)$ spectra using the Fresnel equations for a single interface.
Figure 6-10: A comparison of pseudo-dielectric functions is provided for the same sample of Ag (DS028) obtained initially before deposition of ZnO and then after complete removal of the ZnO layer by etching in a 1:1500 HCl:H2O solution. The starting Ag surface roughness thickness for this sample is 105 Å, and the surface layer thickness after etching is 117 Å. The pseudo-dielectric function is calculated directly from the \((\psi, \Delta)\) spectra using the Fresnel equations assuming a single interface.

The results in Figure 6.10 for sample DS028 suggest that the surface layer analysis presented in Table 6.2 is valid since a weak feature is observed in the pseudo-dielectric function at ~ 2.8 eV after etching of ZnO. In other words, the processed \((\psi, \Delta)\) data support the deduced energy of the plasmon band at 2.76 eV in Table 6.2, indicating that in the fitting the Lorentz oscillator has locked on to the weak feature in Fig. 6.10. In
this case, the plasmon band energy is consistent with $Q_m \sim 0.43$. Replacing the ambient by laboratory air in this case would be expected to shift the plasmon band to 3.3 eV. For this sample, the interband onset is particularly broad, and so in this case, the closer proximity to the interband transition tail may lead to the suppression of the plasmon band when the ambient is air. Furthermore, the plasmon band even as measured within the liquid is weak, and so only the residual low energy side of the band predicted to be centered near 3.3 eV may be observable.

The pseudo-dielectric function data are not available for the Ag film of the ECD back-reflector sample before deposition of ZnO, and as a result no comparisons are available corresponding to those in Figs. 6.9 and 6.10. Instead in Fig. 6.11, the pseudo-dielectric function of the sample prepared by ECD and etched to remove the ZnO is compared with the corresponding results for the two samples DS020 and DS028 prepared at University of Toledo. The pseudo-dielectric function for the etched ECD sample appears more closely similar to sample DS028 with the initial Ag surface roughness thickness of 105 Å to the extent that it exhibits a larger $\varepsilon_2$ spectrum at low energies. This may be an indication of lower energy plasmon modes as investigated in Chapter 3. In addition, these two samples also exhibit plasmon features that are relatively weak, given the thick surface layer. The etched ECD back-reflector sample exhibits a clear plasmon band at 3.1 eV, again providing support to the analysis of Table 6.2 that yielded a Lorentz oscillator with a resonance energy at 3.09 eV. Clearly this band is higher in energy than that of sample DS028 that started from an initial Ag layer with $d_s = 105$ Å.

Most importantly, the pseudo-dielectric functions reveal the plasmon bands identified as weak but clear features in the processed data, i.e. the data converted from
$(\psi, \Delta)$ to $(\langle \varepsilon_1 \rangle, \langle \varepsilon_2 \rangle)$ without fitting, where the triangular brackets indicate the pseudo-dielectric function. Thus the presence of these bands and their energy locations do not rely on the detailed analysis used to extract the Ag surface layer thickness and oscillator parameters. The primary interest in Fig. 6.11 is the demonstration that for two samples the plasmon bands have shifted to higher energies relative to the Ag/ZnO interface layer as a result of the reduced screening of the water ambient relative to ZnO. For one sample the shift is not as large as expected based on Eq. (6.1), and for another sample a shift is not observed at all, and this behavior may be attributed to an increase in $Q_m$, or densification of the surface layer (relative to the interface layer) that occurs upon removal of the ZnO layer by etching. In fact, further evidence for densification occurs from real time spectroscopic ellipsometry as shown in Figure 6.12. Here the results are shown for the surface layer plasmon energy as a function of time near the end of the etching process when the ZnO has been removed. For all samples, the plasmon energy is decreasing, which is the reverse of the trend observed at earlier times that results due to the elimination of the ZnO. This suggests that with increasing time densification (i.e. an increase in $Q_m$) is occurring in accordance with Eq. (6.1).

Finally, it should be pointed out that the weak plasmon bands are not the only features of interest in Fig. 6.11. The relative amplitudes of the interband features starting at 3.75 eV are expected to decrease with increasing surface roughness, and this trend observed in the raw data supports the thickness results in the models of Fig. 6.1 (sample DS020 with $d_s = 12$ Å and $d_i = 23$ Å, before deposition and after etching), Fig. 6.3 (sample DS028 with $d_s = 105$ Å and $d_i = 117$ Å, before deposition and after etching), and Fig. 6.5 (sample fabricated by ECD with $d_i = 78$ Å).
Figure 6-11: The pseudo-dielectric functions are compared for three back-reflector samples after etching with a 1:1500 HCl:H₂O solution that completely removes the ZnO and leaves a Ag surface. The samples include two back-reflector samples prepared at the University of Toledo with starting Ag surface roughness layer thicknesses of 12 and 105 Å (DS020 and DS028, respectively), and a back-reflector prepared at ECD.

6.3 Summary of Plasmon Band Energy Shifts Upon ZnO Etching

The three samples studied here were fabricated so as to obtain different roughness thicknesses on the starting Ag surface and different bulk thicknesses of ZnO. As a result
of the different ZnO bulk layer thicknesses, the time required to completely remove the ZnO layer in the etching process varies considerably and real time spectroscopic ellipsometry is used to identify the etching endpoint. In Figure 6.12, which shows the time dependence of the plasmon energies for the three samples in the last ~ 30-100 min of etching, the plasmon peak energies ultimately stabilize, indicating that the ZnO layer has been removed and any densification process at the surface has stabilized as well. For the smoothest sample with initial Ag surface roughness of 12 Å and a ZnO bulk thickness of 607 Å, this endpoint point occurs near 115 min. For the sample with Ag surface roughness of 105 Å and a ZnO bulk thickness of 1250 Å, the plasmon band energy stabilizes near 120 min. Finally, for the back-reflector prepared by ECD with ZnO bulk thickness of 3164 Å, 240 minutes of etching were required to remove the ZnO completely. A comparison of the RTSE results obtained in this study suggests either that there is not a constant etch rate versus time during the process, or that the average etch rate varies considerably from process to process. Increases in the energy of the plasmon bands earlier in the etching process than is depicted in Fig. 6.11 can be attributed to elimination of the ZnO and its replacement by water as an ambient medium, whereas the decreases in energy near the very end of the process can be attributed qualitatively, as noted earlier, to the densification of the Ag surface layer.

As a summary, the plasmon band energies for the Ag/ZnO interface layer before etching are compared in Table 6.3 with the corresponding result after etching. Clear blue-shifts of the plasmon band are observed for two out of the three samples. The primary reason for the shift of the plasmon band to higher energy is believed to be the change in the dielectric function of the ambient material upon etching, from ZnO with $\varepsilon_a \sim 2.75$-
3.30 to water with $\varepsilon_a \sim 1.80$, although changes in the metal volume fraction of the interface/surface layer also play a role. Thus, if the index of refraction of ZnO in the back-reflectors could be further reduced from the observed range of 1.65-1.82 to 1.3 through the use of voids and a free carrier contribution as described earlier, both plasmon excitation and associated dissipative losses in the range of interest for back-reflectors operation may be reduced or avoided altogether.

For the samples before etching, Table 6.3 includes the values of $Q_m$ deduced from Eq. (4.3a) using the best fit values of the Lorentz oscillator parameters, along with the values of $\varepsilon_a$ deduced from the resonance energy via Eq. (6.1) that predict a resonance energy in agreement with experiment. The resulting values of $Q_m$ for all three samples are in a relatively narrow range of 0.110-0.175, yielding overall sample-to-sample consistency. In addition, a consistent reduction in screening with $\varepsilon_a = 2.75-3.3$ is required compared to $\varepsilon_a = 4.0$ for ZnO. It should be recalled that in the derivation of Eq. (6.1), the Drude expression for the dielectric function of Ag is substituted into the Maxwell-Garnett effective medium approximation with the host being a non-absorbing material with dielectric function $\varepsilon_a$. The result approximates a Lorentz oscillator with an energy maximum given by Eq. (6.1).

In contrast to this approach, Equation (4.3a) is not used for the etched surface measured in situ under aqueous solution. The reason is that a suppression of the plasmon resonance may occur as its energy increases above 3 eV due to the presence of a tail in $\varepsilon_2$ associated with the interband absorption onset. In fact, applying Eq. (4.3a) yields values of $Q_m$ for the plasmon resonance at the etched surface that appear unreasonably low. As a result of these observations, the volume fraction $Q_m$ is initially assumed to be
unchanged upon etching. This assumption works well for the smooth sample; however, for the two rough samples, a densification effect or increase is needed to explain the energy position of the plasmon band after etching. Evidence for this densification is also observed in the RTSE results for which the plasmon energy is observed to decrease with increasing time at the end of the etching process. Although the effective medium calculations may be oversimplified, the observed trends appear to provide qualitative information on the relationship between the interface or surface structure and the plasmon resonance energy.

![Figure 6-12](image)

Figure 6-12: Plasmon band resonance energies based on a Lorentz oscillator model are plotted versus etching time in minutes near the etching endpoint for the three Ag/ZnO back-reflector samples, including DS020 and DS028 fabricated at University of Toledo with initial Ag surface roughness values of $d_s = 12$ Å and 105 Å, respectively, and one sample fabricated at ECD. Among the back-reflector samples, the one fabricated at ECD exhibits the longest etching time due to its thick ZnO layer deposited on top of the Ag coated steel substrate. DS020 and the ECD sample show a final plasmon band energy that is clearly blue-shifted after etching, as measured relative to that obtained for the Ag/ZnO interface layer before etching. The plasmon band resonance energies before and after etching are listed in Table 6.3.
Table 6.3: Thicknesses of the surface layer on three etched back-reflector samples as obtained after etching are shown in the second column. The experimentally determined plasmon band resonance energies for the Ag/ZnO interface layer before ZnO etching and for the Ag surface layer after complete removal of the ZnO by etching are shown in the third and fifth columns. Predicted values of Q, the volume fraction of protrusions that support localized plasmons, and E₀, the plasmon resonance are included in the fourth and sixth columns based on the Lorentz oscillator and Drude parameters for the samples. Also provided are the εₐ values used in the calculations. The last column provides the predicted plasmon energy for the Ag surface layer as measured with a vacuum ambient in the limit of Q = 0 and for the final Q value deduced after etching.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ag surface layer thickness on etched sample</th>
<th>Observed Ag/ZnO plasmon peak energy</th>
<th>Predicted Ag plasmon peak energy before etching ZnO (εₐ = 2.75 - 3.3)</th>
<th>Predicted Ag plasmon peak energy after etching away ZnO (εₐ = 1.8)</th>
<th>Predicted Ag plasmon peak energy in vacuum (εₐ = 1) with Qₘ = 0 and Qₘ values from Col. 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>DS020: Ag ds = 12 Å</td>
<td>23 Å</td>
<td>2.886 ± 0.015 eV (εₐ = 2.75; Qₘ = 0.126)</td>
<td>2.89 eV (εₐ = 2.75; Qₘ = 0.126)</td>
<td>3.315 ± 0.006 eV (εₐ = 1.8; Qₘ = 0.09)</td>
<td>3.85 eV (Qₘ = 0)</td>
</tr>
<tr>
<td>DS028: Ag ds = 105 Å</td>
<td>117 Å</td>
<td>2.758 ± 0.013 eV (εₐ = 2.9; Qₘ = 0.175)</td>
<td>2.76 eV (εₐ = 2.9; Qₘ = 0.175)</td>
<td>2.761 ± 0.003 eV (εₐ = 1.8; Qₘ = 0.43)</td>
<td>3.85 eV (Qₘ = 0)</td>
</tr>
<tr>
<td>ECD: Ag ds unknown</td>
<td>78 Å</td>
<td>2.753 ± 0.019 eV (εₐ = 3.3; Qₘ = 0.110)</td>
<td>2.75 eV (εₐ = 3.3; Qₘ = 0.110)</td>
<td>3.092 ± 0.008 eV (εₐ = 1.8; Qₘ = 0.24)</td>
<td>3.85 eV (Qₘ = 0)</td>
</tr>
</tbody>
</table>
6.4 Normal Angle Reflectance Study

The normal incidence reflectance $R$ of a single interface between vacuum or air and a reflecting medium can be expressed in terms of the refractive index, $n$, and the extinction coefficient, $k$, of the reflecting medium according to

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}.$$  \hfill (6.2)

This expression helps one to understand highly reflective metals such as Ag that sustain plasmon modes. The conditions for sustaining propagating and localized plasmons include $\varepsilon_2 \sim 0$ and $\varepsilon_1 < 0$. Given that $\varepsilon_1 = n^2 - k^2$ and $\varepsilon_2 = 2nk$, in order to meet the condition that $\varepsilon_2 \sim 0$, then either $n \sim 0$ or $k \sim 0$ (or both). In order to further meet the condition that $\varepsilon_1 < 0$, it must mean that $k > n$. Thus, it is $n$ that must be vanishingly small. Under these conditions, the reflectance of the metal given in Eq. (6.2) is near unity.

In this section, the reflectance spectra are shown as measured in air for two samples of the previous section. The two samples selected, DS028 and the ECD back-reflector, are those with the largest Ag/ZnO interface layer before etching and the largest Ag surface layer after etching. Figure 6.13 shows the reflectance for the back-reflector sample DS028 with a 105 Å thickness of initial Ag surface roughness before deposition of the ZnO. These results were obtained before and after the etching process that completely removes the ZnO. The reflectance for this sample in the range of back-reflector operation increases significantly upon etching, in fact from the level of 0.5 at 1.5 eV for Ag/ZnO before etching to nearly 0.9 for the Ag surface after etching. At the higher energies (> 4 eV), however, the reflectance is very weak for the sample both
before and after etching. Similarly, for the ECD back-reflector shown in Fig. 6.14, the increase in the reflectance upon etching is even larger at the energies of back-reflector operation. At 1.5 eV, the reflectance for this sample increases from ~ 0.20 for Ag/ZnO before etching to ~ 0.9 for the Ag surface after etching. Again, the reflectance is very weak over the corresponding high energy range for the sample before and after etching.

Figure 6-13: The normal incidence reflectance data for the back-reflector sample DS028 with initial Ag surface roughness of 105 Å are compared before and after etching away the ZnO in a 1:1500 HCl:H₂O solution. Before etching, the back-reflector sample consists of a ZnO bulk layer with a thickness of 1250 Å and a Ag/ZnO interface layer with a thickness of 233 Å. After etching, the sample consists of a ~ 117 Å thick surface layer on top of an opaque Ag layer which serves as a semi-infinite substrate. The reflectance measurements were performed in air.
Figure 6-14: The normal incidence reflectance data for the ECD back-reflector are compared before and after etching away the ZnO in a 1:1500 HCl:H₂O solution. Before etching, the back-reflector sample consists of a ZnO bulk layer with a thickness of 3164 Å and a Ag/ZnO interface layer with a thickness of 250 Å. After etching, the sample consists of a 78 Å thick surface layer on top of an opaque Ag layer which serves as a semi-infinite substrate. The reflectance measurements were performed in air.

In Fig. 6.15, a comparison of the reflectances is provided for the two samples, DS028 and the ECD back-reflector, having the thickest surface layers after etching. It is clear that the etched back-reflector fabricated at ECD exhibits a higher reflectance than the one fabricated at the University of Toledo, the latter with a starting Ag surface roughness layer of 105 Å in thickness. This result is in contrast to the results of the
comparison made before etching as observed previously in Chapter 5 (see Fig. 5.21), in which case the University of Toledo sample exhibited a higher reflectance.

Next, the results of Figures 6.13 to 6.15 will be discussed in an attempt to better understand the effects of etching and the differences between the two samples. The discussion begins by emphasizing that there is no transmission through any of the sample structures. As a result, the differences between the two reflectance spectra must be understood in terms of differences in absorbance and scattering between the two sample structures. For these samples, however, the scattering spectra have not been measured, which introduces challenges and ambiguity in the interpretation. Such measurements must be performed as part of a more comprehensive future study on a controlled set of back-reflector samples that have been deposited and etched.

An effective future study must involve an initial, independent study of uncoated Ag, and then second and third studies of the Ag/ZnO back-reflector before and after etching, respectively. The latter two studies must use Ag samples deposited under identical conditions as those of the first study. Each of the three studies must involve (i) real time spectroscopic ellipsometry (RTSE) measurements during deposition or etching; (ii) in situ spectroscopic ellipsometry at the end of the process in (i) (using a longer averaging time than that used for RTSE, in order to achieve higher precision); (iii) ex situ variable angle SE and reflectance spectroscopy, along with reflectance deficit calculations; and (iv) total integrated scattering measurements with reflectance performed simultaneously, and (v) angular dependence of scattering.

The most obvious difference between the reflectance spectra of the same sample before and after etching, as expected, is the presence of the interference fringe pattern due
to the ZnO layer observed before etching. Because the ZnO layer removed in the etching process does not absorb below its bandgap, then the increase in the reflectance spectra below 3.0 eV can derive from only two possible sources, namely, either elimination of Ag absorption processes or elimination of scattering processes, as a result of the removal of the ZnO. In fact, the only absorption processes in the sample structure occur in the Ag, and below 3 eV these can arise from absorption by free electrons and by confined plasmons. The presence of interference fringes show that these absorption processes can be either enhanced or suppressed through the presence of the ZnO layer, yielding either interference minima or maxima, respectively, in the reflectance spectra. For both sample structures, however, the interference maxima in the reflectance spectra for the Ag/ZnO structures remain lower than the reflectance of the etched structures. Thus, either the absorption processes are eliminated upon etching by shifting of the plasmon bands above 3 eV, or if not, one must conclude that elimination of scattering upon etching is the dominant effect causing the difference. For the sample DS028 prepared with an initial surface roughness thickness of $d_s = 105 \, \text{Å}$, the plasmon band shift is negligible. Thus we must conclude, for this sample at least (and likely for the ECD sample as well) that the etching process yields significantly suppressed scattering.

Thus, suppression of scattering appears to be the dominant effect that occurs upon removal of the ZnO by etching. Removal of the ZnO eliminates the scattering processes that occur at the ZnO surface, and also eliminates multiple internal reflection processes within the ZnO that randomize the direction of incident radiation. Thus, it is clear that the goal of the ZnO in the back-reflector is to contribute to an optical cavity that randomizes the direction of the radiation within the cavity using a design in which the
only absorbing material in the cavity is the solar cell i-layer. Such a design is clearly an idealization since it has been found throughout this research that the Ag/ZnO interface layer and the Ag bulk itself absorbs radiation, primarily through confined plasmons for the former, but possibly also through propagating plasmons. Although this is not a problem in itself, one must design the microstructure at the interface such that these excited plasmons relax radiatively through scattering processes without dissipation. Even a small amount of dissipation is a problem due to the requirement of multiple reflections at the ZnO/Ag interface for an effective back-reflector that generates multiple passes of light through the i-layer. Given the concept of the solar cell as embedded within an optical cavity for enhanced collection, it would also be important to develop both p and n type layers that do not absorb in the range of back-reflector operation, since the electron-hole pairs generated within these layers are not collected.

Finally, it should be noted in Figs. 6.14 and 6.15 that the ECD sample has a lower reflectance before etching, but a higher reflectance after etching. Because this structure has been optimized for high solar cell performance in triple junction a-Si:H-based devices over many years of research and development, it is likely that such a large difference is a key to high performance. What this behavior suggests, in particular, is that the top-most ZnO surface (which will form the interface to the n-layer of the bottom cell of the multijunction) is optimized to generate significant scattering even before the light reaches the Ag/ZnO interface. The thicker ZnO layer may then result in a larger distribution of incidence angles when the light reaches the Ag/ZnO interface. The higher reflectance of the Ag is likely to result from a trade-off between the additional scattering effect desirable at the Ag/ZnO interface (via a rough Ag layer on which the ZnO is deposited)
and the absorption leading to dissipation which is enhanced as the Ag roughness increases.

The concept for back-reflector improvement arising from this chapter is a reduction in the real part of the dielectric function of the ZnO material closest to the Ag interface over the photon energy range where back-reflector operation is desired, $\sim 1.2 - 1.8$ eV. This can be done either through the introduction of voids or free electrons, while ensuring that free carrier absorption is not generated. The latter condition requires ZnO with the longest possible relaxation time $\tau$ for a given carrier concentration $N_e$. The goal is to blue-shift the plasmon absorption (that may result in dissipation) to energies outside the range of operation of the back-reflector. Another problem identified in Chapter 5 is the observation that the condition leading to rough Ag, specifically elevated substrate temperature, is also generating greater absorption within the bulk Ag. This suggests that the roughness on the Ag surface should be produced in alternative ways, for example by generating a rough film of Ag in an initial deposition at elevated temperature and then reducing the substrate temperature to generate a room temperature deposition with roughness induced by the underlying Ag film.
Figure 6-15: A comparison is shown between the normal incidence reflectance spectra for two completely etched back-reflectors, one sample DS028 prepared at the University of Toledo with an initial Ag surface roughness thickness of 105 Å and the other prepared at ECD. The etching process completely removes all ZnO by immersion in a 1:1500 HCl:H2O solution. The reflectance measurements were performed in air.
Chapter 7

Summary and Future Direction

7.1 Summary

Real time and ex-situ spectroscopic ellipsometry (SE) has been applied to study the growth process, and the optical and electrical properties of the thin film materials that are used as back-reflectors and transparent conductors in thin film photovoltaics. This section summarizes the major results obtained in each chapter of this dissertation.

In Chapter 3, a study was described that has focused on magnetron sputter deposition of silver thin films onto oxide covered silicon substrates. These films were monitored in real time by SE. The growth rate of the Ag thin films as deduced by RTSE was found to be dependent as expected on the RF power applied to the Ag sputtering target. For elevated substrate temperatures used in these experiments, the surface roughness thickness of the final Ag films was observed to be larger as will be described in greater detail in subsequent paragraphs. The dielectric functions of the Ag films obtained by inversion were parameterized using a photon energy independent contribution to the real part of the dielectric function, a Drude contribution to describe the intraband transitions, and a critical point (CP) contribution to describe the interband transitions.
Even at room temperature, variation of Ar pressure or RF power produced Ag films with different optical and electrical properties due to differences in the resulting grain structure of the polycrystalline films. The average value of the carrier concentration of Ag films deposited at room temperature was found to be $5.85 \times 10^{22}$ cm$^{-3}$, very close to the predicted value of $5.86 \times 10^{22}$ cm$^{-3}$ for single crystal Ag. The dc electrical resistivity at room temperature ranged from $3.98 \times 10^{-6}$ to $6.21 \times 10^{-6}$ Ω-cm, values that are higher than that reported for the single crystal, $1.59 \times 10^{-6}$ Ω cm, due to grain boundary and defect scattering.

As noted earlier, the Ag films deposited at elevated substrate temperature were found to exhibit thicker Ag surface roughness layers than the samples deposited at room temperature. When the surface roughness layer was modeled using the Bruggeman effective medium approximation, it was necessary to add a second low photon energy (1.2 - 1.6 eV) CP oscillator in the expression for the dielectric function of bulk layer Ag of the rougher films -- in addition to the higher energy CP oscillator representing the interband transitions. Yet there are no band-to-band transitions in bulk Ag within the 1.2 – 1.6 eV energy range. As a result, the Bruggeman EMA model for the surface roughness layer was deemed insufficient for films with thicker roughness layers and was replaced by an analytical model that includes a Lorentz oscillator representing the low energy plasmon resonance and a CP oscillator for the interband transitions. As the substrate temperature increased, the plasmon resonance energy was found to red shift in conjunction with the increase in surface roughness layer thickness.

In the study described in Chapter 3, one of the room temperature deposited Ag samples was annealed to 200°C in steps of 20°C. In an initial analysis, the annealed Ag
sample was modeled using a Drude component and a single CP oscillator for its bulk layer dielectric function and using the Bruggeman EMA for the surface roughness layer dielectric function. For annealing temperatures of 100°C and lower, an acceptable fit was obtained with this model. For higher annealing temperatures, however, the MSE increased and this problem could be addressed by incorporating an additional low energy CP oscillator into the dielectric function of the bulk layer. Because this is not a suitable model, for annealing temperatures above 100°C as noted earlier, the data were re-analyzed using a surface roughness layer whose dielectric function is modeled, not by the Bruggeman EMA, but rather as an analytical function consisting of a Lorentz oscillator and a CP oscillator. This enabled expression of the bulk layer dielectric function using physically reasonable Drude and single CP oscillator terms. The Lorentz oscillator in the dielectric function of the surface could be understood as representing a confined plasmon resonance. A clear red-shift in this resonance energy and an increase in broadening were observed with increasing annealing temperature. This is attributed to the excitation of confined plasmon modes in the surface layer that span a wider range of energies with increased interaction between those modes due to the increase in surface roughness. The CP oscillator energy representing the bandgap of the interband transitions in the bulk Ag has been plotted versus the annealing temperature, yielding best fit linear temperature coefficients of $-2.3 \times 10^{-4}$ eV/K and $-8.6 \times 10^{-4}$ eV/K for the lower (20 - 120°C) and upper (120 - 200°C) temperature ranges, respectively, that use the two different surface roughness models. Although these results bracket the reported value of $-6.5 \times 10^{-4}$ eV/K in the literature, they represent the combined effects of annealing and the intrinsic temperature dependence of the optical properties and so are difficult to interpret.
Improved experimental procedures have been applied in the studies of Chapter 4 to avoid this complication.

Chapter 4 of this dissertation describes research performed on intrinsic and doped ZnO thin films. The intrinsic ZnO films were deposited on different substrates using a range of sputter deposition conditions. These thin films were analyzed by spectroscopic ellipsometry to determine their optical and electrical properties. The dielectric functions of intrinsic ZnO films thus obtained were parameterized using two generalized critical point (CP) oscillators that describe the interband transitions. The ZnO samples of this study exhibit bandgaps in the range of 3.3 - 3.4 eV. Samples deposited on glass substrates were found to exhibit a higher density bulk layer microstructure in comparison with that of samples deposited on c-Si substrates.

A selected ZnO sample deposited on glass was annealed to study the temperature dependence of its optical and electrical properties. The resistivity of this sample before heating was $1.73 \times 10^4 \ \Omega \cdot \text{cm}$, but after the first cycle of annealing, i.e., heating the sample to 700 K and then cooling it to room temperature, the resistivity was found to decrease sharply to $67.8 \ \Omega \cdot \text{cm}$. One possible reason for this effect is a reduction in defect density in the crystallites and an increase in the crystallite size due to the annealing. Another possible effect is a reduction in p-type compensating defects, which can in turn increase charge carrier concentration. A slight increase in band gap by $0.007 \pm 0.004 \ \text{eV}$ (just outside of the confidence limits of the analysis) is observed, which is consistent with an increase in carrier concentration via the Burstein-Moss effect.

From the temperature dependence of the first CP oscillator energy for ZnO, the optical bandgap is found to exhibit a linear red-shift as the measurement temperature is
increased, in accordance with a temperature coefficient of $-2.57 \times 10^{-4}$ eV/K. Thus, for a temperature increase from room temperature to 650 K, the bandgap energy decreases by 90 meV. This linear coefficient was obtained in the second heating cycle and so represents the measurement temperature dependence of the optical properties of the annealed ZnO. A linearly decreasing bandgap with temperature is expected due to the effects of lattice expansion and increased electron-phonon interaction.

A set of aluminum doped ZnO (AZO) thin films were deposited on soda lime glass (SLG) at room temperature using a target consisting of 2 wt.% Al$_2$O$_3$ and 98 wt.% ZnO. In this study, the AZO films were characterized by IR, visible and UV spectroscopic ellipsometry over the photon energy range from 0.08 to 5 eV. The model used to extract the structural and optical properties consisted of multiple layers on the SLG substrate. These layers include (i) an interface layer between the SLG and the AZO, (ii) an AZO bulk layer, and (iii) a surface roughness layer on the AZO. The dielectric function of the bulk AZO was simulated using an analytical expression consisting of a Drude term, two Lorentz oscillators, and a CP oscillator. The resonance energy of the latter defines the optical bandgap. For all four AZO samples on SLG, the optical bandgaps were found to span a relatively narrow range, from 3.65 to 3.69 eV, as determined from the resonance energy of the CP oscillator. This is expected given that all samples were deposited from a single target, with a presumably uniform doping level throughout its thickness. The observed large blue-shift of the AZO bandgaps relative to those of intrinsic ZnO (band gap ~ 3.30 eV) is to be expected for a degenerately-doped, wide bandgap semiconductor according to the Burstein-Moss (BM) effect.
Interesting features appear in the experimental dielectric function data at photon energies below the band gap in the NIR and IR regions. First, a feature appears at ~0.75 eV, modeled as a Lorentz oscillator, in three of the samples having AZO thicknesses of ~3000 Å on SLG substrates. Because this feature is missing in the thickest sample (thickness ~5900 Å) also on SLG, this feature is likely to be extrinsic in nature. The 0.75 eV feature may arise from contamination by water vapor which leads to electronic defects and an associated absorption band. Alternatively dopant clustering may occur and this may lead to a plasmon associated absorption band due to localized regions of higher carrier concentration. The second feature, also modeled as a Lorentz oscillator, appears at ~0.20 eV and is observed in all samples. This suggests an intrinsic origin associated with the vibrational modes of the Zn-O bonds. The Drude component deduced from the IR and NIR-UV spectroscopic ellipsometry (SE) study can be validated through a free carrier analysis based on the parameters that describe this component. The resistivity derived from IR and NIR-UV SE is in reasonably good agreement with the dc resistivity measured directly by a four point probe instrument. The electrical properties including not only resistivity $\rho_0$, but also relaxation time $\tau$, carrier concentration $N$, and mobility $\mu$ are in close agreement with values reported in literature for a similar composition target and a similar range of film thicknesses.

The dielectric functions of 11 samples of AZO and gallium doped ZnO (GZO) deposited on a variety of substrates were compared in the NIR - UV photon energy range (0.7 - 5 eV). The dielectric functions of GZO were reported previously in the literature by Fujiwara and Kondo (2005). Only the AZO samples deposited on glass, with the exception of the thickest sample, required the 0.75 eV Lorentz oscillator in order to fit the
dielectric functions. For the samples on SLG, the Lorentz oscillator resonance appears in the range of ~ 0.75 - 0.77 eV. For a single AZO sample deposited on borosilicate glass (BSG), the Lorentz oscillator is observed at a somewhat higher energy position of 0.81 eV. This result suggest that the low energy band appearing for the thinner AZO on glass substrates is not specific to the type of glass. Thus, it seems unlikely that the band is caused by Na or other alkali metal contaminants that diffuse from the glass side. For all other AZO samples deposited on c-Si or Ag coated substrates, as well as the GZO deposited on c-Si substrates, only a Drude term and a single CP oscillator, the latter representing the bandgap, are required in fitting the data spanning the NIR – UV range.

The AZO thin films deposited on SLG have a narrow optical bandgap range of ~ 3.65 - 3.70 eV, as determined from the resonance energy of the CP oscillator in each case. The corresponding value for AZO on BSG is somewhat higher, 3.72 eV. The AZO deposited on bare c-Si exhibits an optical gap of 3.73 eV, whereas the other AZO samples deposited on Ag coated substrates have wider optical gaps of 3.76 and 3.85 eV. These results suggest possible diffusion of Ag atoms into the AZO, leading to additional doping and a widening of the optical band gap. For the GZO samples different targets were used to achieve a range of doping levels. As a result, the optical gap was observed to shift to higher energy according to the Burstein-Moss effect as would be expected with the increase in the free electron concentration.

An AZO sample deposited on BSG was selected for study of the effects of annealing and measurement temperature on the structural, optical, and electrical properties. Throughout the measured photon energy range (0.7 - 5 eV), the AZO structure and optical properties were modified in the annealing process. The observed behavior is
in contrast to the case of intrinsic ZnO whereby changes upon annealing were observed only over the higher energy range of the spectra above the optical bandgap. Both sets of room temperature data for AZO before and after annealing, were modeled using a Drude term, a Lorentz oscillator and a CP oscillator. Structurally, the results suggest that the film has become more compact, and the total thickness decreases upon annealing. The observed effects of annealing reflected in the dielectric function include not only the increase in the film density, but also a decrease in the resistivity and an increase the free electron concentration. The blue shift in optical bandgap from 3.72 to 3.85 eV, modeled using the CP oscillator, is consistent with the increase in electron concentration according to the Burstein-Moss effect.

One interesting result of annealing the AZO is the blue shift of the low energy band, modeled as a Lorentz oscillator, from 0.80 to 1.26 eV upon annealing. A continuous shift in such a well-defined band appears inconsistent with electronic defect transitions or vibrational modes due to contaminants. Alternatively, the low energy feature may be a plasmon-related band originating from inhomogeneous doping. In the latter case, the blue shift would be associated with an increase in the doping inhomogeneity upon annealing.

Upon heating the AZO sample during a second cycle to 650 K in order to observe measurement temperature effects, the optical bandgap of the material as measured at the elevated temperatures was observed to red-shift linearly. This again is expected due to the effects of lattice expansion and increased electron-phonon interaction. The red-shift is ~ 104 meV when the sample is heated from room temperature to 650 K, yielding a temperature coefficient of $-2.975 \times 10^{-4}$ eV/K. The measurement temperature
dependences of the Drude parameters show that the resistivity increases linearly whereas the scattering time decreases linearly. The linear increase in resistivity is expected for temperatures near and above the Debye temperature, whereas the linear decrease in scattering time with temperature is a consequence of an inverse proportionality over a narrow range of temperature. Finally, the change in electron concentration is found to be negligible, ~ 1%, compared with the changes of 10 - 20% in resistivity and scattering time over the temperature range of study (~ 300 – 650 K).

The research effort described in Chapter 5 focuses primarily on the Ag/ZnO interface layer. The initial approach applied in the analysis of RTSE data for the deposition of ZnO on Ag was to neglect the interface layer between the two materials. This approach resulted in a poor fitting quality and an unphysical oscillation in the ZnO bulk layer thickness. A more advanced approach resulted in similarly poor results. This latter approach relied on the incorporation of an interface layer whose dielectric function was determined using the Bruggeman EMA. Subsequently, the dielectric function of the Ag/ZnO interface layer was extracted directly by exact mathematical inversion of the (ψ, Δ) spectra collected by RTSE. This led to much improved fits to the RTSE data for several samples. The imaginary part of the resulting interface dielectric function, $\varepsilon_2$, shows a strong resonance at ~ 2.8 eV that is present neither in the Ag bulk layer dielectric function nor in the ZnO dielectric function. This resonance was interpreted as due to confined plasmons and was reasonably well fit using a single Lorentz oscillator. Additionally, a Drude term for the free (or intraband) electron component and a CP oscillator for the bound (or interband) electron absorption feature were required to fit the dielectric function of the Ag/ZnO interface layer throughout the photon energy range. An
interesting physical property of this interface layer is that its average thickness $d_i$ is found to correlate with the starting roughness on the Ag surface $d_s$ with extrema values of $\text{Ag/ZnO } d_i = (40, 233) \text{ Å}$ for $\text{Ag } d_s = (6, 105) \text{ Å}$, respectively. The Lorentz oscillator parameters of the plasmon band have been plotted versus the $d_s$ values of the starting Ag surface. A trend is observed in the resonance energy of the plasmon band indicating that this energy decreases as the Ag $d_s$ value increases. For the narrow range of $d_s$ investigated for a set of relatively smooth samples without macroscopic roughness, the shift is $\sim 0.2 \text{ eV}$.

When the initial surface roughness of Ag reaches the macroscopic range (as in the highest efficiency solar cell structures), a more rapid red-shift of the plasmon band may lead to resonance energies that fall in a region where it will impact solar cell quantum efficiency. In order to explore this possibility, an industry-prepared back-reflector was analyzed ex-situ by SE. This analysis resulted in 250 Å as the total thickness of interface layer and 175 Å as the ZnO surface roughness layer thickness. Such a thick interface layer implies that the starting Ag surface exhibits macroscopic roughness. The interface dielectric function for the industry back-reflector shows evidence of a lower energy absorption features, consistent with resonances due to larger isolated Ag structures in the interface layer. As the interface layer thickness increases, the separation between the plasmon and the interband transition becomes less distinct due to the broad absorption tail of the latter. Starting from the plasmon band centered at 2.9 eV in smooth films, a shift to lower energies is observed with increasing interface thickness into the macroscopic regime. This behavior is an extension of the effect observed for smoother interfaces and interpreted as resulting from an increase in the volume fraction of Ag.
protrusions in the interface layer as it increases in thickness. With increasing Ag/ZnO interface thickness, a clear trend is observed toward increasing $\varepsilon_1$ at low energies associated with the Drude component and the ultimate development of a low energy band from this component as indicated in $\varepsilon_2$.

The normal incidence reflectance spectra of the back-reflector were measured to characterize further the plasmonic effect as observed in the dielectric functions deduced by RTSE. The measured reflectance spectra cannot be modeled successfully without including an interface layer of approximately the same thickness as that deduced by RTSE. The normal incidence spectra reveal a strong minimum in the measured and simulated reflectance, which corresponds to an expected maximum in the absorbance at the plasmon resonance energy. In contrast, the simulations without the interface layer predict a very high reflectance with no absorbance feature. For relatively smooth surfaces without macroscopic roughness, this feature occurs at sufficiently high energies that no significant losses are observed in the near-infrared below ~ 1.7 eV. Thus, since the spectral range of interest for solar cell back-reflector is 1.2 to 1.8 eV, the interference enhanced plasmon absorption observed for smooth surfaces is of marginal importance as a loss mechanism in a solar cell that uses this particular back-reflector structure (i.e., for the observed intermediate $d_1$ range and associated dielectric function).

As the Ag/ZnO interface roughness increases into the macroscopic regime, however, due to a thicker initial Ag surface roughness layer, the reflectance spectrum is strongly affected. A large difference is observed in this case between the simulated and measured reflectance spectra which can be attributed to the increased level of light scattering. This light scattering can also be measured directly. The scattering studies
suggest that as the interface thickness increases into the macroscopic regime the direct scattering and re-radiation of energy absorbed by confined plasmons increases. Thus, the mechanics for optimization of back-reflectors used by industry is suggested to involve interference-enhanced localized plasmon excitation in protrusions, which can lead to efficient re-radiation observed to be as high as 65% for microstructures on the scale of the optical wavelength.

Studies of the Ag/ZnO interface demonstrate that microscopic surface and interface roughness layers are ubiquitous and exert considerable influence on the specular reflectance, the absorbance, and hence the quantum efficiency of solar cells. As an example, models of the multilayer optical structure of a triple-junction a-Si:H based solar cell in the substrate/BR/n-i-p configuration are used to simulate the absorbance within the Ag/ZnO interface layer, the reflectance spectra for the entire solar cell structure, and the current generated by the matched absorber layers. The key point observed here is that when the Ag/ZnO interface roughness layer is relatively thick, as generated by a thick initial Ag surface roughness layer, the associated dielectric function leads to stronger absorption in the range of solar cell operation. Thus the matched current from the three active layers is predicted to decrease with increasing interface thickness for two reasons. First, the increased thickness itself generates losses, and second, the greater dissipation associated with the dielectric functions of the thicker layers enhances these losses. Thus, as is well known, back-reflector design involves a trade-off between light scattering gains and absorption losses.

In Chapter 6, the focus is on a description of the effect of screening on the plasmon band energies. A problem associated with back-reflectors is the red-shift of
plasmon band at the interface of Ag/ZnO back-reflector as the surface roughness thickness on the initial Ag film increases. In fact, this band should be blue-shifted in order to mitigate plasmon absorption and dissipation in the solar cell. A blue-shift of the plasmon energies is expected if the screening effect of ZnO can be reduced.

For previously deposited Ag/ZnO back-reflectors, the effect of the dielectric function of the ambient medium on the plasmon characteristics can be explored by etching away the ZnO layer in an aqueous medium and observing possible plasmon peak energy shifts. The Ag/ZnO back-reflector samples were immersed in 300 mL of deionized water at room temperature in a pyrex cell that provides optical access to the sample surface, and 0.2 mL of hydrochloric acid (HCl) was added to form an aqueous solution with a 1:1500 HCl:H2O volume ratio. The entire etching process was monitored in real time using the same spectroscopic ellipsometer as was applied for monitoring the Ag/ZnO back-reflector depositions. Since the HCl:H2O solution does not etch Ag, the etching process naturally terminates when the ZnO is removed. This etching endpoint is early identified by RTSE.

The Ag films remaining after etching were modeled using a bulk Ag layer, a surface roughness layer, and an ambient medium of deionized water. The dielectric function of the surface layer was modeled using an analytical function consisting of a Drude term, a Lorentz oscillator, and a CP oscillator. The plasmon bands of the Ag surfaces measured after etching were modeled using the Lorentz oscillator expression. The deduced energy positions were different than those of the Lorentz oscillator associated with the Ag/ZnO interface before etching. The smoothest sample with an
initial Ag $d_s = 12 \text{ Å}$ shows a blue-shift of 0.43 eV from the value for Ag/ZnO interface when ZnO is replaced by water in the etching process.

For the thicker roughness layer ($d_s = 105 \text{ Å}$) sample, no shift in plasmon energy is observed upon removal of the ZnO and replacement by water. For the industry prepared back-reflector sample, the plasmon is blue-shifted by 0.34 eV after the etching process. The primary reason for the shift of the plasmon band to higher energy is believed to be the change in the dielectric function of the ambient material upon etching, from ZnO with $\varepsilon_a \sim 2.75\text{-}3.3$ to water with $\varepsilon_a \sim 1.8$. The lack of a blue shift for the sample with $d_i = 105 \text{ Å}$ is attributed to simultaneous densification of the surface layer upon etching. An interesting feature observed is a reduction in the amplitudes of the plasmon band upon etching for the two samples with greater initial Ag roughness. This behavior may be attributed to the overlap of the tail of the interband absorption with the plasmon band which suppresses the plasmonic behavior due to a dissipation pathway.

The normal incidence reflectance spectra were also measured before and after etching. The reflectance in the range of back-reflector operation increases significantly upon etching. In fact, the reflectance at 1.5 eV for the sample with initial Ag surface roughness of 105 Å increased from 0.5 before etching to $\sim 0.9$ after the etching process that exposes the Ag surface. Similarly, for the industry prepared back-reflector, the reflectance at 1.5 eV increased from 0.20 for Ag/ZnO before etching to $\sim 0.9$ for the Ag surface after etching. The reflectance is very weak over the corresponding high energy range for the sample before and after etching due to absorbance by the interband transitions. Also, suppression of the plasmonic characteristics and reduction of scattering appear to be the dominant effects that occur upon removal of the ZnO by etching.
7.2 Future Directions

This dissertation describes comprehensive real time and ex-situ spectroscopic ellipsometry analysis of the Ag/ZnO back-reflector and its component Ag metallic and ZnO transparent conductive oxide layers used in thin film photovoltaics. A brief discussion of future work is presented in this section as required to advance the understanding and performance of back-reflectors.

Since the starting surface roughness of Ag films determines the thickness of Ag/ZnO interface and the location of the plasmon band, increasing the surface roughness thickness beyond the range applied in this dissertation research will be helpful. Analysis of the resulting interface in similar manner as described in this dissertation will help to identify the optimum thickness and deposition parameters for improvement of the back-reflector performance.

Data analysis was found to be quite challenging in studies of Ag films with relatively thick surface roughness layers. In these studies, the dielectric functions of the surface roughness layers were modeled by a mathematical expression with the potential to vary numerous parameters. In such cases, however, it was found necessary to fix parameters to ensure convergence of the least squares regression routine. Further modeling with a larger number of samples is necessary in order to identify the parameters that should be fixed. Such samples can be generated by varying the deposition conditions or by annealing previously deposited samples. Since the annealing and temperature dependence of Ag films are measured simultaneously, the results of this dissertation suggest an improved, two-step experimental approach for such experiments in the future.
The aluminum doped zinc oxide (AZO) thin films deposited on two different types of glass substrates, soda lime and borosilicate glass, show Lorentz oscillator features in thinner samples, but not in a thicker samples. This feature appears within an energy range of 0.7-0.8 eV in as deposited samples. This energy is well below the bandgap energy, of course, and well above the energies of the vibrational modes of ZnO. Moreover, the resonance energy of the oscillator is blue-shifted upon annealing the sample. Complicating the matter is the observation that this feature is absent from AZO materials deposited on c-Si or Ag coated substrates. Further investigation is required in future in order to identify the origin of this resonance.

In studies of Ag/ZnO back-reflectors involving the etching of ZnO in an HCl:H₂O solution, the surface layer thickness after etching is much thinner than the Ag/ZnO interface layer determined before etching. The origin of the evolution from the thick interface layer to the much thinner surface layer upon etching is not clear. The reverse behavior is observed to occur upon deposition of the ZnO. This effect should be explored in future experiments with a subsequent ZnO deposition on the etched Ag surface. In conjunction with such a study, it would be helpful to explore various properties of the Ag/ZnO interface. Solar cell simulations performed with those properties will motivate fabrication of solar cell device structures in the future when simulations suggest that quantum efficiency improvements are possible.

To better understand the normal incidence reflectance spectra and the associated absorbance spectra before and after etching, scattering measurements must be carried out as part of a more comprehensive future study on a controlled set of back-reflector samples. Overall, an effective future study must involve an initial study of uncoated Ag, a
second study of Ag/ZnO structures, and a third study after etching away the ZnO. All studies must use Ag samples deposited under different conditions to achieve a range of surface roughness thicknesses from atomically smooth to macroscopically rough.
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