A Dissertation

entitled

Real Time Spectroscopic Ellipsometry Studies of
Thin Film Materials and Structures for Photovoltaic Applications

by

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Spectroscopic ellipsometry (SE) is a powerful tool to characterize multilayered thin films, providing structural parameters and materials optical properties over a wide spectral range. Further analyses of these optical properties can provide additional information of interest on the physical and chemical properties of materials. In situ real time SE (RTSE) combines high surface sensitivity with fast data acquisition and non-destructive probing, thus lends unique insights into the dynamics of film growth.

In this thesis, the methods of SE have been applied to investigate the growth and properties of material components used in the major thin film photovoltaic technologies, including cadmium telluride (CdTe), hydrogenated silicon (Si:H), and copper indium-gallium diselenide (CIGS). The magnetron sputtering of polycrystalline CdTe, CdS, and CdTe$_{1-x}$S$_x$ thin films has been studied by RTSE. The growth rate, nucleation behavior, evolution of surface roughness, and development of void structures in CdTe and CdS show strong variations with deposition temperature and Ar pressure. The complex
dielectric functions $\varepsilon$ of CdTe and CdS films also sensitively depend on preparation conditions. In-depth analyses of $\varepsilon$ provide consistent estimates of temperature, excited carrier mean free path, group speeds of excited carriers, and intrinsic stress in the films. Thus, SE has the potential to monitor not only film thickness, but also materials properties on a solar cell production line. Major SE analyses results are compared with other characterization techniques, including atomic force microscopy and X-ray diffraction. RTSE has been applied to establish deposition phase diagrams that describe very high frequency plasma enhanced chemical vapor depositions for Si:H thin films on various substrates. Close correlations between RTSE results and solar cell performance have been observed. Finally, \textit{ex situ} SE has provided $\varepsilon$ for a novel In$_2$S$_3$ window layer used in CIGS technology which can then be applied in quantum efficiency simulations.

Significant generalizations from previous studies have been achieved for the study of a dual rotating compensator ellipsometer system. Computer software was developed to verify the generalized approach, to simulate the operations of such a system under non-ideal conditions, and to predict the best hardware design, experimental configuration, and data reduction strategies.
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5-1 (left) A graded sample structure approximated as an opaque multilayer that reflects the incident light at an angle of incidence $\theta$ and generates the ellipsometric angles $(\psi, \Delta)$. (right) An ambient/substrate structure that generates the same $(\psi, \Delta)$ values with a hypothetical dielectric function called the “pseudo-dielectric function” and labeled $(<\varepsilon_1>, <\varepsilon_2>)$.

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5-3 Experimental apparatus for the development of PECVD phase diagrams and their...
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Contour lines in the crystallite volume fraction $f_{\mu c}$ are also plotted. This figure was reproduced from (Stoke, 2008) with permission of the author.

5-7 Open circuit voltage ($V_{oc}$, upper left), efficiency ($\eta$, lower left), fill factor (FF, upper right), and short circuit current ($J_{sc}$, lower right) versus the hydrogen dilution ratio $R$ used for the intrinsic Si:H layer in the fabrication of vhf PECVD Si:H solar cells. These solar cells are incorporated into multijunction devices as the top cell. This figure was adapted from (Stoke, 2008) with permission of the author.

5-8 (a, top) Microcrystalline volume fraction in the top 10 Å of the bulk layer plotted versus the i-layer deposition time for identically-prepared R=100 Si:H i-layers on e-Si/(native-oxide) substrates over-deposited with either an a-Si:H n-layer or a nc-Si:H n-layer. (b, bottom) RTSE-determined surface roughness layer thickness plotted versus the i-layer deposition time for the samples of (a). This figure was adapted from (Cao, 2008) with permission of the author.

5-9 The initial dark and light J–V characteristics for the R=100 vhf PECVD $\mu$c-Si:H solar cell fabricated on a (stainless steel)/Ag/ZnO back-reflector over-deposited
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5-10 External quantum efficiency (QE) for R=100 vhf PECVD $\mu$c-Si:H solar cells with identical i-layer growth conditions and fabricated using either a nc-Si:H or an $a$-Si:H n-layer. Results are shown for the QE in the initial state as well as after 1000 h light soaking. This figure was adapted from (Cao, 2008) with permission of the author.

5-11 The initial dark and light J–V characteristics for vhf PECVD $\mu$c-Si:H solar cells fabricated with R=105 i-layers on (stainless steel)/Ag/ZnO back reflectors over-deposited with: (a, upper left panel) an $a$-Si:H n-layer; (b, lower panel) a nc-Si:H n-layer; and (c, upper right panel) an $a$-Si:H n-layer coated with 15 nm nc-Si:H seed layer. The i-layer thickness is ~ 1.2 $\mu$m for all cells. This figure was adapted from (Cao, 2008) with permission of the author.

5-12 Dielectric functions (a, top) at the deposition temperature of 190°C and (b, bottom) after cooling to 15°C for CdTe$_{1-x}$S$_x$ alloy thin films prepared by co-sputtering using different CdS and CdTe target rf powers to achieve different values of x.
5-13 Composition profiles $x(d_b)$ in CdS$_{x}$Te$_{1-x}$ for depositions at $T_d = 190^\circ$C for CdTe on CdS (a, top) and CdS on CdTe (b, bottom). Also shown in each panel is the optical model used for virtual interface analysis.

6-1 An optical system consisting of two bi-plate compensators with retardance values of $\delta_1$ and $\delta_2$. The fast axis of the second bi-plate is oriented at 45º relative to the first. The dashed lines denote the fast and slow axes of the second bi-plate.

6-2 (a, top) MgF$_2$ index of refraction for the ordinary wave ($n_o$) and the extraordinary wave ($n_e$); (b, bottom) deduced retardances of the individual bi-plate compensators described by Johs et al. (2001).

6-3 (a, top) Optical rotation; (b, center) effective compensator azimuthal angle; and (c, bottom) effective compensator retardance for the dual bi-plate system shown in Fig. 6-1 assuming the parameters reported by Johs et al. (2001). These results were calculated from Eq. (6.7) and the deduced retardance values for the individual
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6-4 Development sequence of multichannel ellipsometers: (a, top) the first generation using a rotating polarizer and no compensator; (b, middle) the second generation using a rotating compensator after the sample; (c, bottom) the third generation using dual compensators, one on each side of the sample, rotating at different angular frequencies. This figure was adapted from (Collins et al., 2000) with permission of the authors.

6-5 Flowchart for the systematic determination of 15 Mueller matrix elements from 24 distinct Fourier coefficients of the irradiance waveform in dual-rotating compensator ellipsometry.

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6-7 Average magnitude of the errors (left scale) in the real and imaginary parts of the cross-polarization complex amplitude reflection ratios $\rho_{sp}$ and $\rho_{ps}$ plotted as functions of the common compensator retardance for random noise in the detector given by $|\delta I(t)/I(t)| \leq 0.005$, assuming a dual-rotating compensator multichannel ellipsometer with a 5:3 rotation frequency. In converting Fourier coefficients to
Mueller matrix elements, the lowest frequency options are used. Two different methods of extracting the real and imaginary parts of $\rho_{sp}$ and $\rho_{ps}$ from the Mueller matrix elements are employed as indicated. The magnitude of the errors as a percentage of the signal appears on the right scale.

6-8 Average magnitude of the errors (left scale) in the real and imaginary parts of $\rho_{sp}$ and $\rho_{ps}$, and the same errors as percentages of the signal (right scale), both plotted versus compensator retardance analogous to Fig. 6-7. In converting Fourier coefficients to Mueller matrix elements, the highest frequency options are used. Two different methods of extracting the real and imaginary parts of $\rho_{sp}$ and $\rho_{ps}$ from the Mueller matrix elements are employed.

6-9 Average magnitude of the errors (left scale) in the real and imaginary parts of the cross-polarization complex amplitude reflection ratios $\rho_{sp}$ and $\rho_{ps}$ plotted as functions of compensator retardance as in Figs. 6-7 and 6-8, but for systematic errors due to rotating compensator misalignments. In converting Fourier coefficients to Mueller matrix elements, the low frequency options are used. The errors as percentages of the signal are shown on the right scale (right scale).
Chapter 1

Introduction

1.1 Background and motivation

As the problem of global climate change is causing increasing worldwide concern, renewable energies, including solar cells based on the photovoltaic effect, have become key fields of research at the forefront of science and technology. Progress in the field of photovoltaics has led to an emerging market for solar modules on a scale unimaginable before, a scale that could potentially involve most roof tops. This huge thrust in the industrialization and commercialization of solar modules in turn drives research for new technologies with higher efficiency and lower cost.

Traditional solar cells are based on single crystal materials, such as crystalline (c) silicon (c-Si) and c-GaAs, grown through costly processes such as the Czochralski method and molecular beam epitaxy (MBE). Single crystal ingots are difficult to cut and process, and each solar cell uses high purity materials which, in the case of c-Si, are subject to price fluctuations due to supply. As a result, the manufacturing cost of these so-called 1st generation solar modules are relatively high to compete effectively with conventional sources of electricity in large scale utility markets without subsidization.
In recent years, thin film technologies have drawn considerable attention. This 2nd generation of solar cells is based on thin film materials, such as cadmium telluride (CdTe), hydrogenated silicon (Si:H), and copper indium-gallium diselenide (CuIn_{1-x}Ga_xSe_2 or CIGS). These solar cell materials are fabricated through simpler processes such as magnetron sputtering, close space sublimation (CSS), plasma enhanced chemical vapor deposition (PECVD), and multi-source evaporation which are suitable for large scale automated production. The thicknesses of the films used in these solar cells are at least an order of magnitude smaller than those in c-Si cells. As a result, although thin film cells have relatively lower conversion efficiencies, they can be manufactured at much lower costs. Additional details can be found in (Luque and Hegedus, 2003).

Although thin film materials for solar cells have obvious potential advantages including low cost, they have well known drawbacks as well. The amorphous, nanocrystalline, or polycrystalline nature of these thin film materials requires significant effort in optimization of the growth procedure and often it is difficult to identify the resulting basic film properties that serve as an indicator of solar cell performance. As an example, CdTe has the potential to serve as excellent solar cell material as its ~1.5 eV band gap closely matches the optimum value for the photon absorber in a photovoltaic device (Green, 1982; Zdanowicz et al., 2005). Magnetron sputtering is of great interest for the deposition of thin film CdTe, and this technology has been exploited in efficient polycrystalline CdS/CdTe heterojunction solar cells (Gupta and Compaan, 2004) with the advantage of low processing temperatures. Sputtering is notoriously difficult for
electronic materials fabrication, however, due to the high density defects in deposited films, especially at or near grain boundaries in the fine grained materials. The grain size of deposited materials and hence their optical and electronic properties, can also vary significantly, depending on the deposition conditions and even on the film thickness (see Sections 4.3 and 4.5).

In thin film materials used in photovoltaics, the variation of material properties with film thickness poses special challenges. For example, in plasma enhanced chemical vapor deposition of Si:H, the thin film material may nucleate in the amorphous phase (a-Si:H) and then evolve gradually into the nanocrystalline phase (nc-Si:H), or vice versa depending on the substrate. The resulting amorphous-to-nanocrystalline (a → nc) and nanocrystalline-to-amorphous (nc → a) transition thicknesses depend on growth parameters such as hydrogen dilution flow ratio, substrate temperature, gas pressure, and plasma power (see Section 6.2). Small variations in any of these parameters could potentially determine the success or failure of the solar cell device. Therefore, in situ, real time analyses of photovoltaic thin films are important in general owing to the insights they provide into the structural evolution. This includes the evolution of thickness and surface roughness, void fraction, grain size, crystalline phase, and stress and their correlations with the ultimate film and device properties. Such insights can be used to control multi-step processing and to optimize interface, bulk, and surface properties separately for high performance cells. Thus, optimization can be based on an in-depth understanding of the process, rather than by trial-and-error.
A powerful real time approach relies on spectroscopic ellipsometry (SE), which requires optical access to the film surface at the desired angle of incidence and operates passively from ultrahigh vacuum to atmospheric pressure. The spectral dependence of the p-to-s complex amplitude reflection ratio, defined by $r_p/r_s = \tan \psi \exp(i\Delta)$, provides information on the multilayer film structure and on the complex dielectric functions of the layer components, the latter in turn lending insights into other important properties of these components. The phase angle $\Delta$ from SE data provides monolayer sensitivity to the thickness of ultrathin films. This makes SE a preferred method to accurately determine a film’s thickness and/or a material’s optical properties, including both the index of refraction and extinction coefficient. The problem of material property variations with film thickness can be studied effectively by the development of in situ real time SE (RTSE), which is capable of determining the evolution of the layered structure and layer properties. The extremely high surface sensitivity of SE, combined with in situ real time probing capabilities, makes RTSE a unique tool that has been widely used in thin film technologies. In the field of thin film photovoltaics, RTSE was first successfully applied for optimization of PECVD process for a-Si:H and nc-Si:H based solar cells and is now being applied more broadly to study CdTe and CIGS based solar cells, for optimization of magnetron sputtering, hybrid deposition methods, and post-deposition annealing processes (Collins et al., 2003).
1.2 Thesis structure

In this Thesis, Chapter 1, Section 1.1 introduced thin film photovoltaic technologies, and the motivation for applying spectroscopic ellipsometry in this field, whereas this Section provides a chapter-by-chapter list of the Thesis structure.

Chapter 2 will introduce the basic concepts and principles of ellipsometry in Sections 2.1–2.5. This introduction includes the concept and mathematical description of polarization and the modulation of polarization state upon transmission through or reflection from an optical system, applying the Jones vector and the Jones matrix formalism as well as the Stokes vector and the Mueller matrix formalism. Also addressed in these Sections include the generic structure of ellipsometers, the specific experimental apparatus, and the operational principles of ellipsometers. After introducing the basic concepts and hardware designs, Section 2.6 covers the primary data analysis strategies used to deduce film structure, structural evolution, and optical properties of static and growing materials from SE and RTSE data. An example is given in Section 2.7 that demonstrates ex situ data analysis on a static sample related to CIGS solar cells.

In Chapter 3, the application of RTSE is demonstrated for analysis of the structural evolution in thin film deposition, including bulk layer thickness and surface roughness evolution, nucleation and clustering (growth modes), void development, and the effective growth rate. Four series of depositions with different process variables are analyzed: (1) magnetron sputtering of CdTe versus deposition temperature; (2) magnetron sputtering of CdS versus deposition temperature; (3) magnetron co-sputtering of CdTe$_{1-x}$S$_x$ versus
composition, and (4) magnetron sputtering of CdTe versus Ar pressure. The large variation in surface roughness observed in the samples of series (4) above makes it possible to correlate SE surface roughness with AFM surface roughness. In fact, a clear linear correlation in surface roughness thickness is obtained. AFM images also show consistent variation in surface morphology versus Ar pressure, which can be used to understand the optimum pressure based on the cell performance.

Chapter 4 provides a discussion of the complex dielectric functions of the thin film materials and their variations with the physical properties. The parabolic band model for the semiconductor critical point is used to parameterize the dielectric functions of the series of CdTe and CdS films. From the systematic variations of the parameters, other important material properties can be estimated including carrier mean free path or grain size, in-plane stress, and temperature. Grain size estimation techniques are compared including SE, atomic force microscopy, and X-ray diffraction. In this Chapter, SE analysis of the stepwise etching of a CdCl₂ treated CdTe/CdS solar cell is presented as a demonstration of the potential of SE as the basis of an online scanning system for quality monitoring in manufacturing. Characteristics of the critical points in the dielectric function of differently-processed CdTe are also compared.

The topics of Chapter 5 include the continuous evolution of phase and chemical composition with film thickness. These changes in material properties require a more sophisticated approach than those described in Chapter 4. In this case the virtual interface approximation is a suitable approach for the analysis of RTSE data. Section 5.1
includes a description of the basic approximations of the virtual interface model. The best known example of this analysis strategy is presented in Sections 5.2 and 5.3, namely, the development of deposition phase diagrams for PECVD Si:H films. In Section 5.4, a similar approach is described for the investigation of atomic inter-diffusion at the CdTe-CdS interface when sputtering one of the two materials on top of the other.

In Chapter 6, explorations at the frontiers of advanced SE instrumentation are described. First, a Jones matrix approach is developed to explain the design and function of a dual bi-plate optical system intended for weakly achromatic retardance. Second, the theoretical principles of an advanced dual rotating compensator ellipsometer system is established for measuring a sample’s full 4x4 Mueller matrix. Several generalizations are possible in broad analytic expressions, including an arbitrary ratio of rotation frequencies and dichroic effects for both rotating compensators. Computer software was developed, initially to verify the generalized instrument analysis, and subsequently to simulate the operation of a generalized dual rotating compensator ellipsometer system under non-ideal conditions, predicting the best hardware design, experimental apparatus, and data reduction strategies.

Chapter 7 summarizes the main observations made and conclusions drawn in the previous Chapters. As the science and technology of thin film photovoltaics is expanding greatly, inevitably there are phenomena, capabilities, and applications of SE yet to be explored. Examples of these are presented in a final Section that describes the future work.
Chapter 2

Basic Concepts and Principles of Real Time Spectroscopic Ellipsometry

2.1 The polarization state of light

Polarization refers to the time evolution of one of the field vectors that describes the light wave, observed at a fixed point in space. For light waves, there are four possible field vectors that can be used to describe polarization:

\[ E \]: electric field;
\[ D \]: displacement field;
\[ B \]: magnetic induction;
\[ H \]: magnetic field.

\( E \) and \( D \) describe the electric forces on the medium within which the wave propagates, whereas \( B \) and \( H \) describe the magnetic forces. If ferromagnetic materials are not considered, which is the case for this Thesis research, then either \( E \) or \( D \) is selected to represent the polarization state since the electric force \( F_E = qE \) on a charge \( q \) in the medium is dominant over the magnetic force \( F_M = qvB = qvE/c \) for charged particle velocities \( v \ll c \). In studies of wave propagation in isotropic media in which case \( D \) and \( E \) are parallel, the electric field \( E \) is selected to describe the state of polarization. The time
evolution of each of the other field vectors is determined from Maxwell’s Equations and the constitutive relations.

2.2 The Jones vector and the Jones matrix formalism

The plane wave solutions of Maxwell’s Equations in a uniform isotropic medium have the form (Jackson, 2001):

\[ E(z, t) = [E_{0x} \cos(\omega t - kz + \delta_x) \mathbf{u}_x + E_{0y} \cos(\omega t - kz + \delta_y) \mathbf{u}_y] \exp(-\alpha z/2), \]  

(2.1)

where the propagation direction is along the z axis; \( \mathbf{u}_x \) and \( \mathbf{u}_y \) are the two orthogonal unit vectors along the x and y axes, respectively, that form a right handed Cartesian coordinate system along with the z axis; \( E_{0x} \) and \( E_{0y} \) are the amplitudes of the electric field along the x and y axes, respectively; \( \omega \) is the angular frequency of the light wave; \( k \) is the magnitude of the wave vector \( \mathbf{k} \) which is also along z axis; \( \delta_x \) and \( \delta_y \) are the phase angles of oscillation along x and y axes, respectively; \( \alpha \) is the absorption coefficient of the medium that reduces the light irradiance exponentially along the propagation direction. The group velocity of light wave inside the medium is given by

\[ v = k/\omega = 2\pi/(\lambda \omega) = c/n, \]

where \( \lambda = 2\pi/k \) is the wavelength in vacuum, \( c \) is the speed of light in vacuum, and \( n \) is the index of refraction of the medium. Both \( n \) and \( \alpha \) are functions of \( \omega \) due to the dispersion of the medium. A frequently used alternative way of describing a medium’s optical properties is the complex dielectric function \( \varepsilon = \varepsilon_1 + i\varepsilon_2 \), where the real and imaginary parts are given as functions of \( n \) and \( \alpha \) by \( \varepsilon_1 = n^2 - [\lambda \alpha/(4\pi)]^2 \) and \( \varepsilon_2 = n \lambda \alpha/(2\pi) \).

The dielectric function \( \varepsilon \) is a more fundamental property that relates the \( E \) and \( D \) fields.
according to $D = \varepsilon_0 \varepsilon E$, where $\varepsilon_0$ is the permittivity of vacuum and $\varepsilon$ is also referred to as the relative permittivity of the medium.

Equation (2.1) can also be expressed in column vector notation:

$$
\begin{pmatrix}
E_x(z, t) \\
E_y(z, t)
\end{pmatrix} =
\begin{pmatrix}
E_{0x} \cos(\omega t - k z + \delta_x) e^{-\alpha z/2} \\
E_{0y} \cos(\omega t - k z + \delta_y) e^{-\alpha z/2}
\end{pmatrix}.
$$

(2.2)

Then, phasor notation can be used to simplify Eq. (2.2):

$$
\begin{pmatrix}
E_{0x} e^{-ikz} e^{-\alpha z/2} e^{i\delta_x} \\
E_{0y} e^{-ikz} e^{-\alpha z/2} e^{i\delta_y}
\end{pmatrix} = e^{-ikz} e^{-\alpha z/2} \begin{pmatrix}
E_{0x} e^{i\delta_x} \\
E_{0y} e^{i\delta_y}
\end{pmatrix}.
$$

(2.3)

It is to be noted that the time dependent part of the wave $\exp(i\omega t)$ is removed in the phasor notation. The true field can be restored by multiplying each field component phasor by $\exp(i\omega t)$ and then taking the real part.

It can be shown (Azzam and Bashara, 1977) that at any fixed point $(x, y, z)$ in space, the end point of the electric field described by Eqs. (2.1 ~ 2.3) sweeps out an ellipse in the most general situation. This ellipse is located within the x-y plane with a tilt angle $Q$ relative to the x axis and an ellipticity $e$ defined by the ratio of the semi-minor axis to the semi-major axis. The handedness (right or left) of the polarization state is determined by the rotation direction (clockwise or counterclockwise) of the electric field vector when viewing the beam from the detector. With this convention, the ellipticity $e$ is assigned a positive value for right handed polarization, and a negative value for left handed polarization. The prefactor $e^{-ikz} e^{-\alpha z/2}$ in Eq. (2.3) describes the absolute phase and amplitude of the electric field, which are of little or no interest in ellipsometry. So $Q$
and \(e\) (including its sign) uniquely define the polarization state (ignoring the absolute phase and amplitude). It can be proved (Azzam and Bashara, 1977) that the complex vector in Eq. (2.3) 
\[
\begin{pmatrix}
E_0 x e^{i\delta_x} \\
E_0 y e^{i\delta_y}
\end{pmatrix}
= \begin{pmatrix}
\tilde{E}_x \\
\tilde{E}_y
\end{pmatrix},
\]
which is called the Jones vector, also uniquely defines the polarization state (again ignoring the absolute phase and amplitude). Relationships can be derived between the shape parameters \(Q\) and \(e\) and the phasor parameters \(E_{oy}/E_{ox}\) and \(\delta_y - \delta_x\).

In the case of linear optics, which is of relevance in this Thesis, the function of a component of an optical system in modifying the polarization state of light can be fully described by a 2x2 complex Jones matrix. This matrix left multiplies the Jones vector of the incident light to generate the Jones vector of the output light:

\[
\tilde{E}^o = \tilde{E}^i J \\
\tilde{E}^o = \begin{pmatrix}
\tilde{E}_x^o \\
\tilde{E}_y^o
\end{pmatrix} = \begin{pmatrix}
J_{11} & J_{12} \\
J_{21} & J_{22}
\end{pmatrix} \begin{pmatrix}
\tilde{E}_x^i \\
\tilde{E}_y^i
\end{pmatrix}.
\] (2.4)

The Jones vectors of some special polarization states, the Jones matrices of some frequently used polarization modifying optical system components, as well as the Jones matrix for a coordinate rotation operation all can be found in Azzam and Bashara (1977).

2.3 The Stokes vector and the Mueller matrix formalism

The Jones vector and matrix formalism has the advantage of being concise but the disadvantage of being able to describe only completely polarized light, or light of a single definite polarization state. Thus, the Jones vector and matrix formalism is not sufficiently powerful to describe (i) unpolarized light, which includes a mixture of completely
random polarization states, (ii) partially polarized light, which includes a component with a single polarization state and another component with a random mixture of polarization states, or (iii) depolarizing optical systems that act to randomize a component of the polarization state of light. To deal with these challenges, the Stokes vector and the Mueller matrix formalism is introduced.

A **Stokes vector** is a 4x1 real column vector defined operationally as:

\[
\vec{S} = \begin{pmatrix}
S_0 \\
S_1 \\
S_2 \\
S_3
\end{pmatrix} = \begin{pmatrix}
I_0 \\
I_x - I_y \\
I_{\pi/4} - I_{-\pi/4} \\
I_R - I_L
\end{pmatrix}.
\]  

where \(I_0\) is the total light irradiance including all polarization states; \(I_x\) and \(I_y\) are the irradiance of the components of light that are linearly polarized along x and y directions respectively; \(I_{\pi/4}\) and \(I_{-\pi/4}\) are the irradiance of the components of light that are linearly polarized along \(\pi/4\) and \(-\pi/4\) (radians) relative to the x axis respectively; and \(I_R\) and \(I_L\) are the irradiance of the components of light that are right and left circularly polarized, respectively. Note that \(I_0 = I_x + I_y = I_{\pi/4} + I_{-\pi/4} = I_R + I_L\). If a beam of light is completely polarized, it can be shown that \(S_0^2 = S_1^2 + S_2^2 + S_3^2\). Otherwise \(P\) is the degree of polarization defined such that \(P = [(S_1^2 + S_2^2 + S_3^2)/S_0^2]^{1/2} < 1\). This quantity describes the fraction of irradiance with a single polarization state, and thus \(1 - P\) is the fraction of irradiance that is completely unpolarized.

Within the Stokes vector formalism, the function of a system optical component in modifying the polarization state of light can be described fully by a 4x4 real **Mueller**
matrix that left multiplies the Stokes vector of the incident light beam to generate the Stokes vector of the output light beam:

\[
\begin{pmatrix}
S'_0 \\
S'_1 \\
S'_2 \\
S'_3
\end{pmatrix}
= \begin{pmatrix}
M_{11} & M_{12} & M_{13} & M_{14} \\
M_{21} & M_{22} & M_{23} & M_{24} \\
M_{31} & M_{32} & M_{33} & M_{34} \\
M_{41} & M_{42} & M_{43} & M_{44}
\end{pmatrix}
\begin{pmatrix}
S_0^i \\
S_1^i \\
S_2^i \\
S_3^i
\end{pmatrix}.
\] (2.6)

The Stokes vectors of some special polarization states, the Mueller matrices of some frequently used polarization modifying optical components, and the Mueller matrix for a coordinate rotation operation can be found in Azzam and Bashara (1977) and Chen et al. (2003). The transformation between the Jones and Mueller matrix formalisms has been described by Azzam and Bashara (1977).

The Stokes vector and the Mueller matrix formalism greatly broadens the applications of spectroscopic ellipsometry, enabling the inclusion of scattering and other depolarizing effects (for example, see Chen et al., 2005). The specific ways of measuring, manipulating, and understanding the Mueller matrix of a sample define the frontiers of research in ellipsometry. Research of this nature will be discussed in Chapter 6.

2.4 The reflection from a sample surface

In the most widely used geometry for ellipsometry, polarized incident light is specularly reflected from a sample surface. Ellipsometry in the transmission geometry is also used, but much less widely. The configuration for the reflection ellipsometry
measurements is shown schematically in Fig. 2-1. Here the propagation direction of the incident and reflected light beams form a plane of incidence that is perpendicular to the plane of the sample surface. A natural coordinate system is shown in the figure, with \( \vec{s} \) oriented perpendicular to the plane of incidence and \( \vec{p} \) lying within the plane of incidence. If the multilayered sample does not exhibit a depolarizing effect, the polarization modification that it imposes upon reflection of the beam can be described with a Jones matrix \( \tilde{J} \) where:

**Figure 2-1.** Reflection of a polarized light beam from the surface of a sample having a multilayer structure. The \( \vec{s} \) and \( \vec{p} \) directions of both the incident and reflected light beams are identified. The incident light beam is described by a Jones vector \( \tilde{E}^i \) and the reflected (outgoing) light beam is described by a Jones vector \( \tilde{E}^o \). The reflecting sample is described by a Jones matrix \( \tilde{J} \).
Here the notation \( \tilde{r}_{ij} \) \((i, j = p, s)\) is used instead of \( \tilde{J}_{ij} \) to emphasize the fact that \( \tilde{r}_{ij} \) is actually the \( j \)-to-\( i \) complex amplitude reflection coefficient for the electric field. As stated earlier in this chapter, the absolute phase and amplitude of a polarization state are of little or no interest in ellipsometry. Thus, the sample’s Jones matrix can be rewritten without loss of information as:

\[
\tilde{J} = \begin{pmatrix} \tilde{\rho}_{pp} & \tilde{\rho}_{ps} \\ \tilde{\rho}_{sp} & 1 \end{pmatrix},
\]

where \( \tilde{\rho}_{ij} = r_{ij} / r_{ss} \equiv \tan \psi_{ij} e^{i\Delta_{ij}} \) is the ratio of complex reflection coefficients and generally describes the quantities of interest. The relative amplitude and phase change parameters \( \psi_{ij} \) and \( \Delta_{ij} \) are called ellipsometric angles. If the reflecting sample is isotropic, the \( p \) component will be reflected only into the \( p \) direction and the \( s \) component will be reflected only into the \( s \) direction, i.e., linear \( p \) and \( s \) waves are the eigen modes. Thus, the off-diagonal elements of \( \tilde{J} \) become 0, and the only quantity of interest is \( \tilde{\rho}_{pp} \), which is simply denoted \( \tilde{\rho}_{pp} = \tilde{\rho} = r_{pp} / r_{ss} = \tan \psi \ e^{i\Delta} \). It is the phase change parameter \( \Delta \) that gives ellipsometry its extremely high sensitivity to film thicknesses, in fact, at the \( \sim 0.1 \) Å level. In the Stokes vector and the Mueller matrix formalism, the operation of reflection from a sample surface can be described by a reflection Mueller matrix that contains information about the sample properties. Such examples will be given in Chapter 6.
2.5 Instrumentation and experimental setup

A schematic of the ellipsometer (M2000-DI by J. A. Woollam Company) and the sputter chamber used in this research is shown in Fig. 2-2.

In the lower right corner of Fig. 2-2, the polarization generation and modulation components of the ellipsometer are depicted. These consist of a tandem light source (deuterium and quartz tungsten halogen) and its collimator (not shown), a fixed polarizer, and a rotating compensator. The polarization detection components of the ellipsometer are shown in the lower left corner. They consist of a fixed analyzer and an irradiance detector. A computer analyzes the detector output and calculates and stores spectra in $(\psi, \Delta)$. 

Figure 2-2. A schematic of the ellipsometer and the sputter chamber used in this study. The polarization generation and modulation components of the ellipsometer are shown in the lower right corner. These components consist of a dual light source and its collimator (not shown), a fixed polarizer, and a rotating compensator. The polarization detection components of the ellipsometer are shown in the lower left corner. They consist of a fixed analyzer and an irradiance detector. A computer analyzes the detector output and calculates and stores spectra in $(\psi, \Delta)$. 

$\frac{r_p}{r_s} = \tan \psi e^{i \Delta}$
degree of polarization (~ 0.99999), and the compensator generates a phase difference \( \delta \) (called retardance) between the two orthogonal components of the fields aligned along its fast and slow axes. The lower left corner of Fig. 2-2 depicts the polarization detection part of the ellipsometer, consisting of a fixed analyzer (denote “A”) which is simply another linear polarizer. In fact, this component is called an “analyzer” instead of a “polarizer” because it is on the polarization analysis and detection side of the ellipsometer. An irradiance detector is the final component of the polarization detection side of the ellipsometer, consisting of an InGaAs photodiode array and a Si charge coupled device designed to cover a wide spectral range (photon energies of 0.75 to 6.5 eV with 706 spectral points).

In this PCrSA ellipsometer configuration (“S” denotes the sample), the compensator continuously rotates at an angular frequency of \( \omega_C \) (not to be confused with the angular frequency of the light wave itself as defined in Section 2.2). The net effect is a modulation of the polarization state of the light incident on the sample. As a result, the irradiance of light entering the detector has an optical period of \( 2\omega_C \). A computer is utilized for waveform analysis of the irradiance to determine the \( 2\omega_C \) and \( 4\omega_C \) Fourier coefficients, from which \( \psi \) and \( \Delta \) of the sample can be calculated. This analysis requires information from a system calibration that must be performed before the measurement. The \( \psi \) and \( \Delta \) data are saved as a function of photon energy for later processing in terms of sample information. If the sample is changing over time and real time SE is performed, then the \( \psi \) and \( \Delta \) spectra are each collected as an array versus time. In the ellipsometer
system used in this study, $\omega_c$ is set at $\sim 190$ \text{rad/s}, corresponding to a rotation frequency of the compensator of $\sim 30$ \text{Hz}. For a compensator, a rotation of $180^\circ$ generates the minimum optical cycle because of the symmetry of the device (Azzam and Bashara, 1977). Thus, it is possible to collect full spectra in $(\psi, \Delta)$ over the full range of $0.75 \rightarrow 6.5$ eV within $\sim 17$ \text{ms}. If the method of zone averaging is adopted (Azzam and Bashara, 1977), then at least two optical cycles are needed to acquire full spectra in $(\psi, \Delta)$. The shortest data acquisition time achieved here ($\sim 17$ \text{ms}) enables real time measurement with single monolayer resolution at growth rates up to $\sim 100$ Å/s. If the deposition rate is not extremely high ($\leq 10$ Å/sec), it is preferred to use longer data acquisition times so that the data acquisition system can average over at least $\sim 10$ optical cycle pairs to generate data with improved signal-to-noise ratio, as long as monolayer resolution is maintained.

The stress free fused silica windows on the chamber walls in Fig. 2-2 are used to allow optical access while minimizing polarization modification due to built in stress. The calibration process used here can correct the data for weak polarization modification effects. Additional discussion on the principles of ellipsometers can be found in texts by Azzam and Bashara (1977) as well as by Tompkins and Irene (2005).

### 2.6 Data analyses strategies

In the experiments performed in this Thesis, the pair of SE spectra consists of 1412 measured quantities, or 706 pairs of ellipsometric angles $(\psi, \Delta)$, over the 0.75--6.5 eV spectral range. The quantities sought include structural parameters and optical properties,
namely thicknesses and complex dielectric functions of one or more layers in a multilayer thin film sample. Here, the thicknesses are independent of photon energy whereas the dielectric functions may have a known analytical form that is dependent on photon energy (Collins and Ferlauto, 2005). Usually it is preferred to determine the appropriate form as part of the data analysis rather than to assume a specific analytical form prior to data analysis. Thus, it is preferred to let the 1412 parameters, namely 706 pairs associated with a single \( (\varepsilon_1, \varepsilon_2) \) over the 0.75 ~ 6.5 eV spectral range, vary independently rather than forcing them to assume some specific functions of photon energy or wavelength. With this method, it would appear to be impossible to determine both thicknesses and optical properties simultaneously from a single pair of spectra of \( (\psi, \Delta) \) because the number of unknown quantities is larger than the number of measured quantities.

In order to elucidate the general data analysis problem just described, Fig. 2-3 depicts the multi-layer structure for the sample of Fig. 2-1. Here it is assumed that the sample has \( m \) layers of different materials, whose thicknesses are enumerated from \( d_1 \) to \( d_m \) with respective complex dielectric functions \( (\varepsilon_1, \varepsilon_2)_1 \) to \( (\varepsilon_1, \varepsilon_2)_m \). The ambient is denoted with the subscript 0 and the substrate is denoted with the subscript \( m+1 \), with dielectric functions \( (\varepsilon_1, \varepsilon_2)_0 \) and \( (\varepsilon_1, \varepsilon_2)_{m+1} \), respectively. If all of the following are known: (1) the thicknesses \( d_1, d_2, \ldots, d_m \); (2) the dielectric functions \( (\varepsilon_1, \varepsilon_2)_0, (\varepsilon_1, \varepsilon_2)_1, (\varepsilon_1, \varepsilon_2)_2, \ldots, (\varepsilon_1, \varepsilon_2)_m, (\varepsilon_1, \varepsilon_2)_m+1; \) and (3) the angle of incidence \( \theta \), then \( (\psi, \Delta) \) of the sample can be uniquely determined over the entire spectral range. The calculation is performed using the scattering matrix method (Azzam and Bashara, 1977) which is valid as long as the optical...
path length $L$ in a single reflection is much less than the coherence length of the light wave (Born and Wolf, 1997). (Here $L$ is given by $L = \frac{2}{\cos \theta_j} \sum_{j=1}^{m} n_j d_j / \cos \theta_j$, where $n_j$ is the index of refraction of the $j$th layer and $\theta_j$ is the angle of transmission in layer $j$.) If $L$ is on the order of or larger than the coherence length incoherent sums of light irradiance must be considered instead of coherent sums of field vectors, thus causing a depolarization effect.

If all of the above information is known except for the thickness and optical properties of the $j$th layer ($1 \leq j \leq m$) -- which is the information sought by SE, then a single pair of SE

Figure 2-3. A reflecting sample with $m$ thin film layers. The ambient is denoted by the subscript 0, and the substrate is denoted by the subscript $m+1$. The angle of incidence at the 0-1 interface is $\theta$. The angle of transmission in the $j$th layer ($1 \leq j \leq m$) is $\theta_j$. The $j$th layer has a thickness $d_j$ and a complex dielectric function $(\varepsilon_1, \varepsilon_2)_j$. 
spectrum \((\psi, \Delta)\) would appear insufficient because the total number of unknown parameters, 1413 which includes 706 pairs of \((\varepsilon_1, \varepsilon_2)\) plus \(d_j\), is larger than the total number of measured quantities – 1412. Several approaches can be used to solve this problem:

First, \(d_j\) is fixed at an estimated value. With \(d_j\) fixed, the number of unknown parameters is the same as the number of measured quantities. Under these conditions, it should be possible to determine all 706 pairs of \((\varepsilon_1, \varepsilon_2)\) exactly through numerical inversion of the non-linear equations. This procedure is called inversion because mathematically it is simply a transformation between 706 pairs of \((\psi, \Delta)\) and 706 pairs of \((\varepsilon_1, \varepsilon_2)\) related through the scattering matrix elements (Azzam and Bashara, 1977). The inverted 706 pairs of \((\varepsilon_1, \varepsilon_2)\) will be incorrect if the estimated \(d_j\) is not equal to the correct value. In this case, often times artifacts are observed in the inverted dielectric function. These artifacts may have different origins including: (a) substrate artifacts, which arise due to coupling of dielectric function features of the substrate or any other layers into the inverted \((\varepsilon_1, \varepsilon_2)\) of the \(j^{th}\) layer; (b) interference artifacts, which arise due to coupling of interference oscillations versus photon energy or wavelength into the inverted \((\varepsilon_1, \varepsilon_2)\) of the \(j^{th}\) layer; and (c) semiconductor artifacts, arising when \(\varepsilon_2\) of the \(j^{th}\) layer material is non-zero below a known band gap. A detailed description of these artifacts and the procedure of artifact minimization by varying the film thickness estimate can be found in (Collins and Ferlauto, 2005). Once the artifacts are minimized, the final \(d_j\) and \((\varepsilon_1, \varepsilon_2)\) can be treated as the correct one.
If the nature of the material is sufficiently well known, its dielectric function can be
constrained to follow a specific appropriate function of wavelength or photon energy.
For example, if the jth layer is a transparent material having a band gap much wider than
6.5 eV, then it is reasonable to assume that its index of refraction below 6.5 eV should
follow a Cauchy function of the wavelength and its absorption coefficient should be zero
(Collins and Ferlauto, 2005). In such case, the Cauchy function is defined by only a very
limited number of free parameters (< 10) which can be used in the analysis of $(\psi, \Delta)$.
Now the total number of unknown parameters is very much less than the total number of
measured quantities even taking the thickness $d_j$ as an additional free parameter in the
analysis. The analysis approach no longer relies on exact inversion, but rather on least
squares regression in which case one finds the set of free parameters that generates
spectra in $(\psi, \Delta)$ that best fit the measured spectra. The quality of fit is evaluated by the
mean squared error (MSE). A commonly used MSE is defined by:

$$MSE = \sum_{i=1}^{N} \left[ \frac{(\psi_i^{\text{gen}} - \psi_i^{\text{exp}})^2}{\delta\psi_i^{\text{exp}}^2} + \frac{(\Delta_i^{\text{gen}} - \Delta_i^{\text{exp}})^2}{\delta\Delta_i^{\text{exp}}^2} \right] / (2N - M) \quad (2.9)$$

where “gen.” denotes a generated value and “exp.” denotes an experimentally measured
value. $N$ is the total number of measured $(\psi, \Delta)$ pairs, $M$ is the total number of free
parameters, $\delta\psi$ and $\delta\Delta$ denote the random errors in the measurement of $\psi$ and $\Delta$
respectively due to noise sources. These errors act as the denominators to ensure that low
quality data points are weighted less heavily than high quality data points when the fitting
is performed. The procedure of finding the lowest MSE is called least squares regression.
SE measurements of the same sample can be performed at multiple angles of incidence and the resulting spectra can be analyzed together. This approach is often used in *ex situ* SE whereby the angle of incidence variation can be easily achieved without the optical access constraints of a processing chamber. Now the number of unknown parameters is the same, but the number of measured quantities is 1412 multiplied by the number of angles of incidence. Then it becomes possible to find the best $d_j$ and $(\varepsilon_1, \varepsilon_2)$ simultaneously through a least squares regression method. Although the 706 pairs of $(\varepsilon_1, \varepsilon_2)$ can be allowed to vary spectral point by spectral point independently without assuming any function of wavelength or photon energy, this procedure is not the same as inversion. Instead, it is classified as least squares regression, because the total number of measured quantities is larger than the total number of unknown parameters and there is not a one-to-one correspondence between data values and unknowns as in the case of inversion. This approach is not applicable for *in situ* SE due to the inability of varying the angle of incidence when the sample is mounted in a processing chamber.

If the topmost $j=1$ layer is changing its thickness with time, then real time SE at consecutive time points $t_1, t_2, \ldots t_K$ can be performed. The film will be characterized by different thicknesses at these different time points. If a specific time point $t_i$ ($1 \leq i \leq K$) is selected and the thickness at this point is estimated as $d_j(t_i)$, then an inverted dielectric function $(\varepsilon_1, \varepsilon_2)$ can be obtained corresponding to this estimate of $d_j(t_i)$. The inverted $(\varepsilon_1, \varepsilon_2)$ can then be applied in a least squares regression fit of $(\psi, \Delta)$ spectra taken at other time points. This fit provides the thicknesses versus time and an MSE now summed over
photon energy and averaged over time, serving as a measure of the quality of the fit. This
time averaged MSE can be minimized by iteratively adjusting the estimate of \(d_i(t_i)\) to its
correct value, and the corresponding inverted \((\varepsilon_1, \varepsilon_2)\) can be treated as the correct
dielectric function of the top layer material. Examples of this approach can be found in
(Cong et al., 1991; An et al., 1991). An alternative methodology that is more fitting
intensive is to vary a single pair of spectra in \((\varepsilon_1, \varepsilon_2)\) and the thicknesses at all time points
simultaneously so that they can fit the measured \((\psi, \Delta)\) spectra globally, that is, at all time
points. The resulting \((\varepsilon_1, \varepsilon_2)\) can be treated as the dielectric function of the top layer
material. In either case, the 706 pairs of \((\varepsilon_1, \varepsilon_2)\) are varied spectral point by spectral point
independently without assuming any function of wavelength or photon energy. These
procedures are classified as least squares regression rather than inversion, because the
total number of measured quantities, 1412 multiplied by \(K\), is larger than the total number
of unknown parameters, 1412 added to \(K\), and there is no one-to-one correspondence
between data and variables as in the case of inversion.

2.7 Effective medium approximation (EMA)

The multilayer structure in Fig. 2-3 can be considered as perfect in that each layer
has clear and abrupt boundaries with its two neighbors. This is not the case in reality.
Even on an atomically smooth substrate, the growth of a thin film inevitably generates a
certain amount of surface roughness which can be considered as a physical mixture of the
deposited material and void. If a second material is deposited on top of the first material,
generally there will be an interface roughness layer which can then be considered as a physical mixture of the two materials. In most cases this surface or interface roughness cannot be ignored since SE has extremely high sensitivity to their presence in the multilayer structure. The optical effect of surface or interface roughness can be approximated as discrete layers with dielectric functions determined by an effective medium theory (EMT). A brief introduction to EMT’s is presented next. More detailed discussions can be found in a review by Aspnes (1981).

Figure 2-4 (a) depicts a 3D cubic lattice of atoms in free space with atomic polarizability \( \alpha_a \), which is defined as the ratio of the induced dipole moment \( p \) of an atom to the local electric field \( E_{loc} \) at the atom that produces this dipole moment: \( p = \alpha_a E_{loc} \). The
uniform macroscopic field, existing everywhere in the 3D space except near each atom, is \( E \). If one considers an atom at the center of a sufficiently large sphere and treats the space outside this sphere as a uniform medium with polarization \( \mathbf{P} = N_a \mathbf{p} = N_a \alpha_a \mathbf{E}_{\text{loc}} \), where \( N_a \) is the atomic concentration, then one can deduce (Jackson, 2001; Aspnes, 1981):

\[
\mathbf{E}_{\text{loc}} = \frac{\mathbf{P}}{N_a \alpha_a}
= E + \frac{\mathbf{P}}{(3\varepsilon_0)},
\]  

(2.10)

where \( \varepsilon_0 \) is the permittivity of free space. Equation (2.10) establishes a relation between \( \mathbf{P} \) and \( \mathbf{E} \). According to the constitutive relation for an isotropic linear material (Jackson, 2001), \( \mathbf{P} = \varepsilon_0 \chi \mathbf{E} \) where \( \chi \) is the electric susceptibility, and \( \varepsilon = 1 + \chi \) is the dielectric function of the material that comprises the atomic lattice in Fig. 2-4(a). From Eq. (2.10) and the constitutive relations, one can derive:

\[
\frac{(\varepsilon_a - 1)}{(\varepsilon_a + 2)} = \frac{N_a \alpha_a}{(3\varepsilon_0)}. \]  

(2.11)

Equation (2.11) is a form of the Clausius–Mossotti relation. If some “a” atoms in Fig. 2-4 (a) are replaced by “b” atoms with a different polarizability \( \alpha_b \) as shown in Fig. 2-4 (b), then a similar approach can be applied to deduce a corresponding Clausius–Mossotti relation:

\[
\frac{(\varepsilon - 1)}{(\varepsilon + 2)} = \frac{(N_a' \alpha_a + N_b' \alpha_b)}{(3\varepsilon_0)},
\]  

(2.12)

where \( \varepsilon \) is the effective dielectric function of the material made from a mixture of “a” and “b” atoms in Fig. 2-4 (b). In Eq. (2.12), \( N_a' \) and \( N_b' \) are the atomic concentrations of “a” and “b” atoms, respectively, in such a composite material. Additional equations of importance are:
\[ N_a' + N_b' = N_a \]  

(2.13)

and  

\[ \frac{(\varepsilon_b - 1)}{(\varepsilon_b + 2)} = \frac{N_a}{N_b}/(3\varepsilon_0), \]  

(2.14)

where \( \varepsilon_b \) is the dielectric function of material “b”, i.e., a material with all the “a” atoms in Fig. 2-4 replaced by “b” atoms. Combining Eqs. (2.11) to (2.14), one can derive:

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

(2.15)

where \( f_a = N_a' / N_a \) and \( f_b = N_b' / N_a \) are the atomic (and hence volume) fractions of materials “a” and “b”, respectively, in the composite material of Fig. 2-4 (b). Next, for an atomic lattice in a host medium (instead of free space) with dielectric function \( \varepsilon_h \), \( \varepsilon_0 \) in Eq. (2.10) should be replaced by \( \varepsilon_h \varepsilon_0 \). Following similar steps as in Eqs. (2.11) to (2.14), one can show that:

\[ \frac{\varepsilon - \varepsilon_h}{\varepsilon + 2\varepsilon_h} = f_a \frac{\varepsilon_a - \varepsilon_h}{\varepsilon_a + 2\varepsilon_h} + f_b \frac{\varepsilon_b - \varepsilon_h}{\varepsilon_b + 2\varepsilon_h}. \]  

(2.16)

Eq. (2.16) is the most general effective medium theory for an isotropic mixture of isotropic component materials. Special cases are as follows (Aspnes, 1981).

(1) Setting \( \varepsilon_h = 1 \) returns Eq. (2.15) which is the Lorentz – Lorenz EMT in which case the host is free space.

(2) Setting \( \varepsilon_h = \varepsilon_a \) if material “a” is dominant (i.e., if \( f_a > f_b \)) yields the Maxwell – Garnett EMT.

(3) Setting \( \varepsilon_h = \varepsilon \) for self-consistency yields the Bruggeman EMT. In this special case, the effective dielectric function itself is the host medium dielectric function. With this EMT, \( \varepsilon \) can be calculated using the equation:
The Bruggeman EMT, often simply called the effective medium approximation or EMA, is the most widely used EMT in SE studies. An excellent assessment of different EMT theories in the analyses of semiconductor thin films can be found in the literature (Fujiwara et al., 2000).

\[ 0 = f_a \frac{\varepsilon_a - \varepsilon}{\varepsilon_a + 2\varepsilon} + f_b \frac{\varepsilon_b - \varepsilon}{\varepsilon_b + 2\varepsilon}. \] (2.17)

2.8 A case study of ex situ SE: \( \text{In}_2\text{S}_3 \) for CIGS solar cells

Photovoltaics technology based on the I-III-VI\(_2\) (or chalcopyrite) polycrystalline semiconductors has reached the highest laboratory efficiency among the potentially low-cost thin-film technologies – 19.9% for \( \text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2 \) (CIGS) fabricated in a three-stage process (Repins et al., 2008). Because this PV technology presents significant challenges in industrial scale-up, spectroscopic ellipsometry (SE) can play an important role in better understanding the material properties and fabrication process. In this case study, SE investigations have been performed to characterize the polycrystalline compound semiconductor indium sulphide -- an alternative to CdS as a Cd-free top-contact window in CIGS technology (Barreau et al., 2001; Barreau et al., 2002). The \( \text{In}_2\text{S}_3 \) film was deposited by Barreau et al. (2008) with co-evaporation method onto soda-lime glass (SLG) held at a temperature of 473 K using a deposition pressure of 10\(^{-5}\) Torr. Ex-situ SE has been applied in this research to determine the
dielectric function of In$_2$S$_3$. The dielectric function of this material is important as it enables one to assess the impact of this replacement on the quantum efficiency of the CIGS solar cell (Barreau et al., 2002).

Figure 2-5 shows the results of an analysis of ex-situ SE data for the In$_2$S$_3$ film, obtained using exact inversion along with the artifact-minimization/semiconductor criterion. In this analysis, two structural parameters are used to describe the In$_2$S$_3$ film: the bulk layer thickness $d_b$ and the surface roughness layer thickness $d_s$. The dielectric function of the surface roughness layer is calculated from the Bruggeman EMT, assuming a 0.5/0.5 volume fraction mixture of In$_2$S$_3$ and ambient air whose dielectric function is simply $(\varepsilon_1, \varepsilon_2) = (1, 0)$. In the analysis procedure, $d_b$ and $d_s$ are chosen to
ensure that no interference-fringe-related artifacts appear in the inverted dielectric function of In$_2$S$_3$ (artifact minimization) and that $\varepsilon_2$ is as close as possible to zero below the absorption onset (semiconductor criterion). Such analysis has led to the values $d_b = 1456 \pm 6 \text{ Å}$ and $d_s = 86 \pm 3 \text{ Å}$. Figure 2-6 compares low photon energy $\varepsilon_2$ spectra on an expanded scale from the inversion result of Fig. 2-5 with results obtained by fixing $(d_b, d_s) = (1446 \text{ Å}, 86 \text{ Å})$ and $(d_b, d_s) = (1466 \text{ Å}, 86 \text{ Å})$. With $(d_b, d_s) = (1446 \text{ Å}, 86 \text{ Å})$, the inverted $\varepsilon_2$ exhibits non-zero values in the lower photon energy range where In$_2$S$_3$ is known to have no absorption and hence $\varepsilon_2$ should be zero. With $(d_b, d_s) = (1466 \text{ Å}, 86 \text{ Å})$, however, the inverted $\varepsilon_2$ is pinned at zero over the lower photon energy range. Even the noise in $\varepsilon_2$ associated with the detector transition from the InGaAs to Si array is almost

![Figure 2-6. Comparison of low photon energy $\varepsilon_2$ of the inversion result of In$_2$S$_3$ in Fig. 2-5 ($(d_b, d_s) = (1456 \text{ Å}, 86 \text{ Å})$) with those obtained by fixing $(d_b, d_s) = (1446 \text{ Å}, 86 \text{ Å})$ and $(d_b, d_s) = (1466 \text{ Å}, 86 \text{ Å})$.](image)
completely suppressed. This apparently desirable result is actually an artifact arising because the ellipsometry software used here does not permit negative $\varepsilon_2$ values. Thus, the noiseless $\varepsilon_2$ spectrum pinned at zero over a wide spectral range for the inversion result of $(d_b, d_s) = (1466 \, \text{Å}, 86 \, \text{Å})$ is an indication of negative $\varepsilon_2$ and one or more incorrect thicknesses. Another indication that 1466 Å is an incorrect $d_b$ value is the enhancement in the interference artifact near 2.35 eV when $d_b$ is increased from 1456 Å to 1466 Å. Through such artifact minimization procedures, the uncertainty in determining $d_b$ and $d_s$ is estimated to be ±6 Å and ±3 Å, respectively.

The dielectric function of In$_2$S$_3$ in Fig. 2-5 shows clear critical point structures at the fundamental band gap ($E_0 \sim 2.8$ eV) and at higher energies ($E_{1A} \sim 4.9$ eV and $E_{1B} \sim 5.6$ eV), as well as an absorption tail below the gap with its onset at ~ 2.0 eV. This dielectric function is fitted with an analytical model that includes 4 critical points: (1) the fundamental band gap is modeled with a Tauc-Lorentz line shape; (2) the $E_{1A}$ and $E_{1B}$ critical points are modeled based on the parabolic band approximation; and (3) the broad background absorptions that do not belong to any above critical points are modeled with another Tauc-Lorentz line shape with large broadening parameters (Collins and Ferlauto, 2005). The explicit expressions of the above line shapes and the best fit parameters are listed in Table 2-1. As shown in Fig. 2-5, the inverted dielectric function of In$_2$S$_3$ can be closely fitted to the above analytical model that is consistent with Kramers-Kronig relations as required by basic electrodynamics principles that describe the interaction of
light with polarizable media (Jackson, 2001). This is another indication of the reliability of the inversion result of Fig. 2-5.

Table 2-1. The analytical model used to fit the deduced dielectric function of \( \text{In}_2\text{S}_3 \) of Fig. 2-5 and the best fit parameters.

<table>
<thead>
<tr>
<th>critical point</th>
<th>line shape</th>
<th>expression</th>
<th>parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_0 )</td>
<td>Tauc–Lorentz</td>
<td>( \varepsilon_2(E) = [(E-E_g)/E] L(E) ) (( E \geq E_g )) ( \varepsilon_2(E) = 0 ) (( E &lt; E_g )) ( L(E) = A E_n \Gamma E/[(E^2-E_n^2)^2 + \Gamma^2 E^2] ) ( \varepsilon_1(E) ) from ( \varepsilon_2(E) ) through K–K relation</td>
<td>( A = 47.2 \pm 10.8 \text{ eV} ) ( E_n = 2.77 \pm 0.08 \text{ eV} ) ( \Gamma = 1.15 \pm 0.07 \text{ eV} ) ( E_g = 2.46 \pm 0.03 \text{ eV} )</td>
</tr>
<tr>
<td>( E_1-A )</td>
<td>parabolic band</td>
<td>( A e^{i \phi} (E-E_n-i \Gamma)^\mu )</td>
<td>( A = 2.68 \pm 0.09 ) ( \phi = 0^\circ ) (fixed) ( E_n = 4.92 \pm 0.003 \text{ eV} ) ( \Gamma = 0.71 \pm 0.02 \text{ eV} )</td>
</tr>
<tr>
<td>( E_1-B )</td>
<td>parabolic band</td>
<td>( A e^{i \phi} (E-E_n-i \Gamma)^\mu )</td>
<td>( A = 1.77 \pm 0.07 ) ( \phi = 0^\circ ) (fixed) ( E_n = 5.64 \pm 0.004 \text{ eV} ) ( \Gamma = 0.51 \pm 0.02 \text{ eV} ) ( \mu = 1 ) (fixed)</td>
</tr>
<tr>
<td>background</td>
<td>Tauc–Lorentz</td>
<td>( \varepsilon_2(E) = [(E-E_g)/E] L(E) ) (( E \geq E_g )) ( \varepsilon_2(E) = 0 ) (( E &lt; E_g )) ( L(E) = A E_n \Gamma E/[(E^2-E_n^2)^2 + \Gamma^2 E^2] ) ( \varepsilon_1(E) ) from ( \varepsilon_2(E) ) through K–K relation</td>
<td>( A = 63.2 \pm 2.1 \text{ eV} ) ( E_n = 5.50 \pm 0.03 \text{ eV} ) ( \Gamma = 3.75 \pm 0.07 \text{ eV} ) ( E_g = 1.86 \pm 0.02 \text{ eV} )</td>
</tr>
</tbody>
</table>

\( \varepsilon_1(\infty) = 1.95 \pm 0.02 \)
Chapter 3

Structural Evolution of CdTe and CdS Photovoltaic Thin Films

Studied by Real Time Spectroscopic Ellipsometry

3.1 Effects of deposition temperature on magnetron sputtering of CdTe

Thin film polycrystalline CdTe technology is attracting increasing attention in recent years as the global demand for low cost solar modules is growing rapidly. Magnetron sputtering is of great interest for the deposition of thin film CdTe as this method has been used to fabricate efficient polycrystalline CdS/CdTe heterojunction solar cells (Gupta and Compaan, 2004), with an advantage of low processing temperatures. Among all the sputtering parameters, deposition temperature is widely believed to have the greatest impact on the quality of the deposited films (Messier et al., 1984). In this Chapter and the next, the role of deposition temperature is investigated using the unique capabilities of real time spectroscopic ellipsometry (RTSE).

The experimental setup for this study is shown schematically in Fig. 2-2. A series of polycrystalline CdTe thin films were magnetron sputtered with a radio frequency (RF) power (13.56 MHz) of 60 Watts, an Ar pressure of 18 mTorr, and an Ar flow rate of 23
sccm. These conditions are similar to those yielding efficient solar cells (Gupta and Compaan, 2004). Native oxide covered crystalline Si wafers were used as substrates due to their consistent smoothness and well known optical properties. The design and data reduction principles of the rotating compensator multichannel ellipsometer used in this study are analogous to those developed previously to study a-Si:H based solar cells (Lee et al., 1998). During film deposition, the ellipsometric spectra ($\psi, \Delta$) over the spectral range from 0.75 to 6.5 eV were acquired in 1-3 sec, as averages over ~ 30 – 90 optical cycle pairs, during which less than 3 Å thickness of material has accumulated. This provides sufficient thickness resolution for the characterization of the nucleation processes with sub-monolayer resolution.

Although the deposition temperature $T_d$ is the key process variable in this study, the thermocouple for substrate temperature measurement is distant from the actual substrate in the deposition chamber as shown in Fig. 2-2. As a result, it is necessary to establish a calibration for the true substrate temperature $T_d$ as a function of the nominal temperature $T_{nom}$ read from the thermocouple. In this calibration, the uncoated c-Si substrate prior to CdTe deposition was first heated to the largest value of $T_{nom}$ of interest, and then stepwise cooled to 15°C. This is the equilibrium temperature $T_{nom}$ as read from the thermocouple with cooling water flowing and the substrate heater turned off. At $T_{nom}=15^\circ$C, the true temperature $T_d$ is also considered to be 15°C. During stepwise cooling, RTSE spectra of the c-Si substrate were taken at each temperature step. These spectra were corrected in order to account for the ~15 Å thick native oxide layer on the substrate and extract the
complex dielectric function $\varepsilon = \varepsilon_1 + i\varepsilon_2$ of the c-Si. Figure 3-1 compares $\varepsilon$ spectra of c-Si at two $T_{\text{nom}}$ values, demonstrating the shifts in the E1 and E2 critical point (CP) features with temperature (Lautenschlager et al., 1987a). Second derivatives $\frac{d^2\varepsilon}{dE^2}$ were determined at each $T_{\text{nom}}$ during cooling and then fit to standard CP lineshapes (Lautenschlager et al., 1987a) in order to find precise values of the E1 and E2 CP energies versus $T_{\text{nom}}$. The E1 and E2 energy shifts relative to values obtained at 15°C provide two independent equations for calculating the true substrate temperature $T_d$ (Lautenschlager et al., 1987a) which are in close agreement as shown in Fig. 3-2. The average of these results was considered the desired calibration relationship, through which $T_d$ was deduced from $T_{\text{nom}}$. In this study, $T_d$ was varied over the range of 188-304°C.
Each CdTe film was first sputtered to a thickness of ~1000 Å. Then the deposition was suspended and the film was stepwise cooled from $T_d$ to 15°C under vacuum. During cooling, in situ SE data were collected at several values of the true measurement temperature $T_m$ as determined from the calibration described in the previous paragraph. In this way, the dielectric function of each CdTe film prepared at a given $T_d$ was obtained as a function of $T_m$.

After such a study versus $T_m$, each sample was reheated to $T_d$, and the deposition was continued in order to study the structural evolution in thicker films, prepared at the
given \( T_d \) value. The total deposited thickness in each case is \( \sim3300 \, \text{Å} \). The reason for suspending the depositions in the thin film regime at \( \sim1000 \, \text{Å} \) is to avoid possible inhomogeneity that occurs in thicker films due to the structural evolution versus film thickness. Void development, grain size evolution, stress buildup and relaxation all can cause artifacts in the deduced \( \varepsilon \) if the film structure is over-simplified by the assumption of a uniform, homogeneous material throughout the thickness. A detailed discussion of the variations of the dielectric function of CdTe prepared at different \( T_d \) values will appear in Chapter 4.

In order to analyze the structural evolution of the CdTe films prepared at different \( T_d \) values, the dielectric function of the surface roughness layer is calculated from the Bruggeman effective medium theory (EMT) assuming a 0.5/0.5 volume fraction mixture of the material immediately below the roughness layer and the overlying vacuum (Aspnes, 1981). In the thin film regime (thickness < 500 Å) of the deposition for all the CdTe films in this series, very weak inhomogeneity was observed, so the film structure in this regime is simply modeled using a bulk layer with thickness \( d_b \) and a surface roughness layer with thickness \( d_s \). In this case, the effective thickness \( d_{\text{eff}} \) of the deposited material can be calculated as \( d_{\text{eff}}=d_b+(d_s/2) \). The bulk layers of the CdTe films deposited at different \( T_d \) values were found to incorporate different void volume fractions as explained later in this Section. To take this effect into account, the above \( d_{\text{eff}} \) is further scaled to the lowest void volume fraction CdTe in this series which serves as a reference material – the first \( \sim 500 \, \text{Å} \) of the \( T_d=188^\circ \text{C} \) sample. After this scaling, the effective deposition rate \( R_{\text{eff}} \) in the thin
film regime for the five CdTe films sputtered at $T_d$ values of 188, 215, 237, 267, and 304°C (under otherwise identical conditions) is plotted as a function of $T_d$ in Figure 3-3. An increase in $R_{\text{eff}}$ with increasing $T_d$ is apparent, which appears counterintuitive since the sticking probability – if it did vary with temperature – would be expected to decrease with increasing $T_d$. An increase in $R_{\text{eff}}$, however, appears attributable to a reduction in Ar atom density with the increase in gas temperature at constant pressure and volume. Similar reasoning can account for a decrease in $R_{\text{eff}}$ with increasing Ar pressure at constant $T_d$ as will be demonstrated in Section 3.3.

Figure 3-4 depicts the evolution of $d_s$ with $d_b$ for the CdTe sputter depositions of Fig. 3-3. The evolution of $d_s$ in the initial 500 Å of $d_b$ in Fig. 3-4 was obtained by analyzing
the \((\psi, \Delta)\) spectra over their full spectral range (0.75 - 6.5 eV) using a two-layer [bulk/roughness] model. For \(500 < d_b < 1000 \text{ Å}\), \(d_s\) was obtained using a model that incorporates a second bulk layer with increased void volume fraction (\(f_v\)) on top of the denser underlying bulk layer (\(\sim 500 \text{ Å} \) thick). This was necessary in order to achieve a quality of the fit to the RTSE data close to that when \(d_b < 500 \text{ Å}\). On the right side of Fig. 3-4, the evolution of \(d_s\) is shown for \(d_b > 1000 \text{ Å}\). In this case, the \((\psi, \Delta)\) spectra were analyzed from 3.5 to 6.5 eV where the CdTe films are opaque and high surface

![Figure 3-4](image)

*Figure 3-4. Evolution of the surface roughness layer thickness \(d_s\) with bulk layer thickness \(d_b\) for the CdTe films of Fig. 3-3. The left half of the abscissa (\(d_b < 1000 \text{ Å}\)) is plotted on a log scale to highlight the nucleation behavior; the right half of the abscissa (\(d_b > 1000 \text{ Å}\)) is plotted on a linear scale to depict the longer term evolution. The final surface roughness layer thickness is plotted as a function of \(T_d\) in the inset.*
sensitivity is attained. In this latter analysis, a one-layer model \([\text{semi-infinite bulk/roughness}]\), that avoids the complicated underlying structure, was used. The \(d_b\) value plotted along the abscissas in Fig. 3-4 is obtained in an analysis that uses the full multilayer model for the sample as explained later in this section.

A closer look at the initial nucleation stage is provided in Fig. 3-5. Considering the results for \(T_d=188, 215, \text{ and } 237^\circ\text{C}\) first, the surface roughness thickness of these films describes the nuclei height above the substrate (Fujiwara et al., 2000). This height
increases to 18-22 Å before formation of the first bulk monolayer (~ 3 Å, which is the interatomic spacing for the CdTe lattice), an indication of clustering (islands) from the outset, or the Volmer-Weber (V-W) growth mode (Venables et al., 1984). For the depositions at the two higher $T_d$ values of 267 and 304°C, bulk layers of 3 and 6 Å (~ 1 and 2 monolayers) form on the substrate before the onset of clustering. Thereafter, clustering occurs abruptly leading to roughness layer thicknesses as large as 33 Å. Such behavior suggests the Stranski-Krastanov (S-K) growth mode in which case $\gamma_f + \gamma^*$, the sum of the free energies of the film surface and substrate/film interface, increases from a value less than $\gamma_s$, the substrate surface free energy, to a value greater than $\gamma_s$ upon growth of one or two monolayers (Venables et al., 1984). This change may be due to the build-up of strain in the monolayer(s). The V-W to S-K transition temperature, at which the first monolayer of bulk dense material and the first monolayer of surface roughness form almost simultaneously, is ~ 260°C. This temperature is expected to depend on the material as well as the deposition conditions. In fact, for CdS depositions in a similar study to be described in the next Section, the V-W to S-K transition temperature is ~100°C lower, indicating a lower activation energy for surface diffusion during deposition. This proposal is based on the concept that S-K growth can only occur when sufficient surface diffusion promotes the filling of the void structure of the first one or two monolayers.

Figure 3-6 shows the cluster parameters for CdTe as a function of $T_d$. These include $d_s$ at its maximum (top curve), which is interpreted as the height of the clusters at
the onset of coalescence. The increased nuclei height with increasing $T_d$ is attributed to a decreased density of clusters on the surface; thus, clusters reach a larger size before contact and coalescence. The decrease in cluster nucleation density with increasing $T_d$ is attributed to a longer diffusion length of film precursor species on the uncovered substrate surface (at lower $T_d$) or on the film surface (at higher $T_d$) which, in turn, leads to a larger capture radius for critical nuclei. The second nucleation parameter shown Fig. 3-6 is the $d_b$ value at the $d_s$ maximum. The results in this case support the trend from V-W type growth to S-K type growth with increasing $T_d$. After reaching peak thicknesses of 26-33 Å, the clusters in both the immediate (V-W) and delayed (S-K) nucleation processes coalesce, leaving stable surface roughness layers ~ 9 - 12 Å thick.
After a bulk layer thickness of \( \sim 200 \text{ Å} \), a roughening transition is observed in Fig. 3-4 with the strongest effect occurring for the lowest \( T_d \) film. At the end of the deposition when \( d_b \sim 3300 \text{ Å} \), \( d_s \) is observed to decrease monotonically with increasing \( T_d \) as shown in the inset of Fig. 3-4. This observation is also likely due to the enhanced diffusion of the film precursors on the surface at elevated \( T_d \). In fact, for the lowest \( T_d \) value of 188°C, the roughness passes through an instability near \( \sim 1500 \text{ Å} \) (Fig. 3-4) that is correlated with the rapid development of voids as will be demonstrated in the next paragraph. It is suggested that as strain is relieved through void formation in the bulk layer, the surface passes through a smoothening transition. The bulk layer void evolution and its correlation with surface roughness will be discussed next.

The evolution of the void volume fraction (\( f_v \)) in the bulk layer of CdTe is analyzed using the Bruggeman EMT (Aspnes, 1981). The continuous variation in void volume fraction with thickness is approximated by applying an n-layer optical model for the bulk layer in which case each sub-layer thickness \( d_i \) (i=1, ..., n) and void volume fraction \( f_{v,i} \) along with the evolving surface roughness layer thickness \( d_s \) are chosen to ensure a best fit of RTSE data versus photon energy (0.75 - 6.5eV) and time. The \( f_v = 0 \) CdTe reference dielectric function for each film is taken to be that of the sub-layer at the substrate interface which is the densest material in the profile. After all samples are analyzed, the void fraction for that dense phase is then scaled relative to that of the highest density sample among those prepared at different substrate temperatures -- which is the one prepared at \( T_d=188^\circ \text{C} \). Figure 3-7 exemplifies the model used to analyze the
RTSE data for the film deposited at $T_d=215^\circ\text{C}$ in Fig. 3-8 (a). This model is valid for the full bulk layer thickness range of $1100 < d_b < 2100$ Å. In this model, all parameters associated with the first and second sub-layers are fixed at previously-determined values; only the parameters of the third such layer are varied in the fitting routine, including the time-dependent sub-layer and surface roughness layer thicknesses $d_3$ and $d_s$, and the time-independent sub-layer void volume fraction $f_{v,3}$. As the film evolves, up to $n=6$
sub-layers are needed to model the full bulk layer and maintain a suitable fit to the RTSE data over the full spectral range.

The results of stepwise depth profiles in the void volume fraction $f_v$ are shown in Fig. 3-8 for the films of Figs. 3-3 through 3-6. The evolution of $f_v$ in Fig. 3-8 is found to exhibit interesting trends with $T_d$. For all deposition temperatures, $f_v$ increases monotonically with increasing bulk layer thickness. Within the thin film regime ($d_b < 500 \, \text{Å}$), $f_v$ also increases monotonically with increasing $T_d$. This latter monotonic trend may be related to the trend with $T_d$ in the nucleation density and cluster height in the initial stage of deposition, as demonstrated previously in this section. A lower nucleation density and larger cluster height may give rise to a higher void fraction in the thin film regime due to incomplete coalescence.

The lowest $T_d$ film having the lowest $f_v$ value in the thin film regime exhibits an abrupt structural transition at $d_b \sim 1500 \, \text{Å}$ whereby $f_v$ increases by more than a factor of eight within a narrow range of $d_b$; this yields a final film with near-surface $f_v \sim 0.10$. The structural transition is suppressed in depositions at increasing $T_d$ in conjunction with the incorporation of voids in the thin film regime. For CdTe films deposited at $T_d \geq 267^\circ\text{C}$, the depth profiles in $f_v$ are nearly linear. The low $T_d$ structural transition is attributed to the relaxation of strain which appears to be enhanced at low $T_d$ under low surface diffusion conditions when $f_v$ is very low.

The void volume fraction in the top-most layer of the final film is shown in the inset of Fig. 3-8 (a) as a function of $T_d$. The highest density in the near-surface region of the
The final film (~3300 Å) is obtained at an intermediate \( T_d \sim 230^\circ C \). Here the rapid structural transition to high \( f_v \) at low \( T_d \) is avoided almost completely, whereas the gradual
increase in \( f_v \) as a function of bulk layer thickness at high \( T_d \) is minimized as a tradeoff. The deposition temperature yielding the minimum void fraction in the final film surface approximates that for optimum solar cell performance. As noted previously in this section, there is a clear correlation between the surface roughness thickness and void fraction evolution. It is reasonable that both surface roughness and voids provide the means for strain relief in these films. For the CdTe films deposited at lower \( T_d \) with lower \( f_v \) in the thin film regime (\( d_b < 500 \) Å), the roughening transition starting at \( d_b \sim 200 \) Å is enhanced, leading to significant roughness thicknesses in the thick film regime. As these films undergo their structural transitions to higher \( f_v \), however, the roughness layer thicknesses begin to stabilize. These structural transitions are centered near \( d_b = 1500 \) Å for \( T_d = 188^\circ C \), \( d_b = 2700 \) Å for \( T_d = 215^\circ C \), and \( d_b \sim 3000 \) Å for \( T_d = 237^\circ C \). In fact, for the CdTe film deposited at \( T_d = 188^\circ C \), the structural transition is even accompanied by a surface smoothening effect in Fig. 3-4. Thus, it is clear that higher bulk layer void fractions permit smoother surfaces.

### 3.2 Effects of deposition temperature on magnetron sputtering of CdS

CdS is an important semiconductor material with a variety of applications not only for photovoltaics, but also for sensors and detectors and for infrared optical components (Broser et al., 1992; Ninomiya and Adachi, 1995). In a CdTe based solar cell, CdS is used as the n-type heterojunction partner with p-type CdTe. Therefore, the CdS layer should not be made too thin in order to form an effective junction and to prevent pinholes
and shunting. At the same time, the CdS layer should not be made too thick in order to allow transmission of photons with higher energies than the CdS band gap (~ 2.4 eV). The transmitted photons can then be absorbed in the CdTe layer and thus contribute to the quantum efficiency in the spectral range below ~ 500 nm. So an understanding of the dynamics of the growth process may be helpful for optimizing the CdS layer in solar cells.

In this research, the CdS thin films are magnetron sputtered in the same chamber as that used for sputtering of CdTe thin films, shown in Fig. 2-2.

A series of polycrystalline CdS thin films were magnetron sputtered onto native oxide covered crystalline Si wafer substrates with an RF power of 50 Watts, an Ar pressure of 10 mTorr, and an Ar flow rate of 23 sccm. These conditions are similar to those yielding efficient solar cells (Gupta and Compaan, 2004). The key process variable, deposition temperature $T_d$, was varied within the range of 145–320°C, determined from the c-Si calibration described in Section 3.1. As described in Section 3.1, the deposition of each CdS film was suspended in this case at a thickness of ~ 500 Å. The film was then stepwise cooled to $T_{nom} = T_m = 15°C$ to investigate the variation of the CdS dielectric function as a function of $T_m$ for films prepared at different $T_d$. The results of such investigations will be reported in Chapter 4. The ~ 500 Å thick film was then reheated to $T_d$ to resume the deposition, continuing to a final thickness of 1300 Å, a standard thickness for efficient CdTe based solar cells.

Using analysis techniques similar to those described in Section 3.1, the variations in the CdS film densities versus $T_d$ were found to be weak, as will be demonstrated later in
this subsection. The CdS effective deposition rate $R_{\text{eff}}$ in the thin film regime ($d_b<500$ Å) is plotted as a function of $T_d$ in Figure 3-9, for direct comparison with the CdTe $R_{\text{eff}}$ versus $T_d$ data in Fig. 3-3. In general, opposite trends are observed for the two materials. For CdTe, the increase in $R_{\text{eff}}$ with increasing $T_d$ is counterintuitive, but as noted in Section 3.1, may result from a reduction in Ar atom density with the increase in gas temperature at constant pressure and volume. This effect may not be dominant in CdS due to the lower pressure of the CdS deposition (10 mTorr versus 18 mTorr). The reduction in the deposition rate of CdS with increasing temperature can then be attributed to a reduction in sticking coefficient of the incident growth species with increasing temperature. It is not clear, however, why this effect is not dominant in CdTe, as well.
The evolution of surface roughness after coalescence for this series of CdS depositions was found to occur on a much smaller scale with much less variation versus $T_d$ than the CdTe series in Fig. 3-4. In spite of this, systematic variations in the nucleation behavior and a well-defined transition of the growth mode is observed for this series as well. In fact, the trend is even clearer than for CdTe in Section 3.1 as shown in Fig. 3-10. Here the evolution of $d_s$ with $d_b$ is depicted for CdS sputter depositions at different temperatures. At $T_d=145\, ^\circ C$, $A \sim 6 \, Å$ surface roughness layer appears before the first complete dense monolayer. Here the thickness of one monolayer (ML), either for

![Graph](image)

Figure 3-10. The nucleation behavior of the sputtered of CdS films of Figs. 3-9. At $T_d = 145\, ^\circ C$, surface roughness (nuclei height) reaches $\sim 6 \, Å$ before the first bulk monolayer forms. At $T_d = 160\, ^\circ C$, the first monolayer of surface roughness and bulk CdS appear simultaneously (V-W to S-K transition temperature). At $T_d \geq 225\, ^\circ C$, bulk layers of $\sim 6 \, Å$ (2 monolayers) form on the substrate before the onset of clustering.
$d_b$ or $d_s$, is assumed to be 3 Å, approximately the interatomic spacing. Thus, the $T_d=145^\circ$C data reveal results typical of an island growth mode, or Volmer-Weber (V-W) mode (Venables et al., 1984). At $T_d=160^\circ$C, the first monolayer of surface roughness and bulk CdS appear simultaneously. This is considered the transition point from an island growth mode to a layer-island growth mode, or Stranski-Krastanov (S-K) mode (Venables et al., 1984). At $T_d=225^\circ$C, ~2 dense monolayers appear before the first monolayer of surface roughness. Thus the S-K mode is favored at higher $T_d$ as also observed for CdTe and described in Section 3.1.

Figure 3-11 demonstrates the two ways to determine the V-W to S-K transition temperature (vertical lines). The transition is identified either (i) as the temperature at which the surface roughness layer thickness ($d_s$) drops below a single monolayer at the bulk monolayer thickness ($d_b \sim 3$ Å) (upper panel) or (ii) as the temperature at which the bulk layer thickness ($d_b$) increases above one monolayer for a surface roughness layer thickness of a single monolayer ($d_s \sim 3$ Å) (lower panel). The trends versus $T_d$ in Fig. 3-11 are systematic and reveal the high sensitivity of the methods for extracting transition temperatures, $T_d \sim 160^\circ$C for CdS and $T_d \sim 260^\circ$C for CdTe. As described in Section 3.1, these results indicate a lower diffusion activation energy for CdS.

The peak height of nuclei for CdS was found to increase monotonically with increasing $T_d$ as shown in Fig. 3-12, similar to that observed for CdTe. The CdTe results from Fig. 3-6 are reproduced in Fig. 3-12 for ease of comparison. This comparison shows that the peak nuclei height for CdTe is 10 – 15 Å larger than that for CdS for a
given $T_d$, indicating a lower nuclei density in the initial growth stage. This may result in part from the lower pressure of the CdS deposition (10 mTorr versus 18 mTorr for CdTe).

In fact, the role of pressure in CdTe deposition will be discussed in Section 3.3.

RTSE data over the full spectral range of 0.75–6.5 eV were applied to study the void development for this series of CdS depositions on c-Si substrates to obtain results
corresponding to those of Fig. 3-8. The void volume fraction profiles were observed to
be relatively weak compared to those for the CdTe films over the corresponding thickness
range \((d_b < 1300 \text{ Å})\). Figure 3-13 shows that stepwise void analysis of the CdS film
deposited at \(T_d = 320^\circ\text{C}\) gives a final \(f_v\) value of 0.01. Other samples exhibit similar
weakly varying profiles with no clear trend vs. \(T_d\). Continuous void fraction analyses
using RTSE data over the spectral range of 4.5 ~ 6.5 eV, where greater surface sensitivity
is obtained, lead to final near surface values of within the range of 0.00 to 0.03 for all
CdS films.
In Sections 3.1 and 3.2, the nucleation and coalescence behaviors were described for magnetron sputter deposition of CdTe and CdS on native oxide covered Si wafer substrates. This stage of growth may have intrinsic relationship with the evolution of the surface roughness and void structure for thicker films. It is known that CdTe and CdS can form CdTe$_{1-x}$S$_x$ alloys in the full range of composition, i.e., with $x$ ranging from 0 to 1.

3.3 Nucleation and coalescence during the deposition of CdTe$_{1-x}$S$_x$ alloy thin films fabricated by magnetron co-sputtering

In Sections 3.1 and 3.2, the nucleation and coalescence behaviors were described for magnetron sputter deposition of CdTe and CdS on native oxide covered Si wafer substrates. This stage of growth may have intrinsic relationship with the evolution of the surface roughness and void structure for thicker films. It is known that CdTe and CdS can form CdTe$_{1-x}$S$_x$ alloys in the full range of composition, i.e., with $x$ ranging from 0 to 1.
(Wei et al., 1999). Therefore, it is of interest to investigate the nucleation and coalescence behavior of CdTe$_{1-x}$S$_x$ alloys and their dependence on the composition, under deposition conditions similar to those for CdTe and CdS growth described in Sections 3.1 and 3.2.

For this investigation, a low deposition temperature of $T_d$=190°C was used in the fabrication of the CdTe$_{1-x}$S$_x$ alloys. This temperature is close to the highest temperature without possible CdS – CdTe phase segregation (McCandless et al., 2002). Additional deposition parameters include an Ar pressure of 18 mTorr and an Ar flow of 23 sccm. Native oxide covered crystal Si wafers were used as substrates. The first step of these experiments was to perform an effective deposition rate versus RF power calibration for both CdTe and CdS sputter deposition under the fixed conditions of substrate temperature, Ar pressure, and flow. Once this calibration is completed, CdTe$_{1-x}$S$_x$ alloy films of prespecified S molar fraction x or alloy composition can be deposited by co-sputtering using the experimental apparatus shown in Fig. 2-2. The alloy composition of the films can be controlled by adjusting RF power to the CdTe and CdS target. Figure 3-14 shows the dependence of deposition rate on RF power for the CdTe and CdS targets. The selected rf powers and the corresponding expected x values are shown in Table 3-1. The measured effective deposition rates versus x for the CdTe$_{1-x}$S$_x$ are shown in Fig. 3-15. One point to notice is that over a wide range of x from 0.2 to 0.9, the deposition rate is nearly constant. This makes it easier to relate trends in optical properties and structural evolution over this range to composition rather than to rate deviations.
Considering the nucleation characteristics as shown in Fig. 3-16, all alloys exhibit island-layer growth mode (Volmer-Weber mode) at the beginning of deposition regardless of the x value. In addition, they all have similar surface roughness thickness values, \( d_s = 22 \pm 2 \text{ Å} \), when the first bulk monolayer appears \( (d_b = 3 \text{ Å}) \). Up to this point, the film growth pattern is nearly the same among all alloys. However, the peak amplitude in the nucleating layer thickness (occurring at bulk layer thicknesses from \( d_b \sim 5 \) to \( 10 \text{ Å} \)), the roughness after coalescence, and the roughening rate near the end of deposition vary consistently with x. First, the overall roughness amplitude decreases upon addition of S to CdTe considering the nucleation and coalescence regime. For CdTe\(_{0.72}\)S\(_{0.28}\), the surface is very smooth and stable for the first 200 Å of bulk layer growth -- considerably smoother than pure CdTe. In contrast, the addition of Te to CdS leads to an increase in

![Figure 3-14](image-url)
the roughness amplitude in this regime. For CdTec.41S0.59, the surface is very rough — considerably rougher than pure CdS even after coalescence, and the roughness is increasing rapidly after 100 Å of bulk layer growth. Because increased surface roughness amplitude has been found to be associated with increased compressive stress as indicated by the blue shift of the band gap relative to the single crystal, as will be

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<th>CdTe target power (W)</th>
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Table 3-1. Target power levels used in the fabrication of CdTe1-xSx alloy films by co-sputtering along with the predicted molar fraction of S.

Figure 3-15. Effective deposition rate for the CdTe1-xSx alloy films fabricated by magnetron co-sputtering.
discussed in detail in Chapter 4, then the smoothening with S addition to CdTe is possibly due to the relaxation of compressive stress due to the smaller atomic radius of S relative to Te. Similarly, the enhancement of roughness with addition of Te to CdS may be due to the generation of an additional compressive stress component due to the larger atomic radius of Te. In the composition range between \( x = 0.3 \) and \( x = 0.6 \), there is an abrupt transition from the CdTe-rich smooth surface to the CdS-rich rough surface. This roughening between \( x = 0.3 \) and \( x = 0.6 \) possibly represents the phase transition from more relaxed cubic CdTe to compressively stressed hexagonal CdS. Additional discussion of the stress in the binary compounds will appear in Chapter 4.
Key nucleation parameters are shown in Fig. 3-17, including the peak surface roughness, or nuclei height, and the bulk layer thickness at the peak surface roughness thickness. It is interesting that both curves have the maximum value at an intermediate composition $x \sim 0.6$. Because the peak nuclei height is related to the capture radius for the deposited species during clustering, Fig. 3-17 may indicate a maximum interaction between the deposited CdTe and CdS species when their individual incident fluxes are close to one other.

Figure 3-17.  Key cluster parameters for the CdTe$_{1-x}$S$_x$ alloy depositions of Figs. 3-15 and 3-16 as a function of $x$. These include $d_s$ at its maximum (top curve) and the $d_b$ value at the $d_s$ maximum (lower curve).
3.4 Effects of deposition pressure on magnetron sputtering of CdTe

A second series of polycrystalline CdTe thin films were magnetron sputtered onto native oxide covered crystalline Si substrates for study by RTSE as a collaborative effort (Sestak et al., 2009). For this second series the deposition temperature was fixed at $T_d=230^\circ$C, near the minimum in the void fraction in the inset of Fig. 3-8 (a). The key process variable was Ar pressure $p_{Ar}$, which was varied within the range of 2.5 – 50 mTorr while fixing the RF power at 60 Watts and the Ar flow rate at 23 sccm. The final target film thickness of ~ 1 µm was larger than in the previous CdTe series (~ 0.33 µm) as described in Section 3.1.

One obvious effect of varying the Ar pressure is to vary the number of collisions that the deposited species experience in transit from the target toward the substrate. As the number of collisions increases, the directionality of the flux is lost and the deposition rate $R_{eff}$ decreases as shown in Figure 3-18 for $R_{eff}$ deduced in the thin film regime ($d_b < 500$ Å) versus Ar pressure. At the pressure of 2.5 mTorr, the highest rate of 2.1 Å/s is achieved as determined by RTSE, but this is the minimum pressure for a stable plasma, and no further increase in deposition rate is possible. It is noted that the effective deposition rate for the $p_{Ar}=18$ mTorr point of Fig. 3-18 (1.26 Å/s) is higher than that of the $T_d=237^\circ$C point of Fig. 3-3 (0.89 Å/s), although the deposition parameters for these two films are very close to one another. This is attributed to the fact that the CdTe target used for the sputtering depositions of Section 3.1 is different than that used for the sputtering depositions of this section. Thus, the structural evolution data of this section
are not expected to be directly comparable with those of Section 3.1. Nevertheless, the study of the effect of $T_d$ on CdTe depositions as described in Section 3.1 and that of $p_{Ar}$ as described in this section are still meaningful. Within each study only one target was used and all the depositions were performed consecutively in a relatively short time period in order to minimize possible target effects.

Figure 3-19 depicts the evolution of $d_s$ with $d_b$ in the range of $0 < d_b < 3000$ Å for the CdTe sputter depositions of Fig. 3-18, obtained through analyses similar to those of Fig. 3-4. The evolution of $d_s$ in the initial 500 Å of $d_b$ in Fig. 3-19 was obtained by analyzing the $(\psi, \Delta)$ spectra over their full spectral range (0.75 – 6.5 eV) using a
two-layer [bulk/roughness] model. For $500 < d_b < 1000$ Å, $d_s$ was obtained using a model that incorporates a second bulk layer with increased void volume fraction ($f_v$) on top of the denser underlying bulk layer ($\sim 500$ Å thick). This was necessary in order to achieve a quality of the fit to the RTSE data close to that when $d_b < 500$ Å. On the right side of Fig. 3-19, the evolution of $d_s$ is shown for $1000 < d_b < 3000$ Å. In this case, the ($\psi, \Delta$) spectra were analyzed from 3.5 to 6.5 eV where the CdTe films are opaque and high surface sensitivity is attained. In this latter analysis, a one-layer model

![Figure 3-19. Evolution of the surface roughness layer thickness $d_s$ with bulk layer thickness $d_b$ for the CdTe films of Fig. 3-18. The left part of the abscissa ($d_b < 1000$ Å) is plotted on a log scale to highlight the nucleation behavior; the right part of the abscissa ($1000 < d_b < 3000$ Å) is plotted on a linear scale to depict the longer term evolution. The surface roughness layer thickness at $d_b \sim 3000$ Å is plotted as a function of Ar pressure $p_{Ar}$ in the inset.](image)
[(semi-infinite bulk)/roughness], that avoids the complicated underlying structure, was used. The $d_b$ value plotted along the abscissas in Fig. 3-19 is obtained in an analysis that uses the full multilayer model for the sample, similar to that explained in Section 3.1. The evolution of $d_s$ with $d_b$ in the right panel of Fig. 3-19 is nearly linear for all depositions. The maximum roughness is observed for an intermediate pressure of 14 mTorr as indicated in the inset.

The initial nucleation and coalescence stages of the depositions at different pressures are depicted in Fig. 3-20 which focuses on the surface roughness thickness.

![Figure 3-20](image.png)

Figure 3-20. The nucleation behavior of the sputtered CdTe films of Figs. 3-18 and 3-19.

At $p_{Ar} > 10$ mTorr, surface roughness (nuclei height) reaches 10–31 Å before the first bulk monolayer forms. At $p_{Ar} \leq 10$ mTorr, bulk layers of ~3–7 Å (~1–2 monolayers) form on the substrate before the onset of clustering. This figure was adapted from (Sestak et al., 2009) with permission of the authors.
versus bulk layer thickness in the first 125 Å. It is clear that at lower pressures, layer
followed by island growth or the Stranski-Krastanov mode is favored whereas at higher
pressures, island growth from the onset or the Volmer-Weber mode is favored (Venables
et al., 1984). The trend is characterized by a larger bulk layer thickness at which the
surface roughness starts to grow from zero at the lower pressures. Figure 3-21 shows the
two ways to determine the S-K to V-W transition pressure, similar to those demonstrated
in Fig. 3-11 for the effect of $T_d$. The transition is identified either (i) as the Ar pressure

![Figure 3-21. Two ways to determine the V-W to S-K transition pressure (vertical line), either (i) as the pressure at which the surface roughness thickness ($d_s$) drops below a single monolayer at the bulk monolayer thickness ($d_b \sim 3$ Å) (upper panel) or (ii) as the pressure at which the bulk layer thickness ($d_b$) increases above one monolayer for a surface roughness layer thickness of a single monolayer ($d_r \sim 3$ Å) (lower panel).]
at which the surface roughness layer thickness \((d_s)\) increases above a single monolayer at the bulk monolayer thickness \((d_b \sim 3 \text{ Å})\) (upper panel) or (ii) as the Ar pressure at which the bulk layer thickness \((d_b)\) drops below one monolayer for a surface roughness layer thickness of a single monolayer \((d_s \sim 3 \text{ Å})\) (lower panel). The trends versus \(p_{\text{Ar}}\) in Fig. 3-21 are systematic and reveal that the transition \(p_{\text{Ar}}\) is \(\sim 10\) mTorr (vertical line).

In Fig. 3-22 (upper panel), the peak nuclei height is observed to decrease
monotonically with decreasing Ar pressure on the atomic scale of resolution. Since the incident energy and the directionality of the species arriving at the substrate increases with decreasing pressure, the trends in Fig. 3-22 (a) may be a direct result of this relationship. Energy carried by the incident species may result in a compaction of the film and also enhancement of the local diffusion of surface species resulting in the filling of voids between growing clusters. In this case, the increase in peak nuclei height is not attributed to a reduction in nuclei density and associated increase in surface diffusion, but rather an enhancement in shadowing that promotes columnar microstructure. In Fig. 3-22 (lower panel), the bulk layer thickness at the peak in the nuclei height decreases as the Ar pressure increases from 2.5 mTorr. A minimum is reached near 18 mTorr followed by a weak rise as the Ar pressure increases to 50 mTorr. In fact, this trend versus Ar pressure is the inverse of that for the roughness thickness on the final 1 µm thick film as discussed next. This supports the concept that the conditions under which a large nuclei maximum and a low bulk layer thickness at that maximum occur together are those leading to columnar growth with significant surface roughness.

Figure 3-23 shows the surface roughness evolution for the CdTe films of Figs. 3-18 through 3-22, plotted versus bulk layer thickness from ~ 600 Å to the end of the deposition (Sestak et al., 2009). Over this thickness range, the surface roughness grows almost linearly. The magnitude of the final roughness thickness shows an interesting trend versus Ar pressure. The 2.5 mTorr film has the thinnest roughness layer, remaining ultra-smooth throughout the deposition. As the Ar pressure increases, the final roughness
thickness increases rapidly, reaching a maximum value at ~ 20 mTorr that is ~ 35 times larger than that of the 2.5 mTorr film. As the Ar pressure increases above 20 mTorr, the roughness thickness exhibits a moderate decrease. The final $d_s$ values are plotted as a function of Ar pressure in the inset of Fig. 3-23.

The large variation in the final roughness layer thickness on the CdTe as shown in Fig. 3-23 provides the opportunity for a comparison of RTSE roughness with roughness measured directly by atomic force microscopy (AFM). Similar correlations between
RTSE and AFM roughness values for a-Si:H films have been found to be helpful in evaluating the different sensitivities of both RTSE and AFM (Fujiwara et al., 2000). In this research, the magnetron sputtered CdTe films of Fig. 3-23 were studied ex situ by AFM in the tapping mode with a scan area of 5x5 µm². An example of a 3-dimensional AFM image is depicted in the upper part of Fig. 3-24, which corresponds to the circled point in the correlation of the lower part of the figure. Here the final RTSE roughness values from Fig. 3-23 are plotted versus the root mean square (RMS) values deduced from the AFM images. An approximately linear correlation is observed given by $d_s(\text{SE}) \sim 1.7d_{\text{RMS}}(\text{AFM}) - 81\text{Å}$, which has a similar slope to that in the literature for a-Si:H films (Fujiwara et al., 2000). The major difference in this study is the large negative intercept ($-81\text{Å}$) for the CdTe which may be attributed to components of surface roughness with an in-plane scale on the order of the wavelength of light, which are detectable by AFM but not by RTSE. Additional discussion of the optical detection of surface roughness with such large in-plane scales appears in the literature (Chen et al., 2006).

It should be noted that CdTe films sputtered at a substrate temperature of 230ºC and an Ar pressure of 10 mTorr are found to provide the best solar cell performance. In the fabrication of CdTe for solar cells, other deposition parameters are fixed at those described earlier in this Section. A comparison of the AFM images of six CdTe samples prepared at different Ar pressures, as shown in Fig. 3-25, indicates that the 10 mTorr sample lies in the boundary region between two distinct microstructures. Below 10 mTorr, the surfaces of CdTe samples exhibit very fine-grained or even amorphous characteristics.
The deposition at 2.5 mTorr, for example, exhibits no clear grain structure, while at the same time exhibiting a smooth and relatively uniform surface. The surfaces of CdTe samples prepared at Ar pressures above 10 mTorr exhibit a well defined grain structure,
but at the same time exhibit considerable roughness and non-uniformity. The fact that relative large grains are observed in these images with significant free space surrounding each grain suggests a shadowing mechanism in the growth process which occurs when the directionality of the flux is lost. At 10 mTorr, the CdTe film surface has a well-defined uniform crystalline grain structure without large void structures between the grains. Thus, 7.5 – 10 mTorr represents a transition region separating directional flux with high impact energies from fully thermalized diffuse flux with energies closer to the thermal. This is evident in the surface roughness evolution of Fig. 3-23 where the most significant increase in roughness occurs for these two depositions. The correlation between grain structure, void fraction in CdTe films, and solar cell performance is a subject for future investigation.
Figure 3-25. A comparison of 5x5 \( \mu\text{m}^2 \) AFM images of six CdTe samples sputtered at different Ar pressures as indicated. The shading scale range is given at the upper right of each image.
Chapter 4

Analysis of The Dielectric Functions of CdTe and CdS for Temperature, Grain Size, and Stress: Potential for On-line Monitoring

4.1 Introduction

One of the major research and development challenges in the field of polycrystalline thin film materials arises from the large variation in materials structure that requires extensive materials optimization for each specific application. This is in contrast to the situation for single crystals or glasses where relatively little structural variation exists, in the first case due to near-perfect order and in the second case due to disorder that is well-defined in statistical terms. For photovoltaic applications, both the optical and electronic properties of polycrystalline thin films play important roles in determining the solar cell performance. As a result, it is critical to understand and characterize variations in these properties that arise due to the structural variations.

Spectroscopic ellipsometry (SE) has proven to be a powerful probe in research on thin film materials due to its extremely high sensitivity to film structure including thickness and surface roughness, as well as to film optical properties. Many key material characteristics, such as temperature, void fraction, grain size, defect density, film stress,
crystalline phase, alloy composition, and free carrier concentration, can exert influences on the optical properties. Therefore, in-depth research on the variations of polycrystalline thin film optical properties with preparation procedure can provide not only practical information to guide solar cell fabrication, but also insights into the optical physics of polycrystalline materials.

Over the years, SE has been used successfully to study polycrystalline Si (poly-Si) prepared by several different technologies, including as examples, chemical vapor deposition and ion-beam sputtering (Bagley et al., 1981; Collins et al., 1985; Boultadakis et al., 1992; Jellison et al., 1993). The optical properties of poly-Si films were first explained assuming a mixture of amorphous Si, single crystal Si, and void, based on an effective medium theory (EMT) (Aspnes, 1981). Improvements beyond this basic concept in terms of the ability to fit experimental SE data were achieved by assuming a two layer structure for the deposited poly-Si films with different compositions for the near substrate and near surface components of the film (Bagley et al., 1981). Further improvement has been made possible more recently by varying the optical response of the single crystal Si component based on analytical models in which case parameters in the models vary with crystalline grain size, and film stress (Boultadakis et al., 1992; Jellison et al., 1993). These improvements indicate first of all that the material properties are inhomogeneous versus film thickness even when the deposition parameters are held constant. Second and more recently, it was determined that the polycrystalline phase possesses its own distinct optical properties, which are sensitive to its polycrystalline
structure, and that an EMT mixture of the corresponding amorphous and single crystalline phases is an oversimplification.

In fact, this previous research (Bagley et al., 1981; Collins et al., 1985; Boultadakis et al., 1992; Jellison et al., 1993) was based on *ex situ* SE, which can only provide a “snapshot” of the final film and thus makes analysis of graded structures with depth into the film very difficult. Typically one must deduce a poorly-defined average set of optical properties for the components of the film including bulk, surface, and substrate interface regions. This problem was largely solved by the development of real time spectroscopic ellipsometers with multichannel capability, instruments with the capabilities of analyzing the dynamic evolution of material properties and film structure (Collins et al., 2005). The advantage of spectroscopic ellipsometry compared to reflectance spectroscopy is that the ellipsometric p-s phase shift difference $\Delta$ provides monolayer sensitivity to ultrathin films. Because of its extremely high surface sensitivity combined with its dynamic measurement capability, real time SE (RTSE) is a unique tool that has been used widely in various thin film technologies (Collins et al., 2005). The proposition of a multilayered structure for future improvements in fitting *ex situ* SE data on Si thin films (Bagley et al., 1981) was clearly demonstrated in RTSE studies of thin film hydrogenated Si (Si:H). In fact, clear transitions from purely amorphous Si:H to mixed-phase (amorphous + microcrystalline) Si:H, and finally to single-phase microcrystalline Si:H have been characterized in detail through RTSE studies during plasma-enhanced chemical vapor deposition (PECVD) of thin film Si:H
With such a capability, RTSE has been applied successfully in the field of thin film photovoltaics to guide amorphous and microcrystalline Si:H based solar cells for optimization of the PECVD process (Collins et al., 2003; Cao et al., 2008). RTSE is now also being applied to polycrystalline CdTe/CdS solar cells for understanding and possible optimization of sputtering and CdCl₂ post-processing. For situations in which one or more layer thicknesses are critical, then the motivation exists to develop an SE system designed for high speed spatial scanning over the full solar panel area in order to monitor layer thicknesses on the production line. Furthermore, if the relation between material optical properties and other important properties can be established, then the motivation to develop such a spatial scanner is even greater.

In this chapter, capabilities for on-line optical monitoring are being sought beyond the simple thickness and compositional information described in Chapter 3. The additional information that may be possible to deduce includes temperature, grain size (or defect density), and film stress. Each of these film characteristics can exert a significant influence on the critical point parameters of the CdTe or CdS dielectric functions and so should be determinable from the fitting of optical spectra. Because of the existence of multiple critical points, the capability of extracting several characteristics of the film independently without correlation may be possible. The requirement for such on-line process monitoring development is a database that relates critical point energies and widths to the physical properties of interest.
4.2 Temperature effect

Because the temperature of a solar module will be above room temperature as it progresses out of the CdTe deposition chamber, it is important to determine the temperature in on-line monitoring applications if only to identify the proper database to use for the dielectric functions. Because the critical point parameters of CdTe and CdS and thus the dielectric functions depend on temperature, it is important to establish this information for proper interpretation of other material properties including thicknesses, compositions, grain size, and strain.

To investigate the variation of CdTe and CdS optical properties with temperature, a series of polycrystalline CdTe and CdS thin films were magnetron sputtered with parameters shown in Table 4-1, as also described in Chapter 3. Native oxide covered crystalline Si wafers were used as substrates due to their consistent smoothness and well studied temperature-dependent optical properties. In situ real time SE data were collected during these depositions to determine the structural parameters of the films, such as the bulk layer thickness $d_b$ and surface roughness thickness $d_s$. In each case, the key process variable was deposition temperature $T_d$, which was determined from an in situ calibration.

<table>
<thead>
<tr>
<th>Deposited material</th>
<th>RF power (Watt)</th>
<th>Ar pressure (mTorr)</th>
<th>Ar flow (sccm)</th>
<th>Deposition temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdTe</td>
<td>60</td>
<td>18</td>
<td>23</td>
<td>188-304</td>
</tr>
<tr>
<td>CdS</td>
<td>50</td>
<td>10</td>
<td>23</td>
<td>145-320</td>
</tr>
</tbody>
</table>

Table 4-1. Deposition parameters used in this study of magnetron sputtered CdTe and CdS. The key process variable is the deposition temperature.
based on the c-Si optical properties prior to all the depositions as described in Section 3.1. All depositions were temporarily suspended after a thickness of 500 – 1000 Å. Then the deposited films were stepwise cooled from $T_d$ to 15°C under vacuum as SE measurements were taken, and finally reheated to $T_d$ for continuation of the depositions. Such a thickness for cooling/heating was selected to reduce possible inhomogeneities in material properties versus depth that occurs in the thicker films as described in Chapter 3. During cooling, *in situ* SE spectra ($\psi$, $\Delta$) were acquired at each step in the measurement temperature $T_m$ as calibrated from the c-Si optical properties. These ($\psi$, $\Delta$) spectra were mathematically inverted to deduce the complex dielectric function $\varepsilon = \varepsilon_1 + i\varepsilon_2$ of the film as outlined in Section 2.6, using the $d_b$ and $d_s$ values that were accurately determined from real time SE data taken during film growth. In this way, $\varepsilon$ of each CdTe or CdS film deposited at $T_d$ was obtained as a function of $T_m$.

Figure 4-1 (a) shows a representative dielectric function of a CdTe film, measured both at $T_m = T_d = 188°C$ and $T_m = 15°C$. Four distinct critical points (CP's) are evident and denoted conventionally as $E_0$, $E_1$, $E_1+\Delta_1$, and $E_2$ (Kim *et al.*, 1997). Figure 4-1 (b) shows a representative dielectric function of a CdS film, measured both at $T_m = T_d = 310°C$ and $T_m = 15°C$. Three distinct CP's are evident and denoted in this case as $E_0$, $E_{1-A}$, and $E_{1-B}$ (Hofmann *et al.*, 1993).

Similar to the behavior in Fig. 4-1 (b), the $E_{1-A}$, and $E_{1-B}$ CP's can be observed in the dielectric functions of all the CdS films measured in this study. SE studies of CdS single crystals reveal that the doublet occurs only in the hexagonal polymorph (Hofmann...
et al., 1993). The cubic zincblende crystal exhibits a single peak in this energy region near the higher energy peak of the doublet. In addition, Hofmann et al. shows that the doublet is observed only in the ordinary dielectric function of the hexagonal CdS single crystal. Accounting for the strong refraction of the incident wave in the CdS, implying that the optical electric field in the thin film measurement lies within the plane of the film,
the results suggest that the optic axes of the crystallites are perpendicular to the film surface. Thus, the film must be highly oriented.

In an attempt to corroborate this optical interpretation, x-ray diffraction (XRD) was performed on the CdS films, as shown in Fig. 4-2. The film thicknesses are all near 1300 Å, accurately determined from the real time SE data. The dominant diffraction peak at $2\theta \sim 26.4^\circ$ appears for both hexagonal close-packed (HCP) and zincblende cubic phases of CdS and thus, cannot be used on its own for CdS crystal structure identification. (All other strong peaks in Fig. 4-2 are due to the c-Si substrate.) The fact that very weak peaks associated with the hexagonal polymorph exist at $2\theta \sim 25^\circ$ and $2\theta \sim 28^\circ$ implies that the film structure as deduced solely by XRD could range from purely hexagonal with

![Figure 4-2](image)

Figure 4-2. X-ray diffraction data for CdS films magnetron sputtered on c-Si substrates held at different deposition temperatures $T_d$. 

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strong (002) preferential orientation to (111) oriented zincblende with a small volume fraction of randomly oriented hexagonal phase. Thus, SE can resolve the ambiguity in this case and identifies the correct interpretation of the XRD in terms of hexagonal CdS with the optic axis of the crystallites preferentially oriented perpendicular to the film surface. For the CdS films deposited at lower $T_d$, the two weak features in XRD data -- signs of other hexagonal orientations -- become stronger at the expense of the dominant peak at $2\theta \sim 26.4^\circ$ indicating that the grain orientation becomes more random for CdS films deposited at decreasing $T_d$.

In Fig. 4-1, the major changes in the dielectric function for a given film with increasing $T_m$ include (i) a shift in the CP positions to lower energy, most visible for the sharp $E_0$ transitions of both CdTe and CdS, and (ii) broadened CP features. Previous studies of many single crystal semiconductors, such as Si, GaAs, and CdTe indicate that within the $T_m$ range of this study, all CP energies decrease monotonically with $T_m$ and all CP widths increase monotonically with $T_m$ (Lautenschlager et al., 1987a; Lautenschlager et al., 1987; Kim et al., 1997). The physical reasons for these variations include the thermal expansion of the lattice and the enhanced electron-phonon interactions at higher $T_m$ (Lautenschlager et al., 1987). In this study, similar trends have been observed for the CP's of polycrystalline CdTe and CdS films, whose grain sizes can range from tens of nanometers to microns. To quantify the CP variations, second derivative spectra $d^2\varepsilon/dE^2$ were fit to an analytical model based on the parabolic band approximation:
\[ \varepsilon = \sum_n A_n e^{i\phi_n} (E_n - E - i\Gamma_n)^{\mu_n} \]  
(4.1)

at the critical point where \( E \) is photon energy; \( A_n, E_n, \Gamma_n, \mu_n, \) and \( \phi_n \) are the amplitude, band gap (resonance energy), broadening parameter (or width), exponent, and phase of the \( n^{th} \) critical point, respectively (Collins and Ferlauto, 2005). Examples of second derivative spectra are shown in Fig. 4-3 including data and their fits, the latter using the

Figure 4-3. Second derivative spectra \( d^2\varepsilon/dE^2 \) of the complex dielectric functions measured at \( T_m=15^\circ\text{C} \) for (a, upper) the CdTe film magnetron sputtered at \( T_d=237^\circ\text{C} \), and (b, lower) the CdS film magnetron sputtered at \( T_d=160^\circ\text{C} \). The data are depicted as the points and the fits are based on Eq. (4.1) are depicted as the lines.
expression in Eq. (4.1). It can be seen that upon taking the second derivatives, the CP features become sharper and isolated from one another, and thus easier to fit with less correlation. It is noted that if the dielectric function can be expressed using Eq. (4.1), then any order of the derivative $\frac{d^k \varepsilon}{d E^n}$ can also be expressed using Eq. (4.1) with different values of $A_n$, $\mu_n$, and $\phi_n$. The most interesting parameters – $E_n$ and $\Gamma_n$ – remain unchanged regardless of the order of derivative.

Figure 4-4 shows the variations of CdTe $E_0$, $E_1$, $E_1 + \Delta_1$, and $E_2$ CP energies and widths as functions of $T_m$. Figure 4-5 show the variations of CdS $E_0$, $E_1$-A, and $E_1$-B CP energies and widths as functions of $T_m$. Previous studies of single crystal semiconductors, such as Si and CdTe, indicate that over the $T_m$ range of this study, the variations of the CP energies and widths can be described as approximately linear functions of $T_m$ (Lautenschlager et al., 1987a; Kim et al., 1997). In this study, similar linear dependences are also observed for polycrystalline CdTe and CdS, as exemplified in Figs. 4-4 and 4-5. All linear temperature coefficients of the major CP energies $C_{TE}(E_n)$ and the CP widths $C_{TR}(E_n)$ are summarized in Table 4-3 with other important parameters as described in greater detail in Sections 4.3 and 4.4. It may be possible to use these coefficients in a spatially scanning SE system to deduce temperature maps of CdTe solar modules in process on the production line.
Figure 4-4. The variations of CdTe $E_0$, $E_1$, $E_1+\Delta_1$, and $E_2$ CP energies (left panels) and widths (right panels) as functions of measurement temperature $T_m$. The indicated temperature coefficient within each panel is the slope of the corresponding linear fit. The error bars are 90% confidence limits in the fits similar to those in Fig. 4-3 using Eq. (4.1).
Figure 4-5. The variations of CdS $E_0$, $E_1$-A, and $E_1$-B CP energies (left panels) and widths (right panels) as functions of measurement temperature $T_m$. The indicated temperature coefficient within each panel is the slope of the corresponding linear fit.
4.3 Effects of defect density and grain size

An additional complication that provides further opportunity for advanced on-line analysis of the CdS and CdTe components of the solar cell is the variability in the dielectric functions due to changes in the substrate nature and detailed deposition and post-process conditions. Although variations in void fraction can account for some aspects of the sample-to-sample variations in CdS and CdTe structure and optical properties as described in Chapter 3, it has been recognized that a more sophisticated approach is required to overcome the weaknesses inherent in the oversimplified modeling of Fig. 3-7. This approach can be developed starting from a study of the dielectric functions of CdS and CdTe films sputter deposited at different $T_d$ with other conditions given in Table 4-1. The CdS study will be presented first as its dielectric function shows clear characteristics consistent with a semi-classical model of electron scattering at grain boundaries. From the observed consistent variations in width for different CdS CP's, important information can be deduced, including (i) the average mean free path of excited carriers within the film (obtained in this case as a function of $T_d$) and (ii) the group speeds associated with the electronic excitations in CdS. Once the group speeds are obtained, the optical properties for any hexagonal CdS film having the same scattering mechanism can be interpreted to deduce the mean free path. When the dominant mechanism is excited carrier scattering at grain boundaries, the mean free path will be equal to the grain radius.

To investigate the effects of grain size on the CdS and CdTe optical properties (or the effects of the density of defects which can also scatter excited carriers), it is necessary...
to compare samples measured by SE at the same $T_m$ in order to avoid the temperature variations as described in Section 4.2. Figure 4-6 (a) compares the near room temperature (15°C) dielectric function $\varepsilon$ of the CdTe film deposited at $T_d = 188^\circ C$ with the room temperature $\varepsilon$ of single crystal CdTe (Johs et al., 1998). Figure 4-6 (b) compares the near room temperature (15°C) dielectric functions $\varepsilon$ of two sputtered CdS films, one deposited

![Figure 4-6](image_url)

Figure 4-6. (a, upper) $T_m = 15^\circ C$ dielectric function $\varepsilon$ of the $T_d = 188^\circ C$ CdTe film and room temperature $\varepsilon$ of single crystal CdTe; (b, lower) $T_m = 15^\circ C$ dielectric functions of the $T_d = 145^\circ C$ CdS film and the $T_d = 310^\circ C$ CdS film.
at $T_d=145^\circ C$ and the other deposited at $T_d=310^\circ C$. Clear differences in the widths of CP features can be observed in both Figs. 4-6 (a) and 4-6 (b) (see the insets). Such differences have been quantified by Eq. (4.1) in Section 4.2. Figure 4-7 shows the best fit broadening parameters $\Gamma_n$ near room temperature ($15^\circ C$) for the CdS films plotted as functions of $T_d$. The variations of $\Gamma_n$ with $T_d$ for all CP's are quite consistent, revealing a decrease from $T_d=145^\circ C$ to $310^\circ C$.

Among the CdS films in Fig. 4-7, the sample deposited at $T_d=310^\circ C$ has the smallest broadening parameters (circled) for each of the $E_0$, $E_{1-A}$, and $E_{1-B}$ CP's. In fact, the CP features in $\varepsilon$ for this sample are even sharper than those of single crystal CdS, as reported by Ninomiya and Adachi (1995) and as observed in this study. A comparison of the three dielectric functions, two single crystal and one thin film, are

![Diagram](image-url)

**Figure 4-7.** CP broadening parameters at $T_m=15^\circ C$ as functions of $T_d$ for the $E_0$, $E_{1-A}$, and $E_{1-B}$ CP's of CdS. The smallest values for the three CP's are circled.
shown in Fig. 4-8. The broader CP widths of the single crystal are likely due to the near-surface damage that occurs during the polishing of the single crystal CdS. Thus, $\Gamma_n$ for the $T_d=310^\circ C$ sample can be taken as intrinsic to single crystal CdS (denoted by $\Gamma_{bn}$; b: bulk) -- even more so than results from careful measurements on single crystal CdS itself. Thus, the $E_0$ transition for this sample can be related to the band structure of CdS, shown schematically in Fig. 4-9. Here the broadening parameter associated with the fundamental gap, $\Gamma_{b,E0}$, indicates how far away from the Brillouin zone center an excitation can occur and still contribute significantly to the optical transitions of the $E_0$ CP. So, in Fig. 4-9, the energy increments $\pm \Gamma_{b,E0}/2$ are considered to define the upper (+)

Figure 4-8. Comparison of dielectric functions of single crystal CdS measured at room temperature in a study by Ninomiya and Adachi (1995) and in this study. Also shown is the dielectric function of the $T_d=310^\circ C$ CdS film of this study measured near room temperature.
and lower (-) energy boundaries relative to the E_0 transition, meaning that the measured E_0 transition energy lies in the range of \((E_g - \Gamma_{b,E_0}/2, E_0/2)\) to \((E_g + \Gamma_{b,E_0}/2, E_0/2)\).  At the upper boundary with \(k = k_0\), \(V_{g,E_0} = dE/d(hk)|_{k=k_0}\) (\(h = h/2\pi\); \(h\) is Planck’s constant) is the (maximum) group speed of excited electrons or holes associated with the E_0 transition.

Assuming the parabolic band approximation for both the valence band (VB) and the conduction band (CB) in Fig. 4-9, the following expression for electrons can be derived:

\[
V_{g,E_0} = \left\{ \Gamma_{b,E_0} m_e^* / \left[ m_e^* (m_e^* + m_h^*) \right] \right\}^{1/2} \tag{4.2}
\]

where \(m_e^*\) is the electron effective mass at the bottom of the CB and \(m_h^*\) is the hole effective mass at the top of the VB. With \(m_e^* = 0.2m\) and \(m_h^* = 0.7m\) where \(m\) is the electron mass (Pankove, 1975), \(V_{g,E_0}\) of CdS is calculated to be \(~2.2 \times 10^5\) m/s. The corresponding hole group speed is 3.5 times lower and so hole scattering is less likely to
contribute to the broadening.

If the dominant broadening effect is assumed to arise from the limited excitation lifetime due to electron scattering as a result of the deviations from single crystalline atomic periodicity, then the following equation can be applied (Feng and Zallen, 1989):

\[ \Gamma_n = \Gamma_{bn} + \left( \frac{h V_{gn}}{\lambda} \right) \]  

(4.3)

where \( \Gamma_n \) is the broadening parameter for the \( n^{th} \) CP; \( \Gamma_{bn} \) is the corresponding parameter for the single crystal; \( h \) is Plank’s constant; and \( V_{gn} \) is the (maximum) group speed of excited electrons associated with the \( n^{th} \) CP; and \( \lambda \) is the mean free path. If the scattering mechanism occurs due to grain boundaries in the polycrystalline film, then \( \lambda \approx R \), the grain radius. Using the values of \( V_g, E_0 \) and \( \Gamma_{b,E_0} \) for single crystal CdS and assuming dominant grain boundary scattering by electrons, \( R \) can be calculated versus \( T_d \) as shown in Fig. 4-10. It can be seen that the deposition temperature \( T_d \) has a strong effect on the mean free path and, thus, the apparent grain size in sputtered CdS films. Increasing \( T_d \) from 150°C to 300°C increases the apparent grain size by a factor of ~ 30.

It is noted that Eq. (4.3) applies not only for the \( E_0 \) CP, but for all other CP’s as well. As a check of the validity of the general approach, the other two critical point widths \( \Gamma_{E_1-A} \) and \( \Gamma_{E_1-B} \) are plotted versus \( R^{-1} \) in Fig. 4-11. The linear relation as predicted by Eq. (4.3) is closely followed. From the linear fits, the group speeds for the \( E_1-A \) and \( E_1-B \) electronic excitations are determined as \( 3.3 \times 10^5 \) and \( 8.8 \times 10^5 \) m/s, respectively.

With the above information, a dielectric function parameterization is possible that uses the grain size as a controlling parameter -- similar to what is now possible with void
fraction. In this parameterization the grain size is assigned, and using the known values of $\Gamma_{bn}$ and $V_{gn}$, then the corresponding $\Gamma_n$ values can be determined according to Eq. (4.3). Once the $\Gamma_n$ values are determined, they are substituted into Eq. (4.1) along with the other CP fitting parameters associated with the $T_d = 310^\circ$C film in order to determine the dielectric function of a film having a given grain size. This is the first of several steps needed to demonstrate that physical parameters, including void fraction, grain size, and strain, can be extracted from an *ex situ* measurement of nearly complete solar cells, enabling an on-line mapping capability.

Figure 4-10. Grain size deduced from the $E_0$ CP broadening parameter using Eq. (4.3) for the series of CdS films deposited at different temperatures $T_d$. Here it is assumed that grain boundary scattering limits the electron mean free path. At the “maximum detectable grain size”, $\Gamma_{E0} \approx \Gamma_{b,E0}$, thus the polycrystalline CdS film is optically indistinguishable from the single crystal.
A similar procedure has been performed for extracting the mean free paths and transition group speeds for the series of CdTe films prepared at different $T_d$. In this case, greater challenges are encountered. Most importantly, the CdTe $E_0$ transition has a weaker amplitude than that of CdS as shown in Figs. 4-1 and 4-6. As a result, the $\Gamma_{E_0}$ values are more difficult to determine accurately compared to those of CdS. Inaccurate $\Gamma_{E_0}$ values lead to inaccurate $\lambda$ or $R$ values when determined based on the known $E_0$ CP data, $T_{E_0}$, $\Gamma_{b,E_0}$, and $V_{g,E_0}$. As a result, fluctuations in the abscissa are introduced into the expected linear relationships that establish the group speeds for the other three critical

![Graph](image.png)

Figure 4-11. CdS $E_1$-A and $E_1$-B CP broadening parameters plotted as functions of the reciprocal grain size deduced from the $E_0$ broadening parameter as shown in Fig. 4-10. The indicated group speeds of excited electrons associated with each CP were calculated from the slope of the corresponding linear fit using Equation (4.3).
points $E_1$, $E_1 + \Delta t$, and $E_2$. To circumvent this problem, the $E_2$ transition is used instead of $E_0$ to determine the carrier mean free path or grain size for CdTe. The band structure associated with the $E_2$ transition is not well-known, however, and thus the group speed is not known in advance. In this case, the group speed of excited carriers at $E_2$ is determined iteratively so as to ensure that the group speed of the $E_0$ electrons matches that estimated theoretically from the band structure based on Eq. (4.2) using values of the effective mass of $m_e^* \approx 0.11m$ and $m_h^* \approx 0.4m$ (Marple, 1963; Capper, 1994).

Assuming equality of the mean free path $\lambda$ and the grain size $R$, the results for the CdTe films as a function of $T_d$ are shown in Fig. 4-12. The relationships that establish the group speeds for the different transitions are shown in Fig. 4-13 and lead to the values for

![Graph showing CdTe grain size as a function of $T_d$](image)

**Figure 4-12.** Grain size $R$ deduced from the $E_2$ CP broadening parameters using Eq. (4.3) with $\lambda = R$ for the series of CdTe films deposited at different temperatures $T_d$.  

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$V_g, E_0, V_g, E_1, V_g, E_1 + \Delta_1$ of $2.3 \times 10^5$, $8.1 \times 10^5$, and $6.9 \times 10^5$ m/s, respectively. The $E_0$ value was the target value achieved through adjustment of $V_g, E_2$, resulting in $V_g, E_2 = 4.2 \times 10^5$ m/s.

It can be seen from Fig. 4-12 that the variation of $R$ with $T_d$ for CdTe is much weaker than that for CdS (Fig. 4-10). Nevertheless, these results still show promising features that help support the analysis procedures. First, the relationship that establishes the group
speed of the \( E_1 + \Delta_1 \) transition is followed quite accurately. This is to be expected since the \( E_1 + \Delta_1 \) transition appears prominently in the dielectric function spectra, and next to \( E_2 \) (see Fig. 4-1), its \( \Gamma \) value can be most accurately determined. Second, the group speed of the \( E_1 \) transition is close to that of the \( E_1 + \Delta_1 \) transition; this is to be expected since the \( L_{4,5} \) and \( L_6 \) valence bands of CdTe which are the initial states of the \( E_1 \) and \( E_1 + \Delta_1 \) transitions are closely parallel (Chelikowsky and Cohen, 1976). Finally, although the error bars of \( \Gamma \) for the \( E_0 \) transition are large, the best fit \( \Gamma \) vs. \( R^{-1} \) linear relation almost crosses each error bar with a slope that is in agreement with theory. In general, it can be concluded that analysis of the optical properties of CdTe can provide mean free path and grain size in a similar way as has been observed quite convincingly for CdS.

It should be noted that in the above discussions, grain boundary scattering is assumed to be the dominant broadening mechanism. If scattering by defects other than grain boundaries is dominant, then we can simply change the physical meaning of \( R \) from grain size to mean free path which then depends on the average distance between defects and the scattering cross-section. In this case, the deduced \( R \) should be proportional to \( N_d^{-1/3} \) where \( N_d \) is the defect density. In other aspects, the discussion is still valid including the deduction of group speeds for excited electrons.

To investigate the possibility that scattering sources other than grain boundaries limit the excited carrier mean free path and control the broadening parameters, the CdS films of Fig. 4-10 were characterized using other more direct techniques to estimate the grain radius. First, atomic force microscopy (AFM) in the tapping mode was performed
Figure 4-14. Atomic force microscopy images of four CdS films sputtered onto native oxide covered c-Si substrates at the indicated temperatures. The in-plane scale of these images is 5x5 µm², and the vertical gray scale spans 30 nm.

on the surfaces of these CdS films using a scan area of 5x5 µm². Figure 4-14 depicts AFM images of four films prepared at different deposition temperatures for comparison.
The increase in average grain structure size with increasing $T_d$ is clear. Fourier analysis was applied assuming a 2D isotropic distribution of grains. One half of the peak wavelength in the Fourier power spectrum was selected as an AFM estimate of the grain radius for the CdS films, as shown in Fig. 4-15. In addition, the x-ray diffraction (XRD) data of Fig. 4-2 were used to estimate grain radius $R$ based on the Scherrer formula: $R \sim k\lambda/(2\beta \cos \theta)$. In this equation, $k$ is set to unity, $\lambda$ is the x-ray wavelength (Cu K$_{\alpha}$: 1.54 Å), $\beta$ is the full width at half maximum of the 26.44° XRD peak corrected for the diffraction background, and $\theta=26.44°/2=13.22°$ (Patterson, 1939; Klug and Alexander, 1974). The XRD results are compared with the SE and AFM estimates in Fig. 4-15.

The accumulated results of Fig. 4-15 provide interesting information. The grain size estimated from all techniques increases with increasing $T_d$, which is at least a confirmation of the trend observed by SE. At lower $T_d$, however, SE appears to be dominated by intragrain scattering presumably by point defects or dislocations rather than by grain boundaries. The larger apparent grain size by AFM may indicate that the directly observed grains are actually composed of smaller grains. At higher $T_d$, SE and XRD estimates cross one another, and both AFM and SE suggest a larger grain size than the estimate by XRD. The nearly constant grain size from XRD for $T_d > 230^\circ$C may indicate that the resolution limit of the instrument is being approached as the diffraction peak becomes narrower. Another possible reason is that XRD may be more sensitive to the grain size along the direction normal to the sample surface. As explained earlier, these CdS films are hexagonal phase and highly oriented with the $c$ axis normal to the surface.
Thus, it is possible that the grains grow faster along the laminar (or in-plane) direction which is the direction that both AFM and SE probe. In the case of SE, the light wave is highly refracted toward the surface normal, so that the electric field has a larger component along the laminar direction. A final possibility is that one needs to incorporate a grain-size independent “grain boundary reflection coefficient” into Eq. (4.3) that is less than unity and whose reciprocal describes the number of scattering event needed to randomize the excited carrier momentum. This would lead to a higher apparent group velocity and larger grain size in the SE measurement than actually exists.

Figure 4-15. Comparison of grain radius deduced from SE, AFM, and XRD for CdS films magnetron sputtered onto native oxide covered crystal silicon substrates held at different deposition temperatures $T_d$. The results for SE are based on the assumption that grain boundary scattering limits the excited carrier mean free path.
The differences in the optical properties of CdS films deposited at different $T_d$ have a direct impact on the solar cell performance, without even considering possible variations in the electronic properties that may be the result of different grain sizes or defect densities. From Fig. 4-6, it is clear that CdS with smaller grain size, deposited at lower $T_d$, has longer and stronger absorption tail below the band gap, hence reducing the available sunlight in this spectral range for absorption in the active CdTe layer. To demonstrate this quantitatively, an optical model that simulates a superstrate CdTe solar cell structure was established as shown in Fig. 4-16. This model from top to bottom consists of: soda lime glass, the TEC-15 TCO stack (using optical property results from a separate study), a 0.13 micron thick CdS layer, a 2.0 micron thick CdTe layer, and an opaque (semi-infinite) Au substrate. Based on this model, a computer simulation was

Figure 4-16. A superstrate CdTe solar cell structure used to simulate the performance of solar cells with CdS layers deposited at different $T_d$. 

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performed under the following assumptions: (i) normal incidence AM1.5 spectrum; (ii) each photon absorbed by CdTe generates one electron-hole pair; (iii) all photo-excited electrons and holes in the CdTe are collected and contribute to the short circuit current $J_{sc}$; (iv) no collection occurs due to electron-hole pairs generated in the CdS; and (v) specular reflection and transmission occur at interfaces without scattering. In the simulations of Fig. 4-17, the variations in QE with CdS deposition temperature arise due to differences

Figure 4-17. Quantum efficiency (QE) generated by the simulations based on the optical model shown in Fig. 4-16. Different curves correspond to CdS films sputtered at different temperatures $T_d$ as indicated.
in the optical properties of CdS. It is clear that the longer absorption tails for CdS films deposited at lower $T_d$ decrease the QE in the spectral range of 500~700 nm. As a result, the simulated $J_{sc}$ generated by integrating the QE has higher values at higher $T_d$, as shown in Fig. 4-18. An increase in $T_d$ from 150 to 200°C leads to an increase in $J_{sc}$ by ~ 4%. The optimum range of deposition temperature for CdS is quite broad, extending from 200 to 300°C.

Figure 4-18. Short circuit current density ($J_{sc}$) generated from the simulations with the optical model shown in Fig. 4-16.
4.4 Stress effect

In addition to the clear differences in the CP widths between the CdTe thin films and the single crystal caused by grain size effects as discussed in Section 4.3, differences in the CP energies also occur most visibly in $E_0$ as shown in the upper left inset of Fig. 4-6 (a). Here it can be observed that the $E_0$ CP feature of the $T_d=188^\circ C$ CdTe film as measured near room temperature is significantly blue shifted relative to that of single crystal CdTe. Similar shifts are observed for all the sputtered CdTe films in this study. These shifts become even more obvious considering results obtained near room temperature for the second derivative spectra $d^2\varepsilon/dE^2$ at the $E_0$ CP as shown in Fig. 4-19. Here the $E_0$ peaks for the films are not only broader, but also $\sim 20 – 50$ meV higher in photon energy than for the single crystal.

In fact, similar shifts are also observed not only at $T_m=15^\circ C$ but also at elevated measurement temperatures. Figure 4-20 (a) shows the $E_0$ CP energy versus $T_m$ for the $T_d=304^\circ C$ CdTe film, reproduced from Fig. 4-4 (a). Also shown are the corresponding results for single crystal CdTe reported by Kim et al. (1997). The two curves are nearly parallel, indicating nearly the same average slope or temperature coefficient, $C_{Te}(E_0)$, for the $E_0$ CP energy. Figure 4-20 (b) provides a comparison of the linear fits of the $E_0$ CP energy data plotted versus $T_m$ for five CdTe films magnetron sputtered at different deposition temperatures $T_d$, including the data shown in Fig. 4-20 (a) for the film with $T_d=304^\circ C$. Also included in the comparison are the data and fits from the work on single crystal CdTe by Kim et al. (1997). All the linear fits, including the one for single
crystal CdTe, are nearly parallel within this range of $T_m$. The average temperature coefficient for the sputtered CdTe films is given by $<C_{\text{Te}}(E_0)> \sim -3.70 \times 10^{-4}$ eV/°C, within ~1% of the temperature coefficient of single crystal CdTe ($-3.66 \times 10^{-4}$ eV/°C).

In spite of the nearly parallel data sets in Fig. 4-20 (b), the magnitudes of the $E_0$ band gap energies are clearly shifted, by as much as ~55 meV relative to the single crystal. This behavior has important implications for substrate temperature calibration from a CdTe surface. The linear trends in Fig. 4-20 makes it possible to determine the temperature of...
a CdTe film, but not from a single measurement of the $E_0$ energy; instead, an energy difference $E_0(T_{m2}) - E_0(T_{m1})$ is required whereby $T_{m1}$ is a known temperature, typically near room temperature.

It has been reported both theoretically and experimentally that stress can shift the band gaps of semiconductors (Camphausen et al., 1971; H. Windischmann, 1987).
Camphausen et al. (1971) explained this effect based on the dielectric theory of chemical bonds. Given the relatively low $T_d$ range of the CdTe films prepared in this study by sputtering, as compared to other deposition technologies such as close space sublimation which is normally performed near ~ 600°C and given the significant compressive stress observed in sputtered thin films in general (Windischmann, 1987), it is reasonable to attribute the band gap shifts observed in Figs. 4-19 and 4-20 to the associated stress.

An estimate of the stress level in these films can be obtained based on previous measurements that relate hydrostatic pressure to the fundamental band gap in single crystal CdTe by Dunstan et al. (1989). These measurements have established a pressure coefficient $C_P(E_0)$ of 0.065 eV/GPa. Although the stress in the CdTe films is likely to be uniaxial rather than hydrostatic, the estimate may be a reasonable one because the optical electric field is strongly refracted into the material and thus probes the high stress direction. Furthermore the effects of uniaxial stress in a cubic polycrystalline film with a random distribution of grain orientation may be simulated by the effects of hydrostatic pressure. Figure 4-21 depicts the $T_m=15^\circ$C $E_0$ CP energy also defining the fundamental band gap $E_g$ of the CdTe films in Fig. 4-20 as a function of $T_d$, and compares them with $E_0$ CP energy of single crystal CdTe which is assumed to be stress free. The left scale shows the $E_0$ CP energy and the right scale uses the indicated pressure coefficient to estimate the compressive stress in the CdTe films. Values from 0.4 to 0.9 GPa are obtained, consistent in order of magnitude with stress levels often observed in sputtered thin films by Windischmann (1987).
Several observations support the trend in Fig. 4-21, if not the absolute values. For $T_d$ above 220°C, the ~1000 Å thick CdTe films pass through a relaxation transition whereby the stress decreases by a factor of two over a ~50°C range. The very high stress levels in the two lowest $T_d$ films are consistent with the observed low void fractions in this thickness range as shown in Fig. 3-8. For thicknesses greater than 1000 Å, these low $T_d$ films undergo abrupt structural transitions in which the void fractions increase significantly. For the two higher $T_d$ films, the void fraction in the thin film regime ($d_b$<500 Å) is higher and no structural transition is observed in Fig. 3-8. Thus, a high
initial stress in Fig. 4-21 is correlated with the appearance of a subsequent microstructural transition in the evolving film.

It is also important to assess the effect of stress on the other critical points of CdTe. If relationships between stress and the $E_1$, $E_1+\Delta_1$, and $E_2$ CP energies can be established, then the short penetration depth of the light at these energies compared to that at the $E_0$ energy provides higher surface sensitivity to the film stress. These relationships in conjunction with stepwise etching of CdTe enable depth profiling of the stress in the film. In Figure 4-22 the variations of the $T_m=15^\circ C$ $E_1$, $E_1+\Delta_1$, and $E_2$ CP energies are plotted for the CdTe films sputtered at different $T_d$. These variations are given relative to the corresponding single crystal CdTe CP energies and plotted versus stress deduced from $\Delta E_0$ of Fig. 4-21. Similar results are presented in Fig. 4-22 (open points) for two ~ 1000 Å thick CdTe films that were CdCl$_2$ treated after sputtering at $T_d \sim 188^\circ C$. All other deposition parameters for these films are the same as those in Table 4-1. Reasonable linear trends are observed in Fig. 4-22 which are fit with the constraint of zero stress in single crystal CdTe. The slopes or stress coefficients are indicated in Fig. 4-22 and summarized in Tables 4-2 and 4-3. For comparison, the stress coefficients and the zero stress energies calculated from the linear fits with and without the constraint of intersecting the zero stress points of single crystal CdTe are summarized in Table 4-2. For the $E_1$ and $E_1+\Delta_1$ critical points, the stress coefficients do not depend on the constraints imposed by single crystal CdTe, whereas for the $E_2$ transition, the stress coefficient is lower without the constraint. This may suggest inaccuracies not necessarily in the critical
point energies for the $E_2$ transition of the polycrystalline films, but rather in the corresponding energy for the single crystal. The results of Fig. 4-22 are important in two ways. First they imply that the deduction of the existence of stress shifts in these CP's do not depend on the quality of the single crystal CdTe CP data. Second, they demonstrate
that one role of the CdCl$_2$ treatment is to relax the stress in the CdTe films.

A similar study of stress has been performed on the CdS films magnetron sputtered at different deposition temperatures $T_d$. For these films, the $E_0$ CP energies are nearly constant with $T_d$ and much higher than the corresponding value deduced from the single crystal. Using the hydrostatic pressure coefficient reported by Batlogg (1983), a stress of ~1.5 GPa is deduced for the thin films, a constant value versus $T_d$ within the error bars of the measurement, as shown in Figure 4-23. This stress level is a factor of two higher than that observed for CdTe as shown in Fig. 4-21. A nearly constant, high level of stress in CdS is consistent with the observed very low void fraction in all films as described in Section 3.2. This in turn suggests that a higher substrate temperature is needed for stress relaxation in CdS through void development. Due to the weak variation of stress for the CdS thin films in Fig. 4-23, the $E_{1-A}$ and $E_{1-B}$ CP energies cluster around values which, along with those of single crystal CdS, define the stress

Table 4-2. Comparison of the stress coefficients and the zero stress energies for the $E_1$, $E_{1+\Delta_1}$, and $E_2$ CP's of CdTe, deduced from the linear fits in Fig. 4-22, with and without the constraint of passing through the single crystal CP energies at zero stress.

<table>
<thead>
<tr>
<th>CdTe critical point</th>
<th>with constraint</th>
<th>without constraint</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>stress coefficient (eV/GPa)</td>
<td>zero stress energy (eV)</td>
</tr>
<tr>
<td>$E_1$</td>
<td>-0.20</td>
<td>3.310</td>
</tr>
<tr>
<td>$E_{1+\Delta_1}$</td>
<td>0.23</td>
<td>3.894</td>
</tr>
<tr>
<td>$E_2$</td>
<td>0.16</td>
<td>5.160</td>
</tr>
</tbody>
</table>
coefficients for these CP’s as shown in Fig. 4-24 (left). In this case, however, in contrast to the case of CdTe, the stress coefficients depend critically on the correctness of the single crystal results. For example, much higher stress coefficients are deduced in Fig. 4-24 (right) when the CP energies of single crystal CdS from Ninomiya and Adachi (1995) are used to define the zero stress points. In the future, greater confidence in the stress coefficients may be obtained by measuring CdS films with differing degrees of stress relaxation. This may be possible by increasing the range of deposition temperature $T_d$ to include higher values, or increasing the Ar pressure to reduce the momentum per arriving atom and, thus, bombardment induced compressive stress. Stress coefficients for CdS CP energies using the results of Fig. 4-24 are summarized in Table 4-3.

Figure 4-23. The $T_m=15^\circ$C $E_0$ CP energy (also defining the fundamental band gap $E_g$) of sputtered CdS films as a function of $T_d$. The horizontal dashed line represents the room temperature $E_g$ for single crystal CdS which is assumed to be stress free. The right scale uses the indicated pressure coefficient of the band gap to estimate the compressive stress in the CdS films.
4.5 Parameterization of $\varepsilon$ and its application

In this section, potential capabilities for on-line optical monitoring will be evaluated beyond the fundamental function of SE for determination of film thicknesses and surface and interface roughness thicknesses as described in previous Chapters. The additional
information that may be deduced for a CdTe or CdS film includes mean free path, stress, and temperature. As described in previous Sections, film characteristics exert significant influences on the CP energies and/or widths, and so should be determinable from fitting the optical spectra. Over the parameter range of this study, the effect of measurement temperature $T_m$, inverse mean free path $\lambda^{-1}$, and stress $P$ on the energy and width of a specific CP can be approximated by the linear dependences as established in Sections 4.2 to 4.4:

$$\begin{align*}
\Gamma &= \Gamma_b(T_0) + C_{\Gamma T} (T_m - T_0) + [(h \cdot V_g / \lambda)] \\
E &= E_b(T_0) + C_{TE} (T_m - T_0) + C_P \cdot P
\end{align*}$$

(4.4)

Here $\Gamma_b(T_0)$ and $E_b(T_0)$ are the widths and CP energies of the single crystal at $T_0$, a reference measurement temperature which is normally room temperature; $C_{\Gamma T}$ and $C_{TE}$ are the temperature coefficients of the CP width and CP energy, respectively; $h$, $V_g$ and $\lambda$ have the same meanings as in Section 4.3; $C_P$ is the stress coefficient of the CP energy, and $P$ is the stress. Equations (4.4) apply to all CP's for CdTe and CdS. The corresponding coefficients and single crystal values for all the major CP's are summarized in Table 4-3. Because the dielectric function $\varepsilon$ of a CdTe or CdS film can be expressed in terms of the analytical model based on the critical point parabolic band approximation [Eq. (4.1)], which includes the CP energies and widths, then they can be further parameterized with Eqs. (4.4) directly as functions of key material characteristics including temperature, mean free path, and stress.

The characteristics of the coefficients in Table 4-3 to be described next are valid as
Table 4-3. Single crystal CP energies and widths, temperature coefficients of CP energies and widths, excited carrier group speeds, and stress coefficients of CP energies for the major CP’s of CdTe and CdS.

<table>
<thead>
<tr>
<th>Material</th>
<th>E_b(T_o) (eV)</th>
<th>(\Gamma_b(T_o)) (eV)</th>
<th>(C_{TT}) (eV/°C)</th>
<th>(C_{TE}) (eV/°C)</th>
<th>(V_g) (m/s)</th>
<th>(C_p) (eV/GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdTe</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E_0</td>
<td>1.49</td>
<td>0.041</td>
<td>1.2x10^{-4}</td>
<td>-3.7x10^{-4}</td>
<td>2.3x10^5</td>
<td>0.065</td>
</tr>
<tr>
<td>E_1</td>
<td>3.31</td>
<td>0.30</td>
<td>2.2x10^{-4}</td>
<td>-7.3x10^{-4}</td>
<td>8.1x10^5</td>
<td>-0.20</td>
</tr>
<tr>
<td>E_1+\Delta_1</td>
<td>3.89</td>
<td>0.29</td>
<td>5.1x10^{-4}</td>
<td>-2.5x10^{-4}</td>
<td>6.9x10^5</td>
<td>0.23</td>
</tr>
<tr>
<td>E_2</td>
<td>5.16</td>
<td>0.92</td>
<td>18x10^{-4}</td>
<td>-2.7x10^{-4}</td>
<td>4.2x10^5</td>
<td>0.16</td>
</tr>
<tr>
<td>CdS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E_0</td>
<td>2.38</td>
<td>0.071</td>
<td>2.0x10^{-4}</td>
<td>-4.1x10^{-4}</td>
<td>2.2x10^5</td>
<td>0.045</td>
</tr>
<tr>
<td>E_1-A</td>
<td>4.82</td>
<td>0.21</td>
<td>4.8x10^{-4}</td>
<td>-5.3x10^{-4}</td>
<td>3.3x10^5</td>
<td>0.089</td>
</tr>
<tr>
<td>E_1-B</td>
<td>5.50</td>
<td>0.64</td>
<td>16x10^{-4}</td>
<td>-8.6x10^{-4}</td>
<td>8.8x10^5</td>
<td>0.028</td>
</tr>
</tbody>
</table>

long as inhomogeneity throughout the thickness does not generate significant artifacts in \(\varepsilon\) when deduced in the data analysis. As a result, it can then be inferred that the film consists of a uniform material throughout the optical probe depth. First for a given CdTe or CdS film, all the CP’s share the same measurement temperature \(T_m\), mean free path \(\lambda\), and stress \(P\). Second, for a series of CdTe or CdS films with different characteristics, the single crystal CP values, \(E_b\) and \(E_b\), the temperature coefficients, \(C_{TT}\) and \(C_{TE}\), and the group speeds of excited electrons, \(V_g\), are all constants. As a result, not only can Eqs. (4.4) directly reflect interesting film properties, but also provide very useful characteristics that can significantly reduce correlation and confidence limits in best-fit models of the optical properties, relative to those obtained in models that use only Eq. (4.1) without the linkages among parameters.
To demonstrate the parameterization described above, a CdCl$_2$-treated CdTe superstrate solar cell (without back contact) was stepwise chemically etched in a solution of Br$_2$ in methanol with 0.04 volume percent Br$_2$ (Chen et al., 2006a). Depending on the length of the etching time, each etch step removed from 100 to 1400 Å of CdTe. \textit{Ex situ} SE data were collected after each etch. For better depth resolution, only those data in the spectral range of 3.7 to 6.0 eV were analyzed since the penetration depth in this range is no more than 200 Å and thus, only the near surface of the film was probed. As a result, the complexity of the underlying CdS and TCO/glass layers was avoided in the optical model. The optical model shown in Fig. 4-25 consists of: (1) a semi-infinite CdTe layer of temperature $T_m$, mean free path $\lambda$, stress $P$, and void volume fraction $f_v$; (2) a surface roughness layer whose dielectric function is calculated with the Bruggeman effective medium theory (Aspnes, 1981) assuming a 0.5/0.5 volume fraction mixture of material (1) and void.

Figure 4-25. Optical model used to analyze stepwise etching data on CdTe, consisting of two media: (1) a semi-infinite CdTe layer of temperature $T_m$, mean free path $\lambda$, stress $P$, and void volume fraction $f_v$; (2) a surface roughness layer whose thickness is $d_s$ and whose dielectric function is calculated with the Bruggeman effective medium theory assuming a 0.5/0.5 volume fraction mixture of medium (1) and void.
In the spectral range of 3.7 to 6.0 eV, the CdTe dielectric function has two major critical points, \(E_{1+\Delta_1}\) and \(E_2\) (Fig. 4-1), which were parameterized with Eq. (4.1) and parameters linked according to Eqs. (4.4). Since the experiments were performed at room temperature, \(T_m\) was fixed at 25°C. This study and a previous one have shown that the stress effects on the CP's of CdCl\(_2\)-treated CdTe are small (Chen \textit{et al.}, 2006a), so \(P\) was fixed at 0. Thus, the information of interest includes \(f_v\) and \(\lambda\). Figure 4-26 shows a typical fit to the ellipsometric \((\psi, \Delta)\) spectra collected after the 42\(^{\text{nd}}\) etch that yields \(\lambda=39.8\pm8.0\) nm and \(f_v=0.038\pm0.004\).

Figure 4-26. A fit to the ellipsometric \((\psi, \Delta)\) spectra taken after the 42\(^{\text{nd}}\) etch of a CdCl\(_2\)-treated CdTe superstrate solar cell without back contact processing. The fit returned the indicated structural results, based on the optical model in Fig. 4-25 with parameterization of Eqs. (4.1) and (4.4).
Figure 4-27 depicts the depth profile in void volume percent versus CdTe bulk layer thickness. The latter was determined from the ellipsometric data in the lower photon energy range with a more complicated optical model that includes all the layers of the solar cell structure due to the semi-transparency of CdTe (Chen et al., 2006). In the depth range of \( \sim 3.8 - 2.8 \mu m \) as measured from the CdS/CdTe interface, a steady drop of \( f_v \) is observed from \( \sim 0.3 \) to \( \sim 0.0 \) as the etching progresses, i. e., as the depth from the interface decreases. This large amount of void is a result of surface roughness and its enhancement during CdCl\(_2\)-treatment. From \( \sim 2.8 \mu m \) to \( \sim 0.25 \mu m \), \( f_v \) remains low (\( \sim 0.0 \)), indicating a uniform and dense film in this depth range after the CdCl\(_2\)-treatment. The rapid increase in \( f_v \) as the CdS/CdTe interface is approached (depth < \( 0.25 \mu m \)).
measured from the CdS/CdTe interface) may be attributed to the lattice mismatch at the interface which prevents complete grain coalescence upon CdCl₂ treatment. The role of the voids then is to relax the stress upon CdCl₂ treatment in a similar manner as was described in Section 3.1 for as-deposited CdTe.

Figure 4-28 shows the depth profile of the mean free path, which can be divided roughly into 4 regions. (1) In the CdTe depth range of 0 – 25 nm as measured from the CdS/CdTe interface, an apparent sharp drop in λ is observed as the CdTe depth decreases from 25 nm to the interface. This may be attributed to sulfur diffusion and alloying which enhances electron scattering. Thus, in this first region, λ may indicate the mean free path due to the scattering centers in the alloy rather than an actual grain size. Alternatively, λ in this depth range may be an effective value due to a combination of grain boundary and defect scattering. In fact, a CdTe/CdS intermixed layer was also included in the model for CdTe etching in this depth range, and this layer was removed by etching after the CdTe itself was etched away. The removal of this material is indicated by the negative values of thickness in Fig. 4-28. (2) In the CdTe depth range of 25 – 150 nm, the mean free path is nearly constant at 40 nm with little increase with increasing depth. Apparently the desired effect of the CdCl₂ treatment, which is to significantly reduce the defect density and increase the grain size, was not achieved in this depth range of the CdTe film. This may be a residual effect of the lattice mismatch associated with the void structure that results from the suppression of coalescence of grains during CdCl₂ treatment. (3) In the CdTe depth range from 150 to 300 nm, the mean free path undergoes a steady increase which is
attributed to an increase in grain size. In fact, in this range it is expected that $\lambda = R$, the grain radius. (4) For CdTe depth greater than $\sim 300$ nm from the CdS/CdTe interface, the grains are so large that the optical model cannot distinguish between the polycrystalline film and single crystal CdTe. In fact, regions (3) and (4) are consistent with the expected effect of the CdCl$_2$ treatment. Similar depth profiles in the grain size were observed by Rogers et al. (2000) for thermally annealed CdTe films without the use of CdCl$_2$. These studies employed the characterization techniques of X-ray diffraction and Rutherford backscattering spectroscopy. In this thesis research, both the void distribution and the enhanced electron scattering near the CdTe/CdS interface are of interest due to their possible effects on solar cell performance, in particular on the open circuit voltage.

Figure 4-28. Depth profile in mean free path versus CdTe bulk layer thickness deduced from fits to SE data similar to those of Fig. 4-26. The SE data were collected during stepwise etching of a CdCl$_2$-treated CdTe superstrate solar cell without back contact processing.
4.6 Comparison of the critical point broadening characteristics of differently processed CdTe

In Section 4.3, it was shown how the group speeds associated with excited carriers in CdTe thin films could be deduced from the dielectric functions of a series of samples fabricated by magnetron sputtering at different deposition temperatures \( T_d \). This approach led to samples with different electron mean free path values \( \lambda \); however, the range of \( \lambda \) was much smaller than that obtained for the corresponding set of CdS samples. As a result, alternative approaches have been investigated to generate CdTe samples with a wider distribution of \( \lambda \) values. These include (i) stepwise etching of the thick CdTe layer on CdS in a CdCl\(_2\) treated solar cell, (ii) stepwise etching of much thinner sputtered CdTe films deposited on crystal Si wafers and exposed to different post-deposition treatments, and finally (iii) ion-implantation of single crystal CdTe (c-CdTe) at different fluences.

Through an investigation of the dielectric functions of these three sample sets, information can be obtained on the ratios of group speeds for excited electrons associated with the different CP's, including \( V_{g,E1+\Delta}/V_{g,E2} \), \( V_{g,E1}/V_{g,E2} \), and \( V_{g,E0}/V_{g,E2} \). Here, \( V_{g,E2} \) is used as the common denominator because of the mean free path \( \lambda \) for CdTe is calculated from \( \Gamma_{E2} \) in Section 4.3. As noted previously, \( \Gamma_{E0} \) is not used for this purpose due to the weakness of the \( E_0 \) feature in the dielectric function and the associated difficulty of determining the width of the feature. Furthermore the penetration depth of the light at the \( E_0 \) energy is very large, and so the use of \( \Gamma_{E0} \) would require a uniform sample throughout the penetration depth, which is typically not the case for the above CdTe samples. Based
on this limitation, information can be obtained by correlating $\Gamma_n$ with $\Gamma_{n'}$ (n and $n'$ denote two different CP's) according to Eq. (4.3) through a common $\lambda$ value that is the same for all CP's:

$$\Gamma_n = \Gamma_{nb} + hV_{gn}/\lambda, \quad (4.5a)$$

$$\Gamma_{n'} = \Gamma_{n'b} + hV_{gn'}/\lambda. \quad (4.5b)$$

Eliminating $\lambda$ from these two equations yields

$$\Gamma_n = (\Gamma_{nb} - \frac{V_{gn}}{V_{gn'}}\Gamma_{n'b}) + \frac{V_{gn}}{V_{gn'}}\Gamma_{n'}. \quad (4.5c)$$

Thus, the slope of the expected linear correlation between $\Gamma_n$ and $\Gamma_{n'}$ is the ratio of group speeds $V_{gn}/V_{gn'}$ which is the quantity of interest in this study.

This more detailed analysis approach applied to understand the depth profile in $\lambda$ for a CdCl$_2$ treated solar cell through stepwise etching stems from the results presented earlier in Fig. 4-28, where $\lambda$ of CdTe was shown to vary with etching step or CdTe thickness. In Section 4.5, the ellipsometric ($\psi$, $\Delta$) spectra collected during stepwise etching of a CdTe solar cell are fitted with a CdTe dielectric function that is parameterized at two levels. The parameters of the first level are associated with the oscillators of the parabolic band approximation to the critical points (CP's) [Eq. (4.1)]. At the second level, the CP parameters [Eqs. (4.4)] are expressed in terms of mean free path $\lambda$, stress $P$, and measurement temperature $T_m$. By parameterizing at two levels, $\lambda$ can be deduced directly in the fit, so that the method is suitable for online monitoring. In this section, however, only the first level of parameterization is used to analyze the ($\psi$, $\Delta$) spectra in order to deduce the CP widths of CdTe. The further interpretation of the CP
widths is done separately in order to gain additional insights. Thus the motivation is not online monitoring, but rather analysis of the effects of different types of defects on the scattering of excited carriers.

Figure 4-29 depicts $\Gamma_{E1}$ and $\Gamma_{E1+\Delta1}$ plotted as functions of $\Gamma_{E2}$. As noted earlier, the $E_0$ CP is not included in this analysis because the CdTe layer is not uniform over the penetration depth of the light at the $E_0$ energy. Excellent linear correlations are evident in Fig. 4-29, as predicted by Eq. (4.5c); however, the deduced ratios of group speeds, $V_{g,E1}/V_{g,E2}$ and $V_{g,E1+\Delta1}/V_{g,E2}$, are both smaller than the values deduced from the series of CdTe films deposited at different temperatures as described in Section 4.3. In that section, $V_{g,E1}/V_{g,E2} \approx 8.1 \times 10^5/4.2 \times 10^5 \approx 1.9$ and $V_{g,E1+\Delta1}/V_{g,E2} \approx 6.9 \times 10^5/4.2 \times 10^5 \approx 1.6$, whereas in Fig. 4-29, $V_{g,E1}/V_{g,E2} \approx 1.0$, and $V_{g,E1+\Delta1}/V_{g,E2} \approx 0.8$. Thus, both ratios are lower by a factor of $\sim 2$ compared to the previous values. A common factor of two would suggest that $V_{g,E2}$ in the CdTe layer of the solar cell has increased by a factor of $\sim 2$ compared to the sputtered CdTe films of Section 4.3, whereas $V_{g,E1}$ and $V_{g,E1+\Delta1}$ remain unchanged. Considering that the solar cell has undergone CdCl$_2$ treatment at elevated temperatures ($\sim 387^\circ$C), a plausible reason for the larger $V_{g,E2}$ is a modified band structure in the energy region of the CdTe E$_2$ transition due to S diffusion. It should be recalled that CdS exhibits two CP's (E$_1$-A and E$_1$-B) near the E$_2$ CP of CdTe, but no CP near the E$_1$ and E$_1+\Delta_1$ CP's of CdTe as shown in Sections 4.1 and 4.3. Based on this reasoning, improved results would be obtained in Fig. 4-28 by applying a new set of group speeds appropriate for CdTe modified by S in-diffusion. The net effect of such a re-evaluation would be to increase the
CdTe mean free path \( \lambda \) by a factor between 1 and 2 since both \( E_{1+\Delta_1} \) and \( E_2 \) have been used in deducing \( \lambda \) in Fig. 4-28; however, such a factor is small in view of the variation in the figure and the overall trend and conclusions will remain unchanged.
In order to assess the proposal that the observed modifications in $V_{g,E1}/V_{g,E2}$ and $V_{g,E1+\Delta1}/V_{g,E2}$ described above are due to S incorporation, a series of CdTe films magnetron sputtered directly onto c-Si wafer substrates and exposed to different post-deposition treatments have been similarly stepwise etched and analyzed using the parabolic band model for the critical points. In this case, there is no CdS layer beneath the CdTe and so no S in-diffusion. The CdTe films were deposited at $T_d=188^\circ$C with an rf power of 60 W, an Ar pressure of 18 mTorr, and an Ar flow of 23 sccm, to a final thickness of ~3300 Å. These films were then studied in three different states: (i) as-deposited, (ii) thermally annealed at 387°C for 30 min, and (iii) CdCl$_2$ treated also at 387°C for 5 min. After the treatments, each sample was etched with Br$_2$+methanol (0.04% Br$_2$ volume fraction), and each etch step corresponds to a ~300 Å reduction in the bulk layer thickness.

The results of this study show that the mean free path $\lambda$ in the as-deposited film is small throughout the thickness. In contrast, the $\lambda$ values for the CdCl$_2$ treated film are homogeneously large throughout the thickness. For the thermally annealed film $\lambda$ is smaller close to the surface and larger close to the substrate (Chen et al., 2006a). Combining samples in all three states, Figure 4-30 shows the variations of $\Gamma_{E1}$ and $\Gamma_{E1+\Delta1}$ as functions of $\Gamma_{E2}$. Again, the $E_0$ CP is not included in this data set due to the inhomogeneity over the penetration depth of the light at $E_0$ for some data sets. Although there is greater scatter in the data points in Fig. 4-30 compared to Fig. 4-29, the linear trends predicted by Eq. (4.5c) are approximately followed. The deduced ratios of the
group speeds, $V_{g,E1}/V_{g,E2} \sim 1.8$ and $V_{g,E1+\Delta1}/V_{g,E2} \sim 1.2$, are at least closer to the values deduced in Section 4.3 (1.9 and 1.6 respectively) in comparison to the ratios for CdTe in
the solar cell configuration. Thus, this second study among those of this Section independently confirms the relative amplitudes of the previously deduced group speeds of excited electrons associated with different CdTe CP's. This result also supports the proposition that S diffusion into a significant thickness of CdTe and hence the modification of E$_2$ band structure is the most plausible reason for the group speeds observed for CdCl$_2$ treated solar cells as shown in Fig. 4-29.

The third approach applied to generate crystalline CdTe with different mean free paths $\lambda$ will be discussed next. In this approach, ion implantation is used to generate disordered regions of different area concentrations, which may be analogous -- in terms of their abilities to scatter optically excited carriers -- to the grain boundary regions in sputter deposited thin film polycrystalline CdTe of different grain sizes. The polycrystalline CdTe samples were prepared as part of this Thesis, whereas the ion implantation and characterization were performed by collaborators at the Research Institute for Technical Physics and Materials Science (MTA-MFA) of the Hungarian Academy of Sciences in Budapest, Hungary (Petrik et al., 2008a). The analysis methodology for the critical points widths was also performed as part of this Thesis. In this work, single crystal CdTe [Nippon Mining & Metals Co., (111)B] samples have been implanted using Bi$^{2+}$ ions accelerated through 175 kV at fluences, i. e., time integrals of the ion flux, ranging from $3.75\times10^{13}$ cm$^{-2}$ to $6.00\times10^{14}$ cm$^{-2}$. The high-mass Bi ions were chosen because the damage created in previous studies using Xe implantation was insufficient for the goal of simulating grain structure in CdTe (Petrik et al., 2008). Using
doubly-charged Bi ions implies that each Bi ion will have an energy of 350 keV.

The ellipsometry spectra ($\psi$, $\Delta$) of the virgin and ion-implanted samples were measured at multiple angles of incidence (AOI) over the spectral range of 1 – 6 eV, covering the four major CdTe CP's. Although depth distribution of disordered atoms simulated by the freely available software Stopping and Range of Ions in Matter (SRIM) as well as measured by Rutherford backscattering spectrometry and channeling (RBS/C) techniques indicate a damaged layer ~ 100 nm thick (Petrik et al., 2008a), for simplicity in this early study, the optical model is selected to be a semi-infinite substrate covered by a thin oxidized over-layer as shown in the Fig. 4-31 inset. Here, the dielectric function of the over-layer is determined from the SE data of the virgin CdTe whose bulk dielectric function has been well studied (Aspnes and Arwin, 1984; Johs et al., 1998). The over-layer is assumed to exhibit a dielectric function given by the Cauchy expression with an absorption onset. The best fit result as shown in Fig. 4-32 (a) is then fixed and incorporated into the optical model for the ion implanted samples. Since SE data were taken at multiple AOI, it is possible to deduce the over-layer thickness and the optical properties of the ion implanted samples simultaneously as described in Section 2.6. Figure 4-32 (b) compares the deduced dielectric functions of four CdTe samples with different fluences of the Bi$^{2+}$ ion implantation. The results in Fig. 4-32 (b) suggest that re-crystallization of the CdTe occurs for the highest fluence of 6.00×10$^{14}$ cm$^{-2}$. This can also be observed in the RBS/C data (Petrik et al., 2008a).

The deduced optical properties of Fig. 4-32 (b) have been fitted with the parabolic
Figure 4-31. Spectroscopic ellipsometry data acquired at three angles of incidence (AOI): 65°, 70°, and 75°, for the Bi²⁺ implanted CdTe with a fluence of 1.50 x 10^{14} \text{ cm}^{-2}. These data were analyzed simultaneously based on the optical model plotted in the inset.

Figure 4-33 shows the variations of the E₀, E₁, and E₁+Δ₁ CP broadening parameters as functions of the E₂ CP broadening parameter for the Bi²⁺ ion implanted CdTe series. In this figure, Γ_{E₁+Δ₁} shows the clearest linear behavior, whereas Γ_{E₀} and Γ_{E₁} tend to be relatively constant as a function of Γ_{E₂}. This behavior

band approximation [Eq. (4.1)].
suggests that as the penetration depth of the light increases, the relationships of Eq. (4.5c) are invalidated due to the different penetration depth coupled with the depth non-uniformity of these samples. In spite of this problem, the correlation of $\Gamma_{E1+A1}$ with $\Gamma_{E2}$ does yield a well defined group speed ratio which is $\sim 4$ times smaller than that

Figure 4-32. The deduced dielectric function of (a, upper) the native oxide over-layer, and (b, lower) un-implanted and Bi$^{2+}$ ion implanted CdTe with the indicated fluences.
deduced from the deposition temperature series of sputtered samples. This result suggests that the nature of the defects in the ion implanted samples is different, e.g., they may exhibit a smaller scattering cross-section for lower energy excitations. One cannot rule out the possibility of depth non-uniformities, however, whereby the density of scattering centers just below the over-layer where the $E_2$ excitations are generated is much higher than that deeper into the bulk. Although the SRIM simulation may suggest that this is not

Figure 4.33. The broadening parameters of the (a, top) $E_0$, (b, middle) $E_1$, and (c, bottom) $E_1^{+\Delta_1}$ CP's plotted as functions of the $E_2$ broadening parameter for the Bi$^{2+}$ implanted CdTe with different fluences. The indicated ratio of group speeds is the slope of the linear fit in each panel.
the case (Petrik et al., 2008a), the calculation in that simulation does not include the possibility of in-diffusion of ambient gases which lead to oxidization. A possible solution to the inhomogeneity problem is to assume grading of the optical properties vs. depth; however, a better approach is to generate uniformly polycrystalline CdTe films with less inhomogeneities vs. depth.
5.1 Introduction

In this chapter, the optical analysis of thin films that exhibit continuous changes in their material properties with thickness is addressed. Such material property changes may include phase transitions in which case the material maintains a constant chemical composition; however, it evolves through different degrees of crystallinity e.g., from a pure amorphous phase through a mixed amorphous + microcrystalline phase to a single microcrystalline phase with thickness. Property changes may also include compositional variations with thickness which may occur due to interactions of the film and substrate materials. In either case, real time spectroscopic ellipsometry (RTSE) in conjunction with data analysis via the virtual interface (VI) approximation constitute a powerful approach for materials characterization.

An explanation of the principle of the virtual interface approximation begins with the concept of the pseudo-dielectric function ($\langle \varepsilon_1 \rangle$, $\langle \varepsilon_2 \rangle$). The multilayer structure on the left side of Fig. 5-1 has been reproduced from Fig. 2-3. One can consider the situation in which the multilayer stack is opaque and stepwise approximates a single graded layer in
which the optical properties change gradually from \((\varepsilon_1, \varepsilon_2)_{m+1}\) to \((\varepsilon_1, \varepsilon_2)_1\) in a continuous manner. Next, the various levels of approximations to this structure will be considered based on the pseudo-dielectric function concept.

First, if one were to reduce the multilayer structure to the simplest possible optical model – a semi-infinite “pseudo–substrate” with a perfectly abrupt interface to the ambient (medium 0), then the so-called “pseudo-dielectric function” \((<\varepsilon_1>, <\varepsilon_2>)\) of the pseudo-substrate can be directly calculated from the ellipsometric spectra \((\psi, \Delta)\) and the angle of incidence \(\theta\) (Azzam and Bashara, 1977) as described in Chapter 2. Thus, the pseudo-dielectric function \((<\varepsilon_1>, <\varepsilon_2>)\) is simply a mathematical transformation of the

![Figure 5-1.](image)
experimental data \((\psi, \Delta)\) and \(\theta\) that reduces to the true dielectric function when the multilayer optical property gradient vanishes and the sample approaches a semi-infinite substrate with a perfectly abrupt interface to the ambient. The pseudo-dielectric function can be viewed as a weighted average of the dielectric functions of the multilayer components shown on the left side of Fig. 5-1 such that the weighting is determined by the layer thicknesses, the angle of incidence, and the component dielectric functions themselves. The simplification of Fig. 5-1 is too extreme to be of any value in the analysis of RTSE data. A more useful approach is the virtual interface approximation which relies on the pseudo-dielectric function concept at a higher level of complexity than that of Fig. 5-1. This second approach will be explained next.

Considering Fig. 5-1, if layer 1 is increasing in thickness during deposition and RTSE data are collected during this process, then both \(d_1\) and \((\psi, \Delta)\) vary with time. Thus, considering two successive time points \(t\) and \(t'\), the thickness increases from \(d_1\) to \(d_1'\) and \((\psi, \Delta)\) changes as a result to \((\psi', \Delta')\), as shown on the left side of Fig. 5-2. Under the virtual interface approximation, the true sample structure reproduced on the left side of Fig. 5-2 is treated as the simplified optical model on the right side of Fig. 5-2 consisting of:

1. a semi-infinite substrate with a dielectric function equal to the pseudo dielectric function \((<\varepsilon_1>, <\varepsilon_2>)\) determined at the earlier time point \(t\);
2. a layer “x” with thickness \(d_x\) and dielectric function \((\varepsilon_1, \varepsilon_2)_x\) on top of the semi-infinite pseudo-substrate;
The term “virtual interface” refers to the interface between the pseudo-substrate and layer “x” that artificially separates the material grown before and after time t. Even with such a simplified model, $d_x$ and the dielectric function $(\varepsilon_1, \varepsilon_2)_x$ cannot be determined simultaneously because the number of unknown parameters is larger than the number of measured quantities $(\psi', \Delta')$ as described in Section 2.6. If the growth of the topmost layer is continuous and RTSE is performed continuously as well, several consecutive spectra acquired at time points $t'$, $t''$, $t'''$, … can be analyzed together based on the virtual interface.

(3) the ambient which is unchanged during the deposition,
interface model for the sample structure at the right side of Fig. 5-2. This analysis is based on the assumption that the optical properties of material x, i.e. \((\varepsilon_1, \varepsilon_2)_x\), are not changing within these consecutive time points and that the thickness of layer x, \(d_x\), is a linear function of time with the slope being the deposition rate. With these assumptions, it is possible to extract \((\varepsilon_1, \varepsilon_2)_x\) and the deposition rate, the latter specifying \(d'_x\), \(d''_x\), \(d'''_x\), …, simultaneously through a regression analysis that minimizes the MSE as described in Section 2.6. In this analysis, \((\varepsilon_1, \varepsilon_2)_x\) represents the optical properties of the near surface region of the growing film whose thickness depends on the number of consecutive time points that are analyzed together as well as the deposition rate.

As a result, the virtual interface approximation is particularly useful for the characterization of growing films with continuously changing optical properties. Once \((\varepsilon_1, \varepsilon_2)_x\) is determined, it can be further analyzed in terms of material composition. For example, if the film is known to be a mixture of amorphous and microcrystalline phases, an effective medium theory can be used to determine the volume fractions of the components. Alternatively, if the film is known to be an alloy, the molar concentrations can be determined using a previously established optical property database. The importance of virtual interface analysis lies in its repetitive application versus time. After determining \((\varepsilon_1, \varepsilon_2)_x\) and the deposition rate from \(t', t'', \ldots t^{(n)}\), then the pseudo-substrate can be redefined as the sample at \(t'\) and then the analysis proceeds using the data collected at the consecutive time points \(t'', t''', \ldots t^{(n+1)}\). Because it is easy to establish the relationship between total film thickness and time using the successive values of the
deposition rate, the final result of virtual interface analysis versus time is a depth profile of a material property such as crystallite content or composition. Examples will be given in the next two sections.

The virtual interface approximation is a considerable simplification of the multilayer structure (Fig. 5-2). Nevertheless, since its first application by Aspnes (1993) using the approach described above, VI analyses have become more complicated. For example, Kim et al. (1995) have first developed a two-layer VI method consisting of surface roughness and “bulk” layers on top of the pseudo-substrate. The results of such advanced VI methods are surprisingly close to those obtained by destructive depth-profiling techniques (Ferlauto et al., 2004). In addition, very good correlations between VI based RTSE results and device performance have been reported. A well known example is the deposition phase diagram that is used to guide the optimization of plasma enhanced chemical vapor deposition (PECVD) of Si:H solar cells (Collins et al., 2003; Cao et al., 2008). Valid results are obtained with such considerable simplification because the interfaces and materials nearest to the sample surface in a multilayered structure exert the greatest influence on the ellipsometric data ($\psi$, $\Delta$). In fact, the virtual interface approximation becomes exact in the limit whereby layer “x” is opaque, meaning that the virtual interface is not detected by the ellipsometry beam. Thus the VI approach is only applicable to the analysis of RTSE data over the spectral range of strong absorption and small penetration depth.
5.2 Virtual interface analyses for plasma enhanced chemical vapor deposition (PECVD) of hydrogenated silicon (Si:H)

State-of-the-art solar cells based on Si:H prepared by PECVD employ an n-i-p triple junction design (Yang et al., 1997; Deng et al., 2000). The top cell i-layer is purely amorphous Si:H (a-Si:H) with a band gap of ~ 1.8 eV. The bottom cell i-layer consist of either Si_{1-x}Ge_x:H or microcrystalline (nanocrystalline) Si:H [µc-Si:H (nc-Si:H)] with a lower band gap within the range ~ 1.1 – 1.4 eV. Optimization of the a-Si:H i-layer of the top cell has been widely successful through the maximal H_2 dilution concept (Tsu et al., 1997; Collins and Ferlauto, 2002). This entails operating the PECVD process at the highest possible H_2 dilution flow ratio while avoiding the tendency of the film to evolve to a mixed-phase amorphous + microcrystalline structure with increasing thickness that occurs at very high dilution ratios. The benefits of the atomic H generated in the plasma through H_2 dilution include enhanced surface passivation and hence diffusion of film precursors in the PECVD process, as well as enhanced relaxation of sub-surface strained Si–Si bonds (Collins and Ferlauto, 2002). The resulting “protocrystalline” nature of the i-layer prepared under these maximal H_2 dilution conditions provides the highest device performance and stability. Previously, deposition phase diagrams were successfully established for Si:H i-layers deposited by radio frequency (rf) PECVD from SiH_4 on both crystalline Si wafer and amorphous Si:H film substrates. In this study, phase diagrams have been developed for Si:H i-layers deposited by very high frequency (vhf) PECVD from Si_2H_6 on amorphous Si:H (a-Si:H) n-layers substrates under the conditions used for
high-efficiency multijunction n–i–p cells. These diagrams have been correlated with single-junction solar cell performance in order to further explore applicability of the maximal H₂ dilution concept for the highest quality a-Si:H i-layers. The methodologies for extracting the dielectric functions of microcrystalline Si:H and for virtual interface analysis of RTSE data were developed in this study. The PECVD depositions and the acquisitions as well as the analyses of RTSE data were performed by collaborators (Stoke, 2008; Stoke et al., 2008; Cao, 2008; Cao et al., 2008).

The Si:H i-layers for phase diagram development by RTSE were deposited on c-Si/(native-oxide)/(n-type a-Si:H) substrate structures using multichamber vhf (70 MHz) PECVD (Stoke et al., 2008). Such substrates ensure a specular surface to aid in the utilization of RTSE with the highest possible sensitivity. This is the first such study that directly correlates PECVD phase diagrams for a-Si:H i-layers with the performance of solar cells incorporating these i-layers. In order to establish these correlations, additional samples ~2000 Å thick were co-deposited onto textured (stainless steel)/Ag/ZnO/(n-type a-Si:H) structures, the standard device configuration, simultaneously with the specular c-Si/(native-oxide)/(n-type a-Si:H) substrates. The experimental apparatus, along with the configuration of the co-deposited samples on the substrate holder are shown in Fig. 5-3. The key process variable is the hydrogen dilution ratio given by $R = [H_2]/[Si_2H_6]$ where $[H_2]$ and $[Si_2H_6]$ represent the gas flows. All other parameters were selected as those used for the previously-optimized top i-layer of a multi junction solar cell. These parameters include a vhf power of 8 W, a low source gas
Si$_2$H$_6$ partial pressure less than 0.004 Torr, a total gas pressure of $p \sim 0.2$ Torr, and a nominal substrate temperature of $T = 200^\circ$C, corresponding to a calibrated value of $T = 107^\circ$C determined by RTSE (Lautenschlager et al., 1987a) as described in Section 3.1. The growth rates range from $\sim 2.3$ to $\sim 0.8$ Å/s as $R$ increases from 60 to 150.

For films whose optical properties are independent of thickness, analysis of RTSE data acquired using the rotating-compensator multichannel ellipsometer described in Section 2.5 enables the determination of the single complex dielectric function $\varepsilon$ that characterizes the growing film, as well as the evolution of the bulk layer thickness $d_b(t)$ and surface roughness layer thicknesses $d_s(t)$. From $d_b(t)$, the instantaneous deposition
rate \( r(t) \) can be determined. For films whose phase and thus optical properties are evolving continuously with thickness, a virtual interface analysis technique is applied to the RTSE data that yields the near surface dielectric function continuously with time \( \varepsilon(t) \), as well as \( r(t) \) and \( d_s(t) \). By integrating \( r(t) \), a depth profile of the dielectric function \( \varepsilon(d_b) \) can be established which in turn can be interpreted via effective medium theory to extract a depth profile in the microcrystalline volume fraction \( f_{\mu c}(d_b) \).

Figure 5-4 (a) shows typical results for the evolution of the surface roughness layer thickness with bulk layer thickness during Si:H growth with two different \( \text{H}_2 \) dilution levels. Examples are provided for a Si:H film that remains amorphous throughout growth \((R = 60)\) and for one in which microcrystallites nucleate from the amorphous phase, grow preferentially, and ultimately coalesce to a single-phase microcrystalline structure \((R = 150)\). In particular, the \( R = 150 \) data reveal the (single phase) amorphous-to-(mixed-phase) microcrystalline roughening transition, denoted \( a \rightarrow (a + \mu c) \), and the (mixed-phase)-to-(single-phase) microcrystalline smoothening transition, denoted \((a + \mu c) \rightarrow \mu c \). The notation \( a \rightarrow (a + \mu c) \) describes a nucleation transition in which the \( \mu c \) phase nucleates from the amorphous phase whereas the notation \((a + \mu c) \rightarrow \mu c \) describes a coalescence transition in which isolated microcrystallites coalesce to a single \( \mu c \) phase.

The RTSE data for the \( R = 150 \) film can be analyzed in three steps.

1. Before the \( a \rightarrow (a + \mu c) \) transition, the film is homogeneous. Standard analysis strategies can be used to extract the dielectric function of amorphous phase Si:H \( \varepsilon_a \) and the bulk and surface roughness layer thicknesses versus time \( d_b(t) \) and \( d_s(t) \), respectively.
After the \((a + \mu c) \rightarrow \mu c\) transition, the topmost region of the film is purely microcrystalline phase Si:H. Thus virtual interface analysis can be performed to extract the dielectric function of this Si:H \(\varepsilon_{\mu c}\). Typical \(\varepsilon_a\) and \(\varepsilon_{\mu c}\) spectra within the range of 3.0 – 6.5 eV are compared in Fig. 5-5. Below 3.0 eV the absorption of Si:H is not sufficiently

Figure 5-4. (a, top) Surface roughness evolution for vhf PECVD Si:H films in the fully amorphous regime \((R = 60)\) and in the microcrystalline evolution regime \((R = 150)\); (b, bottom) the microcrystallite volume fraction in the top 10 Å of the bulk layer plotted versus the accumulated bulk layer thickness for the \(R = 150\) Si:H film, as determined from a VI analysis of RTSE data. This figure was adapted from (Stoke, 2008) with permission of the author.
strong for reliable application of the virtual interface approximation. It can be seen in Fig. 5-5 that \( \varepsilon_{\mu c} \) has sharper critical point features than \( \varepsilon_a \) due to the ordering to Si atoms within the network. A similar effect for CdTe and CdS was discussed in Section 4.3.

(3) The virtual interface approximation can also be applied to data collected between the \( a \rightarrow (a + \mu c) \) and the \( (a + \mu c) \rightarrow \mu c \) transition times in order to extract the dielectric function of the top \( \sim 10 \) Å of the bulk layer as well as the instantaneous deposition rate versus time and thus to generate a depth profile of \( \sigma(d_b) \). This analysis is restricted to the photon energy range from 3.0 to 6.5 eV so as to ensure reliability of the virtual interface approximation. The depth profile \( \sigma(d_b) \) is then interpreted assuming an effective medium mixture of the amorphous and microcrystalline phases of Si:H using the

Figure 5-5. A comparison of the dielectric functions of typical amorphous phase Si:H \( \varepsilon_a \) and that of typical microcrystalline phase Si:H \( \varepsilon_{\mu c} \). These results were extracted through virtual interface analyses.
Bruggeman effective medium theory as described in Section 2.7 (Aspnes, 1981). The result is a depth profile in the microcrystalline fraction $f_{\mu c}(d_b)$ as shown in Fig. 5-4 (b).

Similar depth profiles $f_{\mu c}(d_b)$ were compiled for Si:H films prepared versus R in order to establish the contours of the phase diagram in Fig. 5-6. This diagram demonstrates that, under the vhf PECVD conditions used here, the Si:H films remain amorphous throughout at least $\sim 2000$ Å of bulk layer growth for $R \leq 80$. At higher H$_2$ dilution ($100 \leq R \leq 150$), the Si:H films initially nucleate as $a$-Si:H but undergo $a \rightarrow (a + \mu c)$ transitions at thickness values that decrease with increasing R. The surface roughening onset which identifies a “nominal” $a \rightarrow (a + \mu c)$ transition appears at $d_b=150$ Å for $R = 150$ in Fig. 5-4, and is given as a function of R by the solid line in Fig. 5-6. This onset provides sensitivity to the $a \rightarrow (a + \mu c)$ transition at a microcrystalline volume fraction of less than 0.02 within the near-surface of the bulk layer.

The n–i structures co-deposited on the textured ss/Ag/ZnO stacks, which serve as the substrate and back-reflector, were fabricated into single junction solar cells with i-layer band gaps of $\sim 1.8$ eV ($25^\circ C$ Tauc gap) (Ferlauto et al., 2002). The current-voltage characteristics of the solar cells were measured to extract the open circuit voltage ($V_{oc}$), short circuit current ($J_{sc}$), fill factor (FF), and efficiency ($\eta$). Results are given in Fig. 5-7.

The phase diagram for vhf PECVD of Si:H from Si$_2$H$_6$ in Fig. 5-6 shows features in common with previous diagrams for films from SiH$_4$. Thus, by understanding the nature of microcrystallite evolution and quantifying the phase composition as in Fig. 5-6, it may be possible to select H$_2$ dilution levels in order to maximize film quality for
one-step, multi-step, or graded layers. In the case of a 2000 Å thick $a$-Si:H i-layer, the optimum one-step deposition process is predicted on the basis of the phase diagram to occur at the maximal value of $R = 80$, i.e., the largest possible $R$ value such that the

Figure 5-6. A deposition phase diagram for vhf PECVD top cell Si:H i-layers as deposited on $a$-Si:H n-layers, depicting the thicknesses of the $a \rightarrow (a+\mu c)$ transition (solid line, squares) and the $(a+\mu c) \rightarrow \mu c$ transition (dashed line, solid circles). Upward arrows indicate that the transitions occur at thicknesses above the indicated values. Contour lines in the crystallite volume fraction $f_{\mu c}$ are also plotted. This figure was reproduced from (Stoke, 2008) with permission of the author.
i-layer remains amorphous throughout its thickness during growth. This prediction is borne out in the device performance results of Fig. 5-7. At \( R = 100 \) the \( a \rightarrow (a + \mu c) \) transition occurs at 600 Å, however, and the Si:H microcrystallite fraction in the near-surface of the 2000 Å i-layer is \( \sim 0.09 \). These crystallites appear to degrade \( V_{oc} \) significantly due to their presence at the i/p interface. Next \( V_{oc} \) and FF will be discussed further with possible strategies for future multistep processes yielding improvements in device performance.

Considering first the variation in \( V_{oc} \) for Si:H in Fig. 5-7, this parameter increases with increasing \( R \) for i-layers below the optimum at \( R = 80 \) due to the increase in band gap; however, a more abrupt increase occurs that defines the optimum as the \( a \rightarrow (a + \mu c) \)}
transition is approached. This is the protocrystalline regime, characterized by an improvement in ordering as well as an increase in gap. Because \( V_{oc} \) is strongly influenced by the film properties at the very top of the i-layer near the i/p interface, there is an abrupt decrease in its value above \( R = 80 \) due to the presence of crystalline nuclei at the top of the film. When the top of the film is mixed-phase Si:H, \( V_{oc} \) lies between the values for protocrystalline Si (\( \sim 1 \) eV) and \( \mu c\)-Si:H (\( \sim 0.5 \) eV). For \( R \) values above the \((a + \mu c) \rightarrow \mu c\) transition for a 2000 Å thick film, a \( V_{oc} \) value appropriate for \( \mu c\)-Si:H is expected.

The behavior of the fill factor (FF) with \( R \) suggests the possibility of an improvement in the cell performance with multistep processing. Figure 5-7 shows that, although the FF increases with \( R \), its maximum of 0.74 is reached at an \( R \) value larger than that which maximizes \( V_{oc} \). The presence of crystallites that evolve to a small volume fraction in the upper portion of the film, protrude at the i/p interface, and reduce \( V_{oc} \), however, does not adversely affect the FF because it is controlled predominantly by the bulk i-layer. The FF actually seems to benefit from the incorporation of microcrystallites in the bulk of the Si:H. This improvement may in fact be due to an improvement in the properties of the amorphous component of the mixed phase material (i.e., increases in the band gap and protocrystalline ordering) when it is deposited with increasing \( R \) from 80 to 100. One may be able to take advantage of an optimum \( V_{oc} \) and FF simultaneously by depositing the bulk (\( \sim 1800 \) Å) of the i-layer with \( R = 100 \), then depositing a thin (\(< 100 \) Å) substrate-memory-erasing low \( R \) layer – similar to the starting n-layer, before finally completing the solar cell with a second \( \sim 200 \) Å \( R = 100–120 \) layer. The key, however, is
to ensure that the memory-erasing layer first is successful at suppressing the continued
growth of crystallites, and second is not detrimental to the FF.

5.3 Virtual interface analyses for μc-Si:H bottom cell

It should be emphasized that the Si:H i-layer phase evolution is very sensitive to the
phase of the underlying n-layer, even though the thickness of this layer is only ~100 Å. The deposition phase diagram in Fig. 5-6 applies only to i-layer growth on a fully
amorphous n-layer. In the standard process for the a-Si:H top cell of a multijunction
device, a-Si:H n-layers which serve effectively as memory erasing layers have been used
as the underlying films in the i-layer phase diagram development. In contrast, in the
standard process for the μc-Si:H bottom cell fabrication, a nc-Si:H n-layer is used. In
order to establish the effect of the n-layer phase on the structure of the bottom cell i-layer,
the phase evolution of the i-layer, as characterized by RTSE along with the virtual
interface analysis, has been compared for Si:H i-layer depositions on a-Si:H and nc-Si:H
n-layers (Cao et al., 2008). All other deposition conditions were kept constant for these
120 min, ~1.5 μm Si:H i-layer depositions, including a H₂ dilution ratio of R =
[H₂]/[Si₂H₆] = 100, a nominal substrate temperature of T = 400°C, a pressure of p = 0.2
Torr, and a plasma power of P = 8 W. These conditions are the same as those used for the
phase diagram of Fig. 5-6 with the exception of the higher nominal substrate temperature
of 400°C, which corresponds to a c-Si calibrated temperature of 210°C as described in
Section 3.1 (Lautenschlager et al., 1987a). After fabrication of the n–i–p single-junction
structures, the cells were completed, measured, and compared.

Figure 5-8 (a) shows the microcrystalline volume fraction \( f_{\mu c} \) in the topmost 10 Å of the bulk i-layer versus the deposition time as determined from virtual interface analysis of RTSE data for i-layers deposited on the \( a\)-Si:H n-layer and on the nc-Si:H n-layer.
Figure 5-8 (b) shows the corresponding results for the surface roughness evolution. The combined results for the R = 100 i-layer deposited on the a-Si:H n-layer demonstrate that the Si:H i-layer remains predominantly amorphous for the first ~ 5 min. Microcrystallites then nucleate from the amorphous phase after 5 min and their preferential growth leads to surface protrusions that account for the rapid increase in surface roughness. At t ~ 44 min, corresponding to an i-layer thickness of ~ 5500 Å, the microcrystalline volume fraction of the bulk i-layer reaches unity. At the same time, the surface roughness reaches its maximum value of ~80 Å, indicating fully contacting crystallites at the surface and thus the \((a + \mu c) \rightarrow \mu c\) transition. A smoothening effect occurs with increasing bulk i-layer thickness over the deposition time from 44 to 80 min due to the coalescence of contacting crystallites, a process that is completed by t ~ 80 min. For t > 80 min, the surface roughness first stabilizes at a thickness of ~ 60 Å and then begins to increase gradually. Thus, for t = 44–100 min, the growth of the single-phase microcrystalline structure is maintained. For the phase evolution of the R = 100 i-layer deposited on the nc-Si:H n-layer, the Si:H i-layer grows initially as an \((a + \mu c)\)-Si:H mixed-phase material. The initial microcrystalline volume fraction \(f_{\mu c}\) quickly reaches > 0.8 at t ~ 4 min with a corresponding i-layer thickness of ~ 500 Å. In this case, a nearly pure single phase \(\mu c\)-Si:H material dominates throughout the entire 1.5 µm bulk i-layer. As the nearly single-phase \(\mu c\)-Si:H film grows, the surface roughness increases gradually with deposition time and reaches a maximum value of ~ 48 Å at the end of i-layer deposition, which is smoother than the \(\mu c\)-Si:H i-layer deposited on the a-Si:H n-layer.
This observation is likely to result from the fact that when the underlying n-layer is nc-Si:H, the i-layer is likely to grow by local epitaxy, which continues the structural evolution of the starting n-layer. When the n-layer is amorphous, the i-layer must nucleate from a growing a-Si:H i-layer, which is likely to lead to a more non-uniform morphology and thus greater roughness due to a low nucleation density.

The corresponding device performance was measured and compared for solar cells fabricated using the a-Si:H and nc-Si:H n-layers on (stainless steel)/Ag/ZnO back-reflectors. Figure 5-9 (a) shows the initial dark and light J–V curves for the μc-Si:H solar cell made using the a-Si:H n-layer. The dark and light J–V curves exhibit cross-over associated with a low fill factor of FF = 0.520 which is expected to be a result
of the high volume fraction of the amorphous phase in the initial stage of i-layer evolution on the a-Si:H n-layer. The other initial cell parameters include $V_{oc}=0.522$ V, $J_{sc}=23.45$ mA/cm$^2$, and $\eta = 6.37\%$. After 1000 h of light soaking, cell parameters of $FF = 0.550$, $V_{oc} = 0.496$ V, $J_{sc} = 21.96$ mA/cm$^2$ and $\eta = 5.99\%$ have been obtained. Figure 5-9 (b) shows corresponding results for the µc-Si:H cell fabricated using the nc-Si:H n-layer process. For this cell, very well-behaved initial dark and light J–V curves have been obtained, and the FF has been greatly improved relative to that of Fig. 5-9 (a). An initial efficiency of $\eta_{init} = 9.22\%$ and a stabilized efficiency after 1000 h of light soaking of $\eta_{stab} = 9.46\%$ have been obtained for the vhf PECVD µc-Si:H cells with the R=100 i-layer deposited on a nc-Si:H n-layer. The other cell parameters in the initial and light-soaked states include $V_{oc} = 0.516$ V, $J_{sc} = 25.17$ mA/cm$^2$, FF = 0.701 and $V_{oc} = 0.516$ V, $J_{sc} = 24.65$ mA/cm$^2$, FF = 0.744, respectively. Table 5-1 summarizes the performance of these two solar cells in the initial, 100 hr intermediate light soaked, and

<table>
<thead>
<tr>
<th>Cell Nr.</th>
<th>n-layer phase</th>
<th>light soaking</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GD2342</td>
<td>a-Si:H n-layer</td>
<td>initial</td>
<td>0.522</td>
<td>23.45</td>
<td>0.520</td>
<td>6.37</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100 hrs</td>
<td>0.495</td>
<td>22.47</td>
<td>0.535</td>
<td>5.95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1000 hrs</td>
<td>0.496</td>
<td>21.96</td>
<td>0.550</td>
<td>5.99</td>
</tr>
<tr>
<td>GD2343</td>
<td>nc-Si:H n-layer</td>
<td>initial</td>
<td>0.516</td>
<td>25.17</td>
<td>0.701</td>
<td>9.22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100 hrs</td>
<td>0.512</td>
<td>24.69</td>
<td>0.748</td>
<td>9.44</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1000 hrs</td>
<td>0.516</td>
<td>24.65</td>
<td>0.744</td>
<td>9.46</td>
</tr>
</tbody>
</table>

Table 5-1. Performances for R=100 vhf PECVD µc-Si:H solar cells fabricated using identical i-layer growth conditions but with a-Si:H and nc-Si:H n-layers. This Table was reproduced from (Cao, 2008) with permission of the author.
1000 hr stabilized light soaked states. Figure 5-10 shows the external quantum efficiency (QE) curves plotted for the cells of Fig. 5-9 in the initial state and after 1000 h light soaking. These results show clearly that the μc-Si:H solar cell incorporating the nc-Si:H n-layer has much improved long-wavelength spectral response and more stable QE values after 1000 h light soaking compared with that incorporating the a-Si:H n-layer. Calculations of the short circuit current densities for the μc-Si:H solar cell with the nc-Si:H n-layer were undertaken from the integrals of the QE curves in Fig. 5-10 with the AM1.5G spectrum over the wavelength range from 650 to 1000 nm. The results yield
initial and stabilized values of 10.36 and 10.08 mA/cm², respectively. In contrast, for the solar cell with the a-Si:H n-layer, the corresponding initial and stabilized QE J_{sc} values were 9.30 and 8.20 mA/cm², respectively, over the 650 to 1000 nm range. The short circuit current densities were also calculated from the integral of the QE curves over the range from 380 nm to 1000 nm. The µc-Si:H solar cell with the nc-Si:H n-layer yields AM1.5G initial and stabilized J_{sc} values of 24.25 and 23.89 mA/cm², respectively. In contrast, the solar cell with the a-Si:H n-layer yields corresponding initial and stabilized QE J_{sc} values of 22.89 and 20.96 mA/cm², respectively. In comparison with the J_{sc} values from the J–V measurements of Table 5-1, the integrated QE J_{sc} values are somewhat lower with differences of less than 1 mA/cm².

The strong light induced degradation in performance caused by the Staebler-Wronski effect (Staebler and Wronski, 1977) for the cell grown on the a-Si:H n-layer relative to the smaller light-induced enhancement in performance for the cell grown on the nc-Si:H n-layer indicates the existence of a significant amount of a-Si:H in the i-layer for the former cell, consistent with the RTSE results in Fig. 5-8 (a). The thick layer of mixed-phase (a + µc)-Si:H i-layer material resulting from growth on the a-Si:H n-layer is generally responsible for the poor device performance and stability.

To further explore the strong dependence of Si:H i-layer phase evolution on the underlying n-layer phase and its effect on solar cell performance, another set of Si:H cells was fabricated (Cao, 2008). The i-layer deposition conditions of Fig. 5-8 were used with the exception that the H₂ dilution was increased from R = 100 to R = 105 and the i-layer
thickness was decreased from \( \sim 1.5 \mu m \) to \( \sim 1.2 \mu m \). Three different films were deposited onto (stainless steel)/Ag/ZnO back-reflectors before i-layer deposition.

(1) \( \alpha \)-Si:H n-layer as in the deposition of Fig. 5-8.

(2) nc-Si:H n-layer as in the deposition of Fig. 5-8.

(3) The same as (1) but with a 15 nm nc-Si:H seed layer at n/i interface.

In this case, the i-layer phase evolution and performance for the cell incorporating deposition (3) are expected to be similar to those for the cell incorporating deposition (2), due to the dependence of i-layer growth on the underlying material. Such expectations are clearly verified in the comparisons of cell performance in Fig. 5-11. The nearly constant \( V_{oc} \sim 0.49 \) V among all samples indicates that the top part of these i-layers are \( \sim 100\% \) \( \mu c \)-Si:H which is similar to the situation shown in Fig. 5-8 (a) since \( V_{oc} \) is determined primarily by the i/p interface properties. A lower FF and hence lower \( \eta \) for the cell incorporating deposition (1) indicates that a significant amount of mixed-phase \((\alpha + \mu c)\)-Si:H exists within the i-layer, whereas for cells incorporating depositions (2) and (3), the i-layers are almost purely \( \mu c \)-Si:H. Thus, the \( \sim 15 \) nm nc-Si:H seed layer successfully erased the memory of the underlying \( \alpha \)-Si:H n-layer and as a result forced the overlying i-layer to follow a phase evolution similar to that observed for the i-layer on the nc-Si:H n-layer in Fig. 5-8 (a).

Combining the results of this Section and those of Section 5.2, one can conclude that the phase of the underlying Si:H n-layer has a dominant controlling influence on the phase evolution of the overlying Si:H i-layer under optimized i-layer conditions of
deposition and hence greatly affects the corresponding device performance. In order to achieve high-efficiency $\alpha$-Si:H top and $\mu$-c-Si:H bottom cells in multijunction devices, one should avoid significant portions of the bulk i-layer in the form of $(\alpha + \mu c)$-Si:H mixed-phase material.

![Graphs showing J-V characteristics](image)

Figure 5-11. The initial dark and light J–V characteristics for vhf PECVD $\mu$c-Si:H solar cells fabricated with R=105 i-layers on (stainless steel)/Ag/ZnO back reflectors over-deposited with: (a, upper left panel) an $\alpha$-Si:H n-layer; (b, lower panel) a nc-Si:H n-layer; and (c, upper right panel) an $\alpha$-Si:H n-layer coated with 15 nm nc-Si:H seed layer. The i-layer thickness is ~ 1.2 $\mu$m for all cells. This figure was adapted from (Cao, 2008) with permission of the author.
5.4 Atomic inter-diffusion at CdTe-CdS interface

The procedure for fabricating thin film CdTe solar cells involves exposing the CdS/CdTe heterojunction to elevated temperatures. This can occur either during the deposition process, such as close space sublimation which requires temperatures in the range of 500 – 600°C, or during post-deposition CdCl₂ treatment which requires temperatures near 400°C. Under such elevated temperature conditions, atomic species at the CdTe-CdS interface inter-diffuse as indicated by conventional chemical depth profiling tools such as secondary ion mass spectroscopy and Auger electron spectroscopy (Godines, et al., 2004; Castro-Rodríguez, et al., 1998). Normally an ideal crystalline p-n homojunction should have an abrupt boundary between the p-type and n-type regions for optimum solar cell performance, however, it is widely believed that inter-diffusion at the CdS/CdTe heterojunction and the formation of CdTe₁₋ₓSₓ alloys can actually benefit the heterojunction solar cell performance (Luque and Hegedus, 2003).

In order to investigate inter-diffusion at the CdS/CdTe interface during the sputtering process used in this study, the optical properties of CdTe₁₋ₓSₓ alloys versus composition have been determined. RTSE has been applied for this purpose because it provides accurate bulk and surface roughness thicknesses that enable accurate determination of the dielectric functions of the alloy films. In addition, since such measurements are performed in situ, contamination and oxidation effects are avoided that can distort the deduced optical properties. In addition to determining the optical properties of possible interface components for use as a reference database, it is also of
interest to apply RTSE in conjunction with this database to understand how CdS and CdTe interact during interface formation under idealized conditions, i.e., in the absence of microscopic interface roughness layers.

The detailed process of depositing CdTe$_{1-x}$S$_x$ alloy thin films of prespecified S molar fraction x or alloy composition by co-sputtering, using the experimental apparatus shown in Fig. 2-2, has been described in Section 3.3. The optical properties of the CdTe$_{1-x}$S$_x$ alloy films as a function of composition at the deposition and measurement temperatures of $T_m = 190^\circ$C and after cooling to room temperature of $T_m = 15^\circ$C are both shown in Fig. 5-12. The general behavior observed directly by inspection can be described as follows. (i) In most cases the dielectric functions vary consistently with the x value, and lie between those of CdTe and CdS -- the two endpoint compositions. (ii) All dielectric functions of the alloys show critical point (CP) features; however, these are much broader than the endpoint features – an indication of a much higher density of defects or a much smaller grain size in the alloy films as described in Section 4.3. (iii) The band gap shows a clear bowing effect vs. x, observed most clearly in the peak of $\varepsilon_1$, in consistency with previous studies (Wei et al., 1999). The dielectric function spectra in Fig. 5-12 are analyzed in order to compile a database that enables prediction of $\varepsilon$ for CdTe$_{1-x}$S$_x$ of any x value.

This database was applied in turn to the analysis of RTSE data collected during depositions of CdTe on CdS/c-Si, and the inverted sequence of CdS on CdTe/c-Si, both at $T_d = 190^\circ$C. In this study, a crystalline Si substrate was used in order to minimize
microscopic roughness at the interface between the two materials so that the dominant deviation from interface perfection is the inter-diffusion effect. The virtual interface

Figure 5-12. Dielectric functions (a, top) at the deposition temperature of 190°C and (b, bottom) after cooling to 15°C for CdTe$_{1-x}$S$_x$ alloy thin films prepared by co-sputtering using different CdS and CdTe target rf powers to achieve different values of $x$ (indicated).
approximation was applied to the RTSE data to find x for the topmost ~ 8 Å of deposited material during interface formation. Figure 5-13 shows a schematic of the optical structure for the normal sequence of CdTe deposition on CdS as well as for the inverted sequence of CdS deposition on CdTe. The virtual interface analyses results are also shown in Fig. 5-13. These results exhibit a compositional sensitivity of ~ 0.005 – 0.009 and a depth resolution of ~ 2 monolayers. In both deposition sequences, there is a ~ 40 Å layer with a strong gradient in x, possibly generated by ion impact in the sputtering process. Beyond this thickness, S diffusion into CdTe exhibits a tail with x ~ 0.02; whereas for the inverted structure, Te diffusion into CdS exhibits a much weaker tail, suggesting a lower diffusion coefficient.
Table 5-13. Composition profiles $x(d_b)$ in CdS$_x$Te$_{1-x}$ for depositions at $T_d = 190^\circ$C for CdTe on CdS (a, top) and CdS on CdTe (b, bottom). Also shown in each panel is the optical model used for virtual interface analysis.
Chapter 6

Theoretical Analyses for Advanced Ellipsometry Instrumentation and Measurements

6.1 Dual bi-plate compensator

A state-of-the-art multichannel ellipsometer based on the rotating compensator principle shown in Fig. 2-2 has been used throughout this thesis research. For this ellipsometer, the compensator is the critical component that determines the quality of the system. A compensator is a linear anisotropic optical device that shifts the phase of one polarization eigenmode by $\delta$ with respect to the other eigenmode. The eigenmodes of a linear optical device are those polarization states that are unchanged in ellipticity and tilt angle when acted upon by the device. The compensator type considered in this Section is a transmission device meaning that the incident and transmitted waves have the same propagation vector. The eigen modes of the most common type of compensator, which describes that used throughout this thesis research, are the linear polarization states with tilt angles along two orthogonal directions. These directions are called the fast and slow axes, respectively, which along with the optical axis of the device form an internal coordinate system for the so-called “linear compensator”. External alignment of the
compensator involves aligning the internal optical axis of the device with the incident wave propagation vector. If the device is properly aligned internally, then the propagation vector will not change upon transmission.

In the Jones matrix and Jones vector formalism (Azzam and Bashara, 1977) described in Section 2.2, the Jones matrix of a linear compensator in its internal fast-slow coordinate system is:

$$\begin{pmatrix} 1 & 0 \\ 0 & \cot \psi_C * e^{-i\delta} \end{pmatrix}$$  \hspace{1cm} (6.1)

Here $\psi_C$ is the dichroic angle which describes a possible difference in amplitude transmission coefficients of the device for incident waves with orthogonal linear fast and slow axis polarization states. Specifically, $\psi_C = \tan^{-1}(|t_F|/|t_S|)$ where $t_F$ and $t_S$ are the complex amplitude transmission coefficients for the fast and slow linear eigenmodes. In addition, $\delta$ is the retardance describing the phase shift difference $\delta = \delta_F - \delta_S$ for incident waves with orthogonal linear fast and slow axis polarization states. For an ideal compensator without a dichroic effect, $|t_F| = |t_S|$ or $\psi_C = 45^\circ$, which is closely satisfied for many optical devices. In this case, Eq. (6.1) becomes:

$$\begin{pmatrix} 1 & 0 \\ 0 & e^{-i\delta} \end{pmatrix}$$  \hspace{1cm} (6.2)

where $\delta$ is a critical parameter that determines the performance of the ellipsometer system.

The phase shift difference or retardance $\delta$ is a function of wavelength or photon energy, an effect called dispersion. The simplest compensator is a transparent,
anisotropic, single crystal plate with its optic axis lying in the surface plane (Azzam and Bashara, 1977; Tompkins and Irene, 2005). In proper alignment, the optical axis of the device is parallel to the optic axis of the crystal, but coincides with its rotation axis. The retardance of this type of single plate compensator has the dispersion 
\[ \delta = 2\pi \Delta n d / \lambda , \]
where \( \Delta n = |n_o - n_e| \). Here \( n_o \) is the index of refraction for the ordinary wave with its electric field \( E \perp c \) and \( n_e \) is the index of refraction for the extraordinary wave with its electric field \( E \parallel c \) where \( c \) designates the optic axis. In addition, \( d \) is the thickness of the plate, and \( \lambda \) is the wavelength of the incident light in vacuum.

In designing a single plate compensator, the thickness of the plate cannot be reduced to arbitrarily small values due to the brittleness of optical materials. Thus, inevitably \( d \gg \lambda \) and the resulting retardance has a very strong dispersion. Such strong dispersion is detrimental to the performance of a spectroscopic ellipsometer due to zero-wave crossings of the retardance. This occurs at wavelengths such that \( \delta = 2\pi m \) radians where \( m \) is an integer, and in this case the compensator cannot serve as a polarization modifying device as can be seen from Eq. (6.2). Thus, the ellipsometer provides no information on the sample properties at these wavelengths. As emphasized in the next section, ellipsometry measurements with a rotating compensator instrument have the highest sensitivity to sample properties when \( \delta = \pi / 2 \), or under quarter wave conditions.

To deal with the problem of multiple zero-wave wavelengths, the concept of a bi-plate compensator was introduced (Azzam and Bashara, 1977; Tompkins and Irene,
In this concept, the fast axes of the two individual plates of the bi-plate compensator are fixed perpendicular to one another. The resulting retardance of the bi-plate is given by \( \delta = 2\pi \Delta n \Delta d / \lambda \), where \( \Delta d = |d_1 - d_2| \) is the thickness difference for the two single plates. The fast axis tilt angle for the bi-plate is the same as the fast axis tilt angle of the thicker plate. The use of a bi-plate can avoid the necessity of mechanically polishing a single plate to an impossibly thin layer while enabling zero-order operation of the compensator. In the bi-plate design, the \( 1/\lambda \) dependence still exists in the dispersion formula, leading to spectral ranges where \( \delta \) is still far from \( \pi/2 \).

Significant effort has been spent to fabricate a rotatable achromatic compensator with a weaker wavelength dependence of the retardance, and with \( \delta \) as close as possible to \( \pi/2 \) over the widest possible spectral range. A dual bi-plate design, with the fast axes of the two bi-plate compensators oriented 45° apart, was proposed by (Johs et al., 2001). In the publication by Johs et al. (2001), experimental results were presented but no accompanying theoretical treatment. In this Section, the theoretical analysis of such a device, based on the Jones matrix formalism, will be presented. This analysis demonstrates that (1) the calculated dispersions in \( \delta \) can reproduce the experimental results; and (2) the proposed dual bi-plate device is not strictly a compensator, but rather a device that generates both retardance and rotation of the incident polarization state. In the analysis, the optical rotation of the dual bi-plate is also deduced.

In the schematic of the proposed dual bi-plate system shown in Fig. 6-1, the reference coordinate system is chosen to be the fast-slow axes coordinate system of the
first bi-plate. Therefore, the Jones matrix of the entire dual bi-plate system is

\[
J = \begin{pmatrix}
\cos 45^\circ & -\sin 45^\circ \\
\sin 45^\circ & \cos 45^\circ
\end{pmatrix}
\begin{pmatrix}
1 & 0 \\
0 & e^{-i\delta_2}
\end{pmatrix}
\begin{pmatrix}
\cos 45^\circ & \sin 45^\circ \\
-\sin 45^\circ & \cos 45^\circ
\end{pmatrix}
\begin{pmatrix}
1 & 0 \\
e^{-i\delta_1}
\end{pmatrix}
\]

\[
\Rightarrow J = \begin{pmatrix}
1 + e^{-i\delta_2} & -e^{-i(\delta_1 + \delta_2)} + e^{-i\delta_1} \\
1 - e^{-i\delta_2} & e^{-i(\delta_1 + \delta_2)} + e^{-i\delta_1}
\end{pmatrix}
\]

where \( \delta_1 \) and \( \delta_2 \) are the retardances of the first and second bi-plates, respectively. The above Jones matrix can be expressed as a unity matrix \( U \) upon division by the square root of its determinant:

Figure 6-1. An optical system consisting of two bi-plate compensators with retardance values of \( \delta_1 \) and \( \delta_2 \). The fast axis of the second bi-plate is oriented at 45º relative to the first. The dashed lines denote the fast and slow axes of the second bi-plate.
As described in Chapter 2, the absolute amplitude and phase are not of interest in describing a polarization state or the polarization manipulation function of an optical system. So the above unitary matrix $U$ can be used in place of $J$ as the Jones matrix of the system in Fig. 6-1. It is known that a general 2x2 unitary matrix can be written as (Van der Waerden, 1932):

$$U = \frac{1}{\sqrt{\det(J)}} \begin{pmatrix}
1 + e^{-i\delta_2} & -e^{-i(\delta_1 + \delta_2)} + e^{-i\delta_1} \\
1 - e^{-i\delta_2} & e^{-i(\delta_1 + \delta_2)} + e^{-i\delta_1}
\end{pmatrix}$$

$$= \frac{1}{2e^{-i(\delta_1 + \delta_2)/2}} \begin{pmatrix}
1 + e^{-i\delta_2} & -e^{-i(\delta_1 + \delta_2)} + e^{-i\delta_1} \\
1 - e^{-i\delta_2} & e^{-i(\delta_1 + \delta_2)} + e^{-i\delta_1}
\end{pmatrix}$$

$$= \begin{pmatrix}
e^{i\delta_1/2} \cos(\delta_2/2) & e^{i[-(\delta_1/2) + (\pi/2)]} \sin(\delta_2/2) \\
-e^{i[(\delta_1/2) - (\pi/2)]} \sin(\delta_2/2) & e^{-i\delta_1/2} \cos(\delta_2/2)
\end{pmatrix}
$$

$$= \begin{pmatrix}
u_1 & u_4 \\
u_3 & u_2
\end{pmatrix}
$$

(6.3)

As described in Chapter 2, the absolute amplitude and phase are not of interest in describing a polarization state or the polarization manipulation function of an optical system. So the above unitary matrix $U$ can be used in place of $J$ as the Jones matrix of the system in Fig. 6-1. It is known that a general 2x2 unitary matrix can be written as (Van der Waerden, 1932):

$$U = \begin{pmatrix}
u_1 & u_4 \\
u_3 & u_2
\end{pmatrix} \equiv \begin{pmatrix}
e^{i\phi} \cos \theta & -e^{-i\psi} \sin \theta \\
e^{i\psi} \sin \theta & e^{-i\phi} \cos \theta
\end{pmatrix}
$$

(6.4)

where $e^{2i\phi} = u_1 / u_2$, $-e^{2i\psi} = u_3 / u_4$, $\sin \theta = e^{-i\psi} u_3$, and $\cos \theta = e^{-i\phi} u_1$. The above matrix $U$ can also be written in the form (Henry and Clark, 1941):

$$U = R(A)G(\gamma)R(B) = R(A)G(\gamma)R(-A)R(A + B)
$$

(6.5)

where $R(A)$ is the Jones matrix for a rotation transformation by an angle $A$, and

$$G(\gamma) \equiv \begin{pmatrix}
e^{i\gamma} & 0 \\
0 & e^{-i\gamma}
\end{pmatrix}
$$

It is clear that $G(\gamma)$ is the Jones matrix of an effective compensator with retardance of $2\gamma$. Furthermore, Eq. (6.5) is the Jones matrix of a single optical system that first acts as a
rotator by an angle A+B then acts as an effective compensator whose retardance is 2γ and whose fast axis is oriented at – A relative to the starting reference coordinate system. Therefore, A+B is called the optical rotation angle of the optical system. The relation between Equations (6.4) and (6.5) can be manipulated to provide A+B, A−B, and γ in terms of the matrix elements and parameters that define U (Henry and Clark, 1941).

The results are:

\[
\begin{align*}
\tan(A + B) &= \frac{\cos \psi}{\cos \phi} \tan \theta = \frac{u_3 - u_4}{u_1 + u_2}, \\
\tan(A - B) &= \frac{\sin \psi}{\sin \phi} \tan \theta = \frac{u_3 + u_4}{u_1 - u_2}, \\
\tan \gamma &= \frac{\cos(A + B)}{\cos(A - B)} \tan \phi = \frac{\sin(A + B)}{\sin(A - B)} \tan \psi.
\end{align*}
\]

(6.6)

Comparing Eqs. (6.3) and (6.4), one can observe that: \(\phi = \delta_1/2, \ \psi = (-\pi/2) + (\delta_1/2),\)
and \(\theta = -\delta_2/2.\) Then Eq. 6.6 can be applied to express A+B, A−B, and γ in terms of \(\delta_1\) and \(\delta_2.\) The results in this case are:

\[
\begin{align*}
\tan(A + B) &= -\tan(\delta_1/2) \tan(\delta_2/2), \\
\tan(A - B) &= \cot(\delta_1/2) \tan(\delta_2/2), \\
\tan \gamma &= \frac{\cos(A + B)}{\cos(A - B)} \tan(\delta_1/2).
\end{align*}
\]

(6.7)

These are the relationships that provide the system optical rotation angle, the effective compensator azimuthal angle, and the effective compensator retardance in Eq. (6.5) in terms of the retardances of the two bi-plate compensators in Fig. 6-1. There is no simple
way of expressing $\gamma$ as a function of $\delta_1$ and $\delta_2$. To apply Eq. (6.7) and simulate an actual device, it is necessary to properly construct $\delta_1$ and $\delta_2$ versus $\lambda$, i.e. the retardance dispersion for the individual bi-plate compensators. The total system retardance $\delta=2\gamma$ versus $\lambda$ can then be calculated and compared to the experimental results reported in literature (Johs et al., 2001).

Johs et al. (2001) report that $\delta_1(266\text{ nm})=\delta_2(633\text{ nm})=\pi/2$ describe the quarter wave points of the two bi-plate compensators. If these two compensators are assumed to operate in zeroth order, then $\delta_1=2\pi\Delta n\Delta d_1/\lambda$ and $\delta_2=2\pi\Delta n\Delta d_2/\lambda$. Because MgF$_2$ is the most widely used as a UV transparent anisotropic material, it can be assumed that all plates are made from MgF$_2$. From the known optical properties of MgF$_2$ (Palik, 1991) shown in Fig. 6-2 (a) and from the two specific quarter wave points, one can deduce that $\Delta d_1\approx 5.2554$ $\mu$m and $\Delta d_2\approx 13.4763$ $\mu$m. From this information, the dispersion in $\delta_1=2\pi\Delta n\Delta d_1/\lambda$ and $\delta_2=2\pi\Delta n\Delta d_2/\lambda$ can be easily calculated as shown in Fig. 6-2 (b). By substituting these dispersion data into Eq. (6.7), the total system optical rotation $A+B$, the effective compensator azimuthal angle $-A$, and the effective compensator retardance $2\gamma$ were calculated and plotted in Fig. 6-3. The retardance dispersion in Fig. 6-3 (c) is a close simulation of the experimental results reported in the literature (Johs et al., 2001).

The dispersion of the total system optical rotation $A+B$ and the effective compensator azimuthal angle $-A$, as shown in Fig. 6-3 (a) and (b) respectively, are reported here for the first time. In an ellipsometer system that incorporates the dual bi-plate optical element in Fig. 6-1 serving as the compensating component, all three parameters in Fig.
6-3 must be accurately determined in calibration before any meaningful measurements are possible. It can be seen that the design in Fig. 6-1 leads to the much weaker retardance dispersion shown in Fig. 6-3 (c) as compared to the individual bi-plate compensators whose retardance dispersions are shown in Fig. 6-2.

Two interesting points are observed in both the dispersion of Fig. 6-3 (c) and the closely matching experimental data in the literature (Johs et al., 2001). At $\lambda=266$ nm and $\lambda=633$ nm where either $\delta_1=\pi/2$ or $\delta_2=\pi/2$ holds, the total system retardance $\delta$ also equals
This result can be demonstrated theoretically as follows.

First, if \( \delta_i = \pi/2 \), then from Eq. (6.7):
\[
\tan(A+B) = -\tan(\delta/2), \\
\tan(A-B) = \tan(\delta/2).
\]
This implies that \(A+B = -\delta/2\), \(A-B = \delta/2\), and
\[
\tan \gamma = \cos(-\delta/2)\tan(\delta/2)/\cos(\delta/2) = \tan(\delta/2).
\]
So \(\gamma = \delta/2 = \pi/4\). As a result, \(\delta = 2\gamma = \pi/2\).

Second, if \(\delta = \pi/2\), then from Eq. (6.7):
\[
\tan(A+B) = -\tan(\delta/2) \\
\tan(A-B) = \cot(\delta/2)
\]
This implies that \(A+B = -\delta/2\), \(A-B = (\pi/2) - (\delta/2)\), and
\[
\tan \gamma = \cos(-\delta/2)\tan(\delta/2)/\cos[(\pi/2) - (\delta/2)] = 1
\]
So \(\gamma = \pi/4\). As a result, \(\delta = 2\gamma = \pi/2\).

The above two quarter wave points are highlighted with dashed lines in Fig. 6-3 (c) as well as in the experimental data of Johs et al. (2001).

6.2 Mueller matrix determination by dual rotating compensator ellipsometry:

a general treatment

In Parts (a-c) of Figure 6-4, development sequence of multichannel spectroscopic ellipsometry instrumentation spanning the last two decades is depicted. Although improvements in the light source, spectrograph, and multichannel detectors have been made, the major difference between successive instruments illustrated in the sequence in Fig. 6-4 lies in the nature and number of mechanically rotating elements.
Figure 6-4. Development sequence of multichannel ellipsometers: (a, top) the first generation using a rotating polarizer and no compensator; (b, middle) the second generation using a rotating compensator after the sample; (c, bottom) the third generation using dual compensators, one on each side of the sample, rotating at different angular frequencies. This figure was adapted from (Collins et al., 2000) with permission of the authors.
The first instrument depicted in Fig. 6-4 (a) is in P,SA configuration, where P represents the polarizer, the subscript r indicates that the polarizer is continuously rotating; S represents the reflecting sample; and A represents the analyzer (a second polarizer on the polarization detection side of the instrument). There is no compensator in this first generation of multichannel ellipsometer. The configuration of Fig. 6-4 (a) has the capability of measuring \((\psi, |\Delta|)\) of a sample. The fact that it cannot determine the sign of \(\Delta\) implies that it cannot detect the handedness of the polarization state, i.e., it cannot distinguish left and right elliptical polarization of the same ellipticity, neither can it measure the depolarization effect.

The second generation of multichannel ellipsometer shown in Fig. 6-4 (b) applies the PSC\(_r\)A configuration, where \(C\) represents a rotating compensator. The introduction of the rotating compensator can generate more complex modulation of the polarization state, i.e., both the tilt angle and ellipticity are modulated, and thus additional Fourier coefficients are introduced into the detected irradiance, without significant loss of the dc coefficient. This type of instrument can measure the full Stokes vector of a light beam reflected from the sample, but it cannot determine the full Mueller matrix of the reflecting sample, a point treated in Section 2.3. Presently, this second generation single rotating compensator instrument is the most widely used multichannel ellipsometer. For example, the instrument used to study CdTe deposition in real time in this Thesis research employs the PC,SA configuration as shown in Fig. 2-2.

The third generation of multichannel ellipsometer shown in Fig. 6-4 (c) applies the
PC_1r(\omega_1)SC_2r(\omega_2)A configuration, which means there are two compensators, one on each side of the sample, rotating at different angular frequencies. In Fig. 6-4 (c), for example, \(\omega_1:\omega_2=5:3\). In this configuration, the polarization state in front of the fixed analyzer is highly modulated, and the number of Fourier coefficients in the irradiance waveform at the detector is greatly increased compared to the first two generations. These coefficients provide additional information on the properties of the reflecting sample as well as providing partial self-calibration capabilities. Specifically, this type of instrument can measure the full 4x4 Mueller matrix of the reflecting sample which can then be used to characterize more complicated samples, i.e., those that are anisotropic or that scatter or depolarize the wave (Chen et al., 2003; Chen et al., 2005). Significant progress has been made on the development of dual rotating compensator multichannel ellipsometers and Mueller matrix ellipsometry within the last decade (see for example, Collins and Koh, 1999). Even today, instrumentation development for the third generation of multichannel ellipsometry along with the theories for interpreting the full 4x4 Mueller matrix of a sample define the forefront of research in the ellipsometry field.

The full 4x4 (real) Mueller matrix of a sample can over-determine the quantities that define the non-diagonal (complex) Jones matrix, the latter providing a means for analysis of non-depolarizing, specularly-reflecting surfaces exhibiting optical anisotropy (Azzam and Bashara, 1977; Tompkins and Irene, 2005). One particular application of relevance for in situ and real time studies of the vacuum deposition of cubic single crystalline solids is the simultaneous measurement of the bulk optical properties and the
surface-induced anisotropic optical properties (Chen et al., 2003). In this way one can analyze monolayer level anisotropic phenomena specific to the surface while simultaneously characterizing the underlying bulk isotropic material. Thus, dual rotating compensator multichannel ellipsometry serving as a real time Mueller matrix spectroscopy can play a unique and powerful role in solid state physics. Because the surface-induced dielectric function anisotropy signal is very weak, being derived from Mueller matrix elements and cross-polarization reflection ratios that reach maximum values on the order of $10^{-3}$, such a measurement demands very high precision and accuracy instrumentation, as well as optimized operational parameters, data acquisition, and data reduction strategies. Although it is possible to perform such procedures using multiparameter fitting with an instrument simulator program, the development of analytical expressions enable a more systematic approach that can be applied to identify previously unrecognized errors and establish procedures that correct for these errors.

The dual rotating-compensator configuration analyzed in this Chapter is denoted $\text{PC}_1r(\omega_1)\text{SC}_2r(\omega_2)A$ and, thus, is identical to the one shown in Fig. 6-4 (c) with the exception that the frequency ratio $\omega_1: \omega_2$ is assumed to be an arbitrary rational number rather than the specific ratio 5:3. Thus, mechanical rotation frequencies of the first and second compensators ($\omega_1, \omega_2$) are assumed to be synchronized at a ratio $p:q$ so that $\omega_1 = p\omega$ and $\omega_2 = q\omega$, where $\omega$ is the base frequency and $p$ and $q$ are arbitrary, non-zero, relatively prime integers. The detected waveform for this configuration is given as:
\[ I(t) = I_0 \{1 + \sum_{n=1}^{n_{\text{max}}} [\alpha(2N_{2n}\omega) \cos(2N_{2n}\omega t - \phi_{2n}) + \beta(2N_{2n}\omega) \sin(2N_{2n}\omega t - \phi_{2n})]\}, \]  \hspace{1cm} (6.8)

where \( I_0 = I_{00} M_{11} a_0 \). The summation in Eq. (6.8) employs the positive index \( n \), which takes on only the specific integer values \(|N_{2n}|\) up to its maximum \( n_{\text{max}} \), where \( N_{2n} \) is a signed integer index to be defined as a function of \( p \) and \( q \) in the following paragraph.

The highest frequency component in the waveform can be identified as \( 2N_{2n}\omega=2n_{\text{max}}\omega=4(|p|+|q|)\omega \), so that \( n_{\text{max}}=2(|p|+|q|) \). In the expression for the dc component \( I_0 \), \( I_{00} \) is an instrument response function obtained in reflection from a reflectance calibration sample or in transmission with the sample of interest removed, and \( M_{11} \) is the (1,1) element of the (unnormalized) Mueller matrix of the reflecting or transmitting sample, which is simply the unpolarized reflectance or transmittance. Thus, \( a_0 \) is the dc Fourier coefficient of the waveform for a wavelength independent optical system with no losses \( (I_0=1) \) and a perfectly reflecting sample \( (M_{11}=1) \). The spectra in \{\( \alpha(2N_{2n}\omega) \), \( \beta(2N_{2n}\omega) \)\} are the dc-normalized \( 2N_{2n}\omega \) cosine and sine Fourier coefficients, and \( \phi_{2n} \) is a phase term that depends on the Fourier component as described below.

Because the single rotating compensator ellipsometer configurations \( \text{PSC}_r(\omega)A \) and \( \text{PC}_r(\omega)SA \) generate waveforms with dc, \( 2\omega \), and \( 4\omega \) Fourier terms (Tompkins and Irene, 2005), the dual rotating compensator configuration generates the corresponding terms for the two individual compensators plus all the sum and difference frequencies, possibly 12 frequency components in all (excluding dc). Thus a maximum of 12 distinct frequencies with non-zero \{\( \alpha(2N_{2n}\omega) \), \( \beta(2N_{2n}\omega) \)\} are present in Eq. (6.8), depending on
the values $p$ and $q$. When $n_{\text{max}} = 2(|p| + |q|) < 12$, one or more of the 12 frequencies must be degenerate, whereas when $n_{\text{max}} > 12$, for one or more indices $n=|N_{2n}|$, the Fourier amplitude of $Z(2N_{2n}\omega) \equiv \alpha(2N_{2n}\omega) + i\beta(2N_{2n}\omega)$ must vanish and those indices need not be included. Explicitly, the non-zero frequencies and phases are:

$[2\omega_1, 2\omega_2] = [2p\omega, 2q\omega]$ double frequencies with $N_{2n} = [p, q]$;

$\phi_{2n} = [2pC_{S1}, 2qC_{S2}]$;

$[4\omega_1, 4\omega_2] = [4p\omega, 4q\omega]$ quadruple frequencies with $N_{2n} = [2p, 2q]$;

$\phi_{2n} = [4pC_{S1}, 4qC_{S2}]$;

$[2\omega_1 - 2\omega_2, 2\omega_1 - 4\omega_2] = [2(p-q)\omega, 2(p-2q)\omega]$ difference frequencies with

$N_{2n} = [p-q, p-2q]$; \hspace{1cm} \phi_{2n} = [2pC_{S1} - 2qC_{S2}, 2pC_{S1} - 4qC_{S2}]$;

$[4\omega_1 - 2\omega_2, 4\omega_1 - 4\omega_2] = [2(2p-q)\omega, 4(p-q)\omega]$ difference frequencies with

$N_{2n} = [2p-q, 2p-q]$; \hspace{1cm} \phi_{2n} = [2pC_{S1} - 2qC_{S2}, 4pC_{S1} - 4qC_{S2}]$;

$[2\omega_1 + 2\omega_2, 2\omega_1 + 4\omega_2] = [2(p+q)\omega, 2(p+2q)\omega]$ sum frequencies with

$N_{2n} = [p+q, p+2q]$; \hspace{1cm} \phi_{2n} = [2pC_{S1} + 2qC_{S2}, 2pC_{S1} + 4qC_{S2}]$; and

$[4\omega_1 + 2\omega_2, 4\omega_1 + 4\omega_2] = [2(2p+q)\omega, 4(p+q)\omega]$ sum frequencies with

$N_{2n} = [2p+q, 2(p+q)]$; \hspace{1cm} \phi_{2n} = [4pC_{S1} + 2qC_{S2}, 4pC_{S1} + 4qC_{S2}]$.

Thus, \{ $|p|, |q|, 2|p|, 2|q|, |p-q|, |p-2q|, |2p-q|, 2|p-2q|, |p+q|, |p+2q|, 2|p+q|, 2|p+q|$ \} are the set of non-zero integer indices $n = |N_{2n}|$ in Eq. (6.8) again with the possibility of degenerate values. In the phase terms listed above, ($C_{S1}$, $C_{S2}$) are defined by $C_1'(t) = p(\omega t - C_{S1})$ and $C_2'(t) = q(\omega t - C_{S2})$, where $C_1'(t)$ and $C_2'(t)$ are the true azimuthal angles of the fast axis at time $t$ for compensator 1 and compensator 2, respectively. Thus,
\[ -pC_{S1} \text{ and } -qC_{S2} \text{ are these angles at } t = 0. \]

Because the phases \( \phi_{2n} \) in Eq. (6.8) must be determined in calibration, the dc-normalized Fourier coefficients \( \{ \alpha(2N_2,\omega), \beta(2N_2,\omega) \} \) in Eq. (6.8) are not directly accessible in an experiment. As a result, Eq. (6.8) is considered to be a theoretical expression from which the normalized Mueller matrix elements \( \{ m_{jk} = M_{jk}/M_{11} ; j=1,...,4; k=1,...,4 \} \) are to be extracted after instrument calibration is performed. The corresponding experimental expression that neglects the phase terms is

\[
I(t) = I_0 \{ 1 + \sum_{n=1}^{n_{max}} [ \alpha'(2N_2,\omega) \cos(2N_2,\omega t) + \beta'(2N_2,\omega) \sin(2N_2,\omega t) ] \} \quad (6.9)
\]

Once calibration is performed to extract the phase angles, \( \phi_{2n} \), the theoretical "unprimed" coefficients of Eq. (6.8) can be determined from the experimental "primed" coefficients of Eq. (6.9) by the following \( \phi_{2n} \) rotation transformation:

\[
\alpha(2N_2,\omega) = \alpha'(2N_2,\omega) \cos \phi_{2n} + \beta'(2N_2,\omega) \sin \phi_{2n} \quad (6.10 \text{ a})
\]

\[
\beta(2N_2,\omega) = -\alpha'(2N_2,\omega) \sin \phi_{2n} + \beta'(2N_2,\omega) \cos \phi_{2n} \quad (6.10 \text{ b})
\]

The \((1,1)\) element of the Mueller matrix is determined from the experimental coefficient according to: \( M_{11} = I_0/I_{00}a_0 \), which can be obtained once the calibration for \( I_{00} \) is performed. Of course no phase correction is needed for the dc coefficient.

From the dc-normalized ac Fourier coefficients of Eq. (6.8), written collectively as \( \{ (\alpha_{2n}, \beta_{2n}) ; n=1, ..., n_{max} \} \), the normalized Mueller matrix elements \( \{ m_{jk} = M_{jk}/M_{11} ; j=1,...,4; k=1,...,4 \} \) can be determined (Collins et al., 2009), assuming that the 12 ac frequencies are distinct. The simplicity of the approach and the derived expressions is
remarkable, considering that they incorporate arbitrary:

(i) dual rotating-compensator frequency ratio $p:q$ (distinct frequencies are implicit);
(ii) rotating-compensator fast-axis angular phases $C_{S1}$ and $C_{S2}$;
(iii) compensator retardances, $\delta_{C_j} (j=1,2)$;
(iv) compensator amplitude transmission ratios $\tan \psi_{C_j} (j=1,2)$;
(v) polarizer angle $P'$ and analyzer angle $A'$.

In fact, features (i) and (iv) are new to this research.

Fig. 6-5 shows a comprehensive view of the methods by which the assumed distinct 24 non-zero dc-normalized Fourier coefficients, given in boxes at the left, provide the 15 normalized Mueller matrix elements, given in boxes at the right. In the derivation sequence, it is assumed that the dc Fourier coefficient $a_0$ is known; $a_0$ can be extracted from the dc-normalized Fourier coefficients of the top three boxes in Fig. 6-5, including the frequency components $(4p\omega-4q\omega)$, $(4p\omega+4q\omega)$, $4p\omega$, and $4q\omega$. As the derivation sequence for the Mueller matrix progresses from top to bottom, each new matrix element or group of elements to be determined requires the introduction of new Fourier components which appear in boxes directly to the left of the matrix element box in Fig. 6-5 and the associated boxes are connected by a solid line. The previously introduced Fourier components required in this derivation are connected to the newly-introduced components through broken lines that connect the corresponding boxes. In some cases, two independent groups of new Fourier components can be used to determine the same new Mueller matrix element and this is indicated by the two arrows directed toward the
Figure 6-5. Flowchart for the systematic determination of 15 Mueller matrix elements from 24 distinct Fourier coefficients of the irradiance waveform in dual-rotating compensator ellipsometry.
Mueller matrix box. When the Mueller matrix element is over-determined in this way, it is helpful to distinguish the methods as low frequency, high frequency, or mixed frequency approaches.

a) Mueller matrix elements (2,2), (2,3), (3,2), and (3,3)

The matrix elements of the 2x2 central block are given by:

\[ m_{22} + im_{23} = \left( \frac{a_0}{s_1 s_2} \right) \exp(-2iP') \]
\[ \{ Z(4p\omega - 4q\omega)\exp(2iA') + Z(4p\omega + 4q\omega)\exp(-2iA') \} , \quad (6.11a) \]

\[ m_{32} + im_{33} = \left( \frac{ia_0}{s_1 s_2} \right) \exp(-2iP') \]
\[ \{ Z(4p\omega - 4q\omega)\exp(2iA') - Z(4p\omega + 4q\omega)\exp(-2iA') \} . \quad (6.11b) \]

In these equations, \( Z(X) \) describes the complex quantity formed from the cosine and sine Fourier coefficients according to \( Z(X) = \alpha(X) + i\beta(X) \), where \( X \) denotes the frequency.

The dc Fourier coefficient \( a_0 \) in Eqs. (6.11), first defined in Eq. (6.8) above, is given explicitly in terms of Fourier coefficients in part c) below for Mueller matrix elements (2,1) and (3,1). The quantity \( s_j (j=1,2) \) is solely a characteristic of the compensator \( j \), given by:

\[ s_j = \frac{1}{2}(1 - \sin2\psi_j \cos\delta_j) . \quad (6.11c) \]

b) Mueller matrix elements (1,2) and (1,3)

The two central matrix elements of the first row are given by:

\[ m_{12} + im_{13} = \left( \frac{a_0}{s_1 t_2} \right) \exp(-2iP') \]
\[ \{ t_2Z(4p\omega) - Z(4p\omega - 4q\omega)\exp(4iA') - Z(4p\omega + 4q\omega)\exp(-4iA') \} . \quad (6.12a) \]

In this equation, \( t_2 \) describes the characteristics of the second compensator. For either
compensator \( t_j = s_j/c_j \), where \( s_j \) is given in Eq. (6.11c) and \( c_j \) is given by:

\[
c_j = \sqrt[2]{1 + \sin 2\psi c_j \cos \delta c_j}.
\]  

(6.12b)

c) Mueller matrix elements (2,1) and (3,1)

The two central matrix elements of the first column are given by:

\[
m_{21} + im_{31} = \{(a_0/t_1) \exp(-2iA')\}
\]

\[
\{t_1 Z(4q\omega) - [Z(4p\omega - 4q\omega)]^* \exp(4iP') - Z(4p\omega + 4q\omega) \exp(-4iP')\}
\]  

(6.13)

where the asterisk on \( Z \) denotes the complex conjugate: \([Z(X)]^* = \alpha(X) - i\beta(X)\).

The derivations above leading to the eight normalized Mueller matrix elements in Eqs. (6.11)-(6.13) demonstrate that the upper left 3x3 Mueller matrix block is determined uniquely by the eight unnormalized Fourier coefficients \( a_0\alpha \) and \( a_0\beta \) associated with the \((4p\omega - 4q\omega), (4p\omega + 4q\omega), 4p\omega, \) and \( 4q\omega \) frequency components. Fig. 6-5 exhibits this one-to-one relationship between the frequency components and the Mueller matrix elements.

The analysis of the \( PC_{1r}(p\omega)SC_{2r}(q\omega)A \) configuration shows that the dc Fourier coefficient can be expressed as a function of all the normalized Mueller matrix elements of the upper 3x3 block:

\[
a_0 = t_1 t_2 \left\{ t_1 t_2 + \alpha(4p\omega - 4q\omega) \cos 4(P' - A') + \beta(4p\omega - 4q\omega) \sin 4(P' - A') \right\}
\]

\[
- t_1 [\alpha(4q\omega) \cos 4A' + \beta(4q\omega) \sin 4A'] - t_2 [\alpha(4p\omega) \cos 4P' + \beta(4p\omega) \sin 4P']
\]

\[
+ \alpha(4p\omega + 4q\omega) \cos 4(P' + A') + \beta(4p\omega + 4q\omega) \sin 4(P' + A') \right\}^{-1}.
\]  

(6.14)

d) Mueller matrix elements (4,2) and (4,3)

For the 4th row and column of the normalized Mueller matrix, multiple methods are
possible. Considering $m_{42}$ and $m_{43}$ first:

$$
m_{42} + i m_{43} = \{ \pm i a \exp(-2iP') /[s_1 s_2 \sin 2\psi_{C2} \sin \delta_{C2}] \} \{ 2 s_2 [\exp(\pm 2iA')] Z(4p\omega \mp 2q\omega) 
+ (s_2 \pm 1) \cos 2\psi_{C2} [\exp(4iA')] Z(4p\omega \mp 4q\omega) \} + (s_2 \mp 1) \cos 2\psi_{C2} [\exp(-4iA')] Z(4p\omega \mp 4q\omega) \} .
$$

(6.15a)

The upper signs utilize the $(4p\omega - 4q\omega)$, $(4p\omega - 4q\omega)$, $(4p\omega + 4q\omega)$, and $4p\omega$ coefficients whereas the lower signs utilize the $(4p\omega + 4q\omega)$, $(4p\omega - 4q\omega)$, $(4p\omega + 4q\omega)$, and $4p\omega$ coefficients. If $p$ and $q$ are positive integers with $p > q$, then the upper sign choice corresponds to a lower frequency and the lower sign choice corresponds to a higher frequency. Possible mixed frequency approaches are not independent of these and so are not considered useful.

e) Mueller matrix elements (2,4) and (3,4)

Considering $m_{24}$ and $m_{34}$ next:

$$
m_{24} + i m_{34} = \{ \pm i a \exp(-2iP') /[s_1 s_2 \sin 2\psi_{C1} \sin \delta_{C1}] \} \{ 2 s_1 [\exp(\pm 2iA')] [\alpha(2p\omega \mp 4q\omega) \mp i\beta(2p\omega \mp 4q\omega)] 
+ (s_1 \pm 1) \cos 2\psi_{C1} [\exp(4iP')] [Z(4p\omega - 4q\omega)]^* \pm (s_1 \mp 1) \cos 2\psi_{C1} 
[\exp(-4iP')] Z(4p\omega + 4q\omega) + s_1 \cos 2\psi_{C1} Z(4q\omega) \} .
$$

(6.16a)

The upper signs utilize the $(2p\omega - 4q\omega)$, $(4p\omega - 4q\omega)$, $(4p\omega + 4q\omega)$, and $4q\omega$ coefficients and the lower signs utilize the $(2p\omega + 4q\omega)$, $(4p\omega - 4q\omega)$, $(4p\omega + 4q\omega)$, and $4q\omega$ coefficients. If it is assumed that $p > q > 0$, then the upper sign choice corresponds to a lower frequency and the lower sign choice corresponds to a higher frequency.

f) Mueller matrix elements (4, 1) and (1, 4)
The (4, 1) lower left matrix element is given by:

\[
m_{41} = \{a_0 / [t_1 \sin 2\psi C_2 \sin \delta C_2] \} \{t_1 \left[ \alpha(2q\omega) \sin 2A' - \beta(2q\omega) \cos 2A' \right] \\
\pm 2 \left[ \alpha(4p\omega \mp 2q\omega) \sin (4P' \mp 2A') - \beta(4p\omega \mp 2q\omega) \cos (4P' \mp 2A') \right] \}
\]

\[
+ \{a_0 \cot 2\psi C_2 / [s_1 s_2 \sin \delta C_2] \} \{\pm (1-s_1)(1+s_2) \left[ \alpha(4p\omega \pm 4q\omega) \sin 4(P' \mp A') \mp \beta(4p\omega \pm 4q\omega) \cos 4(P' \mp A') \right] \}
\]

\[
\pm 2 \left[ \alpha(4p\omega \mp 4q\omega) \cos 4(P' \mp A') \mp \beta(4p\omega \mp 4q\omega) \cos 4(P' \mp A') \right] \}
\] (6.17)

This expression results when the proper linear combination of the 2q\omega Fourier coefficients is taken, given by \(\alpha(2q\omega) \sin 2A' - \beta(2q\omega) \cos 2A'\). The upper signs utilize the 2q\omega, (4p\omega-2q\omega), (4p\omega-4q\omega), (4p\omega+4q\omega), 4p\omega, and 4q\omega coefficients and the lower signs utilize the 2q\omega, (4p\omega+2q\omega), (4p\omega-4q\omega), (4p\omega+4q\omega), 4p\omega, and 4q\omega coefficients. Again, if \(p>q>0\), then the upper sign choice corresponds to a lower frequency and the lower sign choice corresponds to a higher frequency.

The (1, 4) upper right matrix element is given by:

\[
m_{14} = \{a_0 / [t_2 \sin 2\psi C_1 \sin \delta C_1] \} \{t_2 \left[ -\alpha(2p\omega) \sin 2P' + \beta(2p\omega) \cos 2P' \right] \\
\pm 2 \left[ \alpha(2p\omega \pm 4q\omega) \sin (2P' \mp 2A') - \beta(2p\omega \pm 4q\omega) \cos (2P' \mp 2A') \right] \}
\]

\[
+ \{a_0 \cot 2\psi C_1 / [s_1 s_2 \sin \delta C_1] \} \{(1+s_1)(1-s_2) \left[ \alpha(4p\omega \mp 4q\omega) \sin 4(P' \mp A') \mp \beta(4p\omega \mp 4q\omega) \cos 4(P' \mp A') \right] \}
\]

\[
\pm s_1 (1-s_2) \left[ \alpha(4q\omega) \sin 4A' - \beta(4q\omega) \cos 4A' \right] + (1-s_1)(1-s_2) \]

\[
\left[ \alpha(4p\omega \pm 4q\omega) \sin 4(P' \mp A') - \beta(4p\omega \pm 4q\omega) \cos 4(P' \mp A') \right] \}
\] (6.18)

Again this expression results in this case when the proper linear combination of the 2p\omega
Fourier coefficients is taken, given by $-\alpha (2p\omega) \sin 2P' + \beta (2p\omega) \cos 2P'$. The upper signs utilize the $2p\omega$, $(2p\omega-2q\omega)$, $(4p\omega-4q\omega)$, $(4p\omega+4q\omega)$, $4p\omega$, and $4q\omega$ coefficients and the lower signs utilize the $2p\omega$, $(2p\omega+4q\omega)$, $(4p\omega-4q\omega)$, $(4p\omega+4q\omega)$, $4p\omega$, and $4q\omega$ coefficients, and in this case also the frequency convention is maintained.

g) Mueller matrix element $(4,4)$

For the $(4,4)$ lower right element of the normalized Mueller matrix, four independent expressions are possible with four different combinations of frequencies,

$$m_{44} = \pm 2a_0 / [\sin 2\psi C_1 \sin \delta C_1 \sin 2\psi C_2 \sin \delta C_2]$$

$$\{ [\alpha (2p\omega \pm 2q\omega) \cos 2(P' \mp A') + \beta (2p\omega \pm 2q\omega) \sin 2(P' \mp A')]$$

$$- \frac{1}{2} [(\cos 2\psi C_1 \cos 2\psi C_2) / s_0] + [((\cos 2\psi C_1) / s_1)(\alpha (4p\omega \pm 2q\omega) \cos (4P' \mp 2A'))$$

$$+ \beta (4p\omega \mp 2q\omega) \sin (4P' \mp 2A')] + [((\cos 2\psi C_2) / s_2)(\alpha (2p\omega \pm 4q\omega) \cos (2P' \mp 4A'))$$

$$+ \beta (2p\omega \mp 4q\omega) \sin (2P' \mp 4A')] + [((\cos 2\psi C_1 \cos 2\psi C_2) / s_1 s_2)$$

$$[\alpha (4p\omega \pm 4q\omega) \cos 4(P' \mp A') + \beta (4p\omega \pm 4q\omega) \sin 4(P' \pm A')] \} . \quad (6.19)$$

The upper signs utilize the low frequency components:

$(2p\omega-2q\omega)$, $(4p\omega-2q\omega)$, $(2p\omega-4q\omega)$, $(4p\omega-4q\omega)$,

and the lower signs utilize the high frequency components:

$(2p\omega+2q\omega)$, $(4p\omega+2q\omega)$, $(2p\omega+4q\omega)$, $(4p\omega+4q\omega)$.

An alternative approach couples (i) the high frequency expressions for $m_{4j}$ and $m_{j4}$ $(j=1,2,3)$ to the low frequency component $(2p\omega-2q\omega)$ and (ii) the low frequency expressions for $m_{4j}$ and $m_{j4}$ $(j=1,2,3)$ to the high frequency component $(2p\omega+2q\omega)$. This approach leads to the pair of more complicated, but independent expressions:
\[ m_{44} = \{ \mp 2a_0 / [\sin 2\psi_{C1}\sin \delta_{C1}\sin 2\psi_{C2}\sin \delta_{C2}] \} \]

\[
\begin{align*}
&\{ [\alpha(2p\omega \mp 2q\omega) \cos (P' \mp A') + \beta(2p\omega \mp 2q\omega) \sin (2P' \mp A')] \\
&- \frac{1}{2}[(\cos 2\psi_{C1}\cos 2\psi_{C2})/a_0] - [(\cos 2\psi_{C1})/s_1][\alpha(4p\omega \pm 2q\omega) \cos (4P' \pm 2A')] \\
&+ \beta(4p\omega \pm 2q\omega) \sin (4P' \pm 2A')] - [(\cos 2\psi_{C2})/s_2][\alpha(2p\omega \pm 4q\omega) \cos (2P' \pm 4A')] \\
&+ \beta(2p\omega \pm 4q\omega) \sin (2P' \pm 4A')] - [(\cos 2\psi_{C1}\cos 2\psi_{C2})/s_1s_2][s_2[\alpha(4p\omega) \cos 4P'] \\
&+ \beta(4p\omega) \sin 4P'] + s_1[\alpha(4q\omega) \cos 4A' + \beta(4q\omega) \sin 4A'] \\
&- (1 - s_1 - s_2)[\alpha(4p\omega \pm 4q\omega) \cos (P' \mp A') + \beta(4p\omega \pm 4q\omega) \sin 4(P' \mp A')] \\
&+ (s_1 + s_2)[\alpha(4p\omega \pm 4q\omega) \cos (P' \pm A') + \beta(4p\omega \pm 4q\omega) \sin 4(P' \pm A')] \}.
\end{align*}
\]

In this case, the upper signs utilize the frequency components:

\((2p\omega - 2q\omega), (4p\omega + 2q\omega), (2p\omega + 4q\omega), 4p\omega, 4q\omega, (4p\omega - 4q\omega), (4p\omega + 4q\omega),\)

and the lower signs utilize the components:

\((2p\omega + 2q\omega), (4p\omega - 2q\omega), (2p\omega - 4q\omega), 4p\omega, 4q\omega, (4p\omega - 4q\omega), (4p\omega + 4q\omega).\)

Thus, among the expressions presented in this section, Eq. (6.20) represents the only one with a mixed frequency selection.

6.3 Simulations for generalized dual rotating compensator ellipsometry

Considering the complexity involved in the derivation of Eqs. (6.11) – (6.20), a computer program in FORTRAN language was written to simulate the operation of a virtual ellipsometer system having the dual rotating compensator design shown in Fig. 6-4 (c). This program calculates the output Stokes vector \( S^O \) of the light beam after it passes through the fixed analyzer and before it enters the detector as follows:
\[ S^O = R(-A')M_\lambda R(A')R(-C_2')M_{C2} R(C_2')M_{jk} \]

\[ R(-C_1')M_{C1} R(C_1')R(-P')M_P R(P')S', \quad (6.21) \]

where \( R(\gamma) \) is the Mueller matrix for a rotation transformation of the coordinate system by an angle \( \gamma \); \( M_\lambda, M_{C2}, M_{jk}, M_{C1}, \) and \( M_P \) are the Mueller matrices of the analyzer, the second compensator, the sample, the first compensator, and the polarizer, respectively; \( S' \) is the Stokes vector of the input light beam from the source. Explicit forms of the matrices in Eq. (6.21) can be found in the references (Azzam and Bashara, 1977; Tompkins and Irene, 2005). For the purpose of verifying Eqs. (6.11) – (6.20), all system parameters except \( \omega_1 \) and \( \omega_2 \) were chosen at random, including \( C_{S1}, C_{S2}, \delta_{C1}, \delta_{C2}, \psi_{C1}, \psi_{C2}, P', A', \) and the \( M_{11} \) normalized Mueller matrix \( m_{jk} \) of the sample, as shown in Table 6-1. The frequencies \( \omega_1 \) and \( \omega_2 \) could not be chosen at random since the ratio \( \omega_1: \omega_2 \) must be rational so that \( \omega_1 = p \omega \) and \( \omega_2 = q \omega \) with \( p \) and \( q \) being relatively prime. Under these circumstances, the simulation can then span a time duration corresponding to an integral number of optical cycles \( T = \pi/\omega \). Thus, in the simulation the frequencies were fixed at \( \omega_1 = 5 \) rad/s and \( \omega_2 = 3 \) rad/s so that \( \omega = 1 \) rad/s and \( T = \pi \) s. In order to assess generality, the simulation was also run with other combinations of \( p \) and \( q \), and all the same conclusions were reached irrespective of the choice of frequencies.

In the calculation of Eq. (6.21), \( C_1', C_2', \) and \( S^O \) are periodic functions of time \( t \). The first element of \( S^O \) is proportional to \( I(t) \) as given in Eq. (6.8), which is the irradiance at the detector. In the simulations performed here, \( t \) was varied from 0 to an integral number of optical periods of the system. Once \( I(t) \) has been generated, the experimental Fourier
Table 6-1. Optical system parameters, including the sample Mueller matrix, used in the simulations to verify the equations of Section 6.2. The simulation results, include the experimental and theoretical dc normalized Fourier coefficients, as well as the sample Mueller matrices calculated using both low and high frequency components.

<table>
<thead>
<tr>
<th>system parameters</th>
<th>input sample Mueller matrix</th>
<th>calculated Mueller matrix (low f)</th>
<th>calculated Mueller matrix (high f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega_1$ (radians/s)</td>
<td>5</td>
<td>-1.46587</td>
<td>-1.36409</td>
</tr>
<tr>
<td>$\omega_2$ (radians/s)</td>
<td>3</td>
<td>-2.83162</td>
<td>-2.02559</td>
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<tr>
<td>$C_{s1}$ (radian)</td>
<td>0.74947</td>
<td>-0.55678</td>
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</tr>
<tr>
<td>$C_{s2}$ (radian)</td>
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<td>2.67738</td>
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<tr>
<td>$\delta_{s1}$ (radian)</td>
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<td></td>
</tr>
<tr>
<td>$\delta_{s2}$ (radian)</td>
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<tr>
<td>$\psi_{C1}$ (radian)</td>
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</tr>
<tr>
<td>$\psi_{C2}$ (radian)</td>
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<tr>
<td>$A'$ (radian)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>$P'$ (radian)</td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>dc normalized Fourier coefficients</th>
<th>experimental ($\alpha$, $\beta$)</th>
<th>theoretical ($\alpha$, $\beta$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_0$</td>
<td>0.592056</td>
<td>0.592056</td>
</tr>
<tr>
<td>$(4\omega_1, -4\omega_2)$</td>
<td>(-2.585062E-02 - 1.106770E-02)</td>
<td>(-3.724758E-02 - 1.073812E-02)</td>
</tr>
<tr>
<td>$(4\omega_1, 4\omega_2)$</td>
<td>(1.245482E-02 - 6.121288E-03)</td>
<td>(-1.031541E-02 - 9.283594E-03)</td>
</tr>
<tr>
<td>$(4\omega_1)$</td>
<td>(-6.314514E-02 - 7.545806E-02)</td>
<td>(5.087719E-02 - 8.372372E-02)</td>
</tr>
<tr>
<td>$(4\omega_2)$</td>
<td>(0.136218 - 0.441585)</td>
<td>(0.304337 - 0.347751)</td>
</tr>
<tr>
<td>$(4\omega_1, 2\omega_2)$</td>
<td>(7.133719E-02 - 5.112283E-02)</td>
<td>(4.922355E-02 - 7.266073E-02)</td>
</tr>
<tr>
<td>$(4\omega_1, -2\omega_2)$</td>
<td>(-4.254286E-02 - 2.455839E-02)</td>
<td>(-4.082673E-02 - 2.731642E-02)</td>
</tr>
<tr>
<td>$(2\omega_1, -4\omega_2)$</td>
<td>(4.080516E-02 - 5.291629E-02)</td>
<td>(6.591100E-02 - 1.099704E-02)</td>
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<tr>
<td>$(2\omega_1, 4\omega_2)$</td>
<td>(-0.137296 - 5.624056E-02)</td>
<td>(-7.951636E-03 - 0.148925)</td>
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<td>$(2\omega_1)$</td>
<td>(-0.553607 - 9.009729E-02)</td>
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<td>$(2\omega_2)$</td>
<td>(-1.17260 - 2.86461)</td>
<td>(2.61820 - 2.55371)</td>
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<td>(-0.348568 - 0.471797)</td>
<td>(2.61246 - 0.305768)</td>
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<td>$(2\omega_1, 2\omega_2)$</td>
<td>(0.856099 - 0.214145)</td>
<td>(-9.434537E-02 - 0.877418)</td>
</tr>
</tbody>
</table>

coefficients as defined in Eq. (6.9) can be calculated through the numerical integrals:

$$
\alpha'(2Nz_1\omega) = \int_0^T \cos(2Nz_1\omega t) \ast I(t) dt / \int_0^T I(t) dt
$$

$$
\beta'(2Nz_2\omega) = \int_0^T \sin(2Nz_2\omega t) \ast I(t) dt / \int_0^T I(t) dt
$$

(6.22)

This method for determining the Fourier coefficients of the irradiance waveform differs from that used in the measurements because the detector used in the measurements

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integrates the current generated by the incident irradiance over relatively large sectors, typically 5°, of the 180° optical cycle (Lee et al., 2001). In contrast, the numerical integrals in Eq. (6.22) are evaluated by numerical means whereby $10^4$ irradiance points over an optical cycle are determined, a method that approaches the limit of continuous sampling. Once the experimental Fourier coefficients have been determined from Eq. (6.22), they can be entered into Eq. (6.10) for a phase correction that provides the theoretical Fourier coefficients in Eq. (6.8). The known $\phi_{2n}$ values are calculated from the randomly selected system optical parameters $C_{S1}$ and $C_{S2}$. The theoretical Fourier coefficients determined in this procedure were then used to calculate the $M_{11}$ normalized sample Mueller matrix $m_{jk}$ applying Eqs. (6.11) to (6.20) for comparison with the randomly chosen input Mueller matrix.

Figure 6-6 shows the simulated irradiance waveform of Eqs. (6.8) and (6.9). It can be seen that within the two generated optical periods, the irradiance oscillates between positive and negative values, the latter values being unphysical. A negative irradiance can be generated by Mueller matrix elements selected at random. Such a randomly generated Mueller matrix cannot exist for a real sample and specific constraints must be placed on the Mueller matrix elements in order to avoid an unphysical irradiance waveform. This problem does not preclude a purely mathematical assessment of the validity of Eqs. (6.11) to (6.20). Upon evaluation of the Fourier integrals of Eq. (6.22) and application of the phase corrections of Eq. (6.10), the experimental and theoretical Fourier coefficients are obtained as shown in Table 6-1. The latter were used to calculate the $M_{11}$ normalized
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sample Mueller matrix through Eqs. (6.11) – (6.20). As shown in Table 6-1, the Mueller matrix of the sample calculated from the above equations is identical within the sampling errors to the input Mueller matrix for both high and low frequency methods. With this simulation, the extensive theoretical derivations of Section 6.2 were found to be correct.

Once the equations of Section 6.2 have been verified, the function of the simulation program can be further extended to instrument performance applications. The extended program can provide a framework for simulating the behavior of the system under non-ideal experimental conditions, incorporating effects such as random noise in the detector output and mechanical misalignment of the rotating elements. Such simulations are critical in identifying the optimum system operational parameters and data reduction strategies.

Figure 6-6. Irradiance waveform generated from Eq. (6.21) with system parameters shown in Table 6-1.
For the purpose of implementing simulations for system optimization, the inputs to the simulations were based on a previously developed dual-rotating compensator multichannel ellipsometer with a rotation frequency ratio \( p:q \) of 5:3, and frequencies of the first and second compensators of \( 5\omega = 10 \text{ Hz} \) and \( 3\omega = 6 \text{ Hz} \), respectively. The simulated experimental non-zero Fourier coefficients correspond to \( n = |N_{2n}| = 1-8, 10, 11, 13, \text{ and } 16 \) (Chen et al., 2003). System optimization in this Thesis research was focused on a sample of (110) oriented single crystal silicon with lattice termination induced surface anisotropy. At 3.5 eV, the (110) Si surface exhibits a relatively strong anisotropic response in the dielectric function compared to other cubic crystalline semiconductor surfaces. The co-polarization and cross-polarization complex amplitude reflection coefficients were assumed to be \( \rho_{pp} = -0.50 + i0.25 \) and \( \rho_{ps} = -\rho_{sp} = 0.0025 + i0.0010 \), where \( \rho_{pp} \equiv r_{pp}/r_{ss} \), \( \rho_{sp} \equiv r_{sp}/r_{ss} \), and \( \rho_{ps} \equiv r_{ps}/r_{ss} \). The following definitions have been adopted for the complex amplitude reflection coefficients:

\[
\begin{align*}
    r_{jj} & = [(E_r)_j/(E_i)_j]_{(E_{ij})=0} \\
    r_{jk} & = [(E_r)_j/(E_i)_k]_{(E_{ij})=0},
\end{align*}
\]

where the inner subscripts indicate the reflected \((r)\) and incident \((i)\) wave electric fields and the outer subscripts \((j, k)\) denote the possible combinations of \((p, s)\) or \((s, p)\) directions. If no depolarization effect is considered, the sample’s normalized Mueller matrix \( m_{jk} \) can be uniquely determined from the above complex \( \rho \) values. For simplicity, identical compensators without dichroism were assumed so that \( \delta_{C1} = \delta_{C2} \) and \( \psi_{C1} = \psi_{C2} = 45^\circ \); and all calibration angles \((P', A', C_{S1}, C_{S2})\) were set to zero so that the theoretical Fourier coefficients were assumed to be the same as the experimental ones.

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A simulated detector output waveform $I(t)$, similar to that of Fig. 6-6, was used to compute first the Fourier coefficients and then the sample’s normalized Mueller matrix $m_{jk}(\text{calc})$, as described previously in this section. When no experimental errors were included in the simulations, $m_{jk}(\text{calc})$ was always found to be identical within the sampling errors to the assumed $m_{jk}$ derived from the assumed complex $\rho$ values. In order to simulate the effect of random noise, an output signal $\delta I(t)$ was added to the error-free detector output $I(t)$ at every time point during the simulations. The ratio of the noise to the error-free detector output, $\delta I(t)/I(t)$, was varied randomly from $-0.005$ to $0.005$, simulating any random errors that may exist in the experimental system, such as source noise or detector thermal noise. The distorted detector output $I(t)+\delta I(t)$, which is designed to simulate the measured data in a real experiment, was entered into Eqs. (6.22), (6.10), and finally Eqs. (6.11) – (6.20) in order to calculate $m_{jk}(\text{calc})$. In this case, $m_{jk}(\text{calc}) \neq m_{jk}$. The specific differences between the calculated and assumed Mueller matrix and the associated differences in the sample properties of interest depend on the operational parameters of the ellipsometer as well as on the sample itself. Systematic simulations can help identify the best operational parameters and data reduction strategy for different samples. An example of key operational parameters includes the retardances of the two compensators.

The noise-generated deviations in the complex amplitude reflection ratios were used (rather than the Mueller matrix elements) to evaluate system performance. This approach is based on the fact that the Mueller matrix is derivable from a Jones matrix in
the absence of depolarization, and it is the Jones matrix elements that are fitted in data analysis. The six parameters that describe the complex amplitude reflection ratios (including both real and imaginary parts) are over-determined by the 15 normalized Mueller matrix elements. Thus, the cross-polarization reflection ratios, which provide the anisotropic response of interest, can be derived in two independent ways, using complementary 2x2 blocks of the Mueller matrix and the upper left (UL) 2x2 block for normalization in both cases. From the upper right (UR) and lower left (LL) blocks, the simplest expressions for $\rho_{sp}$ and $\rho_{ps}$ are derived:

\[
\rho_{sp} = \frac{[(m_{13} - m_{23}) + i(m_{14} - m_{24})]/D_1 , \quad (UR) \quad (6.23a)}{}
\]

\[
\rho_{ps} = \frac{[(m_{31} - m_{32}) - i(m_{41} - m_{42})]/D_1 , \quad (LL) \quad (6.23b)}{}
\]

where

\[
D_1 = 1 - m_{12} - m_{21} + m_{22} . \quad (6.23c)
\]

Then, the two complementary blocks at lower left and lower right (LL+LR) for $\rho_{sp}$ and at upper right and lower right (UR+LR) for $\rho_{ps}$ provide the alternative expressions:

\[
\rho_{sp} = \frac{\{[(m_{33} + m_{44})(m_{31} + m_{32}) + i(m_{41} + m_{42})] - (m_{34} - m_{43})(m_{41} + m_{42}) - i(m_{34} - m_{43})]/D_1 D_2 , \quad (LL+LR) \quad (6.24a)}{}
\]

\[
\rho_{ps} = \frac{\{[(m_{33} + m_{44})(m_{13} + m_{23}) - i(m_{14} + m_{24})] + (m_{34} - m_{43})(m_{14} + m_{24}) + i(m_{13} + m_{23})]/D_1 D_2 , \quad (UR+LR) \quad (6.24b)}{}
\]

where

\[
D_2 = 1 + m_{12} + m_{21} + m_{22} . \quad (6.24c)
\]

Using these expressions, the first system operational parameter considered here is the common retardance $\delta$ for the two (identical) compensators. To minimize possible noise in the simulation results due to the random nature of $\delta I(t)$, 100 rounds of
Simulations were performed at each $\delta$ value. Figure 6-7 shows the average magnitude of the deviations in the real and imaginary parts of $\rho_{sp}$ and $\rho_{ps}$ -- one quantity per panel, plotted versus the single retardance value of the two compensators. In each plot, results are depicted for the two independent ways of extracting $\rho_{sp}$ and $\rho_{ps}$ from a Mueller matrix.

Figure 6-7. Average magnitude of the errors (left scale) in the real and imaginary parts of the cross-polarization complex amplitude reflection ratios $\rho_{sp}$ and $\rho_{ps}$ plotted as functions of the common compensator retardance for random noise in the detector given by $|\delta I(t)/I(t)| \leq 0.005$, assuming a dual-rotating compensator multichannel ellipsometer with a 5:3 rotation frequency. In converting Fourier coefficients to Mueller matrix elements, the lowest frequency options are used. Two different methods of extracting the real and imaginary parts of $\rho_{sp}$ and $\rho_{ps}$ from the Mueller matrix elements are employed as indicated. The magnitude of the errors as a percentage of the signal appears on the right scale.
either from Eqs. (6.23) or from Eqs. (6.24). In deducing the fourth row and column Mueller matrix elements from the Fourier coefficients, the simulations of Fig. 6-7 use the lowest possible frequencies in the waveform, i.e., all the upper sign choices in Section 6.2.

Figure 6-8 shows the results corresponding to those of Fig. 6-7, but using the highest possible frequencies, i.e., the lower sign choices in Section 6.2.

The following conclusions can be drawn from the simulation results shown in Figs.
6-7 and 6-8. First, it is clear that for overall greatest immunity of $\rho_{sp}$ and $\rho_{ps}$ to random noise in the waveform data, the range of compensator retardance should be approximately $90 - 120^\circ$, thus motivating the need for a compensator with a weakly varying retardance with wavelength. Second, the computational methods of Eqs. (6.24) for $\rho_{sp}$ and $\rho_{ps}$ that employ multiple blocks provide improved performance over the simpler single-block methods of Eqs. (6.23), considering the optimum range of $\delta$. Third, the use of the lower frequency Fourier coefficients can lead to better performance for the simpler single-block methods.

The assessments of Figs. 6-7 and 6-8 are based on the assumption of random noise of maximum amplitude $\delta I(t) = 0.005I(t)$; however, it is of interest to consider systematic errors that may be unrecognized or at least uncharacterized, and not generally included in a statistic assessment of fitting quality in data analysis. The error selected for this study is compensator element misalignment, in which case the first compensator is assumed to be tilted by $1^\circ$ about an axis of rotation coincident with the $S$ or slow direction in the plane of the compensator, and the second compensator is assumed to be tilted by the same angle, but about an axis coincident with the $F$ or fast direction. Figure 6-9 shows results, analogous to those of Figs. 6-7 and 6-8, for the misalignment errors of the compensators, using the lowest possible frequencies of the irradiance waveform. In this case, the two primary conclusions are as follows. First, the use of the two-block expressions of Eqs. (6.24) provide a wider range of compensator retardance over which the relative deviations are reduced, for example, below 1%. Second, and more importantly, the
overall errors in $\rho_{sp}$ and $\rho_{ps}$ are minimized when the two-block expressions are used and the compensators are designed for $90^\circ$ retardance. Thus, the simulation of Fig. 6-9 clearly emphasizes the advantages possible with achromatic rotating compensators.

The improved immunity to noise and alignment errors provided by the two-block expressions for $\rho_{sp}$ and $\rho_{ps}$ suggests that even greater performance improvement may be possible by averaging the two different methods for deducing $\rho_{sp}$ and $\rho_{ps}$. Additional
opportunities for averaging arise in the case of optical systems for which \( \rho_{sp} = -\rho_{ps} \), such as uniaxial ultra-thin surface layers that characterize the optical anisotropy on the surfaces of isotropic bulk single crystals. In fact, experimental two-block determinations of \( \rho_{sp} + \rho_{ps} \), which should vanish, have been used to assess the accuracy and precision of the previously described dual-rotating compensator multichannel ellipsometer (Chen et al., 2003). Results of \( \rho_{sp} + \rho_{ps} \) from waveform integrals collected over a time of 12 s, corresponding to a 48 optical cycle average, exhibit standard deviations of \( \sim 1 \times 10^{-4} \) from zero, which provide a measure of accuracy, and standard deviations of \( 8 \times 10^{-5} \) from the average, which provide a measure of the precision, considering a set of data points collected over the 2.0 (620 nm) to 4.5 eV (280 nm) photon energy range.

The optimization of the dual-rotating compensator multichannel ellipsometer is a complicated search in a multidimensional parameter space. Numerical simulations provide a very useful tool to identify the best compensator designs, operational parameters, and data reduction and analysis approaches. Such optimization is an important step to be taken before the design and manufacture of a dual rotating compensator ellipsometer and before the application of the unique measurement capability in future advanced spectroscopic ellipsometry studies. Additional simulations are the subject of future work; in these simulations other system operational parameters will be varied in an attempt to reduce errors introduced by non-ideal conditions.
Chapter 7

Summaries and Future Work

7.1 Summaries

Real time spectroscopic ellipsometry (RTSE) has been applied to study the growth processes and properties of thin film materials and solar cells based on II-VI semiconductors (CdTe/CdS), hydrogenated silicon (Si:H), and copper indium-gallium diselenide (CuIn_{1-x}Ga_xSe_2 or CIGS).

A series of polycrystalline CdTe thin films were magnetron sputtered onto native oxide covered crystal silicon substrates held at different deposition temperatures $T_d$ in the range of 188°C – 304°C. Other deposition parameters include an RF power of 60 Watts, an Ar pressure of 18 mTorr, and an Ar flow rate of 23 sccm. $T_d$ was determined from a temperature calibration based on the shifts of the $E_1$ and $E_2$ critical point energies of the complex dielectric function $\varepsilon = \varepsilon_1 + i\varepsilon_2$ for single crystal Si as a function of the thermocouple readout. The effective deposition rate of CdTe has been found to increase with increasing $T_d$, which can be attributed to a reduction in Ar atom density with the increase in gas temperature at constant pressure and volume. The initial nucleation stages of these CdTe depositions show island growth mode, or the Volmer-Weber (V-W) mode,
at lower $T_d$ and layer-island mode, or the Stranski-Krastanov (S-K) mode, at higher $T_d$. The peak nuclei height increases monotonically with $T_d$. At the end of deposition after a bulk layer thickness of $\sim 3300$ Å is reached, the final film surface roughness thickness is observed to decrease monotonically with increasing $T_d$. These trends are consistent with enhanced surface diffusion at higher $T_d$. For all $T_d$, the void volume fraction $f_v$ in the CdTe film increases monotonically with increasing bulk layer thickness $d_b$. Within the thin film regime ($d_b < 500$ Å), $f_v$ increases monotonically with increasing $T_d$. The lowest $T_d$ film, having the lowest $f_v$ value in the initial stages, exhibits an abrupt structural transition at $d_b \sim 1500$ Å whereby $f_v$ increases by more than eight times within a narrow range of $d_b$. This structural transition is suppressed with increasing $T_d$ in conjunction with the incorporation of voids in the thin film. The low $T_d$ structural transition is attributed to the relaxation of stress; the stress appears to be enhanced under low surface diffusion conditions, i.e., at low $T_d$, where $f_v$ is low. The highest density in the near-surface region of the final film ($\sim 3300$ Å) is obtained at an intermediate $T_d \sim 230^\circ$C, close to that for optimum solar cell performance.

A series of polycrystalline CdS thin films were magnetron sputtered onto native oxide covered crystal silicon substrates held at different deposition temperatures $T_d$ in the range of 145ºC – 320ºC. Other deposition parameters include an RF power of 50 Watts, an Ar pressure of 10 mTorr, and an Ar flow rate of 23 sccm. The effective deposition rate of CdS has been found to decrease with increasing $T_d$ in general, a trend opposite that observed for CdTe. In the initial nucleation stages of these CdS depositions, a trend
similar to that of CdTe was observed. The Volmer-Weber growth mode is evident at lower $T_d$ and the Stranski-Krastanov growth mode at higher $T_d$. The V-W to S-K transition temperature for CdS was found to be $\sim 160^\circ$C, about 100$^\circ$C lower than that for CdTe, indicating a lower diffusion activation energy for CdS. For the CdS films, each with a final thickness of $\sim 1300$ Å, both the surface roughness thickness and void volume fraction remain low throughout the depositions.

A second series of polycrystalline CdTe thin films was magnetron sputtered onto native oxide covered crystalline Si substrates with the key process variable being the Ar pressure, which was varied over the range of 2.5 – 50 mTorr. Fixed deposition conditions for this series include $T_d=230^\circ$C, an RF power of 60 Watts, and an Ar flow rate of 23 sccm. The growth rates determined from RTSE show a monotonic decrease with increasing Ar pressure due to enhanced gas phase scattering that occurs when the species sputtered from the target transit to the substrate. At lower pressures, the layer-island growth mode or S-K mode is favored; whereas at higher pressures, the island growth mode or V-W mode is favored. The peak nuclei height is observed to increase monotonically with increasing Ar pressure. For a 1 µm thickness, the 2.5 mTorr film exhibits the smallest roughness thickness, remaining relatively smooth throughout the deposition. As the Ar pressure increases, the roughness increases rapidly, reaching a maximum at $\sim 20$ mTorr with a final roughness thickness $\sim 35$ times larger than that of the 2.5 mTorr film. As the Ar pressure increases further above 20 mTorr, the roughness thickness returns to an intermediate value. These same CdTe films were studied ex situ by
AFM in the tapping mode with a scan area of 5x5 \( \mu \text{m}^2 \). The SE surface roughness thickness and the RMS roughness from AFM measurements are observed to follow a linear correlation: \( d_s(\text{SE}) \sim 1.7d_{\text{RMS}}(\text{AFM}) - 81\text{Å} \). The negative intercept of \(-81\text{Å} \) was attributed to the components of surface roughness with large in-plane scale (on the order of the wavelength of light) detectable by AFM but not by SE.

AFM images show that the optimum pressure for fabricating efficient solar cells near 10 mTorr lies in the boundary region between two distinct characteristics of the AFM images. Below 10 mTorr, the surfaces of CdTe samples appear nanocrystalline without a clearly defined grain structure, as a result of a relatively smooth and uniform appearance in the AFM images. Above 10 mTorr, the surfaces of CdTe samples have a well defined large grained structure, but at the same time appear very rough and not-uniform. Between crystallites, large voids appear whose average size and volume increases with increasing pressure. In the boundary region, the CdTe film surface has the overall best-defined and most uniform crystalline grain structure.

The optical properties of the CdTe and CdS films were studied in depth for the above \( T_d \) series. The complex dielectric functions of the CdTe films show distinct critical point (CP) features at the \( E_0, E_1, E_1+\Delta_1, \) and \( E_2 \) CP's; the complex dielectric functions of the CdS films show distinct CP features at the \( E_0, E_1-A, \) and \( E_1-B \) CP's. The second derivative spectra \( \frac{d^2\varepsilon}{dE^2} \) were fit to an analytical model based on the parabolic band approximation applied at each CP. Key parameters for the \( n^{th} \) CP were deduced from the fit, including the amplitude \( A_n \), band gap (resonance energy) \( E_n \), broadening parameter
(width) $\Gamma_n$, exponent $\mu_n$, and phase $\phi_n$, $E_n$ for both CdTe and CdS were found to decrease monotonically with increasing measurement temperature $T_m$, in accordance with a linear relationship. $\Gamma_n$ for both CdTe and CdS were also found to vary approximately linearly, in this case increasing with measurement temperature $T_m$. The corresponding temperature coefficients for $E_n$ and $\Gamma_n$, $C_{TE}(E_n)$ and $C_{TT}(E_n)$, respectively, were deduced.

At $T_m$ near room temperature, $\Gamma_n$ for the CdS films show strong and consistent variations with $T_d$ for all the CP's. These variations were explained in terms of different mean free paths $\lambda$ for the excited carriers in the polycrystalline films. The associated scattering mechanisms that control $\Gamma_n$ may be due to phonons, point or extended defects such as vacancies, impurities, and dislocations, as well as grain boundaries. Based on the parabolic band approximation and an assumption of dominant grain boundary scattering, grain sizes of the CdS films were estimated to increase from $\sim 60$ Å at $T_d \sim 150^\circ$C to $\sim 2000$ Å at $T_d \sim 300^\circ$C. The group speed of excited electrons associated with the $n^{th}$ CP $V_{gn}$ was consistently deduced for all the CdS CP's. The grain sizes estimated from SE analyses were compared to those estimated from XRD and AFM measurements. Qualitatively consistent trends versus $T_d$ were observed, but quantitatively the results of these three characterization methods differ. As a result, the possibility must be left open, however, for a more general interpretation in terms of a mean free path, with defect scattering being dominant at low $T_d$ and phonon scattering entering at high $T_d$.

A similar approach was applied to interpret $\Gamma_n$ as a function of $T_d$ for the series of CdTe films. In this case, the grain size was found to vary from $\sim 100$ Å at $T_d \sim 190^\circ$C to $\sim$
250 Å at $T_d \sim 300^\circ$C, a much weaker variation compared to CdS. In this analysis, $V_{gn}$ was also consistently deduced for all the CdTe CP's.

The data for $E_0$ versus $T_m$ associated with each of the sputtered CdTe films in the $T_d$ series were found to be almost parallel to one another and to the corresponding data for single crystal CdTe. Significant blue shifts of $E_0$ for the thin films relative to those of the single crystal are observed; these are constant with $T_m$, but vary with $T_d$. Based on such data, it is possible to deduce the temperature of a CdTe film, not from a single measurement of band gap energy $E_0$, but rather from an energy difference relative to a known $T_m$ value. The observed blue shifts in $E_0(T_m)$ are attributed to the stress in the sputtered films which depends on $T_d$. Previous measurements that provide the fundamental band gap in single crystal CdTe as a function of hydrostatic pressure made it possible to estimate the compressive stress in the CdTe films. Values from 0.4 to 0.9 GPa were obtained, from which linear stress coefficients for other CdTe CP’s $C_p(E_0)$ have been deduced.

A similar approach has been applied to the series of CdS films versus $T_d$, for which the deduced stress is nearly constant at $\sim 1.5$ GPa, a factor of two higher than that observed for CdTe. In this case, the quantitative analysis of stress is more uncertain due to the uncertainty in the $E_0$ or band gap energy of single crystal CdS, which is optically anisotropic and so may exhibit different band gap for fields aligned along the ordinary or extraordinary directions. A nearly constant, high level of stress is consistent, however, with the observed very low void fraction in all these CdS films. Using the stress deduced
from the $E_0$ CP, the stress coefficients $C_p(E_n)$ were also consistently deduced for all the other CP's of CdS.

With the full set of coefficients and group speeds obtained as described above, $\varepsilon$ spectra for CdTe and CdS were parameterized directly as a function of the key film properties such as temperature, mean free path (or grain size), and stress. Such parameterizations make it possible to develop a spatially scanning SE system to monitor film properties on a CdTe solar cell production line. As a demonstration of this capability, SE data collected during stepwise etching of a CdCl$_2$ treated CdTe solar cell were analyzed using the parameterization. Depth profiles in void volume fraction and electron mean free path were deduced for the CdTe film.

Virtual interface analyses were applied to RTSE data collected during very high frequency (vhf) plasma enhanced chemical vapor deposition (PECVD) of Si:H using a source gas of Si$_2$H$_6$. A deposition phase diagram was established for the vhf PECVD Si:H i-layer on an amorphous n-layer substrate film. After finishing the n-i structure with an a-Si:H p-layer, the resulting n-i-p stack serves as the top cell of a multifunction device. The optimum deposition condition for top cell performance was identified as the highest possible H$_2$ dilution ratio while avoiding the tendency of the Si:H to develop a mixed-phase amorphous+microcrystalline structure with increasing thickness. Such an optimization principle is similar to that previously identified by RTSE for radio frequency (rf) PECVD of Si:H from SiH$_4$, with the only difference being the optimum value of the hydrogen dilution ratio. Virtual interface analyses also show that the deposition phase
diagram depends sensitively on the phase of the underlying n-layer. Finally, in order to obtain high efficiencies for single junction devices serving either as the top amorphous Si:H cell or as the bottom microcrystalline Si:H cell, the evolution of any significant portion of the bulk i-layer in the form of amorphous+microcrystalline mixed-phase Si:H material must be avoided.

As a second example of the application of virtual interface analysis, metastable layers of CdTe$_{1-x}$S$_x$ at the CdS/CdTe interface have been explored using RTSE data collected when CdTe is sputter deposited on CdS and vice versa. As a first step in this investigation, a calibration of deposition rate versus rf power was required for magnetron sputtering of CdTe and CdS under a fixed set of other conditions which include $T_d=190^\circ$C, an Ar pressure of 18 mTorr, and an Ar flow of 23 sccm. Using this calibration, a series of CdTe$_{1-x}$S$_x$ alloy films with controlled compositions were fabricated by co-sputtering, by properly adjusting the rf power to the CdTe and CdS targets. As the next step, dielectric functions of the resulting CdTe$_{1-x}$S$_x$ alloy films were determined from RTSE data, and compiled into a database that enables prediction of $\varepsilon$ for CdTe$_{1-x}$S$_x$ of any $x$ value. As a final step, this database was incorporated into the virtual interface approximation for the analysis of RTSE data collected during depositions of CdTe on CdS/c-Si and the reverse sequence of CdS on CdTe/c-Si, both at $T_d = 190^\circ$C. The goal of the virtual interface analysis itself is to determine the depth profile in the alloy content of the growing film in the interface formation process. In both deposition sequences, there is a $\sim$ 40 Å layer with a strong gradient in $x$, possibly generated by ion impact in the
sputtering process as the interface is formed. Beyond this thickness, S diffusion into the deposited CdTe from the underlying CdS exhibits a tail with $x \sim 0.02$. For the inverted structure, Te diffusion into the deposited CdS from the underlying CdTe exhibits a much weaker tail, indicative of a lower diffusion coefficient.

In studies related to instrument development as a component of this research, the Jones vector and Jones matrix formalism was used to characterize the function of an optical system consisting of two bi-plate compensators whose fast axes are oriented 45° apart. The polarization modifying properties of this device were derived, demonstrating that the device acts as a linear rotator followed by a linear phase retarder (or compensator). The rotation angle, the retardance, and the associated fast axis azimuthal angle were explicitly determined as functions of the retardance of the two bi-plate compensators, for a fixed relative orientation of the fast axes of the compensators of 45°.

In a final study also related to novel instrument development, Stokes vector and Mueller matrix formalisms were used to describe the operational principles of the dual rotating compensator ellipsometer system. Additional generalizations were incorporated into the description including: (1) rotation frequencies of the two compensators $p\omega$ and $q\omega$ where $p$ and $q$ are arbitrary relatively prime integers; and (2) arbitrary dichroic effects for the two compensators. A computer program was developed to first verify the derived equations that provide the sample Mueller matrix given the Fourier coefficients of signal waveform at the detector, and second to simulate the operation of the instrument under non-ideal conditions. This program can be used to identify the best hardware design,
experimental configuration, and data reduction strategies.

7.2 Future work

The science and technology of thin film photovoltaics is developing rapidly, and real time SE has the potential to impact the existing knowledge base and state-of-the-art process development in these fields. Because this thesis represents the first real time SE studies of CdTe and CdS thin films, many questions have been raised in addition to those that have been answered in this thesis. As a result, there remain many research activities of interest that have yet to be undertaken, which is inevitably the case for initial research in new directions. Even in a well-studied area of real time SE -- that involving thin Si:H films -- additional recommendations for future research have become evident through this thesis. Such recommendations for future research activities are described in the following paragraphs.

Chapters 3 and 4 show that deposition temperature $T_d$ and Ar pressure $p_{Ar}$ play critical roles in determining the structural evolution and optical properties of the deposited CdTe films. The well-defined structural features in CdTe film growth as a function of $T_d$ and $p_{Ar}$ described in Chapter 3, such as the transition between the Volmer-Weber (V-W) and Stranski-Krastanov (S-K) growth modes, appear to be well correlated with the regimes of optimum CdTe solar cell performance. Further controlled studies of solar cell fabrication as a function of $T_d$ and $p_{Ar}$ are needed to confirm such correlations and understand their physical origins. Similar such studies of CdTe focusing
on other sputtering parameters, such as substrate bias and rf power, are expected to be similarly interesting and potentially important in guiding solar cell fabrication. Variations in the substrate bias can change the incident energies of the deposited species without changing their directionality; unfortunately both such changes occur together in the case of the Ar pressure. Variations in the rf target power will change the flux of the deposited species and thus provide information on the surface kinetic processes. In any new studies that expand processing parameter space, real time SE must be combined with other characterization techniques such as atomic force microscopy and scanning electron microscopy, which provide direct images of the surfaces, as well as with overall solar cell device performance.

Investigations of the effects of deposition parameters used in the magnetron sputtering of CdS should be carried out as well. The goal in this case is to enhance the performance of solar cells by identifying the sputtering conditions that optimize solar cell performance when using ultrathin CdS layers. This will include similar variations in pressure, dc bias, and target power. Additionally the role of O₂ additions to the sputtering gas in the fabrication of wider band gap nanocrystalline CdS:O would also be of interest. In all cases, it is important to ensure that the optical absorption in the film drops abruptly below the CdS layer band gap so that light is not absorbed in the CdS that would otherwise be expected to lead to electrons and holes in the CdTe.

Throughout this thesis, CdTe and CdS thin films were deposited on native oxide covered c-Si wafers due to their consistent smoothness and well studied properties.
However, the CdTe solar cells in the superstrate configuration are deposited on transparent conducting oxide (TCO) coated glass substrates. The TCO-coated glass may be a standard commercial product such as TEC-15, an experimental product such as TEC-15 with a high resistivity transparent layer on top, or a research laboratory prepared TCO such as ZnO:Al on alumino-silicate glass designed to maximize efficiency through the reduction of optical losses. Such TCO-layer substrate materials can lead to significant interface roughness between the TCO and the CdS and between the CdS and CdTe. This complicates any analysis of the structural evolution. In addition CdS-TCO chemical interactions are likely due to penetration of S via ion bombardment and/or diffusion, and these are sure to complicate the analysis as well. Real time SE studies similar to those in this thesis should be performed, but selecting a system first that exhibits minimum surface roughness which would then enable understanding of the chemical interaction separately from the effects of interface roughness. A good candidate is alumino-silicate glass coated with smooth ZnO:Al which could also be studied in advance by RTSE. Studies as a function of the TCO roughness may provide more direct correlations between the ZnO:Al and CdS thin film structural evolution, material optical properties, and solar cell performance. For the CdS, the ability to achieve high performance solar cells with very thin layers is likely to depend not only on deposition process for the CdS, but also the nature of the substrate, i.e., its roughness and reactivity in the deposition process. In contrast, for a very thick film such as the CdTe layer, the ultimate film structure is less likely to be dependent on the starting underlying
roughness on the CdS.

Chapter 4 of the thesis focused on the variability of the CdTe and CdS optical properties deduced along with the structural information in the RTSE analysis. One of the limitations of the optical property determination is the inability to perform such analysis as a function of bulk layer thickness due to the rapid development of surface roughness under most conditions. In fact, the conditions under which surfaces remain sufficiently smooth throughout deposition, e.g., the lowest pressures, are the conditions under which the optical properties remain relatively constant with thickness. Improved analysis methods to handle samples with thick roughness layers would be a very worthwhile goal of future research.

The challenge of measuring CdTe optical properties as a function of thickness as the grain structure coarsens due to the development of significant surface roughness can be overcome in a different way, namely, through the use of ex situ measurements in conjunction with Br₂/methanol etching which smoothens the surface at the same time as it reduces the thickness. This approach can be described as "time-reversed real time SE", but with a smooth surface, and it can also be applied to depth profile the optical properties of CdCl₂ treated samples. When such data for CdTe is combined with those of as-deposited samples from the series studied in this thesis, good consistency is obtained leading to a better understanding of the role of grain size and stress on the optical properties. Given the observed correlations, the optical properties can then be used as a probe of grain size and stress in ex situ measurements of samples, both
non-destructively through the glass and also destructively in etch profiling experiments. It should be pointed out that the correlations between the optical properties and the grain size or defect density and between optical properties and the strain in thin films remains a work in progress. Future studies will increase confidence in the correlations, as well as identify possible deviations from the correlations as described in the next paragraph.

Although very good consistency is obtained in this thesis for a model of the optical property broadening parameters in terms of grain boundary or defect scattering, in which case the group speed associated with each critical point is extracted, the model assumes that the excited carrier crystal momentum is completely randomized in each scattering event. However, different types of defects are expected to lead to different scattering behavior at each of the critical points, and as a result, the group velocity ratios which should be constant in a simple theory may show variations from sample set to sample set. The fact that ion-implanted single crystal CdTe exhibits different group speed ratios relative to polycrystalline CdTe may be an indication of low angle scattering events from the dominant defects -- dislocation loops -- in the ion-implanted samples. This can be taken into account through an empirical factor that describes the number of interactions required to randomize the momentum of the excited carrier. A more complete study of single crystal CdTe in which known defects are intentionally introduced, may enable categorization of the effect of these defects on the optical properties and provide additional insights.

Good consistency, at least for CdTe, is also obtained when correlating stress and
critical point energies, and such correlations have provided insights into the role of strain build-up in the structural evolution of the film as well as the relaxation of strain in the CdCl₂ treatment. Additional research in this area should focus on the determination of the spectroscopic strain-optic tensor of single crystal CdTe. Another approach is to deposit a thin layer of CdTe on a flexible substrate, CdCl₂ treat the resulting sample, and then measure the critical point shifts as a function of the bending radius. Such studies would provide essentially independent verification of the critical point energy shifts.

The corresponding correlations between stress and critical point energies in CdS is less certain due to variations in the measurement of the critical point energies of single crystal CdS which is assumed to be free of stress. In this case, polishing damage of the CdS crystal may be the origin of the variations, and the focus in this case should be to develop surface processing of the single crystal, thereby provide greater confidence in the measurements as characteristic of the single crystal. For CdS as well, it would also be useful to deposit a thin layer on a flexible substrate and measure the critical point energy shifts as a function of the bending radius.

The real time SE studies of CdTe₁₋ₓSₓ alloys in this thesis were limited to a highest temperature of 190°C in order to avoid the complexity of alloy phase segregation. This is useful for generating homogeneous metastable CdTe₁₋ₓSₓ films and hence for establishing the reported database of CdTe₁₋ₓSₓ optical properties as a function of the compositional parameter x. It is also of interest to study stable alloy formation using RTSE at temperatures higher than 190°C. Exposure of CdS/CdTe films to higher
temperatures is necessary in the fabrication processes of solar cells. For example, the highest efficiency processes using close-space sublimation occur at a temperature of ~600°C. Even "low temperature" magnetron sputtered CdTe solar cells are exposed to a temperature of ~387°C in the post-deposition CdCl₂ treatment. Significant inter-diffusion between CdTe and CdS is expected at such temperatures, which may lead to the modification of the compositional and optical properties of the entire CdTe and/or CdS layers, especially when they are thin.

One future study of interest would be to begin with smooth crystalline silicon wafer substrates and to deposit layers of CdTe on CdS and vice versa with thicknesses designed to generate the stable phase composition when complete interdiffusion occurs upon annealing. This study will provide the optical properties of the stable phases at the elevated temperature, and these can also be measured upon cooling. Initial experimental activities in this direction have suggested that challenges occur due to the slow sublimation of the films during the annealing process which makes it difficult to maintain the appropriate composition during interdiffusion. It is important to achieve success in this type of experiment for the characterization of the interfaces of CdCl₂ treated cells at room temperature. In summary in future research, it will be important to determine the compositions and optical properties of the expected two endpoint alloy phases (Te rich and S rich, respectively) after fabrication at high temperature and then maintain these phases upon cooling the alloy films to room temperature for final optical property measurement.
Although ex situ measurements of post-deposition CdCl₂ treatments have been incorporated in this thesis study, and much has been learned, the microscopic processes and the optimum parameters for CdCl₂ treatment are still open to debate. In the future, it is of great interest to apply SE to investigate the dynamics and effects of CdCl₂ treatment on as-grown CdTe and CdS films, especially if such an investigation can be carried out in situ and in real time. For this purpose, the key is to design the appropriate experimental configuration that allows optical access to the films being treated. It may be possible to perform the SE measurement in real time through the glass and focus on the changes that occur at the CdS/CdTe interface where inter-diffusion is occurring.

Future research is also proposed to extend the studies of thin film Si:H described in Chapter 5. As presented in that chapter, the Si:H thin film materials fabricated by PECVD are categorized into two phases: amorphous (a-) and microcrystalline (µc-). This categorization could be further refined which will be useful for understanding the evolution of material properties and for further solar cell optimization. For example, after the $a \rightarrow a + \mu c$ nucleation transition, the average grain size of the microcrystalline phase Si:H is sure to vary with its volume fraction as characterized by the virtual interface analysis in the topmost part of the film. Furthermore after the $a + \mu c \rightarrow \mu c$ coalescence transition, the average grain size of the microcrystalline phase as well as the void volume fraction in the topmost part of the film is likely to continue to vary with film thickness. Therefore, it is of interest to determine the optical properties of the microcrystalline phase Si:H as a function of grain size as has been done for CdS and CdTe in Chapter 4. In this
way, the optical properties of the Si:H microcrystals can be linked to their volume fraction evolution. In the first studies, depositions with very low rates will be needed, so that the acquisition time of the SE data can be extended and hence the noise can be reduced, which is necessary in order to extract multiple parameters in a virtual interface analysis.

Finally, for the generalized dual rotating compensator ellipsometer system described in Chapter 6, additional simulations are warranted in order to optimize the system parameters that are not described in Section 6.3, such as the polarizer angle, the analyzer angle, the dichroism parameters, the ratio of rotation speeds, and the rotation directions. Optimizations of these parameters are particularly important if the retardance of the compensators is significantly smaller than the optimum value of ~ 90°. For advanced sample measurements, depolarization effects should also be included in the simulations. Of particular interest is the ability of the instrument user to correct for measurement errors when characterizing a sample that is known to be isotropic and non-depolarizing and thus characterized by a single \((\psi, \Delta)\) spectrum. For example, one can enter various errors into the simulations such as those generated in calibration, and then extract the ellipsometric parameters as an average of multiple methods (which is possible in such an advanced instrument configuration) in order to improve the accuracy and determine the correct sample parameters even in the presence of instrument errors. Such an approach has been developed in the early four-zone null ellipsometry methods. The promise of the advanced instrument configuration to improve significantly the accuracy of
spectroscopic ellipsometry measurements is one of its great attractions.
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