

A Dissertation

entitled

Enhancement of Cu(In,Ga)Se₂ Solar Cells and Materials via the Incorporation of Silver

by

Scott A. Little

Submitted to the Graduate Faculty as partial fulfillment of the requirements for the

Doctor of Philosophy Degree in Physics

Dr. Sylvain X. Marsillac, Committee Chair

Dr. Terry Bigioni, Committee Chair

Dr. Robert Collins, Committee Member

Dr. Randy Ellingson, Committee Member

Dr. John-David Smith, Committee Member

Dr. Patricia R. Komuniecki, Dean
College of Graduate Studies

The University of Toledo

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As Cu(In,Ga)Se₂ (CIGS) technology has proven itself to be a worthy solar cell technology, research efforts have redoubled to explore ways to enrich the already mature technology or create spin-offs of the technology with specific goals for manufacturing in mind. CIGS technology is now at an efficiency and production level that is competitive with other second generation solar cell devices and c-Si. Further research in CIGS allows for a toolbox of new ideas to try in the technology. This work aims at that goal by generating and presenting many ideas on how that may be possible. Primarily, this work contains information concerning the improvement of the manufacturing process using a hybrid sputter deposition chamber for scaling up and allowing for easy *in situ* monitoring using ellipsometry. It also explores the possibility of the addition of Ag to enhance and control device behavior and properties, and investigates the concept of a two-stage process with a co-sputtering deposition chamber. Monitoring of Ag *in situ* and in real time was explored to possibly improve the back contact of solar cells that use Ag as a back contact (not necessarily CIGS) and as a potential precursor for nanocrystals.

For my parents, brother, friends and family

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Chapter 1

Introduction

1.1. Motivation and Background

Some models predict that the supply of fossil fuels is expected to peak in the next 5 to 20 years [Brandt, 2007]. After that, fossil fuel availability is expected to start to decrease dramatically. Thus, we need to realize that there is a problem with the current situation and develop a sense of urgency. While decreasing the amount of fossil fuels as much as we can and as soon as we can, we have to develop powerful, reliable and inexpensive sources of renewable energy. Out of the popular alternative energy technologies available—geothermal, biomass, wind, hydropower, and solar—the latter appears to be the most promising, albeit under-implemented, and with the capacity to become an inexpensive technology worldwide thanks to continuous technological advances that make solar cells more easily manufactured and widely available.

1.2. Fundamentals of Solar Cell Operation

1.2.1. Introduction

Solar cell technologies have benefited greatly from the wealth of knowledge borrowed from semiconductor research for computing devices. Thus, the knowledge and

understanding of basic semiconductor materials and devices go a long way in the understanding of solar cell devices.

To explain the basic operation of a solar cell device, crystalline silicon (c-Si) is the best place to start pedagogically as well as historically. In this section, it is explained how diodes can be formed from these basic semiconductors and ultimately be used and tested as a solar cell device.

1.2.2. Semiconductor Materials

Simply put, a semiconductor material conducts electricity better than an insulator, such as SiO_2 , but worse than a conductor, such as Cu. The distinction is more than the name “semi” and “conductor” suggests, but is a good starting place. A first glance at the Group IV elements, such as Si, and the name “semiconductor” seems to make the most sense because it contains an equal number filled and unfilled electron positions in the outer valence shell (+4 or -4 charge), unlike the metals left of Group IV and the insulators on the right of Group IV. So when two Si atoms form a bond, the total charge of the molecule is neutral.

1.2.2.1. Band Structure and Band Gap

In the illustration of two Si atoms forming a bond, additional energy levels for an electron to occupy are possible. Likewise, when several hundred Si or other semiconductor atoms construct an atomic lattice, the energy levels as a function of momentum in three dimensions stabilize and can be represented by a figure known as the band structure diagram.

As more atoms are being added to the lattice, some energy states are emphasized more than others called “bands.” Two notable bands within any structure are the

conduction band (at E_c energy) and the valence band (at E_v energy). The conduction band is the higher energy level of the two energy bands. A band gap is formed when there is a separation between the conduction and valence bands. Thus the energy for a band gap is given by $E_g = E_c - E_v$. We can now revisit the definition of a semiconductor. A semiconductor differs from an insulator in the magnitude of the band gap. Usually an insulator's band gap is much larger than the one of a semiconductor (generally greater than 3 eV). At normal operating conditions, an insulator is usually not useful in the kind of applications that use semiconductors (i.e., diodes) because electrons cannot be thermally excited with any reasonable probability from the valence band to the conduction band.

Another distinguishing property within the class of semiconductors is whether or not the band gap is considered direct or indirect. In band gaps that are considered indirect, such as Si, the conduction and valence bands are separated not only in energy but also in momentum. In direct band gaps, which are found in a material such as GaAs, the valence and conduction band are separated in energy at the same momentum (usually denoted Γ or $k = 0$ in momentum space).

1.2.2.2. Intrinsic Carrier Concentration and Doping

Just as a greater band gap will decrease the chances of an electron from “hopping” from one band to another band, there are other mechanisms responsible for the excitation. Just increasing the temperature of the semiconductor increases the number of free electrons within a material according to the statistical Fermi-Dirac distribution of electrons. The amount of these carriers per volume, or concentration, exists intrinsically within all semiconductors (and conductors for that matter) as a function of temperature.

At room temperature, the intrinsic carrier concentration, n_i , is the number of electrons that exist in the valence band. Since the conduction band is normally filled, this number describes the number of vacancies, or holes, in this band. Intrinsically, or undoped, the number of free electrons and free holes within the semiconductor is the same.

The number of holes or electrons within a semiconductor can be increased by replacing some of the atoms in the lattice with a dopant. In the case of a Si lattice, where all of the atoms are made of Si, the dopants usually used are boron (or other Group III element) and phosphorous (or other Group V) atoms. Boron atoms that replace Si in the lattice leave a vacancy for an electron since the outer valence shell of boron contains one less electron, which are called acceptors or p-doped semiconductors. Likewise, phosphorous atoms add an extra electron to the Si lattice, creating an n-doped semiconductor or donors. Now, for doped semiconductors, unlike undoped semiconductors, there is an imbalance in the hole concentration, p_o , to electron concentration, n_o .

1.2.3. Generation and Recombination

Now that we have introduced the basics of semiconductors science, we can look at how light, or photons, interact with semiconductors. Photons can be absorbed by a semiconductor, assuming that the photon is not reflected or transmitted through the material. If the photon is absorbed, then there is a probability that the photon will generate an electron-hole pair within the solar cell material. An electron is excited from the valence band into the conduction band, breaking a covalent bond between lattice atoms and the removed electron. The removed electron leaves behind a hole in the

valence band. The electron in the conduction band and the hole in the valence band are free to move around since the bond is broken, hence the electron-hole pair generation.

It is important to note that a photon is subject to not being absorbed if its energy is less than the band gap energy. Also, an increase in light intensity increases the amount of electron-hole pairs generated. This is why optical concentrators, such as Fresnel lenses, are used to increase photogenerated current.

In a semiconductor, if the electron-hole pair is not further separated, or collected, it will recombine. The electrons and holes must be separated by an electric field before one of the recombinative processes—Shockley-Read-Hall (SRH) process, photon exchange, or Auger recombination—occurs.

For the SRH process, impurities in the lattice create states between the valence and conduction bands that can absorb the difference in momentum between the electron and hole carriers. This kind of recombination is more prevalent in indirect band gap semiconductors than in direct band gap semiconductors because of the extra amount of momentum required in an indirect semiconductor. When this momentum is absorbed through a phonon, or lattice vibration, it is transformed into thermal energy in the semiconductor.

In the photon exchange recombination process, an absorbed photon can be re-radiated as a photon of a different energy. This is known as stimulated emission, and is common in direct band gap semiconductors. In fact, this is the reason why many direct band gap materials are used in solid state lasers or LEDs—because they can produce a wavelength of light desired for a particular application. Unfortunately in a solar cell, this behavior is not desired since all light generated should be collected and not re-emitted.

In the Auger recombination, an electron-hole recombines and gives its energy to a third charge carrier, which is either a hole deep in the valence band or an electron deep in the conduction band. This third charge carrier slowly thermalizes, then, back to an energy closer to E_C or E_V by losing its energy to phonons. The Auger recombination process is most prevalent in a heavily doped semiconductor (which is denoted n_o^+ or p_o^+ instead of n_o or p_o).

1.2.4. Carrier Transport

To prevent recombination, the separated charges must be collected before being recombined. This introduces the concept of transport. The electrons and holes have to physically travel to opposite places as one requirement of a semiconductor to be used as a solar cell. Free carriers, which exist as holes in the valence band and electrons within the conduction band, move randomly until they run into an atom in the lattice. This is known as the mean free path or scattering length of the free carrier. The carriers will continue the random scattering movement until an electric field is applied, at which point the direction of both carriers will be balanced by the other carrier travelling in the opposite direction. When an electric field is applied, the average velocity of the charge carrier is called the drift velocity.

Due to this random movement of carriers, a gradient of electrons or holes is set up. Just like any diffusion in physics, the carriers flow from regions of high concentration to low concentration. Diffusion occurs at a higher rate at higher temperatures. Diffusion allows for all the charge carriers to be spread out in a semiconductor but is not ideal for charge separation. In the next section, the “trick” of the p-n junction can help us solve this problem.

1.2.5. P-n Junctions

When a p-doped semiconductor, say p-type Si, and an n-doped semiconductor, say n-type Si, are atomically bonded together (usually by growing one on top of the other), a p-n junction diode is formed. P-n junction diodes are the foundation of modern solid-state devices, such as transistors, lasers, LEDs, and solar cells. By diffusion, the holes from the p-type Si diffuse into the n-type region and likewise, the electrons from the n-type side diffuse into the p-type Si. This occurs until equilibrium occurs between the diffusion and the drift current, whereby the vacated dopant atoms in the lattice on both the n-doped and p-doped sides set up an electric field between them. This electric field rapidly removes any charge in this intermediate area giving it the name of depleted region or space charge region.

There are several modes of operations for diodes, but only a couple of them are relevant to solar cells. Under no illumination in a solar cell device, there is no net current. This state is known as thermal equilibrium. Under illumination or if an electric field is applied (in the form of an external voltage), then there is a steady-state current. Hence, this state is known as steady state. Another important mode of operation for a diode is the transient mode where voltages or illumination change with a high frequency. Since a solar cell device is not designed to operate at this frequency (as opposed to the modern transistor for computer processors), this mode is irrelevant for solar cells.

1.2.6. Diode Physics for Photovoltaics

The schematic of a solar cell device is shown in Fig. 1.1. Fig. 1.1.a. shows a typical pictorial of a c-Si solar cell device with electrical contacts, diode junctions, etc. depicted. Fig. 1.1.b. on the other hand shows how a solar cell can be described

electrically, where R_S is the series resistance, R_{SH} is the shunt resistance, I_D is the diode current and I_L is the photogenerated current. Using this electrically equivalent circuit for a solar cell, we can better understand the underlying electrical responses of the solar cell device. So, starting with the calculation of the current at the anode node of the diode, we have

$$I = I_L - I_D - I_{SH} , \quad (1.1)$$

where I_S and I_{SH} are the currents running through R_S and R_{SH} respectively. V_D , the voltage across the diode can be calculated by

$$V_D = V_L - V \quad (1.2)$$

The current in a diode can further be described by the Schokley diode equation [Nelson, 2008], which is given by

$$I_D = I_O [\exp(qV_D / nkT) - 1] \quad (1.3)$$

where I_O is the reverse saturation current, n is the diode ideality factor, q is the elementary charge, k is the Boltzmann constant, and T is the absolute temperature of the diode. Substituting equations 1.2 and 1.3 into equation 1.1 and using Ohm's law, we get

$$I = I_L - I_O \left[\exp\left(\frac{q(V + IR_S)}{nkT}\right) - 1 \right] - \frac{V + IR_S}{R_{SH}} \quad (1.4)$$

This diode equation explains the basic operation of the solar cell. Certain approximations of this equation are used to extract importance electrical characteristics that are explained in the following sections.

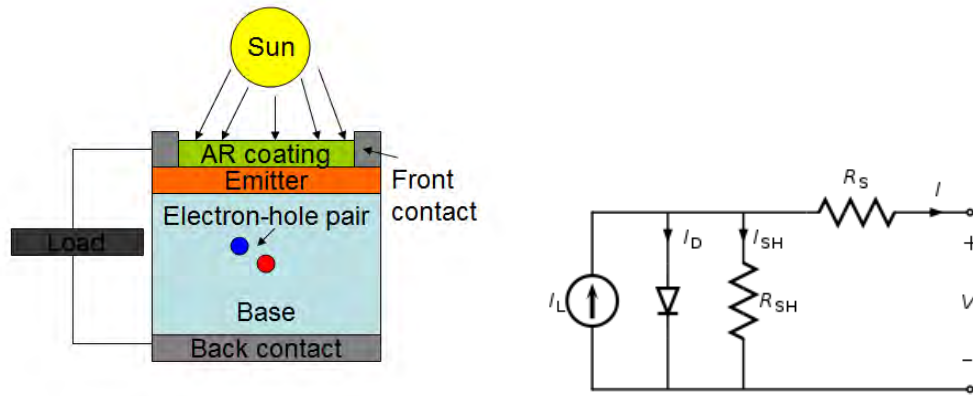


Figure 1-1. Solar cell: a) physical schematic, b) electrical schematic

1.2.7. Quantum Efficiency

Not all of the light incident on the solar cell can be converted into electrical energy. A test to see what percentage of light actually generates an electron-hole pair is quantum efficiency (QE) spectroscopy. When a photon arrives at the surface of a solar cell, it can be absorbed by any of the layers deposited on the solar cell. High energy photons tend to be absorbed nearer to the surface of the cell facing the sun while lower energy photons tend to be absorbed at the opposite side. In addition, layers are designed to absorb different energies of light, with the layers of highest band gap closest to the sun. Thus, each layer between the sun and a deeper layer acts as a window. If every photon over the entire solar spectrum were to be absorbed in the solar cell and collected as current, this would mean that the solar cell would have a 100% or unity quantum efficiency. In reality, a solar cell does not get 100% QE, and the areas of the spectrum that have lower currents can give insight to what layer is causing a problem within the cell. So a solar cell may have less than a unity QE if either: 1) recombination occurs

anywhere in the cell; or 2) the collection probability decreases due to mechanisms governing collection at a specific wavelength.

1.2.8. J-V Curve

Diodes can be identified over resistors by plotting a current density (J) vs. voltage (V) curve or a J-V curve. Resistors demonstrate a linear line shape while diodes exhibit an exponential type line shape after a voltage known as the turn on voltage (see equation 1.4). For a solar cell diode, the current collected from electron hole pairs generated by photons is added *in addition* to the normal diode current, or “dark” current as it is called in solar cell terminology. Thus, it is useful to collect both dark and illuminated J-V curves.

Parameters extracted from the J-V curve are the voltage at open circuit (V_{oc}), the current at short circuit (J_{sc}), the fill factor (FF), and the external efficiency (η). V_{oc} and J_{sc} are self descriptive while FF and η require a little more explanation. FF is defined by multiplying the voltage and current at the maximum power point of the J-V curve and dividing by $V_{oc} \times J_{sc}$. FF measures the “squareness” of the actual diode –thus it is a measure of the “diodeness” of the diode as compared to a resistor. The external efficiency is gotten by $V_{oc} \times J_{sc} \times FF$ divided by the power incident on the solar cell (from the solar simulator). A solar simulator is the machine used to simulate the irradiation of the sun in a controlled environment.

Two types of resistances are important to solar cell operation, which were used in the electrical schematic of the solar cell in Fig. 1.1: the shunt resistance and the series resistance. They can also be calculated directly from the J-V curve. The shunt resistance

is the easiest to understand as it is usually caused by imperfections in the making of the solar cell. Since the defects that cause shunt resistances have a lower resistance than the intended material of the solar cell, shunt resistances short circuit the current through the cell by giving the current another path to follow. In this way, a shunt resistance can be thought of a low resistor placed in parallel with the intended solar cell resistance (as seen in Fig. 1.1), whether that be an individual layer or from metallic contact to metallic contact. Shunt resistances can be estimated by observing the slope of the J-V in the dark in reverse bias.

Series resistances can be caused by several imperfections, such as the contact resistance between the metal contact and semiconductor, the resistance of the metal contacts themselves, and the resistance within the layers of the solar cell. Since the series resistance can be due to several different causes within a solar cell, it can be harder to pinpoint than a shunt resistance. The way to estimate the series resistance is more complex and requires calculating the derivative of dV/dJ . The schematic of a series resistance can also be seen in Fig. 1.1.

1.3. Overview of Photovoltaic (PV) Technology Development

1.3.1. Introduction

Solar cell technology has improved dramatically since its inception some 50 years ago. The first solar cell technologies were based on silicon and are commonly called “first generation” technology. Second generation technology includes research on thin-film materials dating back to around 30 years ago and is based on thin films such as CdTe, a-Si, and Cu(In,Ga)Se₂ (CIGS) absorber layer materials. Third generation

technology includes organic solar cells and nanotechnology-based devices. Even though it may seem like second or third generation solar cells might be the logical successors to first generation technology, first generation solar cells continue to be improved upon as companies invent new ways to manufacture and package this technology. For example, some companies feature Si “vertical integration” where the solar cell is made from Si ingot to finished product within the same plant [Calisolar, 2011]. With a vertical integration model it is the hope of many Americans that solar cells will be practical to make in the United States for employment purposes. For this reason, state and federal money is being invested to research photovoltaics in the hope that they will be able to give back to the community through jobs creation.

All these technologies operate based on the same principles, and the differences are in the cost of production. Although first generation solar cells have been developed and manufactured for many years, second generation solar cells are now at a point where they can be manufactured and sold at a price per Watt lower than the first generation technology. An example includes the company First Solar (USA), which produces most of the solar cells in the United States at less than a US dollar per watt using second generation CdTe thin films as absorber layers [Hutchinson, 2009].

1.3.2. First Generation PV

The first documented observation of the photovoltaic effect was by Edmund Becquerel in 1839 [Williams, 1960]. He accomplished this by illuminating a silver chloride electrode that was immersed in an electrolytic solution. The first predecessor to the modern commercialized Si diode solar cell was not invented until 1953 in Bell Labs by Gerald Person, Fuller, and Chapin [Tsokos 2008]. Thus, first generation crystalline Si

(c-Si) solar cells were born at an efficiency of 6% [Nelson, 2008]. More than 50 years later, we continue to improve on the efficiency and methods of manufacturing c-Si solar cells and several other technologies classified within the “second” and “third” generation hierarchy.

1.3.2.1. c-Si – single and polycrystalline

c-Si semiconductors have an indirect band gap of 1.17 eV, which has two problems: it is not optimized for the maximum absorption of light from the solar spectrum and it is an indirect transition. These two reasons combined mean that even though c-Si has an efficiency around 25% [Green, 2011], the layer has to be around 100 μm to make it optically thick. The technique of slicing a Si wafer from an ingot is borrowed from the computer processor manufacturing industry, but solar cells do not require the same amount of high purity Si that modern computer chips do. Thus, solar-grade Si can be produced at less of a cost and by the company manufacturing the cell for even a further reduced cost [Calisolar, 2011].

1.3.2.2. GaAs

GaAs is a direct band gap material. With the addition of Al, (Al,Ga)As is a tunable material. So with the highest conversion efficiencies (30% to 40% for single and multiple junction devices) out of any technology of any generation, it would seem like this would be the obvious choice. However, the cost of manufacturing is high because the amount of purity is similar to what c-Si requires. We will see that second generation technology has the advantage of being much more forgiving during the manufacturing process. The high purity of GaAs cells means that they are primarily manufactured using molecular beam epitaxy (MBE), which is expensive and the reason why most

applications for this technology are limited to space applications like satellite and space station solar cells, where power density requirements outweigh the price.

1.3.2. Second Generation PV

The expense of single crystals is high because much attention has to be given to the material quality of the crystal. So, it would be desirable to produce a high efficiency solar cell that is not as demanding pertaining to the purification. The thin film technologies, amorphous Si (a-Si), polycrystalline CdTe, and polycrystalline Cu(In,Ga)Se₂ (CIGS), that make up the second generation hierarchy are the best candidates to fit that requirement presently. “Thin” is not the only requirement of second generation since GaAs films are of thicknesses of the same order of magnitude as “thin-film” technologies. Second generation solar cells are placed in this category mainly for the industrial needs of quick production and large area at a low cost.

So, to reduce the amount of material in thin film solar cells compared to c-Si solar cells, it must be a good optical absorber of light. One way thin films achieve this better absorption is to incorporate a direct band gap material, which is accomplished in the CdTe and CIGS absorber materials. Since the density of states and energy band diagram differ in a-Si compared to c-Si because the bond lengths vary and long range order is lost, the transition becomes more like a direct band gap, thus the absorption is better in a-Si [Nelson, 2008]. Absorption in c-Si requires for there to be a phonon for the absorption of a photon. In a-Si, since there is no clear relation between energy and momentum due to the varying lengths of the Si-Si bonds, momentum does not have to be conserved, so the absorption of a photon can be accomplished without the requirement of a phonon.

1.3.2.1. a-Si

This unique Si-Si bond in a-Si may allow for it to have better absorption than in c-Si, but the material comes with other advantages and disadvantages when compared to c-Si. It is good, for example, that a-Si can form at a relatively low temperature, but it is not good that a-Si solar cells degrade several percent after initial production. a-Si, due to its small granularity, has a lower diffusion length and thus charge transport is made more difficult. This is usually remedied with a triple junction (p-i-n) solar cell. The charges on the dangling bonds determine if the a-Si will be p-doped, n-doped, or intrinsic (i). The intrinsic layer is needed to give the photons more space to be absorbed, therefore accommodating the short diffusion length of a-Si.

1.3.2.2. CdTe

After exploring group IV elements for suitable solar cell device materials, the next logical step is to look for good candidates in group III and group V or III-V semiconductors. One finds a decent solar cell device in GaAs and its variants but the cost of production is high. Being a II-VI semiconductor, CdTe is the next step in the search for good solar cell devices as it fits the requirements for a second generation technology. CdTe's band gap is 1.44 eV, which is close to the optimum limit of maximum theoretical efficiency [Nelson, 2008].

For a solar cell device, CdTe is p-doped extrinsically and is put together with n-CdS in an heterojunction configuration [Nelson, 2008]. The CdTe layer requires about 3-5 μm of thickness to achieve optical thickness [Nelson, 2008]. Like a-Si, CdTe is inhibited by defects within the device. These defects, including grain boundaries and areas of excess Te, cause traps that decrease the overall efficiency of the device. To

decrease the effect of these traps, a CdCl_2 treatment and annealing are used to passivate the defects and increase the grain size, resulting in an overall efficiency increase.

1.3.2.3. CIGS

CIGS in many ways is the continuation of CdTe, even moreso than CdTe is the continuation of Si. Thinking of this continuation in terms of elements, the Cd is replaced with Cu and In (or Ga) and Te is replaced with Se. Thus, CIGS is an I-III-VI₂ group semiconductor. The structure of the CIGS solar cell device is very similar to the structure of CdTe. Like CdTe, CdS is also used as the n-type layer for the diode junction. Unlike CdTe, the grain boundaries in CIGS are electrically benign [Yan, 2007] and do not require chemical treatment or extrinsic doping to achieve high efficiency. CIS (without the Ga) has a band gap around 1.0 eV, but with an optimum addition of Ga, the band gap can be tuned up to 1.65 eV.

1.3.3. Third Generation PV

Solar cell technology seeking to overcome the Shockley-Queesser limit of 31-41% efficiency is known as third generation photovoltaics [Kazmerski, 2006]. This is based on the theoretical limit of single layer first generation technology. So, even though multilayered solar cell devices such as GaAs and a-Si can be classified as third generation, third generation technology is usually thought of something that goes beyond the silicon/thin film hierarchy of a solar cell, presenting concepts such as multiple electron-hole generation, or employing nanotechnology or organic materials.

1.3.3.1. Organic PV solar cell devices

Organic solar cells use organic polymers or molecules to absorb light and transport charge [Brabec, 2003]. The local electric fields of organic solar cells can

separate electron-hole pairs better than a conventional solar cell, but the diffusion length is much smaller than a first generation solar cell, making charge transport much more difficult. To get around the problem of a small diffusion length, tricks are applied to the shape of the heterojunction interface to decrease the length needed for the junction while including enough material to make the layer optically thick. The efficiency of this type of solar cell is around 8% [Green, 2011], but its appeal comes from the potential inexpensiveness of the material and manufacturing process, flexibility of the cell, and with the hopes of someday improving the efficiency with future innovations.

1.3.3.2. Nanocrystalline

Out of all nanocrystalline technologies, quantum dot solar cells are the most famous. Quantum dots allow for a tunable band gap, thereby maximizing the absorption of light. A feature that can be utilized by quantum dots is the creation of multiple electron-hole pairs per photon that arrives on the quantum dot, known as multiple exciton generation (MEG) [Ellingson, 2005]. If these electron-hole pairs could be collected, this should allow for higher efficiency solar cells to be fabricated.

1.3.3.3. Dye sensitized

Dye sensitized solar cells use a TiO_2 sponge-like structure and are filled with ruthenium-polypyridine, an organic dye [Regan, 1991]. The dye is held in a liquid electrolytic solution, but the top electrode is a transparent conducting oxide (TCO). Dye sensitized solar cells can be made into a solar stack structure, and the electrolytic cells get better efficiency than the best quantum dot solar cells [Pattantyus-Abraham, 2010] with efficiency reaching 10.9% [Green, 2011].

1.4. Cu(In,Ga)Se₂ thin film properties details

1.4.1. Introduction – History

CuInSe₂ (CIS) solar cells were invented in Bell Laboratories in the early 1970s, but not much attention was given to this technology until Boeing achieved an efficiency of 9.4% in 1981 [Shafarman 2003]. At the time of Boeing's demonstration, CuS₂ was being explored as a thin film technology, but had some problems electrochemically [Shafarman 2003]. So, CIS progressed out of CuS₂ more than CdTe but CuS₂ research has nearly stopped, albeit for nanocrystalline interest.

Recently, the state-of-the-art in CIGS is 20.3% for a small area test cell [Hopwood 2010]. Since it has been demonstrated that it is possible to achieve this on a small scale, the manufacturing processes and procedures need to change so that large scale modules can be produced at a somewhat lesser efficiency. Current deposition temperatures of the substrate are from 400 – 600 °C, but may be able to be decreased or increased to decrease the cost and increase the efficiency. For example, if the substrate temperature could be lowered, then the overall cost of maintaining a higher temperature would be avoided. On the other hand, if the quality of the substrate improves and it is stoichiometrically favorable, a higher temperature may lead to higher efficiency. In addition to substrate temperature, the best CIGS solar cells have been produced by two- or three-stage processes. In these processes, the ratios of Cu, In, and Ga are changed to produce a desired effect, such as larger grain size, which corresponds to a greater conversion efficiency. CIGS is usually co-evaporated, but in this work and in previous work by Dr. Himel Khatri [Khatri, 2009], it can be shown that co-sputtering of Cu, In,

and Ga while evaporating the Se proves to be quite an effective and promising method, as sputtering is much more scalable to industrial sizes than evaporation methods.

1.4.2. Structural properties

1.4.2.1. CIGS semiconductor structure

CIGS belongs to a class of semiconductors known as chalcopyrites. Structurally, the chalcopyrite structure can be thought of two zincblende structures stacked on top of another. The CIS chalcopyrite structure can be built by starting with a zincblende structure of CdSe or ZnSe, for example (and by the way, these two compounds are considered the closest binary compounds to the ternary compound CIS). Cd would be the cation and Se would be the anion. So in CIS, the anion is Se, but the cation is shared with Cu and In. Each Se atom is bonded to two Cu atoms and two In atoms. In one of the two zincblende structures, Se must be nearer to Cu or In atoms to satisfy equilibrium. So if Cu is closer in one of the zincblende structures, then In will be closer in the next zincblende structure. Also, if one of the zincblende structures has been determined, the second joining zincblende can be found by simply replacing Cu atoms with In atoms and vice versa. The electronic energy diagram can then be calculated from this chalcopyrite structure. Ga may be added to replace In in this structure, and because there is conservation of charge, the structure is still called chalcopyrite. This permission of a substitution is known as the Grimm-Sommerfeld rule [Grimm et al., 1926].

1.4.2.2. Solar cell device structure

A typical CIGS solar cell includes a soda lime glass (SLG) substrate, typically 1 – 3 mm in thickness; a Mo layer on top of the substrate, 500 nm thick; the CIGS absorber layer, which is 1 – 2 μm thick; CdS, 50 nm thick; ZnO and transparent conducting oxide

(TCO), 500 nm thick; and metallic grids, a few hundred nanometers thick. SLG actually assists the efficiency of the solar cell due to Na diffusion, and there are several theories why this is so [Shafarman 2003]. Mo is actually a two-layer film, with each layer designed for a specific purpose. The layer deposited on the SLG is designed for adhesion, while the layer next to the absorber layer is designed to have the least resistivity. The addition of Ga actually permits the absorber layer to adhere to the Mo surface better [Nelson, 2008]. The CdS layer forms the n-type diode junction of the solar cell device and is usually deposited by a chemical bath (CBD). ZnO is used to help stop possible shunting caused by surface damage from the next deposition. The TCO layer can be indium tin oxide (ITO) or Al-doped ZnO (AZO). The grids are made with alternating layers of Ni, Al, and Ni. Ni is placed first to prevent Al from diffusing into the cell. Al is placed second for its excellent electrical conductance and low cost. And lastly, Ni is deposited to prevent oxidation of Al.

1.4.3. Compositional properties

High efficiency CIGS solar cell devices depend on several important processes and characteristics of the cell. The CIGS absorber layer must be a single phase. That is, the absorber layer must not contain Cu_{2-x}Se since it is conductive and will shunt the cell. Fig. 1.2 shows that the α phase is the desired phase of CIGS. In the two stage process, it is desirable to have Cu_{2-x}Se for the first stage since it helps in producing large grains, but eliminate it at the end to prevent shunt. Thus, all of the Cu_{2-x}Se must be gone from the absorber layer in the two- or three- stage process. Since Cu_{2-x}Se usually is found in the grain boundaries of CIGS and the grain boundaries are found to be electrically benign, we can conclude that most, if not all, of the Cu_{2-x}Se is gone at the end of the run. Dr.

Vikash Ranjan did a study of the detection of the disappearance of Cu_{2-x}Se in a multi-stage process by monitoring in real time and in situ the signature of Cu_{2-x}Se with ellipsometry [Vikash thesis]. By placing a line at 570 °C (the deposition temperature) on Fig. 1.2, the transition from a mixed phase on the right to a pure chalcopyrite phase by a two- or three-stage process can be traced out.

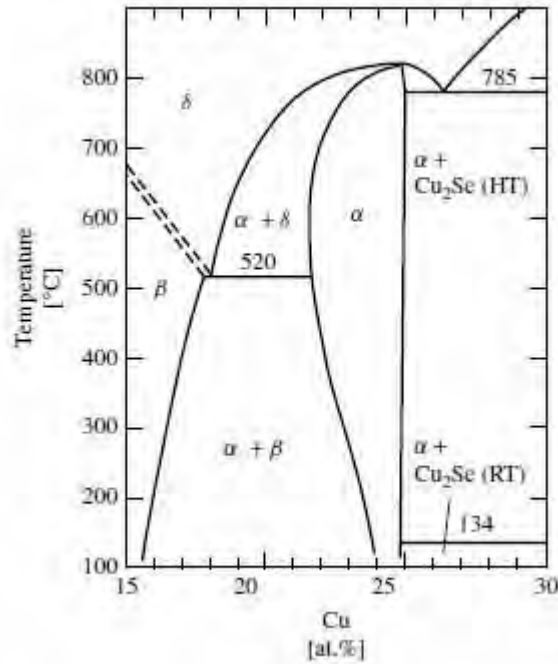


Figure 1-2. Pseudo-binary phase diagram of CIS show Cu% for In_2Se_3 at the left and Cu_2Se at the right. α is the chalcopyrite phase, δ is the sphalerite phase, β is the ordered defect phase, and Cu_2Se is an undesired compound if found at the end of the deposition [Shafarman, 2003].

CIGS is found to be p-type due to naturally occurring defects of Cu atoms at In sites and In vacancies [Nelson, 2008]. These native defects like to congregate near the grain boundaries, which creates trap energies above the valence band so that the hole activation is 0.3 eV [Nelson, 2008]. Dangling bonds on Se at grain boundaries (which are positively charged) must also be passivated by annealing in an O-environment.

1.4.4. Optical properties and absorber problems

Following the discussion in section 1.3.2.3, CIGS is a strong absorber of light since it is a direct band gap absorber and the band gap is tunable by changing the Ga content. Even though CIGS is an excellent absorber layer, it is not without its current set of problems. CIGS has a problem with absorbing the long wavelengths of the spectrum due to the poor collection of carriers generated at the back of the cell near Mo. This is due to the required diffusion length of 2 μm , which is similar to the grain size. The only way to improve this is to passivate the recombination due to the crystallites with the grains by annealing. Absorption in the blue and green region of the spectrum is inhibited by absorption due to the CdS layer—which is why the CdS layer is kept as thin as possible [Nelson, 2008]. Another non-optical problem of CIGS is the poor mismatch between the wurzite structure of CdS and the chalcopyrite structure of CIGS at the diode interface, which causes recombination by introducing more trap states [Nelson, 2008].

1.5. Thesis Objectives and Organization

As the CIGS technology has proven itself to be a worthy solar cell technology, research efforts have redoubled to explore ways to enrich the already mature technology or create spin-offs of the technology with specific goals for manufacturing in mind. CIGS technology is now up to an efficiency and production level to compete with other second generation solar cell devices and c-Si. Further extended research in CIGS allows for a toolbox for new ideas to try in the technology. This thesis aims at that goal by generating and presenting many ideas on how that may be possible. Not as an exhaustive list, this thesis contains information on how to improve the manufacturing process using a sputter deposition chamber for scaling up and allowing for easy in situ monitoring using

ellipsometry, it explores the possibility of the addition of Ag to enhance and control device behavior and properties, and the idea of a two-stage process with a co-sputtering deposition chamber is also explored. The monitoring of Ag in situ and in real time was explored to possibly improve the back contact of solar cells that use Ag as a back contact (not necessarily CIGS) and as potential precursors for nanocrystals.

In chapter 2, material and device characterization methods to explore solar cell materials and performance are discussed.

In chapter 3, noble metals, with special interest in Ag nanoparticles, are explored by in situ spectroscopic ellipsometry via the real time monitoring of the dielectric functions, the thickness and the roughness.

In chapter 4, the basic properties of (Ag,Cu)InSe₂ thin film materials by 1-stage process are discussed.

In chapter 5, the properties of (Ag,Cu)(In,Ga)Se₂ thin films deposited by 1-stage process and devices fabricated from these films are presented.

In chapter 6, the properties of (Ag,Cu)(In,Ga)Se₂ thin films deposited by 2-stage process and devices fabricated from these films are presented.

In the final chapter, a summary and conclusion of the work presented here will be given. In addition, a discussion involving the importance of this work on future directions of research are presented.

Chapter 2

Characterization Methods

2.1. Introduction

Characterization of solar cell materials and devices is fundamentally necessary in solar cell design and manufacturing. Different types of characterization techniques are used to monitor material properties *in situ*, in real time, *ex situ*, and as a completed device. The results of these techniques can then be corroborated for a more complete understanding of defects, morphology, and other material properties. Sections have been grouped with characterization techniques that are similar in measurement objective. An expanded section on ellipsometry is given due to its ubiquitous importance.

2.2. Elemental Composition Analysis

2.2.1. Energy-dispersive Spectroscopy (EDS)

2.2.1.1. Theory

Energy-dispersive Spectroscopy (EDS) allows for a quantitative compositional measurement of a specimen. EDS most commonly uses electrons as probes and measures x-rays emitted from atomic orbitals with specific energies that are characteristic to specific elements. Specifically, when an incident electron collides with inner core atomic

electron, the core electron is ejected, leaving a hole. An outer shell electron fills the core electron and an x-ray photon is emitted.

2.2.1.2. Operation

Typical operating voltages depend on two things: 1) the depth of the site of interest, 2) the inclusion of peaks. Greater operating voltages tend to probe deeper in the specimen. This depth can be estimated using computer simulation software employing Monte Carlo simulations. Greater operating voltages also allow for the inclusion of higher energy peaks, increasing the accuracy of the characterization. Typical operating voltages are twice that of the peak of interest. Characterization accuracy is also increased by longer acquisition times, higher resolution detectors, and lower time spent on processing an x-ray event (dead time).

2.2.2. Auger Electron Spectroscopy (AES)

2.2.2.1. Theory

In a process similar to EDS, Auger Electron Spectroscopy (AES) involves an electron being ejected instead of an x-ray photon. The Auger electron has the energy of an electron transitioning to a lower orbital hole. By detecting the Auger electron and extracting the value of the energy transition, the element can be identified. EDS is more of a volumetric compositional analysis, whereas Auger probes only a few nanometers on the surface and is more of a surface analysis.

2.2.2.2. Operation

Even though AES can detect only the composition on the surface, a depth profile can be accomplished by sputtering the surface material at a known rate while monitoring the composition in time.

2.2.3. Secondary ion mass spectrometry (SIMS)

2.2.3.1. Theory

The objective of SIMS as a surface compositional analysis technique is similar to that of AES. The method in accomplishing this objective, however, is much different. SIMS uses a primary ion beam, such as an Ar or Cs ion, and fires it at the specimen of interest. Ions ejected from the material of the target specimen are known as secondary ions. These secondary ions are then analyzed through a mass spectrometer. SIMS is the most sensitive surface scan analysis measuring in the ppb range and capable of monolayer analysis. The type of mass spectrometer employed by SIMS depends on what mode in which it is operating.

2.2.3.2. Operation

The two different modes of SIMS—static and dynamic—have different objectives and detector types. Static mode is capable of analyzing the surface of an atomic monolayer by using a pulsed ion beam and a time of flight mass spectrometer. Dynamic mode sputters the specimen material using a DC ion beam and measuring with a quadrupole or magnetic sector mass spectrometer.

2.3. Morphological and Topological Characterization

2.3.1. Scanning Electron Microscopy (SEM)

2.3.1.1. Theory

A scanning electron microscope (SEM) is a type of electron microscope that images a sample by scanning it with a beam of high-energy electrons. The electrons interact with the atoms in the sample producing a signal that contains data about the

sample's surface morphology, composition, and other properties such as electrical resistivity.

Signals formed by an SEM include secondary electrons, back-scattered electrons (BSE), characteristic X-rays, cathodoluminescence, as well as specimen current and transmitted electrons. Signals are a result of the scattering of electrons off of atoms near or at the surface of the specimen. In standard or secondary electron mode, the SEM can produce high-resolution images of the specimen surface, revealing features on the order of a nanometer. Because an electron beam is small, a large field of view is possible, allowing three-dimensional study of a specimen's surface.

2.3.1.2. Operation

2.3.1.2.1. Secondary electron mode

Due to the low energy of secondary electrons, these electrons are scattered from within a few nanometers of the surface of the specimen. Accelerated secondary electrons are sufficiently energetic to cause cathodoluminescence which are conducted to a photomultiplier outside the SEM main column. Amplified signal output is displayed as a two-dimensional intensity distribution. Brightness depends on the number of secondary electrons arriving at the detector. If an electron enters the specimen perpendicular to the surface, the activated region is uniform about the axis of the electron beam. Thus, at higher angles of incidence, more secondary electrons will be ejected, so steep surfaces tend to be brighter than flat surfaces, which results in images with a well-defined, three-dimensional image.

2.3.1.2.2. Backscattered electron mode

Back-scattered electrons (BSE) are reflected from the sample by elastic scattering. BSE mode is often used in analytical SEM along with the spectra made from the characteristic x-rays. Due to the intensity of the BSE signal being greatly correlated to the atomic number, BSE images can give one data about the distribution of elements in the specimen.

2.3.2. Profilometry

2.3.2.1. Theory

A profilometer uses a stylus to measure the lateral topography of a specimen. While the vertical resolution is on the nanometer scale range, the lateral resolution is only in the micrometer scale range.

2.3.2.2. Operation

For a thickness measurement, a small scratch on the specimen is made in the area of interest. The specimen is placed on a surface that has been made as perpendicular as possible to the stylus. Using an optical microscope, usually attached to the profilometer, the area of interest is selected and then scanned with the stylus. On screen data allows for “leveling” to be done so that an accurate reading of the specimen thickness can be accomplished.

2.3.3. Atomic Force Microscopy (AFM)

2.3.3.1. Theory

AFM is similar to stylus based profilometry, but scans are carried out over a two dimensional area instead of a single one dimensional line. Generally a cantilever made of SiN is used to probe the surface of the specimen by adjusting the position via control implementations. A laser is reflected on the back surface of the cantilever as a scan is in

progress. If the laser changes positions due to force on the cantilever, a voltage is applied to the piezoelectric to make the laser go back to its origin. Since the force on the cantilever is caused by surface features on the specimen, the voltage corresponds to the height of these features. A calibration between the height and the voltage is accomplished with a sample of a known structure.

2.3.3.2. Operation

2.3.3.2.1. Contact mode

AFM contact mode scans the surface similar to the stylus approach in profilometry, although setting an upper limit for the voltage on the piezoelectric and controlling the response behavior between the piezoelectric voltage and the deflection of the cantilever.

2.3.3.2.2. Tapping mode

Tapping mode, like contact mode, scans a two dimensional area, but does so with a “vibrating” cantilever instead of “dragging” the cantilever. A lock-in amplifier is used to select the strongest resonant frequency of the vibrating cantilever so that deviations in this frequency correspond to voltage changes applied to the piezoelectric. Thus, height information can be extracted from the piezoelectric voltage in the same way as in contact mode. Tapping mode has a couple of advantages over contact mode, including longer cantilever tip life due to less force applied to the cantilever, and the addition of a reading of the phase of the resonant frequency. Differences in the phase amplitude allows for the differentiation of composition within the specimen scan inclusion.

2.4. Structural Characterization

2.4.1. X-ray diffraction (XRD)

2.4.1.1. Theory

Materials that have a crystalline (not amorphous) structure are comprised of atomic lattices, which are atoms spaced periodically in three-dimensional space. If high energy photons, x-rays, hit the specimen, diffraction patterns are produced at different incident angles. The spacing and intensities of these diffraction patterns are analyzed using Bragg's Law and can be used to identify elements, chemical bonds, degree of disorder and other information.

X-ray diffraction patterns plotted as intensity vs. angle can be used to identify elements within alloys, for example, by observing relative peak intensities and the full width at half-maximum. Beyond identifying elements within an alloy, XRD can show lattice constants for constituent phase for polycrystalline films.

2.4.1.2. Operation

2.4.1.2.1. Theta-two theta mode

In theta-two theta mode, both incident and detecting "arms" have the same angle relative to the surface of the substrate. The advantage of this mode is quick scan rates since both arms are moving, and the ability to measure deep into the film.

2.4.1.2.2. Glancing angle mode

Sometimes, it is not desired to probe deeply into the film or not possible to get a good signal if the film is too thin. Glancing angle mode (GAXRD) fixes the incident angle from 1 to 10 degrees while moving the detecting arm. The peaks identified in the

mode will be at the same angles as the theta-two theta mode. For both of these modes the angle that is report on the horizontal axis is usually two theta

2.4.2. Transmission Electron Microscopy (TEM)

2.4.2.1. Theory

In a configuration similar to SEM, transmission electron microscopy (TEM) utilizes the small de Broglie wavelength of electrons to image down to the atomic scale. TEM is an imaging technique in which electrons tunnel through an ultra thin specimen. Images formed are from the interaction of the electrons with the specimen. Images are focused onto a fluorescent screen, for instance, or detected by a digital camera.

TEM image contrast is due to absorption of electrons in the material, which corresponds to the thickness and composition of the material. At higher magnifications interactions that modulate the intensity of the image are rather complex and require a more in-depth analysis. In addition to the regular absorption based imaging, different operating modes allow for the TEM to observe modulations in elemental composition, crystal orientation, electronic structure, and sample induced electron phase shift.

2.4.2.2. STEM mode

Rather than a specific mode of an ordinary TEM, a scanning transmission electron microscope (STEM) is a specific type of TEM. The difference is that STEM focuses the electron beam into a narrow spot which is rastered over the specimen, which makes these microscopes ideal to fit in conjunction with dispersive x-ray (EDS) spectroscopy, electron energy loss spectroscopy (EELS), and annular dark-field imaging (ADF). In addition, by using a high-angle detector with an STEM, it is possible to acquire atomic resolution images with a contrast directly related to the atomic number.

2.5. Optical Characterization

2.5.1. Spectrophotometry

2.5.1.1. Theory

Spectrophotometry quantitatively measures the reflection or transmission properties of a specimen as a function of wavelength. Spectrophotometry can be comprised of visible light, near-ultraviolet, and near-infrared, but not time-resolved spectroscopic techniques. Spectrophotometers measure light intensity as a function of the light source wavelength. Spectrophotometers are usually designed to work in the 200 nm – 2500 nm range, which require calibrations on the machine using standards that are wavelength dependent.

2.5.1.2. Operation

In semiconductor physics, a spectrophotometer is primarily used to extract absorption coefficient and the band gap of a semiconductor. Once the absorption coefficient α is calculated, then the band gap of any direct band gap semiconductor can be extracted by plotting $(\alpha h\nu)^2$ vs. $h\nu$ and by extrapolating the linear portion of the curve to the $h\nu$ axis, where h is Plank's constant and ν is the frequency. If this is the correct order of the transition, the intersection of this linear extrapolation with the $h\nu$ axis gives the band gap. Otherwise, it may be necessary to find the order of the transition by replacing the "2" in $(\alpha h\nu)^2$ with the correct transition number.

2.5.2. Spectroscopic Ellipsometry

2.5.2.1. Introduction

Ellipsometry uses elliptically polarized light to investigate the electrical, structural and optical properties of a thin film material. This information can be extracted indirectly from a material's dielectric function, which is found through measurement and analysis of ellipsometric parameters, Ψ and Δ , which will be discussed. Additionally, ellipsometry is able to probe thicknesses smaller than the photon wavelength because it measures the change in elliptical polarization of light, which is essentially an angle that can have an infinite amount of positions, and is not dependent on the absolute intensity of light. The analysis of multilayer stacks of thin films is facilitated through the usage of analysis software by least squares regression techniques.

Ellipsometry works by measuring the change in polarization that occurs after reflection of the sample. The nature of polarization is dependent on the unique properties of the sample. Generally, the sample is assumed to be isotropic and optically homogenous. If this is not true, more rigorous analysis or even a more complex ellipsometer may be required.

A usual ellipsometer setup includes a light source, polarizer, and an optional compensator on the source side and an optional compensator, analyzer, and detector on the detector side. The incident and reflected beam of an ellipsometer is referred to as the plane of incidence. The light that is perpendicularly polarized to this plane is known as s-polarized light and light that is parallel to this plane is known as p-polarized light. The relationship between s- and p-polarized light is the foundation of ellipsometry.

2.5.2.2. Theory

The description of ellipsometry, like most optics, starts with a solution to the wave equation [Collins *et. al.*, 2005]

$$\nabla^2 \vec{E} = \frac{\epsilon_r}{c^2} \frac{\partial^2 \vec{E}}{\partial t^2} + \frac{4\pi\sigma}{c^2} \frac{\partial \vec{E}}{\partial t} \quad (2.1)$$

where E is the electric field, ϵ_r is the relative permittivity, t is time, c is the speed of light, and σ is the real optical conductivity. The solution to this differential equation can be written as a traveling plane wave:

$$\vec{E}(\vec{r}, t) = \vec{E}_0 \cos(\omega t - \vec{k} \cdot \vec{r}) \quad (2.2)$$

where ω is the angular frequency of the wave, $\vec{k}$ is the complex wave vector along the propagation direction, and $\vec{E}_0$ is the complex electric field vector perpendicular to $\vec{k}$.

Now, if we wanted to generalize the polarization of this wave to two independent components along orthogonal directions x and y :

$$\vec{E}(\vec{r}, t) = E_{0x} \cos(\omega t - kz + \delta_x) \hat{x} + E_{0y} \cos(\omega t - kz + \delta_y) \hat{y}$$

The two components have the same wavelength and frequency but different amplitudes and phases.

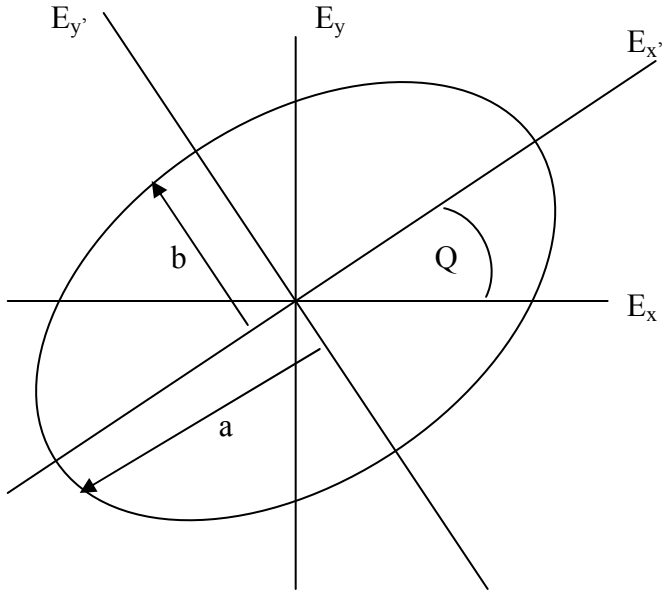


Figure 2-1. The generalized elliptical representation of polarized light.

For Fig. 2.1, the angle of the ellipse is given by $\tan Q = E_{0x} / E_{0y}$ and the ellipse factor $e = b/a$. A shift from the (x, y) coordinate system to the (p, s) coordinate system allows us to define the ellipse in the plane of incidence. Essentially this is done by $Q \rightarrow \Psi$,

$x \rightarrow p, y \rightarrow s, E_{0x} \rightarrow |r_p|, E_{0y} \rightarrow |r_s|$ [Fujiwara, 2007]. Now, the measured ellipsometric parameters may be defined as

$$\tan \Psi = |r_p| / |r_s| \quad (2.3)$$

and

$$\Delta = \delta_p - \delta_s \quad (2.4),$$

where r_p and r_s are reflection coefficients that can be also written as [Guenther, 1990]:

$$r_p = |r_p| \exp(i\delta_p) = \frac{E_p^r}{E_p^i} \quad (2.5)$$

and

$$r_s = |r_s| \exp(i\delta_s) = \frac{E_s^r}{E_s^i} \quad (2.6),$$

where E_p^r and E_s^r are the reflected electric field terms and E_p^i and E_s^i are the incident electric field terms. Thus, the relationship of these reflected coefficients can be written as

$$\rho_r = r_p / r_s = |r_p| \exp(i\delta_p) / |r_s| \exp(i\delta_s) = \frac{|r_p|}{|r_s|} \exp(i(\delta_p - \delta_s)) \quad (2.7).$$

Now, inserting equations 2.3 and 2.4:

$$\rho_r = \tan \Psi \exp(i\Delta) \quad (2.8),$$

which is known as the fundamental equation of ellipsometry.

2.5.2.3. Operation

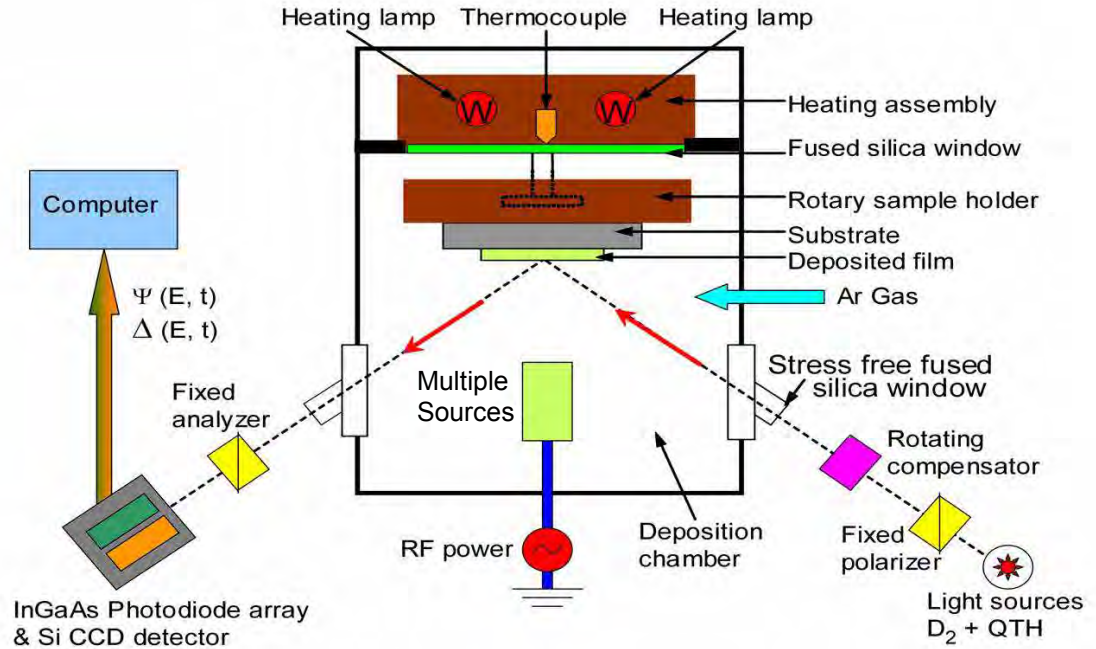


Figure 2-2. Diagram of the hybrid co-sputtering chamber and RTSE system components used in this study. Stress free fused silica windows (manufactured by BOMCO, Inc.) are mounted in both the incident and reflection ports of the vacuum chamber, with the goal of eliminating birefringence due to uneven application of stresses and developed strain.

Figure 2.2 show a schematic of the hybrid sputtering/evaporation chamber along with the ellipsometer used in this work. This rotating compensator ellipsometer (J.A. Woollam 2000) is capable of simultaneously collecting 706 wavelengths over a photon energy range 0.75 eV to 6.5 eV. This ellipsometer use Deuterium (D2) and Quartz-Tungsten-Halogen (QTH) to produce incident light over this broad photon energy range.

A typical measurement originates from these light sources, passes through the fixed polarizer at 45 degrees with respect to the plane of incidence (which is coincident with the plane of the page), through a rotating compensator, through the stress-free window, reflects off of the surface of the sample (substrate plus films), back through the second stress-free window, through the fixed analyzer and finally to the detector. Upon being captured by the detector, the information is sent to the computer from the ellipsometer controller (not shown) where it can be stored, viewed, and possibly analyzed in real-time.

2.5.2.4. Analysis

The computer stores ellipsometric data (Ψ , Δ) as a function of the photon energy and time. This data, however, is not very useful in the study of thin films and must be, then, modeled to give more meaningful information about the sample. The procedure for analyzing the ellipsometric data into “useful” data is given by Figure 2.3.

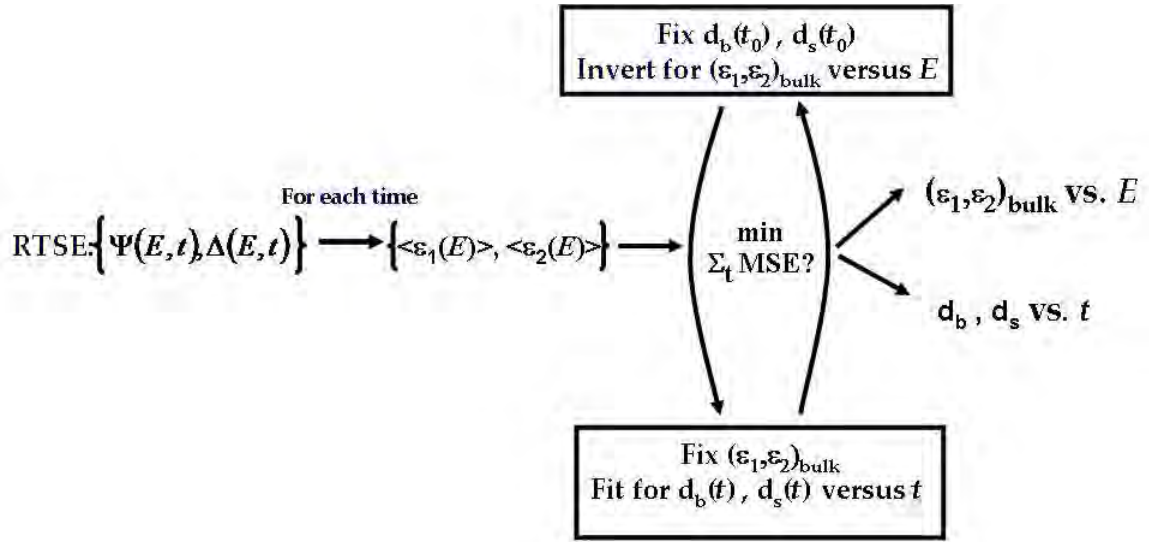


Figure 2-3. Algorithm for data analysis [Ranjan, 2011].

In this procedure, (Ψ, Δ) can be mathematically inverted by the Kramers-Kronig relations [Collins, 2005] to give what is known as the pseudo-dielectric constants $(\langle \epsilon_1, \epsilon_2 \rangle)$. If the material of the sample is optically thick and free of surface effects, then $(\langle \epsilon_1, \epsilon_2 \rangle)$ are more or less equal to the real dielectric constants of the material. If this is not the case, as it usually is not, then a model describing the thin film stack must be produced as in Figure 2.4.

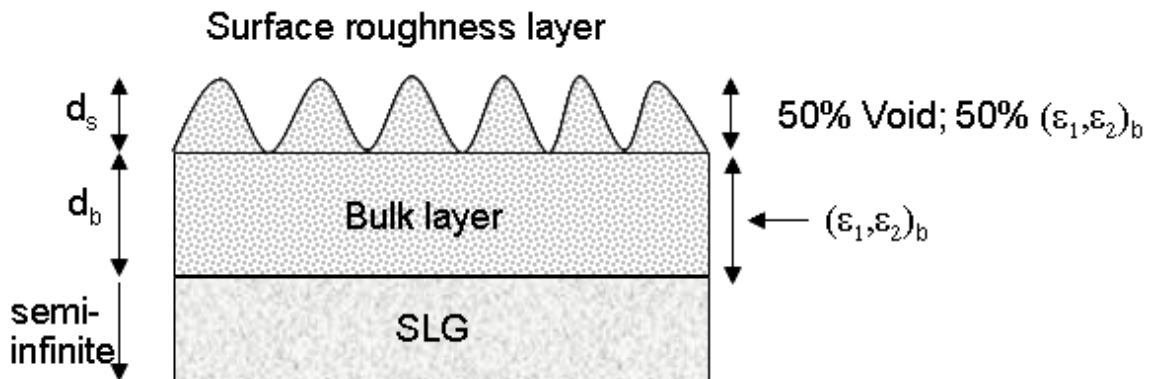


Figure 2-4. Schematic of a two layer sample structure consisting of a bulk layer and surface roughness layer on top of a known substrate. The dielectric response of the surface roughness layer is determined by the Bruggeman effective medium

approximation as a 0.5/0.5 volume fraction mixture of ambient (free space: $\epsilon_1 = 1$ and $\epsilon_2 = 0$) and underlying bulk material. In multilayer structures, such as thin film solar cells, each layer, ambient, and the substrate will have its own optical properties. In most cases, the ambient and substrate media are considered to have an infinite thickness while all other layers in the structure will have a finite thickness [Khatri, 2010].

This modeling is facilitated in optical software packages. Specialized packages that came with the J.A. Woollam ellipsometers are known as CompleteEASE and WVASE. This software uses a least squares regression technique, known as the mean square error (MSE):

$$MSE = \sqrt{\frac{1}{2N - M} \sum_{i=1}^N \left[\left(\frac{\psi_i^{\text{mod}} - \psi_i^{\text{exp}}}{\sigma_{\psi,i}^{\text{exp}}} \right)^2 + \left(\frac{\Delta_i^{\text{mod}} - \Delta_i^{\text{exp}}}{\sigma_{\Delta,i}^{\text{exp}}} \right)^2 \right]} \quad (2.9).$$

In the fitting procedure of Figure 2.3, parameters are modified and repeated until the lowest MSE is achieved. The parameter space of the dielectric constants can be greatly reduced by the use of oscillators that describe the absorption behavior of a particular film. It is usually desirable to define these oscillators in such a way that the parameters that constitute them have physical meaning such as directly related to grain size or the band gap, for instance.

2.6 Electrical Characterization

2.6.1. Four Point Probe Measurement

2.6.1.1. Theory

Four point probe measurement is an electrical conductivity measuring technique that employs two wires for sensing and supplying current and two wires for measuring the voltage. The use of four probes, compared to the two found in common multimeters, allows for increased accuracy. For metals, for example, the reading of the resistance

would be effectively zero with a multimeter, whereas a four point probe can be used to measure a nonzero value to a millionth of an ohm. Due to this great accuracy, four point probes are also used to measure sheet resistance of thin films, for either metals or semiconductors. Four point probes are able to be so accurate by eliminating the resistance contribution of the wires and contacts. Usually, the force (current) probes are the outer two probes, and the sensing (voltage) wires are the inner two probes.

2.6.1.2. Operation

Modern four point probe resistivity measurement machines have semiconductor wafer testing in mind. For example, the film or wafer is placed on the measurement surface and an arm containing the four probes is lowered onto the film or wafer surface. In modern systems, after contact is made, the process to calculate the range by adjusting a resistor value is automatic. In older systems, however, the resistor value may have to be manually changed to select the measurement range, and the resistivity may have to be calculated from these resistor values and the reading on a multimeter, for instance.

2.6.2. Hall Effect Measurement

2.6.2.1. Theory

As current due to holes or electrons move through a conductor or semiconductor, if a magnetic field is applied across the specimen, a force perpendicular to both current and magnetic field is experienced by the charge carrier known as the Lorentz force. The Hall effect is the result of using this force to determine the magnitude and sign (n-type or p-type) of this force. Specifically, when the perpendicular magnetic field is applied, the paths of the charge carriers are curved so that charges accumulate on one side of the material. Equal and opposite charges remain on the opposite side of the wall and a

voltage can be measured from the charge density difference. Thus, the Hall effect is very useful as a means to measure either the charge carrier density or the magnetic field, if the density is known.

2.6.2.2. Operation

Usually a specimen is mounted in the van der Pauw configuration. In this configuration, electrodes are attached (usually soldered for a good ohmic contact) at four opposite corners of the specimen. The error associated with these electrodes is given by the diameter they make on the specimen divided by the distance between them, since their size is ideally supposed to be zero and the distance between them infinite. In this configuration the sheet resistance can be found, and with a magnetic field applied the charge carrier density and sign can be found. It is noted that even though the sheet resistance can be found in this configuration, this is a more destructive method than the previously mentioned four point probe measurement since the electrodes are soldered to the specimen in the van der Pauw configuration.

2.7. Device Characterization

2.7.1. Current Density-Voltage (JV)

2.7.1.1. Theory: please refer to Chapter 1.

2.7.1.2. Operation

The JV collection instrument is designed to simulate the light output of the sun as observed from earth. Different air mass (AM) indexes can be used, but the most commonly reported efficiencies are for AM1.5. As a side note, AM0 is the air mass just above the earth's surface and AM1 is measured at the zenith at sea level. The specimen

is placed directly under the light source, minimizing the distance to the center of the light. Electrical probes are placed on the p-type and n-type sides. The measurement with the light off is called a dark measurement, while the measurement with the light on is called the illuminated measurement. The measurement results are collected by a sensitive and accurate multimeter and sent to a computer, where the data is stored in current and voltage pairs. Calculations on this data can be made as outlined in Chapter 1.

2.7.2. Quantum Efficiency (QE)

2.7.2.1. Theory: please refer to Chapter 1.

2.7.2.2. Operation

A usual QE measurement is done in a dark environment. This is why the measurement system is in a large box or behind an enclosure with a curtain. A specimen is mounted so that the light arrives on one test cell only. One wavelength, usually green, is chosen so that the user can align the test cell properly. Probes are connected to the positive and negative leads of the cell. With the cell secure and the enclosure made dark, a current is collected for each wavelength illuminating the test cell. A chopping frequency and lock-in amplifier is then used to enhance the signal to noise ratio. The signal from the lock-in amplifier is then read by a data acquisition board or multimeter and made ready for storage on a computer. A bias voltage can also be applied to the test cell during a measurement for reasons outlined in Chapter 1. For accurate comparison with J-V measurement, white light bias is used.

2.7.3. Electron Beam Induced Current (EBIC)

2.7.3.1. Theory

Electron beam induced current (EBIC) is a device characterization technique that is used to show defects in semiconductors or minority carrier properties. EBIC works by creating electron-hole pairs in the specimen via an electron beam. Thus, EBIC is usually performed in an SEM or STEM. In specimens with a p-n junction or Schottky junction, electron-hole pairs will separate due to drift due to the internal electric field. EBIC allows for a current response to be measured as the electron beam is rastered over the surface.

2.7.3.2. Operation

An SEM or STEM can display the information of a picoammeter hooked up to the positive and negative leads of the device being tested. A depletion region will have high contrast. The contrast shape can be used to determine the minority carrier properties, such as surface recombination velocity and diffusion length. Places on the specimen with good crystal quality will show high contrast, and places with defects show darker contrast.

2.7.4. Optical Beam Induced Current (OBIC)

2.7.4.1. Theory

Optical Beam Induced Current (OBIC) is a device characterization technique that uses a laser (or other light source) to create electron-hole pairs for the identification of damaged junctions and buried diffusion regions, for example. The laser beam is rastered over the surface of the specimen to collect current information. Variation in current can be shown used to identify features of interest.

2.7.4.2. Operation

Spatial resolution of an OBIC image is limited by the length of absorption of the beam. Depending on the specimen being measured it may be useful to illumination from the backside. Usually OBIC is designed to measure one photon absorption because a two-photon absorption is a non-linear process and requires an instrument adapted for this ability, called a TOBIC, or Two-photon OBIC.

2.8. Conclusion

As one can see, many kinds of characterization techniques are at the disposal of the solar cell engineer. Characterization techniques ranging in measurement settings from *in situ* growth monitoring to the characterization of the final film device have been presented. Use of more than one technique is encouraged to develop a holistic idea of what is happening with a particular specimen or device.

Chapter 3

Growth and Temperature Dependence of Silver Nanoparticles Properties

3.1. Introduction

Three related studies concerning silver nanoparticles will be presented in this chapter. For the first study, the evolution of optical properties was observed as a function of thickness. For the second study, these optical properties were correlated more closely to structural properties. For the final study, the temperature dependence was observed for silver nanoparticles as a function of time.

In the first study, a broadband analysis of the optical properties of silver nanoparticle films over the range from 0.75 to 6.5 eV was performed by applying *in situ* real-time spectroscopic ellipsometry (RTSE) during the nucleation, coalescence, and bulk thin film growth regimes. The dielectric functions of the particulate films were found to depend strongly on the particle size and film thickness from the nucleation regime throughout coalescence. These dependences were analyzed by separately characterizing the three types of transitions evident in the dielectric function: intraband, particle plasmon polariton, and interband. Throughout the film growth regimes, the thickness

evolution of the amplitude, energy, and broadening parameter for each type of transition is discussed in view of the structural characteristics of the films, and corroborated with *ex situ* measurements such as atomic force microscopy, resistivity measurements, and profilometry.

In the second study, the dielectric function of Ag nanoparticle films, deduced by *in situ* real-time spectroscopic ellipsometry (RTSE), is found to evolve with time in close consistency with the film structure, also deduced by RTSE. We studied the intraband, plasmon polariton and interband amplitude, relaxation times and position components as a function of time and will discuss their evolution and trends individually and one compared to another.

In the final study, the temperature dependence of these oscillators was analyzed via RTSE. Based on this evolution, we detected a melting point depression, allowing for the surface energy to be calculated. After annealing, structural changes were observed in the nanoparticles via ex-situ measurements such as AFM, SEM and XRD.

3.2. Silver Nanoparticles Growth

3.2.1. Literature review on Silver Nanoparticle via RTSE

Until recently, *in situ* real time spectroscopic ellipsometry (RTSE) studies of metal film growth were rare. The first *in situ* real time spectroscopic ellipsometry (RTSE) studies of metal film nucleation and growth focused on Al and Ag films (Nguyen, 1993; Collins, 2005). More recently, Oates *et al.* have studied the growth behavior of Ag *in situ* over the photon energy range of 1.25-3.33 eV (Oates, 2005). In this chapter, RTSE measurements spanning the photon energy range of 0.75-6.50 eV are

described in detail for Ag nanoparticle films. This is a broader spectral range than has been previously reported for such measurements, and enables a separation among the contributions due to interband transitions at high energy, intraband transitions at low energies, and nanoparticle plasmon polariton transitions at intermediate energies. The thickness parameters associated with the nucleating nanoparticle layer, as well as the bulk and surface roughness layers for the subsequent thin film growth process, are also reported and correlated with the behavior of the dielectric function components associated with the nucleating and bulk layers.

3.2.2. Surface Plasmon Background

The dispersion in the optical properties of silver and silver compounds has been investigated for more than a century (Hagen 1902; Minor, 1903; Ingersoll, 1910). Silver nanoparticles and other metallic clusters have been studied for almost as long, motivated by the colors that small metal particles impart when embedded within a glass matrix (Kneipp, 2007). More recently, metallic nanoparticles have been investigated for their wide variety of novel functional properties. The optical properties of such nanoparticles result from the resonant oscillation of confined electrons that would otherwise be free in a bulk metal. This mechanism, which is electrodynamic in nature, is different from that of determining the optical properties of quantum dots, for example, which exhibit band gap modifications via quantum size effects. The resonant oscillations that occur within metal nanoparticles and thin films, known collectively as surface plasmons, are commonly understood by studying the optical properties or dielectric functions of specific thin film structures. Surface plasmon resonances exist on metal surfaces and become optically

coupled to incident electromagnetic waves when surface structures such as gratings or nanoparticles are present. In general, the coupling depends on the relationship of the wavelength of the incident light to the Fourier spectrum of the metallic surface profile. Thus, surface engineering allows for a tunable range of desired optical properties (Jensen, 2000). Devices utilizing such technology include sensors (Malmqvist, 1993; Haes, 2004) of biological materials and those based on surface enhanced Raman spectroscopy (Kneipp, 2007) as well as back contact reflectors in thin film solar cells (Carlson, 1989).

3.2.3. Experimental Procedure

Silver thin films were deposited by d.c. magnetron sputtering at room temperature onto a Si (100) wafer with a 39 nm thermal oxide using a high purity (99.99%), 2” diameter silver target in high purity (99.998%) argon. A 4 mTorr Ar pressure and 10 W d.c. target power were maintained throughout the experiment. RTSE data were acquired *in situ* during film growth using a J.A. Woollam Company rotating-compensator multichannel ellipsometer with a photon energy range of 0.75-6.50 eV at an angle of incidence of 65°. Photon energy spacing ranged from 0.002 eV for low energy to 0.05 eV for high energy. Pairs of (ψ , Δ) spectra were collected with a 3 s acquisition time over a total time duration of 85 min. After 10 min of initial data collection from the substrate, a shutter in front of the silver target was opened (defining $t = 0$ min). Complementary *ex situ* characterization of the as-deposited film includes atomic force microscopy (AFM), resistivity measurements, and profilometry.

The *in situ* spectra in ψ and Δ were initially fit using a model having only wavelength independent parameters in order to determine the nucleating and bulk layer

thicknesses by least-squares regression algorithms. The optical model for the film in the nucleation regime consisted of a single layer whereas the model in the bulk growth regime consisted of bulk and surface roughness layers. The dielectric functions of the nucleating and bulk layers were parameterized whereas the dielectric function of the surface roughness (on top of a bulk layer) was determined from the Bruggeman effective medium theory (EMT) as a 0.5/0.5 volume fraction mixture of bulk layer material and void. From the nucleating and bulk layer thicknesses at each time, the ψ and Δ spectra could then be numerically inverted to extract the dielectric functions of these layers for comparison with the parameterized functions. It is also interesting to note that there was no need to incorporate a silver/ silicon dioxide interface layer in the model to fully fit the data. Close agreement in the dielectric functions, which were free of artifacts, provided support for the validity of the parameterizations and the resulting free parameters. In the determination of the dielectric function parameters reported here, it was the dielectric functions themselves (rather than the ψ and Δ spectra) that were fit, eliminating the thicknesses from the final fitting procedure.

3.2.4. Results and Discussion

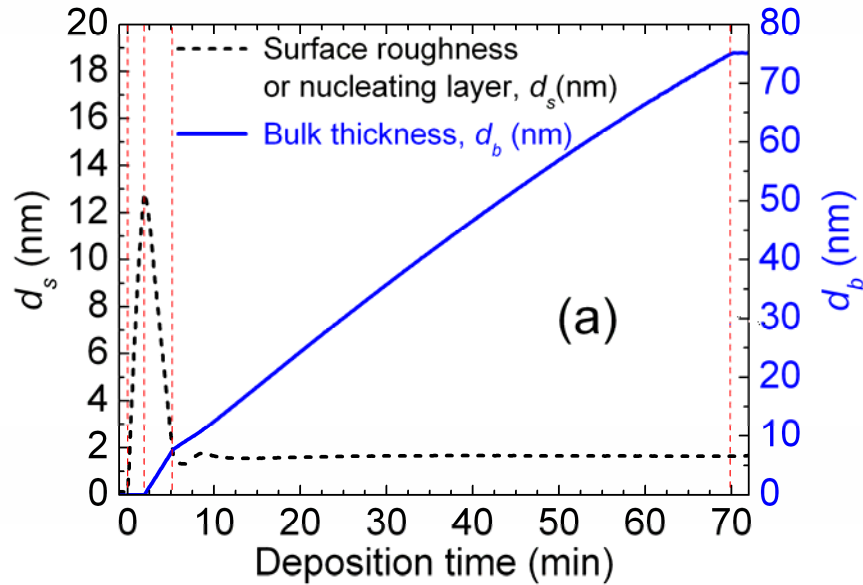


Figure 3-1. Thicknesses of the nucleating layer (dashed line; $t < 2$ min), the surface roughness layer (dashed line; $t > 2$ min), and the bulk layer (full line; $t > 2$ min) vs. deposition time obtained by RTSE for silver depositions.

Fig. 3.1 shows the time evolution of the surface roughness and bulk layer thicknesses for a silver thin film deposited at room temperature. In the first phase in Fig. 3.1 starting at time zero (first dashed line from left), the shutter of the sputter gun is opened to initiate the deposition. The silver film initially nucleates following the Volmer-Weber growth mode, whereby the interaction between adatoms is stronger than that between the adatom and the substrate. This leads to the formation of three-dimensional clusters, a process evidenced by an abrupt increase in the nucleating layer thickness with no increase in bulk layer thickness (An, 1990). In the second phase (starting from the second dashed line at $t = 2$ min), the nuclei make contact and a bulk layer develops simultaneously with island coalescence (or smoothening of the nucleation induced roughness layer). In the third phase (starting from the third dashed line at $t = 5.5$ min) the

surface roughness has fully relaxed, and its thickness saturates at a constant value while the bulk layer continues to grow at a constant rate. The shutter is closed after 70 minutes of deposition (fourth dashed line). Similar growth phases and observations have been previously reported for other metals (Nguyen, 1993). This last phase has been applied in linear extrapolations to deduce thicknesses greater than 15 nm ($t = 13$ min). These extrapolated film thicknesses from RTSE agree well (to within 10%) with those obtained by profilometry.

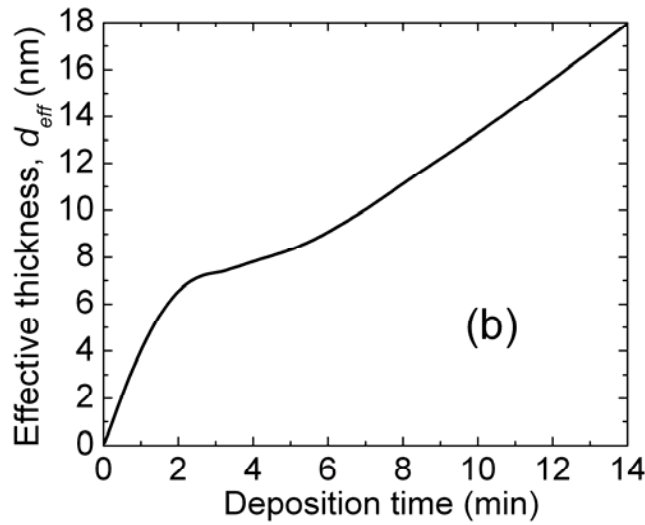


Figure 3-2. Time dependence of the effective thickness, given by the layer thickness multiplied by the volume fraction of material in the layer, summed over all layers of the film.

Fig. 3.2 depicts the effective thickness d_{eff} which is used as a key parameter in correlation with the dielectric function evolution. In the nucleation stage, this thickness is defined as the physical thickness times the variable nuclei volume fraction estimated through an EMT, as described below. In the coalescence and bulk layer growth stages, this thickness is defined as the bulk thickness, d_b , plus one half of the surface roughness thickness, d_s , for consistency with the structural model used in this analysis.

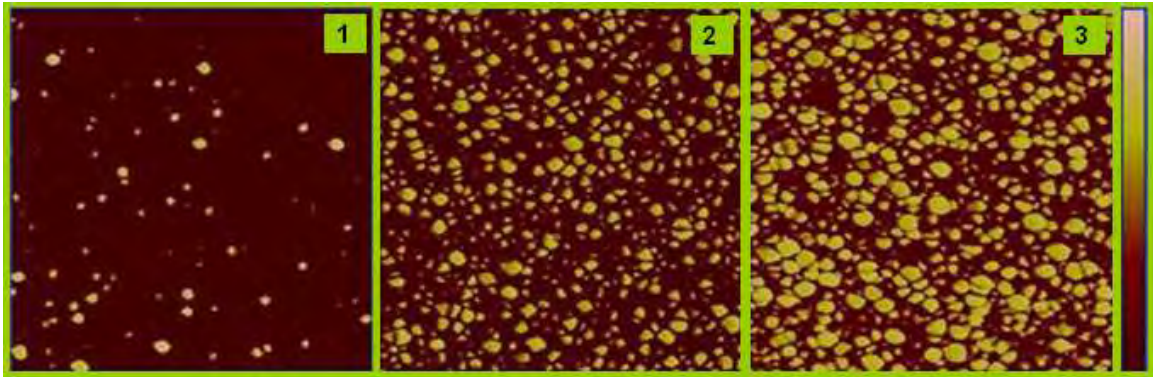


Figure 3-3. AFM phase scans for deposition durations of: (1) 30 s, (2) 1 min, (3) 2 min. Image area is $1 \times 1 \mu\text{m}^2$. Scale bar max is 30 degrees.

To corroborate the formation and coalescence of islands as observed by RTSE, silver films were grown for short deposition times and characterized by AFM. The results of these experiments are reported Fig. 3.3, where $1 \times 1 \mu\text{m}^2$ AFM phase scans are presented for deposition durations of 30 s, 1 min, and 2 min. As one can see, evidence of island formation on top of the thermal silicon dioxide exists at 30 s, an increase in island density is observed at 1 min, and the beginning of coalescence is observed at 2 min. According to Fig. 3.1, the coalescence is also observed to begin at $t = 2$ min which is in good agreement with the *ex situ* AFM observations.

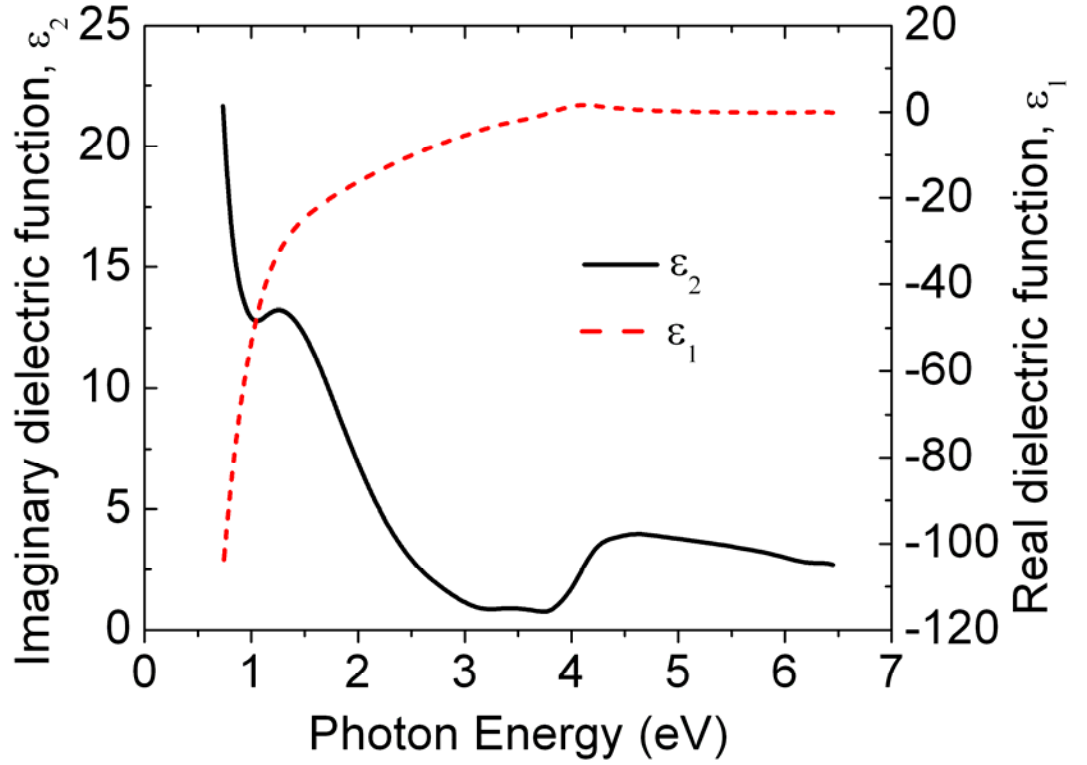


Figure 3-4. Imaginary and real parts of the dielectric function for a silver thin film of an effective thickness 10.9 nm. This thickness was selected to exhibit a film containing features in all three photon energy regions.

In conjunction with the extraction of thicknesses as discussed above, the pair of ellipsometric parameters, ψ and Δ , also allowed for the extraction of dielectric functions at different times. Three clear spectral regions appear for these dielectric functions as reported in Fig. 3.4, each described by a separate term in the following equation:

$$\varepsilon(\omega) = \varepsilon_{\infty} + \left(\frac{A_D^2}{-E^2 - i\Gamma_D E} \right)_{\text{Drude}} + \left(\frac{A_L^2}{E_L^2 - E^2 - i\Gamma_L E} \right)_{\text{Lorentz}} + (G(E))_{\text{Interband}} \quad (3.1)$$

(i) At low photon energies, a Drude expression with variable amplitude (A_D) and broadening (Γ_D) parameters describes the intraband transitions. (ii) In the mid-range of energies, a Lorentz oscillator with variable amplitude (A_L), peak energy (E_L), and broadening (Γ_L) parameters describes the particle plasmon polariton (PPP) transitions. (iii) At high photon energies, a more general critical point oscillator also with variable amplitude, peak energy, and broadening parameters describes the d-band to Fermi level interband absorption onset. Each of these energy regions is elaborated in the sections below, where an explicit expression for the interband function $G(E)$ is given. It is important to note that before 2 min of deposition (i.e., before coalescence) no Drude oscillator is observed, and after 13 min (in the bulk layer growth regime) no PPP oscillator is observed.

3.2.4.1. Intraband transitions

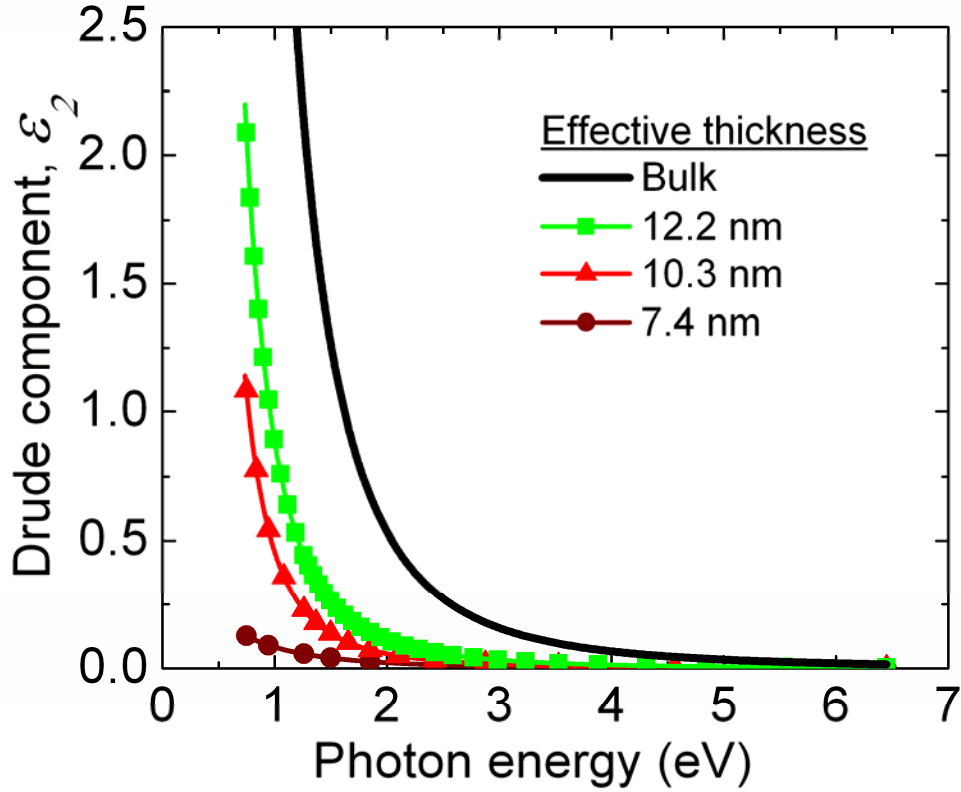


Figure 3-5. Drude component extracted from the dielectric function versus photon energy for different effective thicknesses during the growth of thin film Ag.

The intraband transitions of electrons within an s-band are a common feature among noble metals and are observed easily for the “bulk-like” material in the low photon energy range (see Fig. 3.5). The transitions in this case were modeled using the Drude expression shown in Eq. (3.1). As determined from the Drude amplitude versus time, this component first appears after $d_{eff} = 6.5$ nm ($t = 2$ min), which corresponds to the onset of bulk layer growth as observed in the thin film structural analysis of Fig. 3.1, increases during coalescence, and then saturates when coalescence is complete. The Drude broadening energy Γ_D shows a significant decrease with increasing time, which

can be related to an increase in electron scattering time as the bulk layer thickness increases (Kasap, 2006).

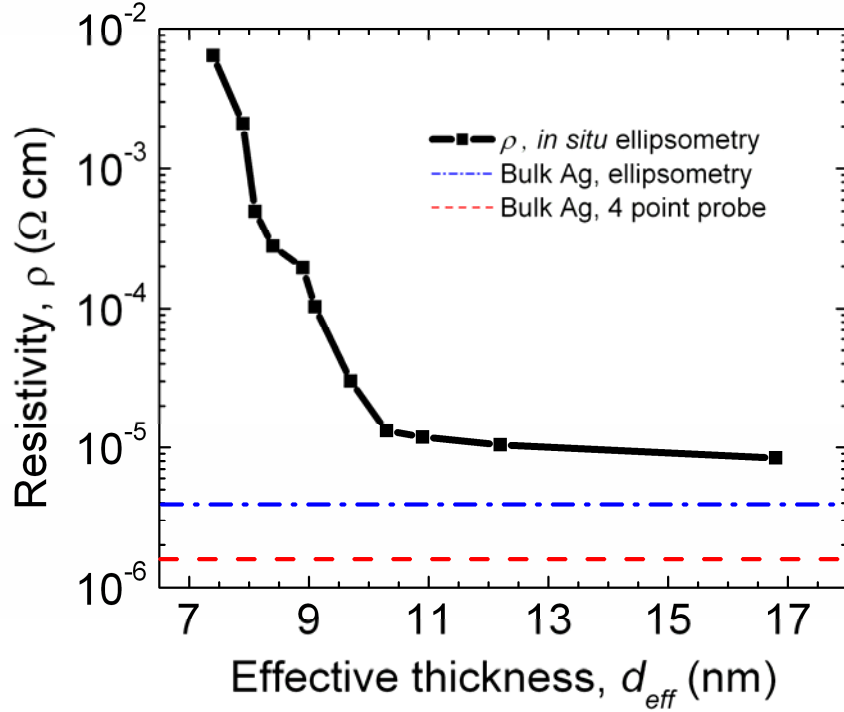


Figure 3-6. Resistivity versus effective thickness for the growth of thin film Ag deduced from the amplitude and broadening parameters of the Drude component.

By combining the Drude component amplitude and broadening parameter, the "optical" resistivity of the film can be estimated versus time or effective layer thickness via the following equation:

$$\rho = \frac{\hbar \Gamma_D}{\epsilon_0 A_D^2} \quad (3.2)$$

A monotonic trend toward lower resistivity with increasing thickness is observed in Fig. 3.6, with an abrupt transition from a strong to a weak dependence near 10 nm, which corresponds to the coalescence endpoint and the formation of a smooth ($d_s = 1.8$ nm), "bulk-like" layer of silver. The final resistivity value of $4 \times 10^{-6} \Omega$ cm at $d_{eff} = 76$ nm is in

reasonable agreement with the *ex situ* dc value for our bulk silver ($1.6 \times 10^{-6} \Omega \text{ cm}$). For a film thinner than the mean free path, the resistivity is inversely proportional to the thickness, $\rho \propto 1/d$ (Kasap, 2006). Various models can account for this behavior including surface and interface scattering, or grain boundary scattering in conjunction with a linear increase in crystalline grain size with thickness (Fuchs, 1938; Sondheimer, 1952; Messier, 1986; Mayadas, 1970). When fitting the latter model (Mayadas, 1970) for thicknesses of 10 nm and greater in Fig. 3.6, the *ex-situ* value of the bulk resistivity was recovered as the ρ -axis intercept of the $\rho \propto 1/d$ plot assuming a grain boundary reflection coefficient of $R = 0.3$ (Kasap, 2006). The same grain boundary scattering model was also found to fit the data in Fig. 3.6 reasonably well even for thicknesses less than 10 nm, below the coalescence transition.

3.2.4.2. Particle Plasmon polariton transitions

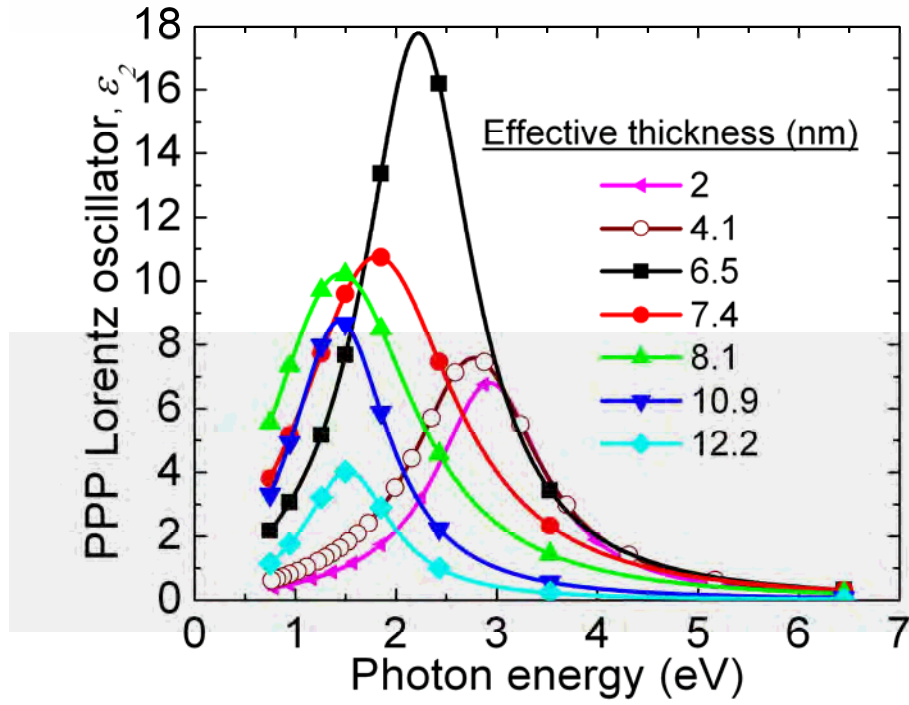


Figure 3-7. PPP oscillator component extracted from the dielectric function versus photon energy for different effective thicknesses of the Ag film.

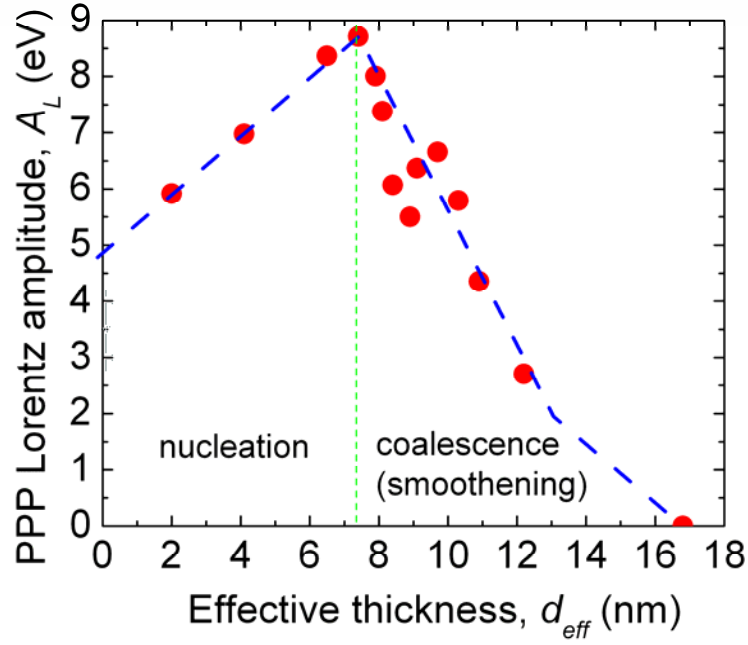


Figure 3-8: Amplitude associated with the PPP oscillator versus the effective thickness of the Ag film.

The particle plasmon polariton (PPP) feature, modeled using a Lorentz oscillator as described in Eq. (3.1), passes through a maximum in amplitude as it shifts continuously to lower energy as a function of time or effective thickness (Figs. 3.7 and 3.8). The maximum in amplitude is readily understood in terms of the film structure shown in Fig. 3.3. For d_{eff} below 7 nm, the amplitude is increasing due to an increase in particle size and coverage. Above this effective thickness, particle coalescence rapidly reduces the volume fraction of Ag material associated with isolated, resonating particles. Note that the correlation with the Drude amplitude limits the accuracy in the later stages of coalescence when the resonance energy is low.

The continuous shift in PPP oscillator energy in Fig. 3.7 has been observed in previous experiments (Nguyen, 1993; Collins, 1998; Oates, 2005; Genzel, 1975; Kreibig,

1970), and below a particle radius of 2 nm, the shift may even be enhanced by quantum size effects (Malmqvist, 1993). Above 2 nm, however, this effect can be sufficiently described using classical electrodynamics by solving Maxwell's equations using Mie theory for an individual particle (Kreibig, 1970) and the Maxwell Garnett EMT to describe the collection of particles (Kreibig, 1995). A simplified equation for calculating peak energies is given by (Wormeester, 2008):

$$E_{\max} = E_p \left[\epsilon_{\infty} + \epsilon_m \frac{(k + f)}{(1 - f)} \right]^{-1/2} \quad (3.3)$$

which can be derived by substitution of the Drude expression for the dielectric function of Ag into the Maxwell Garnett EMT (Wormeester, 2008; Collins, 2005), which best describes particulate metals. This substitution yields a Lorentz oscillator expression. In Eqn. (3.3), E_p is the bulk plasma frequency of the metal, ϵ_{∞} is the constant contribution to the metal dielectric function due to interband transitions at high energies, ϵ_m is the real dielectric function of the surrounding ambient medium, k is a depolarization parameter depending on particle shape, and f is the particle volume fraction. It is interesting to note that for a very low density ($f \rightarrow 0$) of spherical ($k = 2$) particles, formed from an ideal metal ($\epsilon_{\infty} = 1$) in an ambient medium of vacuum or atmosphere ($\epsilon_m = 1$), this peak occurs at $E_p/\sqrt{3}$ or 5.3 eV, the energy predicted by Mie theory for such a sphere (Kreibig, 1998). Considering the peak energy value of 2.88 eV for the Lorentz oscillator in Fig. 3.7 at $t = 2$ min, a spherical particle calculation using $E_p = 9.2$ eV and $\epsilon_{\infty} \sim 4$ (Wormeester, 2008; Collins, 2005) for bulk silver and $\epsilon_m = 1$ for ambient vacuum yields a metal volume fraction of $f \sim 0.58$, for example. This calculated result is in reasonable agreement with the experimental coverage seen in Fig. 3.3; however, the results of such calculations are a

sensitive function of particle shape. Confined size and shape effects have been accounted for in this explanation, but the consideration of metal nanoparticles supported on a substrate involving effects of interparticle dipolar interaction (Atay, 2004; Kelly, 2003), charge interaction with the substrate interface (Haes, 2004; Kelly, 2003), and the anisotropy of a mixed medium environment (Kelly, 2003) should also be incorporated into a future version of our model and analysis.

The broadening parameter of the PPP Lorentz oscillator remains in the range 1.5 ± 0.3 eV over a wide range of effective thickness from 2 to 18 nm. For a collection of particles with the same resonance energy, the broadening parameter is predicted to be the same as that in the Drude expression for the bulk metal. The observed value for the particles is much higher than that of the bulk metal (1.5 eV vs. 0.1 eV), however, suggesting that either surface scattering, or scattering by internal defects specific to the particles controls the PPP broadening parameter. Alternatively, this parameter may be dominated by a distribution of particle shapes which leads to a distribution of resonance energies. The observed constant broadening parameter suggests two results: (i) that the shape distribution of the nanoparticles does not change significantly during nucleation and coalescence, and (ii) that the increase in size of the particles does not influence the broadening, further indicating that defects internal to the particles rather than surfaces control the scattering processes (Nguyen, 1993).

3.2.4.3. Interband transitions

Noble metals exhibit interband transitions due to the presence of d-band states in the range of 2-4 eV below the Fermi level. In silver these transitions can be seen in the

high energy region of Fig. 3.9 and have been attributed to electronic transitions from the completely filled 4d shell to empty states at the Fermi level (Antonangeli, 1974). These interband transitions have been fit using a single, Lorentzian-broadened critical point oscillator given by:

$$G(E) = A_I \Gamma_I^{-\mu} [e^{i\phi} (E_I - E - i\Gamma_I)^\mu + e^{-i\phi} (E_I + E + i\Gamma_I)^\mu] \quad (3.4)$$

which has been used for gold, as well, and is designed to be Kramers-Kronig consistent (Etchegoin, 2006). In this expression, A_I is the amplitude, E_I is the onset energy, Γ_I is the broadening parameter, μ is the Lorentzian exponent, which was fixed at -0.2 , and ϕ is the phase, which was fixed at zero. The values of the fixed parameters μ and ϕ were obtained when using all five oscillator parameters as variables. Because these values were not found to vary with effective thickness within the confidence limits, they were fixed in the final fitting procedure.

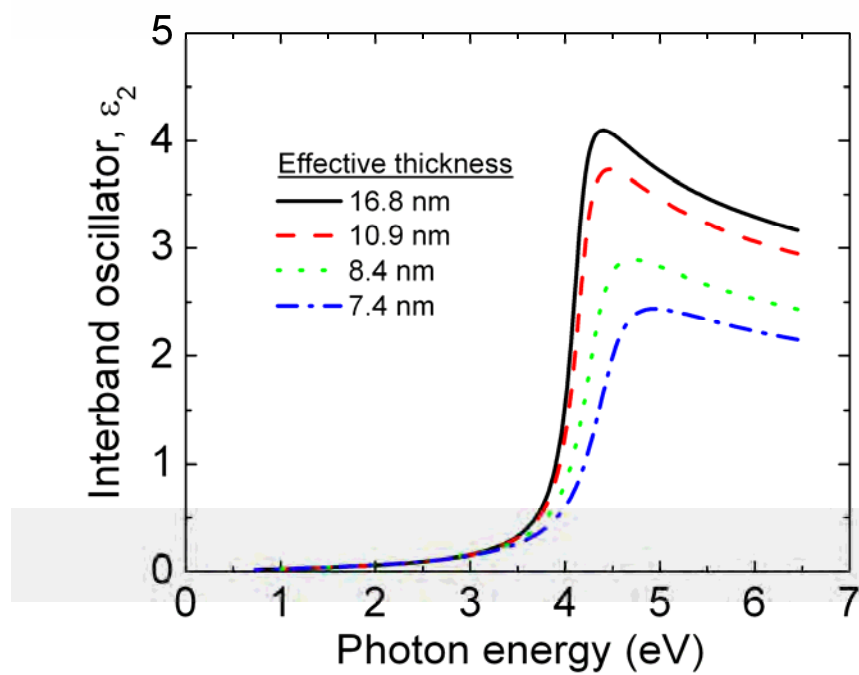


Figure 3-9: Interband oscillator component extracted from the dielectric function versus photon energy for different effective thicknesses of the Ag film.

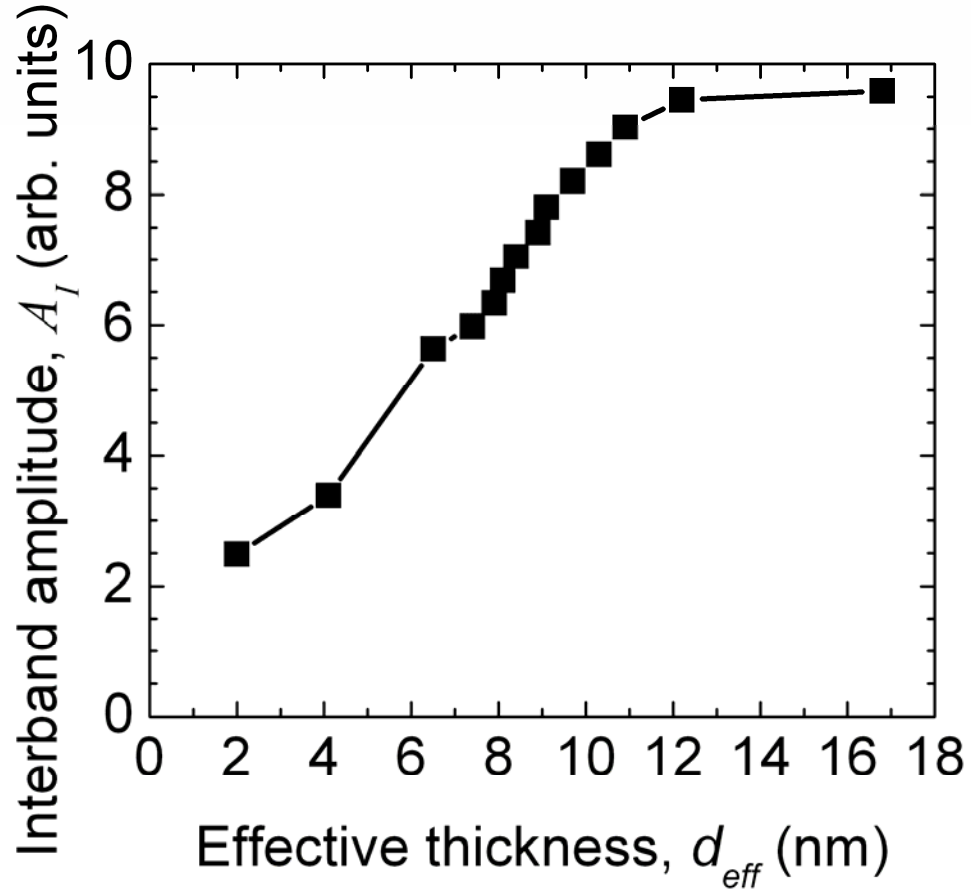


Figure 3-10: Amplitude of the interband oscillator versus effective thickness of the Ag film.

The amplitude of the interband transition is depicted as a function of effective thickness in Fig. 3.10. As one can see, an increase in amplitude with effective thickness is observed, which reflects a decrease in void fraction in the films. Because of the widespread use of the interband transitions in semiconductors for the characterization of void volume fractions via the Bruggeman EMT (Aspnes 1979; Fujiwara, 2000), it is likely that this approach can also be used for quantitative analysis of metal thin films, as well. The energy onset of the interband transitions in this study is observed to decrease with the increase in effective thickness (from 4.57 eV to 4.14 eV) over the effective

thickness range in Fig. 3.10. A possible explanation may be strain-induced distortions of the band structure. Finally, the broadening parameter of the interband critical point oscillator is observed to decrease with increasing effective thickness, similar to the observation for the Drude oscillator. The effect in this case is similarly related to an increase in transition lifetime due to the reduction in defect density as the bulk layer thickness increases.

3.3. Oscillator lifetime comparison

3.3.1. Introduction

Whereas section 3.2 focused on the optical properties of Ag nanoparticles, this section takes those optical properties and analyzes the strong correlation between optical and structural behavior that allow for the extraction of the individual oscillator lifetimes. This section also explores the physical meaning behind these lifetimes. Thus, this study was based on an independent analysis of the structural and optical (intraband electron and plasmon polariton) behaviors, the silver films being readily understood in terms of three growth regimes, characterized by the ranges of effective thickness. These include (i) isolated particle growth, in which case no bulk layer is present and no Drude intraband component is observed ($0 < d_{eff} < 7$ nm); (ii) bulk layer growth before complete coalescence of particles ($7 < d_{eff} < 15$ nm), in which case both Drude intraband and plasmon polariton components are observed; and finally (iii) bulk layer growth after full coalescence of particles, in which case no plasmon polariton component is observed.

3.3.2. Experimental Procedure

(See section 3.2.2)

3.3.3. Results and Discussion

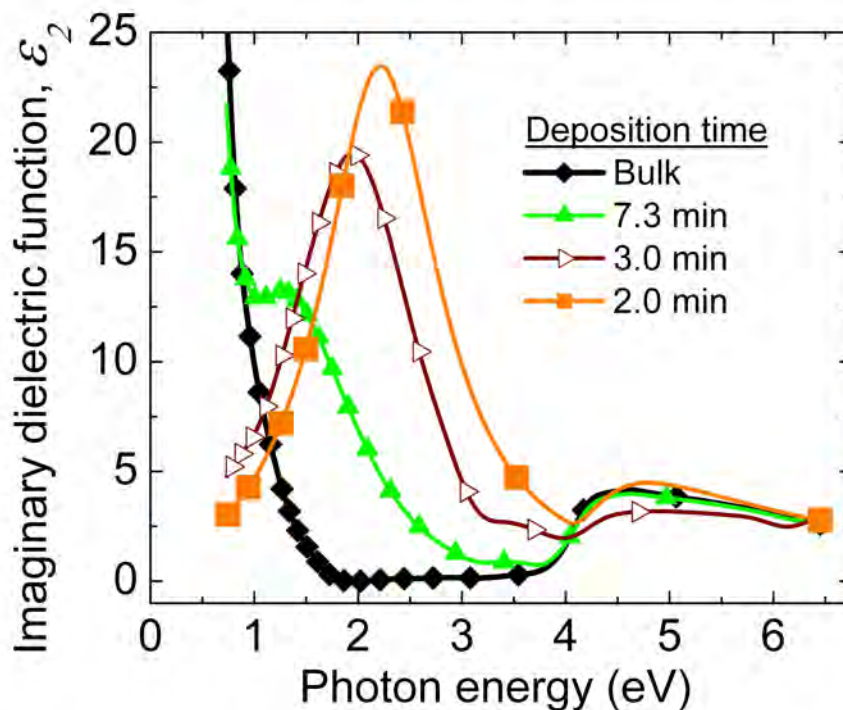


Figure 3-11. Imaginary part of the complex dielectric function ϵ_2 plotted as a function of photon energy for bulk Ag and for Ag obtained at selected deposition times.

The imaginary part, ϵ_2 , of the dielectric functions for selected deposition times are shown in Fig. 3.11. Three main regions were parameterized through Eqn. 3.1 and Eqn. 3.3. At low energy, the rapid decrease of ϵ_2 with increasing photon energy observed at longer deposition times is attributed to free electron or intraband transitions and was fit using a Drude expression with the amplitude A_D and broadening Γ_D as adjustable parameters. In the mid-range energy, a well-defined peak is observed for all three times in Fig. 3.11, which shifts to lower energy with increasing time and merges with the

intraband transitions. This peak is associated with nanoparticle plasmon polariton transitions and is modeled using a Lorentz oscillator with amplitude A_L , resonance energy E_L , and broadening Γ_L , all as adjustable parameters (Collins, 2005). At high energies, the absorption step observed for all times is attributed to the onset of interband transitions originating from the d -band and was modeled using a general critical point oscillator. Again, the free parameters include the amplitude A_G , band gap energy E_G , broadening Γ_G , phase ϕ , and exponent μ .

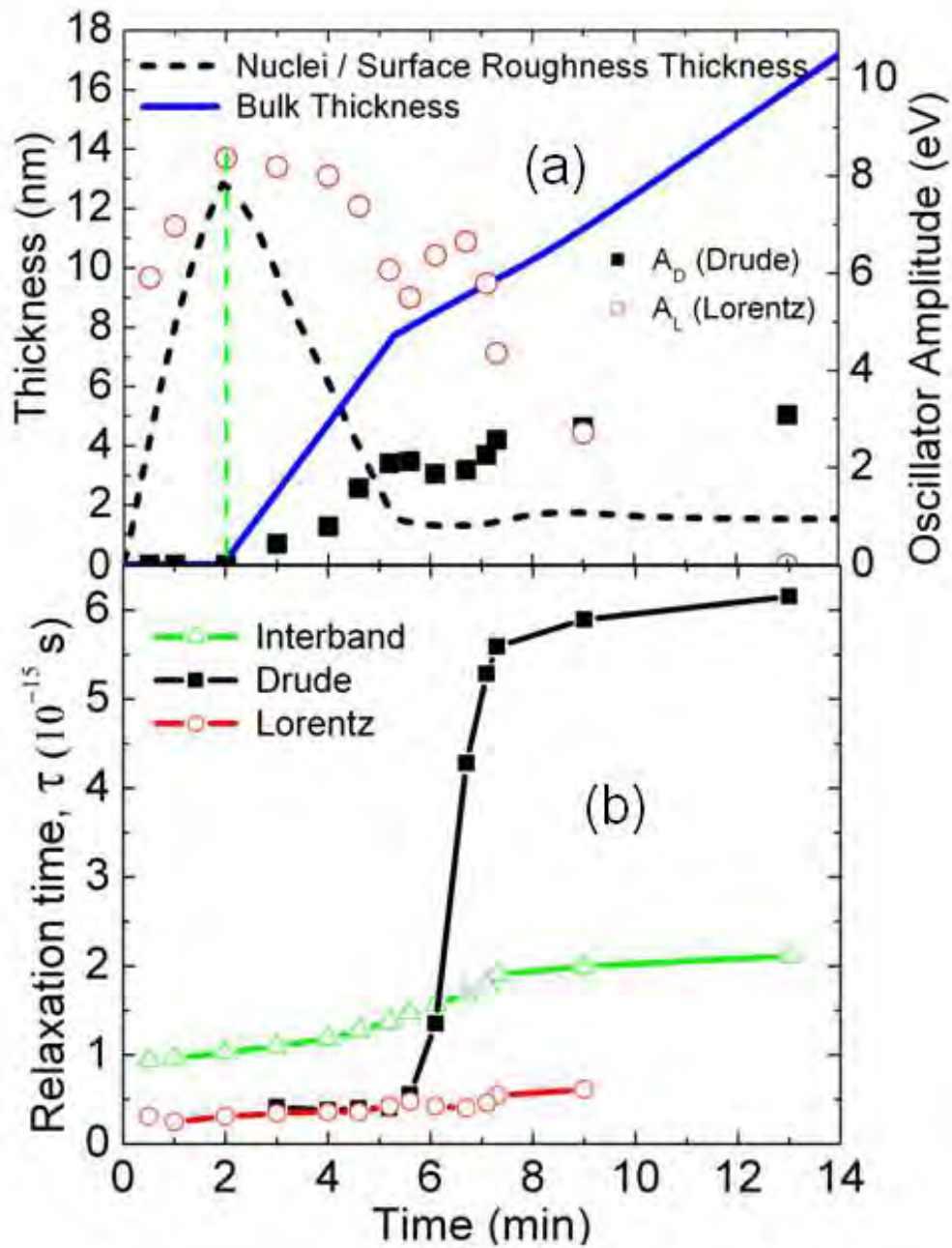


Figure 3-12. (a) Layer thicknesses and amplitudes of Lorentz and Drude components and (b) relaxation times for the interband, intraband (Drude), and nanoparticle plasmon polariton (Lorentz) transitions as functions of the deposition time for a Ag thin film from nucleation through coalescence to bulk film growth.

Fig. 3.12(a) shows the evolution of the nucleation, surface roughness, and bulk layer thicknesses as a function of time. Three stages are clearly identified in the growth

process (Nguyen, 1993; An, 1990). In the first stage after opening the shutter ($t = 0$ min), the Ag film nucleates following a Volmer-Weber growth mode, evidenced by an abrupt increase in d_s with no detectable increase in d_b . In the second stage starting at $t = 2$ min, the enlarging nanoparticle nuclei have made contact and generate a definable d_b . At this point the nucleating layer is treated as a surface roughness layer which decreases rapidly with thickness as the nuclei coalesce into d_b . As a result, the d_b growth rate is larger during coalescence than in steady state. In the third stage ($t > 5$ min), d_s has saturated at a nearly constant value while d_b grows at a constant steady-state rate until the shutter is closed. The final film thickness from RTSE, agrees well (to within 10%) with that from profilometry. The root mean square (rms) surface roughness thickness, d_{AFM} , measured from tapping mode atomic force microscopy (AFM) at the end of the deposition was ~ 1 nm, which compares with the final RTSE value of $d_s = 1.6$ nm. This implies a relationship between the RTSE and AFM roughness values of $d_s \sim 1.6 d_{\text{AFM}}$, which is close to that obtained for silicon thin films (Kawabata, 1998).

Also shown in Fig. 3.12(a) is the Drude component amplitude A_D and Lorentz oscillator amplitude A_L as a function of time for comparison with the structural evolution. At the beginning of deposition, A_L increases as the nucleating layer thickness increases due to the increase in volume fraction of nanoparticles, each serving as source of spatially confined electrons with the ability to couple to the incident wave. During this first stage, A_D is not detectable due to the absence of pathways for free electron conduction in the nucleating film. At the vertical dashed line ($t = 2$ min), however, A_L reaches its maximum just as A_D increases above zero. Thus, the vertical dashed line denotes the onset of free electron behavior which simultaneously corresponds to the onset of a non-zero d_b .

Similarly, the decrease in the Lorentz oscillator amplitude at the onset of A_D indicates that the nanoparticles and structures that confine electrons are absorbed into the conducting film structure. Thus, this stage is associated with coalescence which simultaneously corresponds to surface smoothening in d_s as seen Fig. 3.12(a). This correspondence provides support for the validity of the overall analysis and the close relationship between the structural and optical properties.

Although there is excellent overall consistency between the sets of properties, it is interesting that a weak A_L value is observed even after the surface has fully smoothened (e.g., at 9 min). One possible explanation of this effect is that the responsible crystallites are not fully coalesced at the substrate interface and are no longer observed when the overlying film becomes opaque at the resonance energy, as occurs for $d_b > 10$ nm. Grain coarsening which would lead to a loss of this effect with d_b is confirmed by x-ray diffractometry (XRD) of individual runs at different d_b values and is also suggested by the relaxation times of the RTSE oscillators.

The relaxation times calculated on the basis of the relation $\tau = \hbar/\Gamma$ for different dielectric function contributions are plotted as a function of deposition time in Fig. 3.12(b). The relaxation time of the Lorentz oscillator τ_L corresponds to the mean free time between collisions for the electrons confined within the nanoparticles. As can be observed in Fig. 3.12(b), τ_L is essentially constant within the range of 0.25 - 0.3 fs as a function of time, even as the thickness associated with the nuclei increases from 7.5 to 12.5 nm. This increase in nucleating layer thickness reflects an increase in the size of the nanoparticles as observed directly from AFM. As a result, it is concluded that the relaxation time is limited, not by scattering from nanoparticle surfaces, but rather from

scattering by multiple crystallite boundaries or defects internal to the nanoparticles; otherwise the relaxation time would increase at the same rate as the thickness (Nguyen, 1993). Even throughout coalescence, and as the proposed substrate interface resonances dominate, τ_L remains very short, also indicating dominance of defect scattering.

In a theoretical analysis of the nanoparticle plasmon polariton, obtained by substituting the Drude expression into the Maxwell Garnett EMT (Collins, 2005), τ_L equals the relaxation time in the Drude expression τ_D . This prediction is borne out by the results in Fig. 3.12(b), in which case there is an overlap between Lorentz and Drude values. Thus, the nanoparticles are formed not from bulk-like Ag, but rather from the defective Ag formed in the coalescence stage—which has a factor of 15 shorter relaxation time. The equality of τ_L and τ_D indicates that the dominant broadening mechanism for the plasmon polariton transitions is homogeneous, caused by electron relaxation, rather than inhomogeneous, caused by a distribution of nanoparticle shapes, for example.

A dramatic increase in τ_D occurs starting at $t = 5$ min, which corresponds to the completion of thin film coalescence and the start of the third stage of growth, characterized by a nearly constant surface roughness thickness (see Fig. 3.12a). Thus, in the coalescence process, the defective Ag microstructure abruptly transitions to a larger grain polycrystalline film nearest the surface. The divergence of τ_D and τ_L at this time provides evidence for different structure of the Ag at the near surface (τ_D) versus near the substrate interface (τ_L). In the third stage, a continuous, gradual increase in τ_D occurs and is attributed to grain coarsening with increasing thickness. In this stage, there is a linear increase in $(\tau_D)^{-1}$ with d_b^{-1} , as might be expected if the grain size increases linearly with

bulk layer thickness (Walker, 2009). This evolution in grain size is corroborated by XRD as described earlier. The value of the relaxation time τ_D for the final thin film (70 min deposition) measurement is 9.1 fs, which is to be compared with a multicrystalline Ag value of 37 fs (Johnson, 1972).

Compared to τ_L and τ_D , the interband transition relaxation time τ_G is longer in the nucleation stage. This is evident directly from the data of Fig. 3.11 where the width of the interband onset is observed to be narrower than that of the plasmon polariton. For the interband transitions the initial electronic state is within the *d*-band, which has a weak dependence on electron wave vector *k*. For interband transitions arising from particulate Ag regions of the film, the static dielectric constant is low due to the spatial confinement of free electrons. This may lead to electron and hole Coulomb interaction that would significantly reduce the group speed v_g of the excited electron. For a given mean free path, this would account for the longer relaxation time in the early stage of growth as compared to the plasmon polariton, in which case electron travels in accordance with the Fermi speed. The more gradual increase in τ_G in the third stage of growth is likely to have the same origin as the rapid rise in τ_D , namely the reduction in defect density and an increase in grain size. The rise in τ_G is not as large, however, since defects play a less significant role in scattering for the lower v_g interband transitions.

3.3.4. Conclusion

A broadband analysis of the optical properties of silver nanoparticles over the range from 0.75 to 6.5 eV was performed by applying *in situ* real-time spectroscopic ellipsometry (RTSE). Based on an independent analysis of the structural and optical (intraband electron and plasmon polariton) behaviors, the silver films were readily

understood in terms of three growth regimes, characterized by the ranges of effective thickness. These include (i) isolated particle growth, in which case no bulk layer is present and no Drude intraband component is observed ($0 < d_{eff} < 7$ nm); (ii) bulk layer growth before complete coalescence of particles ($7 < d_{eff} < 15$ nm), in which case both Drude intraband and plasmon polariton components are observed; and finally (iii) bulk layer growth after full coalescence of particles, in which case no plasmon polariton component is observed. RTSE proves therefore to be a powerful tool for *in situ* and real time analysis of metal nanoparticle deposition, enabling the growth processes and film structure to be closely correlated with optical properties -- with the prospect of deposition control for specific functionalities.

3.4. Temperature Dependence of Silver Nanoparticles Properties

3.4.1. Introduction

In situ control of the structural, thermal, electrical, and optical properties of metallic nanoparticles via surface engineering is motivated by their many applications [Little, 2011]. The varied applications of silver in nanoparticle form include low temperature interconnects [Jiang, 2010], nanoantennas [Chen, 2010], sensors for biological materials [Malmqvist, 1993], and back contact reflectors in thin film solar cells [Dahal, 2008] *In situ* control is enabled through thin film processing, as well as through thermal annealing of the resulting nanoparticle films, in conjunction with non-invasive *in situ* measurement techniques. For example, deposition or annealing at elevated temperatures shapes nanoantennas [Chen, 2010] and incorporates surface structure into back reflectors for optical enhancement in photovoltaics [Dahal, 2008]. In research

described in the present article, Ag films – incorporating isolated nanoparticles and having a range of thickness – were deposited at room temperature and then annealed at temperatures up to 773 K while analyzing *in situ* by real time spectroscopic ellipsometry (SE).

3.4.2. Experiment

The Ag nanoparticle films were deposited by dc magnetron sputtering at 288 K onto Si (100) wafers with 500 nm thermal oxides [Little, 2011]. The deposition times were varied from 0.5 to 3 minutes, which led to films of increasing thicknesses characterized by an array of isolated nanoparticles of average size increasing from 2 nm to 10 nm, respectively [Little, 2011; Marsillac, 2011]. To determine the dielectric functions of these films, a rotating-compensator multichannel ellipsometer was used having a photon energy range of 0.75-6.50 eV. Pairs of (ψ, Δ) spectra were collected with a 65° incidence angle and a 3 s acquisition time. These spectra were modeled assuming one or two substrate-supported layers, applying the effective medium theory and dielectric function analytical form given previously [Little, 2011]. *Ex situ* measurements including atomic force microscopy (AFM), x-ray diffraction (XRD), scanning electron microscopy (SEM), and secondary ion mass spectrometry (SIMS) were used to complement as well as corroborate the real time SE results.

3.4.3. Results and Discussion

For generality in fitting (ψ, Δ) data by least-squares regression, the starting structural model consists of two layers, a coalesced or "bulk" layer and a surface roughness layer, with thicknesses d_b and d_s , respectively, incorporated as free parameters. The analytical form for the dielectric function of the nanoparticles was described in Eq. (3.1) and Eq.

(3.4). The first term in Eq. (3.1) describes an offset; the second term describes a Lorentz oscillator for the nanoparticle plasmon polariton (PP) with amplitude A_L , resonance energy E_L , and broadening Γ_L ; the third term describes the interband transition with amplitude A_G , band gap energy E_G , broadening Γ_G , phase ϕ , and exponent μ .

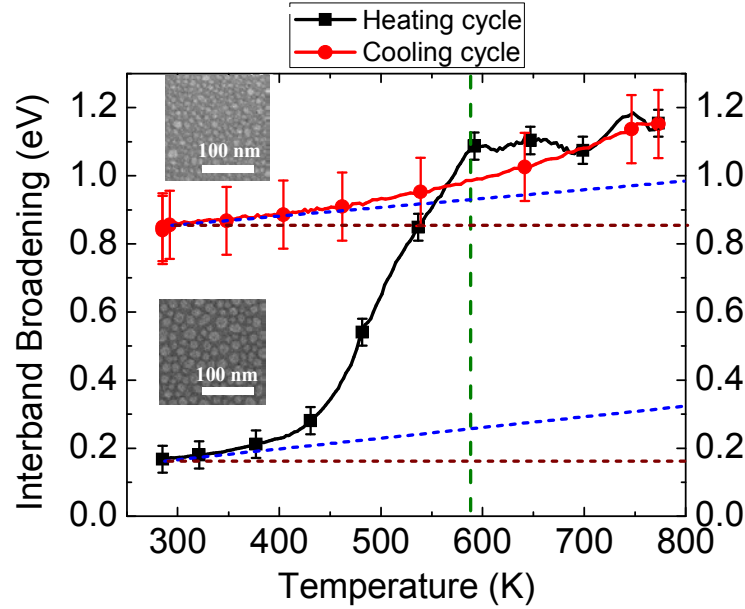


Figure 3-13. Interband broadening parameter as a function of temperature for nanoparticles in a Ag film with $d_s = 8.42$ nm. The vertical line is guide to the eye for the transition point and the broken lines are variations predicted on the basis of electron-phonon interactions alone; insets: scanning electron microscope (SEM) image of the as-deposited film (top left); SEM of the same film after the thermal cycle (bottom right).

The dominant nanoparticle nature of the deposited films was evidenced by the need for the Lorentz oscillator in the dielectric function model. The oscillator resonance energy E_L is observed to redshift with increasing thickness and thus particle size, consistent with increasing dipole-dipole interactions between particles [Marsillac, 2011]. Because no Drude component was needed to fit the dielectric functions and because d_b remained below a single monolayer in a two-layer analysis, it could be verified that all

depositions were terminated prior to coalescence – with the resulting films consisting of *isolated* nanoparticles. This was further corroborated by *ex situ* SEM and AFM images obtained immediately after selected depositions, as depicted in the Fig. 3.13 insets.

After characterization of the as-deposited nanoparticle film, its SE data were acquired *in situ* and in real time during annealing from 288 K to 773 K and then during cooling to 288 K. The continuous temperature (T) evolution of the interband broadening parameter Γ_G , deduced by SE, is shown in Fig. 1 for a nanoparticle film with $d_b = 0$ nm, $d_s = 8.42$ nm. An increase in T can lead to an increase in Γ_G simply due to the increased electron-phonon interactions at higher T [Winsemius, 1976]. This effect is described by the broken lines in Fig. 3.13, most accurately determined in the later stages of cooling when structural changes due to annealing are minimized.

The most obvious feature in Fig. 3.13, however, is the abrupt change in the evolution of Γ_G at $T \sim 595$ K. This is attributed to the melting transition associated with the largest particles of the film which define its physical thickness d_s [Dalacu, J. Appl. Phys., 2000]. During annealing, the broadening that occurs above the broken line dependences in Fig. 3.13 must be due to structural changes in the nanoparticle film. For $400 < T < 595$ K, during annealing the excess broadening may be due to melting of the smallest particles which occur at reduced T . For $500 < T < 595$ K, during cooling the excess broadening may have a similar origin – liquid particles that recrystallize over a range of T due to the distribution of particle sizes. Broadening may also occur upon heating and cooling due to strain-induced lattice deformation [Dalacu, J. Appl. Phys., 2000].

Table 3.1. The oscillators parameters that define the dielectric functions of the Ag nanoparticles at different stages in the thermal cycle. The physical thickness is 6.48 nm for the as-deposited film composed of isolated Ag nanoparticles.

Parameter	Lorentz Oscillator (PPP)						Interband Oscillator					
	A_L	Err.	Γ_L (eV)	Err.	E_L (eV)	Err.	A_G	Err.	Γ_G (eV)	Err.	E_G (eV)	Err.
Room Temperature (before heating)	15.5	0.93	0.83	0.01	2.68	0.01	4.1	0.22	0.18	0.03	4.34	0.02
High Temperature (773 K)	0.5	.060	3.57	0.10	3.21	0.04	3.2	0.07	1.11	0.04	4.51	0.05
Room Temperature (after heating)	0.9	0.30	2.17	0.52	3.01	0.35	3.0	0.23	0.82	0.10	4.19	0.15

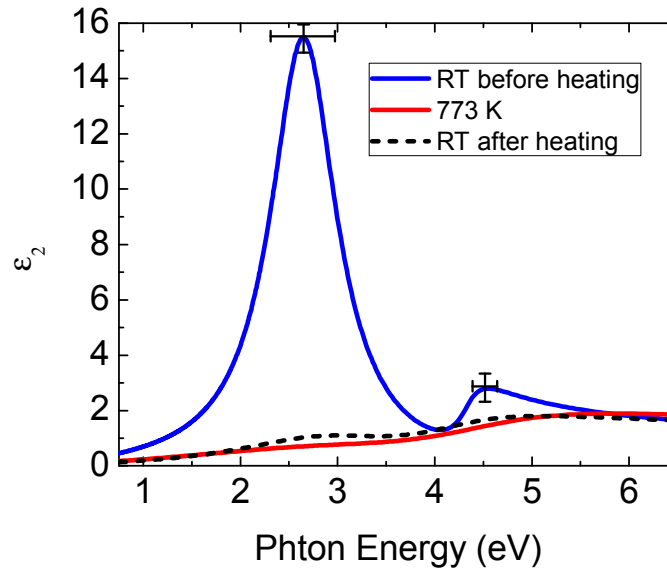


Figure 3-14. Dielectric functions of silver nanoparticles that compose a film with an as-deposited thickness of $d_s = 3.24$ nm; the measurements were performed in the as-deposited state at 285 K, upon annealing at 773 K – above the melting point, and after the full annealing-melting-cooling cycle at 285 K.

Representative dielectric functions are plotted in Fig. 3.14 for nanoparticles in a film with an as-deposited thickness of $d_s = 6.48$ nm (i) at 288 K in the as deposited state, (ii) at 773K during annealing, and (iii) at 288 K after annealing. The parameters of the analytical models for these dielectric functions are provided Table 3.1 and quantitative comparisons of these parameters yield several insights.

Upon heating to 773 K, significant increases occur not only in Γ_G (0.18 to 1.11 eV), as indicated in Fig. 3.13, but also in Γ_L , the broadening parameter of the PP resonance (0.83 to 3.57 eV) [Dalacu, Appl. Phys. Lett., 2000]. This consistent behavior in both interband and PP transitions is attributed to a loss of long range order due to melting which occurs at 595 K and leads to an electron mean free path λ on the order of the atomic spacing. Applying an estimate of $\lambda = \hbar v_F / \Gamma_L$ for the free electrons of the PP band, where $v_F \sim 1.4 \times 10^8$ cm/s is the bulk Fermi velocity and $\hbar$ is Planck's constant, values of Γ_L of 0.83 and 3.57 eV correspond to λ values of 1 nm, approximately one-third the particle radius, and 0.25 nm, approximately the atomic spacing, respectively. Cooling to room temperature leads to only a partial recovery of the broadening parameters (interband: 1.11 to 0.82 eV; PP: 3.57 to 2.17 eV). Recrystallization to a more defective crystalline or a disordered nanocrystalline structure relative to the as-deposited structure is responsible for this behavior [Dalacu, J. Appl. Phys., 2000], a surprising observation that will be discussed in further detail below.

In addition in Table 3.1 a significant decrease in A_L , the PP amplitude is noted (from 15.5 to 0.5 eV). This behavior is attributed primarily to the broadening of the interband transition which gives rise to a larger ϵ_2 value at the PP energy and hence a suppression

of the resonance. An unaccounted for increase in void fraction f_v in the film may also occur during heating due to nanoparticle coarsening, which leads to an increase in d_s , at constant effective thickness (defined as $d_{\text{eff}} = f_v d_s$, or the volume of particles per area). The latter effect is likely to be reflected clearly in the reduction in A_G , the interband amplitude upon annealing. Cooling to room temperature again leads to only a partial recovery of the PP amplitude (0.5 to 0.9 eV), consistent with the sharpening of the interband component and a reduction in ϵ_2 at the PP resonance. The interband amplitude continues to decrease consistent which could result from nanoparticle coarsening during cooling; however, a contribution may also exist due to lattice deformation, as was suggested by XRD with the lowering and broadening of the Ag (111) peak.

For E_L , the PP resonance energy, a blue shift upon annealing from 2.68 to 3.21 eV indicates a decrease in dipole-dipole interactions due to the weaker PP resonance and the larger spacing between particles [Marsillac, 2011] as indicated in the Fig. 3.13 insets. The partial red shift upon cooling is consistent with the accompanying increase in the resonance amplitude. For E_G , the interband energy onset, various competing effects can occur. An increase in temperature leads to a decrease in interband energy due to the electron-phonon interaction, by ~ 0.1 eV over the temperature range of 288 K to 595 K [Winsemeius, 1976]. Annealing can also induce lattice deformation and particle size changes which can also change the band gap due to strain and size effects [Dalacu, J. Appl. Phys., 2000]. The reduction in E_G at room temperature by the heating-melting-cooling cycle may be attributable to the increase in nanoparticle size as shown in Fig. 3.13.

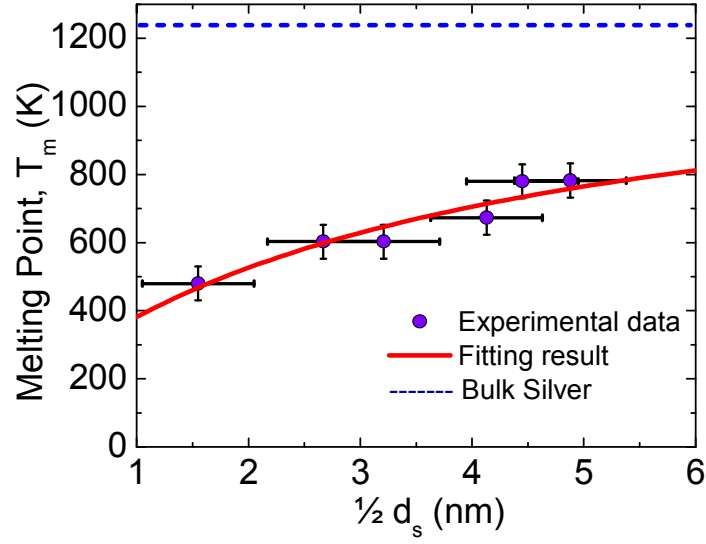


Figure 3-15. Melting point of silver nanoparticles plotted versus the average particle radius, estimated as one-half the physical thickness. The dashed line indicates the melting point of bulk silver. The solid line is the fit of Eq. (3.5), yielding the surface energy density.

A key focus of this research is characterization of the melting point depression for the nanoparticles – in the case of Fig. 3.13 from 1235 K to 595 K for a film with $d_s = 8.42$ nm [Dalacu, J. Appl. Phys., 2000]. This depression is due to the high surface to volume ratio and the lower cohesive energy of surface atoms. The melting point is thus a function of the nanoparticle shape, radius, or any other structural parameters that can modify the surface to volume ratio. The melting point temperature can be described by the following equation [Quaas, 2007]:

$$T_m(d_s) = T_o - \frac{2T_o M \sigma_s}{\Delta H_o \rho_s} \cdot \frac{1}{\frac{1}{2}d_s} \quad (3.5)$$

where σ_s is the surface energy density and is used as a fitting parameter, T_o is the bulk melting point (1235 K); M is the molar mass of Ag (107.87 g/mol); ΔH_o is the enthalpy of

melting (11.28 kJ/mol); ρ_s is the mass density of Ag (10.49 g/cm³); and d_s is extracted from RTSE. In fact, d_s is assumed to be equal to the diameter of the largest particles in the distribution, and thus, dominates the melting behavior. In Fig. 3.15, the nanoparticle film melting point is shown, deduced from data similar to those of Fig. 3.13 and plotted as a function of $1/2d_s$, or the estimated particle radius. Fitting the results in Fig. 3.15 using Eq. (3.5) leads to a surface free energy density of $\sigma_s = 0.9 \text{ J/m}^2$, which is in reasonable agreement with previously reported values for both bulk Ag (1.0 - 1.5 J/m²) [Bernard, 1971; Nanda, 2003] substrate supported nanoparticles (1.1 J/m²) [Blackman, 1968; Castro, 1990], but much lower than values reported for free nanoparticles (~6.4-7.4 J/m²) [Nanda, 2003; Berry, 1952]

Ex-situ analyses were also performed to better understand the influence of the full annealing-melting-cooling cycle on the structure of the Ag nanoparticles. Both scanning electron microscopy (SEM) and x-ray diffraction (XRD) results confirm the melting temperature of the nanoparticles through the significant differences in average size and crystallinity of particles before and after annealing cycles that reach the melting point.

By SEM, nanoparticles particles appeared larger and more uniform in size after an annealing cycle that exceeds the SE-deduced melting point, as shown in the Fig. 3.13 insets. Analysis by XRD performed before heating reveals a characteristic Ag (111) peak, which nearly disappears after a full annealing-melting-cooling cycle, revealing that the bulk-like crystalline component of the nanoparticles has decreased. This result is likely to result from the increase in the volume of grain boundaries and other defective regions of the nanoparticles upon annealing – even to the extent that the nanoparticle material appears to exhibit an amorphous component. This structural change is consistent with

significant broadening of the PP and interband features measured after cooling, as seen in the SE spectra of Fig. 3.14 and the analysis results of Table 3.1. In fact, the increase in broadening of the PP for the thermally-cycled particles over the as-deposited particles can be attributed to decrease in mean free path from ~ 1 nm to 0.4 nm, the latter being much smaller than the observed particle size. The physical reason for the formation of defective particles after cooling from the liquid is unclear; cooling rates are too slow (4 K/min) to quench in such defects. One possibility is that such a structure is stabilized by surface adsorbates that are incorporated as impurities within the bulk nanoparticles upon melting. Secondary ion mass spectrometry has not detected differences between the contaminant levels before and after the annealing cycle; however, it is likely that nanoparticle impurities would be difficult to detect, given the presence of surface contamination in *ex situ* analyses.

3.4.4. Conclusion

In conclusion, sputter deposition of silver onto room temperature SiO₂ surfaces for increasing durations led to films consisting of isolated nanoparticles with increasing average sizes. The thin films were measured by real time spectroscopic ellipsometry (SE) during annealing and subsequent cooling, and the resulting nanoparticle dielectric functions were modeled using parameterized oscillators. By observing the variations in the oscillator parameters upon annealing, at elevated temperature, and during cooling, key information on the nanoparticle structure and phase can be deduced. In particular, the broadening parameters of the particle plasmon polariton and interband transitions provide insights into electronic scattering and defects within the particles. A significant reduction in the free electron mean free path in nanoparticles identifies melting point

depression, and partial recovery upon cooling indicates poorer crystallinity in the thermally-cycled particles relative to the as-deposited particles. These conclusions based on non-invasive real time analysis were further confirmed by direct imaging in *ex situ* studies.

3.5. Conclusion

In conclusion, three studies of silver nanoparticles were presented in this chapter. In the first study, a broadband analysis of the optical properties of silver nanoparticle films over the range from 0.75 to 6.5 eV was performed by applying *in situ* real-time spectroscopic ellipsometry (RTSE) during the nucleation, coalescence, and bulk thin film growth regimes. The dielectric functions of the particulate films were found to depend strongly on the particle size and film thickness from the nucleation regime throughout coalescence. These dependences were analyzed by separately characterizing the three types of transitions evident in the dielectric function: intraband, particle plasmon polariton, and interband. Throughout the film growth regimes, the thickness evolution of the amplitude, energy, and broadening parameter for each type of transition was discussed in view of the structural characteristics of the films, and corroborated by *ex situ* atomic force microscopy for films deposited over different time durations. In the second study, the dielectric function of Ag nanoparticle films, deduced by *in situ* real-time spectroscopic ellipsometry (RTSE), was found to evolve with time in close consistency with the film structure, also deduced by RTSE. In the nucleation regime, the intraband component is absent and plasmon polariton behavior dominates. Only at nuclei contact, does the intraband amplitude increase above zero. Both intraband and plasmon

amplitudes coexist during surface smoothening associated with coalescence. The evolution of the relaxation times for the interband, intraband, and plasmon dielectric function components shows trends that are similarly consistent with the Ag film structure. In the final study, the temperature dependence of these oscillators was analyzed via RTSE and a melting point depression was detected via an abrupt change in the generalized oscillator broadening, allowing for the surface energy to be calculated. After annealing, permanent structural changes, such as the reduction in crystallinity and change in size, were observed in the nanoparticles via ex-situ measurements, thereby confirming that the nanoparticles had melted.

Chapter 4

Growth and Characterization of (Ag,Cu)InSe₂

4.1. Background

As was seen in the last chapter, the study of silver nanoparticles reveals that silver possesses many admirable attributes that make it an ideal material of study. In terms of optics, the sensitivity to light of silver compounds is what made photography possible in the 19th century. Given the rich history of silver as applied in optical, electrical, and thermal conductivity, a solar cell device could benefit from the same properties. In solar cells, silver have been used as a back reflector, transparent conducting layer, and as an electrical contact.

The study in this chapter focuses on the growth of (Ag,Cu)InSe₂ (ACIS). We are going to study the growth and optical properties of this silver compound similarly to the way we studied the growth of Ag nanoparticles in the last chapter. As a material ACIS has not been studied as much in depth as CIGS [Boyle 2011]. ACIS has several advantages through explicit material properties and controllability of growth parameters. The bandgap can be varied between 1 eV and 1.24 eV by changing ratio of Cu and Ag (this is without Ga). This material can be theoretically stable at lower temperature than

CIGS. Also, modification of the growth process to enhance the performance of solar cells should be possible via Ag addition, which would allow the ability to control the grain size by optimizing the nucleation stage and controlling the uniformity and defect concentration. Furthermore, bandgaps of the I-III-VI₂ system (I-Cu,Ag; III-Ga,In; VI-S,Se) cover almost the entire solar spectrum, which make it an ideal system for multijunction solar cells. Overall, the study of Ag in the I-III-VI₂ system is an exploratory study, because most of its properties, including optical properties, are poorly understood.

In this Chapter, *in situ* and *ex situ* characterization methods have been used in order to investigate the growth as well as the physical and chemical properties of (Ag,Cu)InSe₂ (ACIS) thin films deposited by direct current (dc) magnetron sputtering. Data acquired by real time spectroscopic ellipsometry (RTSE) were used to extract growth parameters such as thickness and surface roughness. The complex dielectric functions, (ϵ_1 , ϵ_2), of ACIS at high and room temperatures as a function of $x = Cu/(Ag+Cu)$ were also extracted from the RTSE data. *Ex situ* measurements were used to corroborate RTSE results and included SEM, XRD, AES, EDS, optical spectroscopy, and cryogenic cathodoluminescence (CL). The CL study is explored in detail in section 4.3.

4.2. Study of the growth of ACIS thin films by RTSE and corroboration with *ex situ* characterization

4.2.1. Introduction

The success of optimizing the solar cell performance in the quaternary alloy Cu(In,Ga)Se₂ to a 20.3% efficiency [Hopwood 2010], achieved by substitutionally

replacing the Group III element, leads one to believe that a similar benefit could be possible with Group I elements. Given its many optically reactive compounds, Ag is a very interesting substitution for Cu. Recently, Hanket *et al.* [Hanket 2009] have investigated solar cell devices optimizing the content of Ag in (Ag,Cu)(In,Ga)Se₂ (AgCIGS) and Albornoz *et al.* [Albornoz 2005] conducted *ex situ* ellipsometric experiments on AgCIGS thin films over the photon energy range of 0.5 - 4.7 eV at room temperature. In the present section, *in situ* RTSE measurements are described for (Ag,Cu)InSe₂ thin films over the photon energy range 0.75 – 6.5 eV at deposition temperatures. Models describing the critical points as oscillators were used to extract important material parameters such as broadening and band gap energy. The effects of the composition on the nucleation and growth mechanism that ultimately influence the film morphology and grain structure have been studied. The data were corroborated with *ex situ* measurements. Key characteristics have been deduced including growth modes and final grain size.

4.2.2. Experiment

(Ag,Cu)InSe₂ thin films were deposited by d.c. magnetron sputtering at 550°C onto a Si (100) wafer with a 25 nm thermal oxide using high purity targets (Ag, Cu, In) in high purity (99.998%) argon. The d.c. power of the targets were varied to obtain different compositions of varying Ag/Cu content whereas the Ar pressure was maintained at 2.5 mTorr. Selenium was simultaneously evaporated at a constant rate. RTSE data were acquired *in situ* during film growth using a rotating-compensator multichannel ellipsometer with a photon energy range of 0.75-6.5 eV at an angle of incidence of 65°. The optical model for the data analysis is based on a 2-layer structure consisting of

surface roughness and bulk layer of the deposited film (ACIS) on fully characterized substrate of Si with 25 nm thick SiO₂. The surface roughness was simulated with a Bruggeman effective medium approximation (EMA) composed of a 50/50 mixture of void and ACIS. The experimental data, spectra in Ψ and Δ , were fit assuming this model and then numerically inverted to extract the dielectric functions, thickness, and roughness using least-squares regression algorithms. Complementary *ex situ* characterization of the as-deposited film includes x-ray diffractometry (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and Auger Electron Spectroscopy (AES).

4.2.3. Results and Discussion

The composition of the (Ag,Cu)InSe₂ thin films was controlled by the relative power in each sputtering gun and confirmed by EDS and XRD (assuming Vegard's law), while the single phase was directly confirmed by identifying XRD peaks. AES profiles were also obtained for these films and confirmed that there was no composition gradient throughout the thickness of the films.

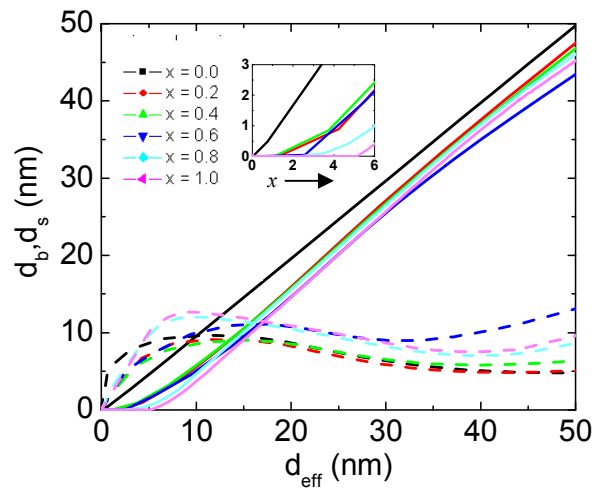


Figure 4-1a. Thickness (d_b) and surface roughness / nucleating layer (d_s) vs. effective thickness d_{eff} for the first 50 nm of deposition. d_b is displayed by solid lines while d_s is

displayed as a dashed line. The inset shows a magnified view of d_b the early nucleating region, where the arrow denotes of increasing x as a function of increasing d_{eff} . Here, d_{eff} evolves proportionally to the deposition time.

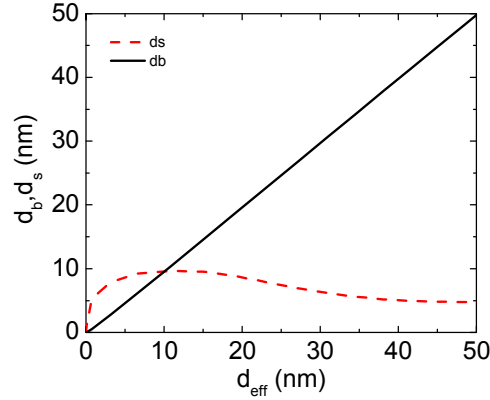


Figure 4-1b. From *in situ* analysis of the growth parameters from RTSE data and according to the copper to silver ratio ($x = Cu/(Ag+Cu)$), different types of growth have been identified. For $x = 0$, the surface roughness layer appears before the first dense monolayer (ML) (~ 0.5 nm). This is typical of the island or Volmer-Weber (V-W) nucleation mode [Venables 1984].

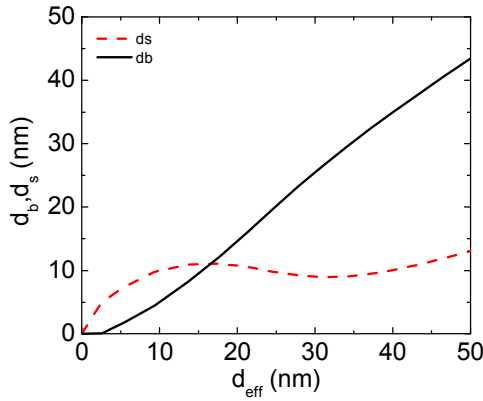


Figure 4-1c. For $x = 0.6$, the first MLs of surface roughness and dense material appear more simultaneously and also display an S-K growth mode.

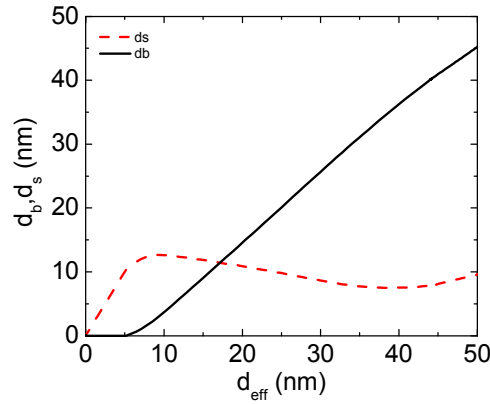


Figure 4-1d. For $x = 1$, a few MLs appear before the first ML of roughness. This is typical of the layer-to-island or Stranski-Krastanov (S-K) growth mode [Venables 1984].

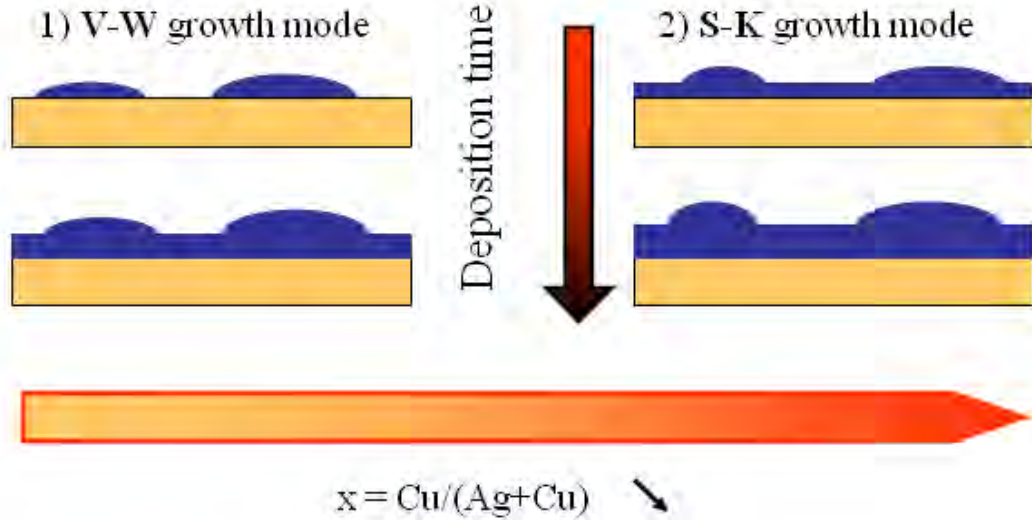


Figure 4-1e. Illustration of growth modes.

During the deposition, pairs of (Ψ, Δ) were acquired and allowed for the extraction of growth parameters. Figures 4.1.a-d. depict the growth parameters describing the first 50 nm of the deposition (out of 500 nm). From the *in situ* RTSE analysis of (d_b, d_s) , slightly different types of growth were identified depending on the copper to silver ratio ($x = Cu/(Ag+Cu)$). For most of the film compositions, the surface roughness layer appears before the first dense monolayer (ML) (~ 0.5 nm). This is typical of an islanding or Volmer-Weber (V-W) nucleation mode [Venables 1984]. However, as

the x decreases, the growth of the first dense monolayer appears earlier, which ultimately lead to layer-by-layer followed by islands based growth or Stranski-Krastanov (S-K) growth [Venables 1984] for $x = 0$. Graphically, this is represented in Fig. 4.1.e. A reduction in the free energy density of the interface in the alloys containing Ag probably allowed for this modification of the growth mode. Nucleation behavior in the initial stage of deposition has been observed to impact the subsequent structural evolution of film and ultimate material properties, as will be shown.

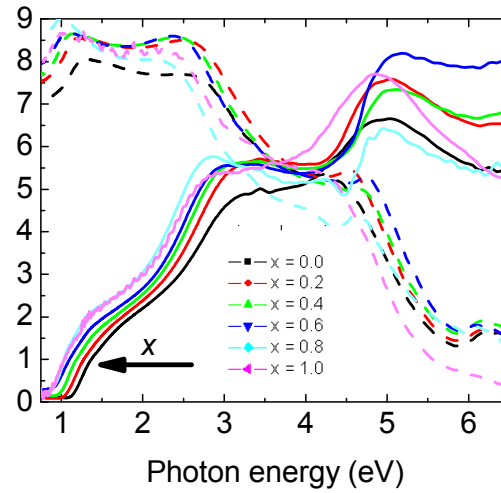


Figure 4-2. Dielectric functions for different compositions at deposition temperature (550 °C). Arrow indicates the direction of increasing x for ϵ_2 near the band gap. d_b is displayed by solid lines while d_s is displayed as a dashed line.

The same ellipsometric parameters (Ψ , Δ) used to fit the growth parameters were also used to extract the dielectric functions (ϵ_1 , ϵ_2). The dielectric functions shown in Fig. 4.2 for ACIS films at the deposition temperature (550 °C) were measured in situ by RTSE. As one can see, the band gap energy shifts towards lower energy as the x content increases. These dielectric functions were then modeled using critical point parabolic

oscillators [Ozaki 2006] to extract more precise information regarding the shift in the band gap as well as in the broadening as a function of x , using:

$$\varepsilon(E) = \varepsilon_{\infty} - \sum_n A_n e^{i\theta_n} (E - E_n + i\Gamma_n)^{m_n}, \quad (4.1)$$

where ε_{∞} is the real dielectric offset, A_n is the amplitude, E_n is the center energy, Γ_n is the broadening, and m_n is the order of the transition.

Table 4.1. Band gaps (E_g or E_o) of various compositions of ACIS films at different temperatures (RT is room temperature).

$x = Cu / (Ag + Cu)$	0.0	0.2	0.4	0.6	0.8	1.0
E_g (RTSE 550 °C)	1.15	1.05	0.98	0.91	0.90	0.90
E_g (RTSE RT)	1.24	1.16	1.10	1.01	0.99	0.98
E_g ([Albornoz 2005] RT)	1.22	1.16	1.09	1.03	1.01	1.01

Band gap via optical spectroscopy of the different compositions have been extracted from ellipsometry at deposition temperature and at room temperature (Table 4.1 and Figure 4.3).

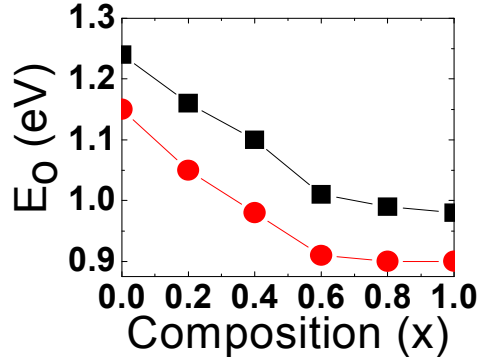


Figure 4-3. Depicted is the fundamental energy gap as a function of composition as extracted by ellipsometry. The higher energy data points represent the energy gaps at room temperature while the lower energy data points depict the energy gaps at deposition temperature.

The room temperature values are in good agreement with the ones found by Albornoz *et al.* [Albornoz 2005]. As expected for a semiconductor, the values for the band gaps at high temperature are lower than the ones at room temperature. The bowing parameter calculated from the RTSE room temperature data is 0.23 (in agreement with the 0.22 for Albornoz *et al.* data), whereas the high temperature bowing parameter is 0.33, which is reported for the first time here. The bowing effect on the band gap is responsible for the similarity between the $x = 0.6$ and $x = 1$ compositions. It is interesting to note that even though the $x = 0.6$ is closer to $x = 1$ in composition and band gap, it favors the S-K growth mode like the $x = 0$ composition.

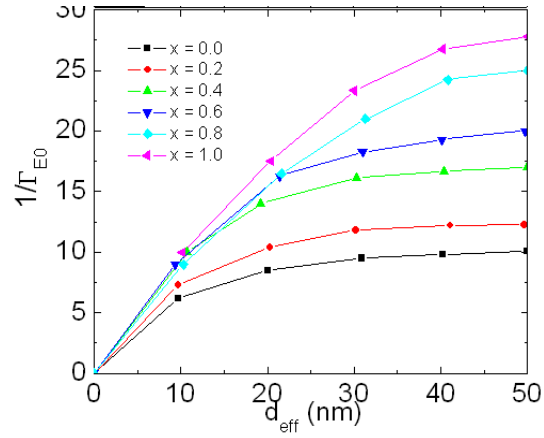


Figure 4-4. Inverse of broadening parameter for the E_0 oscillator. $1/\Gamma_{E_0}$ is expressed in eV^{-1} units.

Since nucleation behavior in the initial stage of the deposition has been observed to impact the subsequent structural evolution of the film and ultimate material properties, grain size evolution as a function of x was also studied. Broadening (Γ_{E_0}), extracted from the same fitting procedure described above, is plotted in Fig. 4.4 as a function of effective thickness. It can be seen in this figure that even at small effective thicknesses, separation between $1/\Gamma_{E_0}$ for $x = 0$ to $x = 1$ can be observed. This separation of $1/\Gamma_{E_0}$ keeps increasing with the growth of the film. Previous studies have shown that the inverse of the ellipsometric broadening is proportional to the physical grain size, assuming that the broadening due to other scatterers are kept constant, following the equation [Li, 2010]:

$$\frac{\hbar v_g}{R} = \Gamma_{E_0} - \Gamma_b \quad (4.2a)$$

where R is the electron mean free path, Γ_b is the theoretical single crystal broadening, and v_g is the group velocity. It is observed in the Fig. 4.4 that the grain growth saturates faster for $x = 0.0$ compared to $x = 1.0$. If v_g is considered to be the speed of light (a

highly conservative estimate since even electrons in a conductor only travel about 0.6 c)

and $\Delta_{E0} = \Gamma_{E0} - \Gamma_b$ with $\Gamma_{E0} \gg \Gamma_b$ [Li, 2010], then it can be shown that

$$R \gg \frac{\hbar v_g}{\Delta_{E0}}, \quad (4.2b)$$

thus proving that R is the dominant parameter in this relation. Even though various physical attributes can affect the mean free path, such as stress, impurities, and other scatterers, it is believed that grain size is the main differentiator of R , as evidenced by XRD, SEM, and CL, for example.

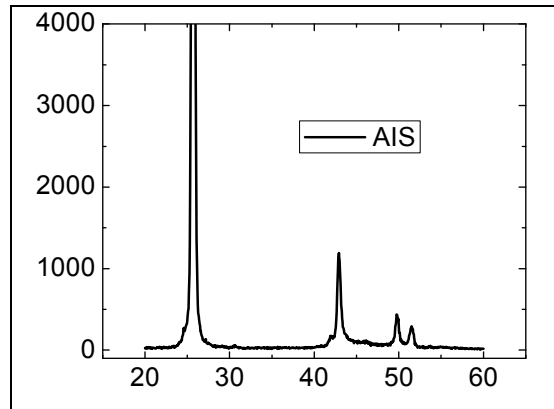


Figure 4-5. Typical XRD data obtained displaying the arbitrary counts vs. the angle in degrees. The first peak is identified as the (112) peak around 25 degrees, followed by the (204) peak just after 40 degrees.

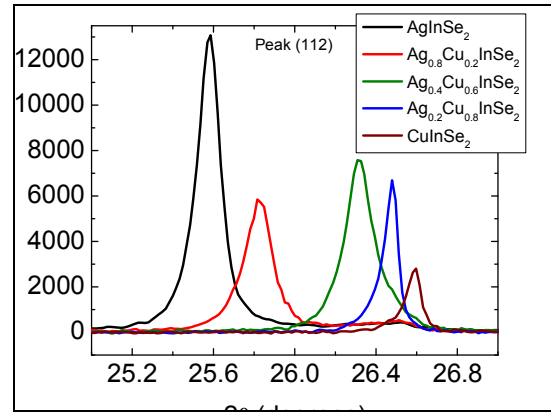


Figure 4-6. XRD zoom of (112) peak for various compositions of ACIS thin films

XRD analysis (see Fig. 4.5 and Fig. 4.6) was performed on the samples and they were found to follow Vegard's law. The band gaps predicted by lattice parameter calculation (Table 4.2) corroborated fairly well with those found from optical spectroscopy and ellipsometry (Table 4.1).

Table 4.2. Data obtained via XRD for ACIS films.

$x = Cu / (Ag + Cu) =$	0.0	0.2	0.4	0.6	0.8	1.0
(112) 2 θ XRD (degrees)	25.6	25.8	26.0	26.3	26.5	26.6
FWHM XRD (degrees)	0.15	0.15	0.14	0.13	0.09	0.10
Grain Size XRD (nm)	110	114	118	128	167	155
Calculated band gap (eV)	1.2	1.12	1.05	1.02	1.01	1.01

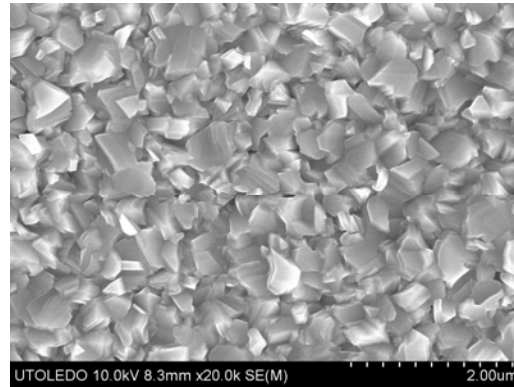
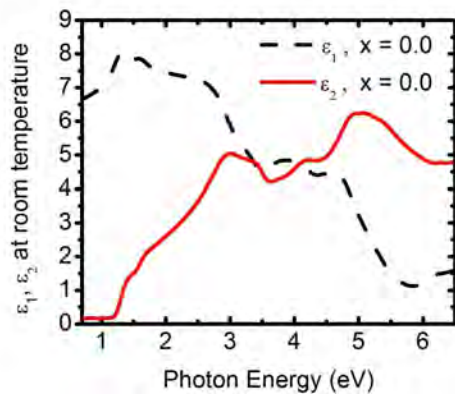


Figure 4-7. a) AgInSe₂ dielectric functions at room temperature, b) AgInSe₂ SEM micrograph

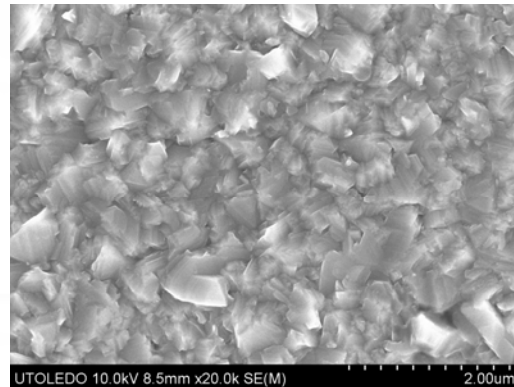
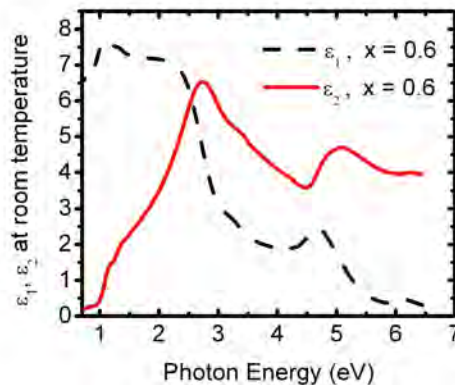


Figure 4-8. a) Ag_{0.4}Cu_{0.6}InSe₂ dielectric functions at room temperature, b) Ag_{0.4}Cu_{0.6}InSe₂ SEM micrograph

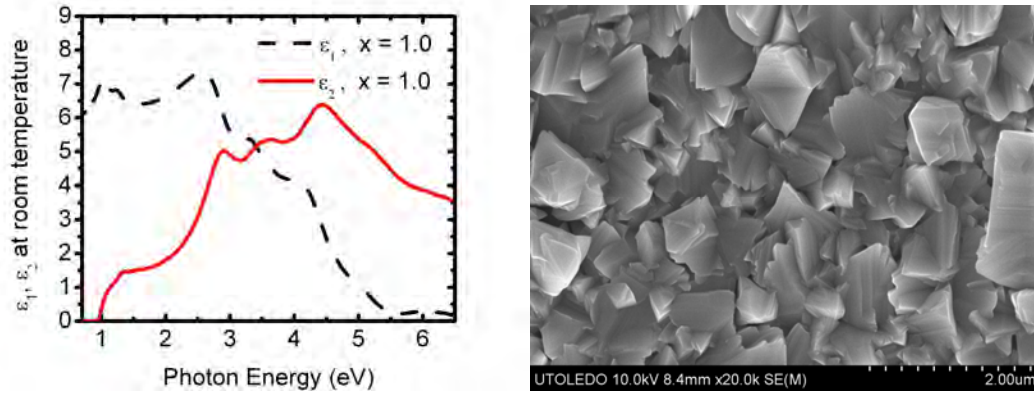


Figure 4-9. a) CuInSe₂ dielectric functions at room temperature, b) CuInSe₂ SEM micrograph

Figures 4.7 to 4.9 show the dielectric function and the top surface after deposition of ACIS films with $x = 0$, 0.6 and 1 . For pure composition layers ($x = 0$ or 1), the dielectric functions, exhibit interesting similarities of their shapes (Fig. 4.7 and Fig. 4.9). For mixed composition ($x = 0.6$), the dielectric function shape is slightly different with higher values of ϵ_2 in the low energy range, compared to ϵ_2 for AgInSe₂ or CuInSe₂ films (Fig. 4.9), which could be related to the growth mechanism and may result from a unique combination of the d-bands of Ag and Cu. From SEM images and absorption peak broadenings extracted from the dielectric function, the grain size appeared to be larger for CuInSe₂ films, which is also confirmed by XRD. The fact that the grain size of the $x = 0.6$ composition (by XRD and SEM appearance) is closer to values of the AgInSe₂ film, reveals that the growth mode is important to the final grain size of the as-deposited film.

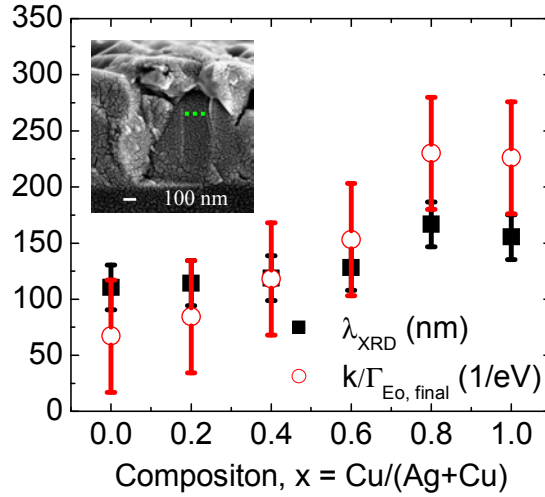


Figure 4-10. λ_{XRD} values are extracted from FWHM of XRD 112 peaks, while $k/\Gamma_{\text{Eo, final}}$ (1/eV) values are extracted from RTSE parameters. Inset is a composition $x = 0.2$ cross-sectional SEM image. Dashed line highlights a grain size demonstration of this particular film. k is 0.85×10^{-7} .

Trends for the evolution of the grain size as a function of x were corroborated with XRD and SEM results for the completed films. Fitting the (112) XRD peak for each composition, the grain size can be found using the Scherrer formula [Scherrer 1918],

$$\lambda_{\text{XRD}} = \frac{K \lambda_l}{\beta \cos \theta} \quad (4.3)$$

where K is the dimensionless shape factor, λ_l is the x-ray wavelength, β is the full width at half maximum (FWHM), and θ is the angle of the peak center. Grain sizes of the completed film were found to vary from 80 nm to 150 nm. Since the grain size calculated from XRD can be shown to be proportional with the inverse of the broadening from RTSE, they are compared side by side in Fig. 4.10. It is clear in this figure that the grain size by XRD as well as the inverse of the broadening of the completed film increases as x content increases. This shows that RTSE can be effective in predicting the relative grain sizes found in XRD early in the deposition while being monitored *in situ*.

4.2.4. Conclusions concerning growth

(Ag,Cu)InSe₂ thin films were grown by dc magnetron sputtering and were characterized by *in situ* RTSE and *ex situ* EDS, AES, XRD and SEM. RTSE has been applied to investigate the structural evolution and dielectric functions, ϵ , of these films. Changes in the growth process with Ag alloying appear to induce changes in grain size; in addition, the alloys present specific characteristics in their dielectric functions making them easily identifiable. The extraction of the band gap at high temperature allowed for the parameterization of the band gap under actual growth conditions, which could be an effective tool for future band gap engineering. Excellent agreement between RTSE and XRD trends demonstrated the effectiveness of RTSE in predicting the relative change in a physics parameter given a change in an input parameter (composition). In the next section, we will see that the study of cathodoluminescence (CL) will allow us to explore the electronic defect states. This will give us a microscopic electronic map of the surface state, allowing us to corroborate the modes of growth in this section, as well as conclusions pertaining to grain size differences between compositions and band gap energies. The next section, along with this previous section, will therefore give us a more complete understanding of ACIS thin films.

4.3. Cryogenic cathodoluminescence from ACIS thin films

4.3.1. Introduction

Cryogenic cathodoluminescence (CL) data was obtained from the ACIS thin films studied in the previous section in collaboration with Dr. Angus Rockett and Angel Acquino from the University of Illinois Urbana-Champaign. Emission peaks were

identified and spectrally-resolved images were recorded at these wavelengths. A power-dependent CL series was also recorded.

The purpose of this section was to study the emission spectrum of grains and grain boundaries in ACIS in order to identify any differences among them. A decrease in emission intensity from the grain boundary would indicate a possible increase in non-radiative recombination there, which could be detrimental for solar cell devices. Spectral image acquisition allows us to see what location a specific emission is coming from, helping us to determine whether certain impurities or defects are responsible for particular parts of the emission spectrum.

4.3.2. Experimental Setup

As described in section 4.2, ACIS polycrystalline samples were deposited via a hybrid process in which Cu, Ag, and In were sputtered and elemental Se was evaporated. These elements were deposited onto a bare glass substrate held at 550°C. Three of these films are studied in this section.

Cryogenic CL was performed on as-deposited air-exposed films. The experiments were carried out in a JEOL (JSM-7000F) scanning electron microscope (SEM) fitted with a liquid nitrogen-cooled stage and a Gatan MonoCL3 cathodoluminescence spectrometer that used a liquid nitrogen-cooled Ge photodetector. The electron beam accelerating voltage was set at 15 kV and the current at 200 pA, except where otherwise noted. Power-dependent CL spectra were also collected in order to study the behavior of the peaks. Accelerating voltages remained constant (15kV) while excitation currents were varied from 22 pA to 160 nA. The sample temperature was 5 K when the spectra were collected.

Monochromatic CL spectra were collected and analyzed. Spectrally-resolved CL images were obtained at selected positions. These spectrally resolved images were then given individual colors and overlaid in order to highlight spatial and spectral variations in luminescence. Panchromatic images (sensitive to all wavelengths of light) were also recorded for each sample.

4.3.3. Results and Discussion

4.3.3.1. AgInSe₂ sample

The surface morphology of a sample of AIS is shown in Figure 4.11a. The image suggests an average grain size of ~200 nm. A monochromatic CL spectrum was taken at 30kx magnification from this area and is shown in Figure 4.12. A best fit to the CL data was obtained for a Gaussian peak at 1020 nm (1.215 eV, FWHM = 34.7 meV) combined with an exponential tail on the lower energy side, which decayed at a rate of 44 meV/decade. Spectral images were acquired at the peak position and along the band tail (1010 nm, 1020 nm, and 1060 nm). The spectral images have been overlaid in Figure 4.11b. The emission at 1060 nm is colorized as red, while the 1010 nm and 1020 nm emissions contribute blue and green to the overlay, respectively. The spectral image at 1010 nm shows better lateral resolution than the 1060 nm spectral image, suggesting that the emission at 1010 nm is more localized than the emission at 1060 nm. A panchromatic CL image was also collected for this sample (see Fig. 4.13). Again, emissions are very uniform. Most dark areas in the panchromatic CL image correspond to dark areas in the secondary electron image (SEI).

The spectral images show no significant difference in distribution of emission with respect to position indicating compositional uniformity, unlike the samples with

$x > 0$, as discussed below. By comparing the SEI to the CL spectral image, we can see that the majority of grains exhibit some type of emission. The AIS sample is affected relatively little by protuberant surface features, meaning moderate non-radiative surface recombination. Another important observation is that grain boundaries in this sample do not appear to luminesce more or less than the surrounding grains. This means that the grain boundaries are not acting as non-radiative recombination centers.

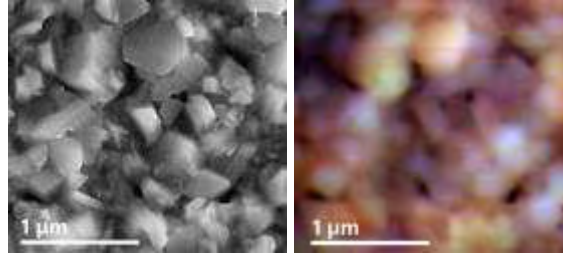


Figure 4-11. a) SEM image of AgInSe₂, b) MonoCL images overlaid with 1010 nm in the blue channel, 1020 nm in the green channel and 1060 nm in the red channel (taken in same area as Fig. 4.11a).

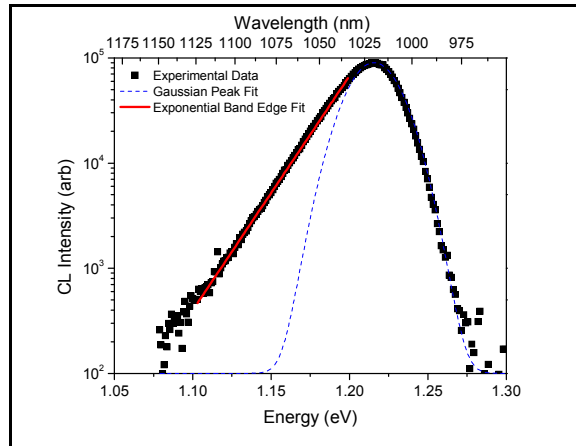


Figure 4-12. AIS MonoCL spectrum with best fits on area shown in Fig. 4.11a.

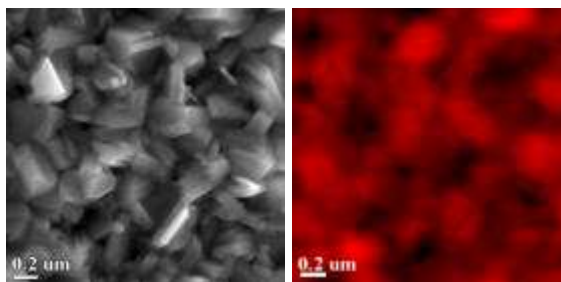


Figure 4-13. a) SEM image of AgInSe_2 , b) panchromatic CL image from Fig. 4.13a.

Power-dependent CL spectra are plotted on a semi-logarithmic scale in Fig. 4.14. The spectra from 22 pA up to 640 pA can be modeled using a Gaussian peak with an exponential band tail. The Gaussian peak undergoes a blue-shift from 1028 nm (1.206 eV) to 1011 nm (1.226 eV) as power increases in this range (22 pA - 640 pA). When the excitation current is increased past 2,560 pA, second and third exponential tails are observed at the low energy (> 1168 nm) and high energy ends (< 950 nm), respectively. The Gaussian peak continues blue-shifting with increasing excitation current until reaching a maximum shift of 41 meV at 40,960 pA (994 nm, 1.247 eV). At higher excitation currents this peak experiences a red-shift.

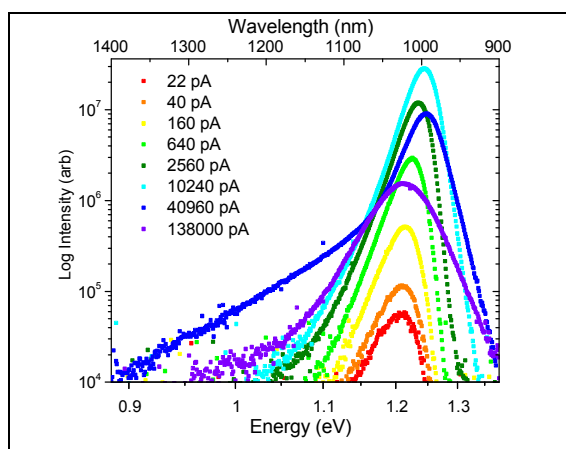


Figure 4-14. AgInSe_2 power-dependent spectra at 5K.

4.3.3.2. $\text{Cu}_{0.6}\text{Ag}_{0.4}\text{InSe}_2$ sample

A secondary electron image from the $\text{Cu}_{0.6}\text{Ag}_{0.4}\text{InSe}_2$ (ACIS) sample is shown in Figure 4.15. This image suggests an average grain size of ~ 500 nm in this sample. CL emission spectra were acquired at 1200 nm (blue channel), 1230 nm (green channel), and 1280 nm (red channel) and the overlay image is shown in Figure 4.15b. This sample exhibits a lot more spatial and spectral variation than the other samples. There was some enhanced emission seen from the grain boundary areas in the mono CL overlay. The white areas (see Fig. 4.15b) indicate the presence of all three emission wavelengths, and these seem to lie across grain boundary or inter-grain areas. This sample has the most variation of emissions from grain to grain. Some grains appear to luminesce only at one wavelength, and others do not luminesce at all. This indicates that there are compositional or electrically-active defect fluctuations between grains.

A panchromatic CL image (see Fig. 4.16) confirms these observations and reveals a severe reduction in emission intensity from protuberant surface features. Enhanced emission intensity from grain boundary areas is also seen. In fact, most of the red areas (more intense emission) in the image correspond to grain boundary areas in the SEM image. The dark areas in the panchromatic CL image correspond to protruding features in the SEM image.

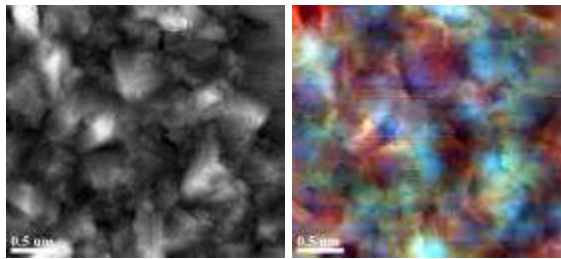


Figure 4-15. a) $\text{Cu}_{0.6}\text{Ag}_{0.4}\text{InSe}_2$ SEM image b) MonoCL images overlaid with 1200 nm in the blue channel, 1230 nm in the green channel and 1280 nm in the red channel (taken in same area as Fig. 4.15a).

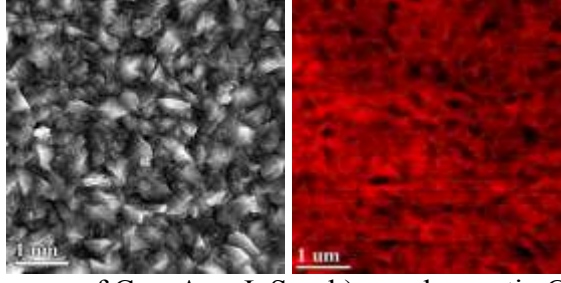


Figure 4-16. a) SEM image of $\text{Cu}_{0.6}\text{Ag}_{0.4}\text{InSe}_2$, b) panchromatic CL image from Fig. 4.16a.

Power-dependent spectra for the ACIS sample are broader than the emissions from the AIS sample. Two Gaussian peaks at 1229 nm (1.01 eV) and 1270 nm (0.976 eV) are required to obtain a best fit for the 22 and 40 pA spectra. As the excitation power is increased, exponential tails appear on both high and low energy sides of the peak, as for the AIS sample. Both Gaussian components blue-shift (20 meV and 15 meV) with increasing excitation power, but not as much as the peaks for the AIS sample (41 meV). A very broad additional Gaussian component is also present at very high excitation powers, as seen in Fig. 4.17 for 160000 pA.

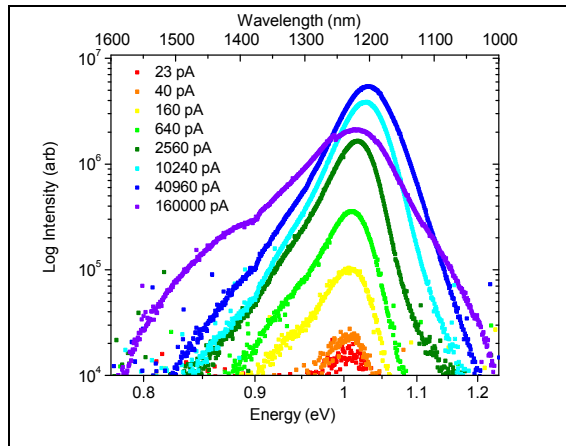


Figure 4-17. $\text{Cu}_{0.6}\text{Ag}_{0.4}\text{InSe}_2$ power-dependent spectra at 5K.

4.3.3.3. CuInSe₂ sample

A secondary electron image for the pure CIS sample is shown in Fig. 4.18a and suggests an average grain size of ~1000 nm. Emission spectra were acquired at 1260 nm (blue channel), 1300 nm (green channel), and 1450 nm (red channel) wavelengths and the overlay image is shown in Fig. 4.18b. This sample also exhibits a lot of spatial and spectral variation. The red emission from this spectrum was fairly uniform throughout the sample, but with higher intensity inside the grains. This was true even close to surface facets and grain boundary edges. The other emission peaks did not luminesce well in these areas. However, the blue and green emissions were very strong near the grain boundaries. This behavior in emissions indicates that there are compositional or electrically-active defects present near or at the grain boundaries.

A panchromatic CL image (see Fig. 4.19) reveals a severe reduction in emission intensity from protuberant surface features and facets. Most grains appear to luminesce fairly well from the center regions. Enhanced emission intensity from grain boundary areas is also seen in the panchromatic CL image, confirming the monochromatic CL results.

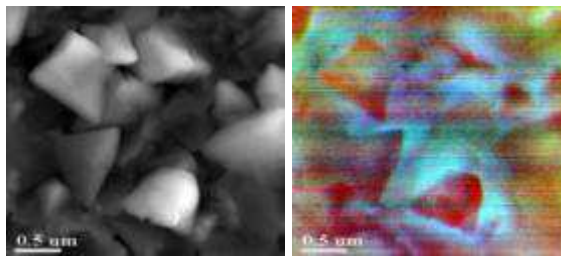


Figure 4-18. a) SEM image of CuInSe₂, b) MonoCL images overlaid with 1260 nm in the blue channel, 1300 nm in the green channel and 1450 nm in the red channel (taken in same area as Fig. 4.18a).

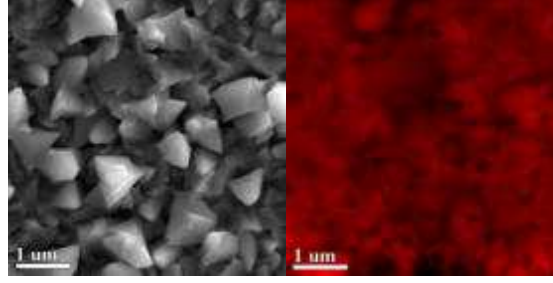


Figure 4-19. a) SEM image of CuInSe_2 , b) panchromatic CL image from Fig. 4.19a.

The power-dependent CL series (see Fig. 4.20) shows even broader emissions for the CIS sample (FWHM = 95 meV for the 160 pA spectrum), even though the individual peaks required to fit the data do not get broader. In fact, 4 or more Gaussian peaks are necessary in order to obtain a best fit for the data. All peaks blue-shift 22-32 meV with increasing power and an additional peak at higher energies (1201 nm, 1.03 eV) is observed above 640 pA. These spectra also seem to have high and low energy exponential tails, especially at high powers, although more analysis will be necessary to fully understand the behavior.

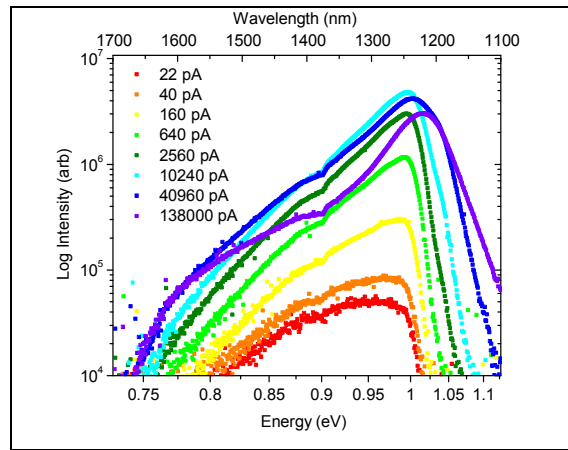


Figure 4-20. CuInSe_2 power-dependent spectra at 5K.

4.3.4. Conclusions about the CL study on ACIS thin films

In summary, cryogenic CL experiments have been performed on ACIS thin films. Emissions from AIS are more uniform both spatially and spectrally than Cu-containing samples. AIS is also less affected by reduced emission from surface features, presumably due to less surface recombination. Cu-containing samples exhibit enhanced luminescence from grain boundaries or inter-grain areas and localized luminescent variations indicative of compositional or electrically-active defect fluctuations. This was more apparent from grain to grain in the ACIS, as it showed the most variation among the samples in emission from one grain to another. The CIS sample showed the most variation in emission from grain to grain boundary, indicating possible chemical fluctuations at the grain boundaries. As the Cu content in the films increases, emissions get broader indicating a larger number of specific defect states (more local chemical variation). Further experiments, such as temperature-dependent measurements of the Hall Effect, CL and PL will be necessary to fully characterize the transitions and assign defect levels to each. Local chemistry probes, such as transmission electron microscopy combined with energy dispersive x-ray spectroscopy, will help confirm changes in chemistry between grains and their boundaries.

The results presented here have implications for device operation. First, the relatively uniform luminescence from the AIS sample suggests that this material may produce more uniform cell performances, because reduced fluctuations in chemical composition and band structure from one location to another would result in more efficient energy collection. Variations in band structure would shunt the device locally, leading to low current high voltage grains with large energy gaps being shunted by

adjacent high current low energy gap grains. The more uniform behavior in the AIS should produce better performance. At the same time, reduced surface recombination in air-exposed samples could result in less air-sensitivity during manufacture of AIS based devices and in less dependence on a particular method for forming the current collecting heterojunction.

4.4. Concluding Remarks and Future Work

The observations in section 4.3 corroborate with those found in section 4.2. The lack of surface defects found in the AIS sample in section 4.3 could add an explanation for the different growth mode of AIS seen in section 4.2. A lowered surface defect condition can be attributed to the S-K growth method through relieving the surface tension via elastic undulations to the substrate in what is known as the Grinfeld instability [Markov 1995]. In general, corroborations of the conclusions pertaining to structural and optical features described in section 4.2 with the conclusions about structural and electrical features described in section 4.3, aid greatly in the complete understanding of the opto-electronic nature of a ACIS thin film material. This full characterization is part of an exploration of how Ag can be used to optimize this chalcopyrite family.

Part of the solution to figuring out the dynamics of how Ag helps in the ACIS system is to study other phases that may exist in the production of these films due to the conditions in which they were grown. Phases such as Ag_{2-x}Se , much like Cu_{2-x}Se were studied in the past [Khatri 2009]. A simple understanding of the reaction pathways and possible phases of a system can also be insightful. A study by Nichols et al. found that

films at higher deposition temperatures than 120 °C were metallic while those deposited lower than this temperature are semiconducting [Nichols 2008].

The melting point of copper is 1068 °C while silver is 962 °C. Similarly, the melting point of Ag₂Se is lower than Cu₂Se according to Miyatani [Miyatani 1973]. Likewise, CIS and AIS have a melting point of 987 °C and 782 °C respectively. Since the deposition temperature is much closer to the melting point of the sample, this could mean the elimination of some of the defects as the composition of Ag increases in ACIS [Ehrhart 1991].

Future studies will include epitaxial growth of ACIS thin films to determine the single crystal properties—allowing for the direct comparison of the polycrystalline samples grown here. In the next chapter, we will explore ACIS thin films in solar cell devices—including the addition of Ga and growth by the two-stage process.

Chapter 5

(Ag,Cu)(In,Ga)Se₂ (ACIGS) materials and devices

5.1. Background

5.1.1. Motivation

As was observed in the previous chapter, alloying Ag with Cu has an effect on growth mechanisms, grain size, and band gap. Two questions can then be asked: (i) How can this information be used to engineer a high-quality solar cell; and (ii) What can a high efficiency solar cell tell us further about the material? It would seem that material and device fabrication are both necessary for a complete understanding. Thus, in this chapter (Ag,Cu)(In,Ga)Se₂ (ACIGS) thin film solar cell devices are fabricated via hybrid d.c. sputtering deposition technique. This deposition technique has not been used to produce ACIGS solar cell devices anywhere else to our knowledge.

5.1.2. Review of ACIGS cells

Much of what was learned in the previous chapter, concerning ACIS, can be directly applied to ACIGS films. The addition of Ga is advantageous because it causes the allowable noble metal (Group I) content ratio, (Ag+Cu)/(In+Ga) (previously called

“Cu content”), to be wider, ensuring that a good solar cell can be made even if the noble metal content fluctuates. In CIGS films, the Cu content should be between 22 and 24 percent [Schock, 2004]. Also, varying Ga as well as Ag allows us to optimize their content, since both increase the band gap from the CIS band gap of 1.0 eV. The price of Ag has usually been comparable to that of Ga, and at points in time, Ag has even been less expensive than Ga [Bloomberg, 2011]. In this chapter’s study, Ag was optimized to reduce Ag content, while focusing on improving the efficiency by exploiting what was learned from the previous chapter concerning the Cu/(Cu+Ag) ratio.

5.2. ACIGS single stage solar cells

5.2.1. Experimental setup

Solar cell devices were produced by a hybrid evaporation and sputtering process. Three targets were used in the deposition: Ag, In, and an alloy of Cu/Ga. The powers of the targets were calibrated so that the individual sputtering rates of the targets produced the desired composition. The “x” used to describe the Cu to Ag ratio is redefined in this chapter to be “z”: $z = \text{Cu}/(\text{Cu}+\text{Ag})$. This was done because “x” is conventionally used to denote the Ga to In ratio in CIGS films, as it is here: $x = \text{Ga}/(\text{Ga}+\text{In})$. As an expansion of the conventionally used “y” ratio used in CIGS, “y” is used to denote the Group I elements to Group III elements: $y = (\text{Ag}+\text{Cu})/(\text{Ga}+\text{In})$.

Solar cells were deposited on soda-lime glass covered with molybdenum. The molybdenum was deposited in 5 mTorr of Argon at 50 W. The final thickness of the layer was between 0.8 and 1 μm . After the ACIGS deposition, a CdS layer was deposited by chemical bath deposition at 60°C, following a standard solution containing 0.0015 M

thiourea, 0.1 M cadmium acetate and 1M ammonium hydroxide. Following the deposition of this 50-60 nm layer, an intrinsic ZnO layer was deposited in 5 mTorr of Argon at 50 W, followed by a ZnO:Al layer in the same conditions, using a 99.999% pure ZnO target and a 99.995% pure ZnO:Al target respectively.

Six types of samples were deposited. They have the following x, y, and z values:

Table 5.1. Samples grown at different compositions.

Run number	x	y	z
10150	0.25	0.74	0.81
10152	0.22	0.73	0.82
10153	0.22	0.85	0.84
10154	0.25	0.90	0.81
10155	0.20	0.76	0.90
10157	0.26	0.96	0.77

These compositions were chosen because the values of x and y are within the range that is typically used for CIGS solar cells without Ag. The value of x was kept within the range of typical values of Ga replacement of In: 20% to 30% [Schock]. Also, the value of 1 - y should be held above 24% [Schock] to prevent phase separation. The ranges of z were varied to sample the amount of Ag content that produced the largest grain size. As grain size vs. composition was shown in the previous chapter, this range of z was chosen to be centered around z = 0.80. Using Ag to substitute for Cu may appear

to be economically unwise since Ag is more costly than Cu. However, since Ag increases the band gap, it can also be used to effectively replace some of the Ga too.

5.2.2. J-V and QE measurements

The J-V results are summarized in the Table 2 below and in Figure 1 and 2.

Table 5.2. Results of the J-V measurements for the various samples, with Voc, Jsc, FF, Rs, Rsh, efficiency and band gap extracted from QE.

Run number	Efficiency (%)	Eg (eV)	Voc (V)	Jsc (mA/cm ²)	Fill Factor (%)	Rshunt (ohms/cm ²)	Rseries (ohms/cm ²)
10150	11.6	1.08	0.54	32.7	65.6	593	5.24
10152	12.6	1.08	0.56	33.5	66.5	337	4.82
10153	11.3	1.10	0.57	31	64.1	770	6.48
10154	11.1	1.10	0.56	28.5	69.3	118	4.72
10155	12.3	1.09	0.57	33	65.5	970	5.56
10157	10.3	1.10	0.53	32.6	59.7	568	7.7

The devices have similar V_{oc} values ranging from 0.53 to 0.57. For this set of fabricated devices, the devices with the largest V_{oc} tended to have higher efficiencies. V_{oc} in ACIGS is related to the bandgap, E_g , by $V_{oc} = E_g / e - 0.5$ V [Konagai, 2004]. A deviation from this relation might indicate that something is wrong with the junction or absorber material. On Fig. 1 and Fig. 2, the V_{oc} can be identified by observing where the J-V curve intersects with the zero current axis. These values of V_{oc} are however lower than the ones we can obtain with CIGS, where for the same band gap values as high as 0.74 V have been obtained. Another formula for V_{oc} is:

$$V_{oc} \propto \frac{E_g}{q} - A_0 - \frac{kT}{q} \ln N_t$$

Where N_t is the trap density. As can be seen from this equation, for a similar band gap as is the case here, V_{oc} will be reduced if the trap density is higher. This is something that we will be investigating in the next section, where we look at the materials properties.

Understanding parasitic resistances in the solar cell can give insight to a problematic solar cell. Usually this is easily observed on the J-V curve as a deviation from normal diode behavior, as can be recalled in Eqn. 1.4,

$$I = I_L - I_O \left[\exp \left(\frac{q(V + IR_s)}{nkT} \right) - 1 \right] - \frac{V + IR_s}{R_{SH}}.$$

This equation allows us to point several things out about R_s and R_{sh} . R_s does not effect V_{oc} since at open circuit, the term $I R_s$ vanishes. However, a high R_s may reduce J_{sc} . Similarly, R_{sh} has no effect of J_{sc} because V/R_{sh} disappears in this equation at short circuit. However, low R_{sh} may be correlated with a low V_{oc} and have a negative gradient at the $V = 0$. An example of the effect of these parasitic resistances may be taken in the case of 10152, the champion solar cell of this series. It has one of the lowest series resistances and the highest J_{sc} . The only cell to have a lower series resistance is 10154. Oddly enough, this cell also has the lowest J_{sc} of the series. This tells us that this cell has a purely optical loss problem that is not due to an electrical parasitic resistance.

J_{sc} for the series of films appears to be fairly consistent, as confirmed by the similar QE plots in Fig. 4. The variation in J_{sc} here is partly due its relation to the band gap, E_g . That is J_{sc} will tend to decrease for increasing E_g due to a loss of absorption at higher wavelengths for larger bandgaps. Since V_{oc} is linearly related to E_g and J_{sc} is inversely related to E_g , this is what is usually known as the “trade-off” of V_{oc} and J_{sc} . On Fig. 1 and Fig. 2, J_{sc} can be identified by observing where the J-V curve intersects the zero voltage axis. In these figures, the current is divided by the area of the cell, 0.5 cm^2 , to get the J_{sc} reported in Table 1.

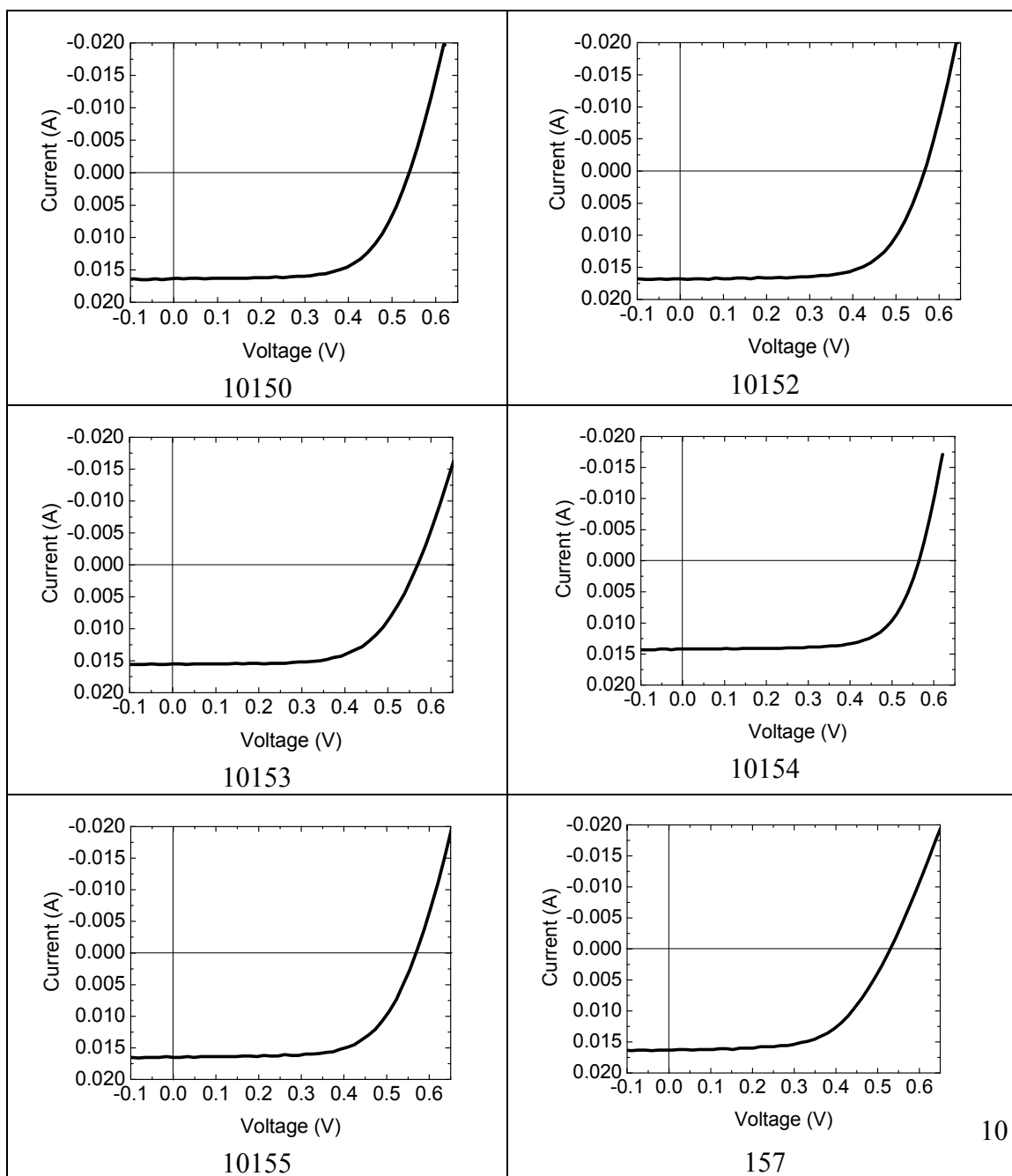


Figure 5-1. J-V curves for the 6 types of sample deposited.

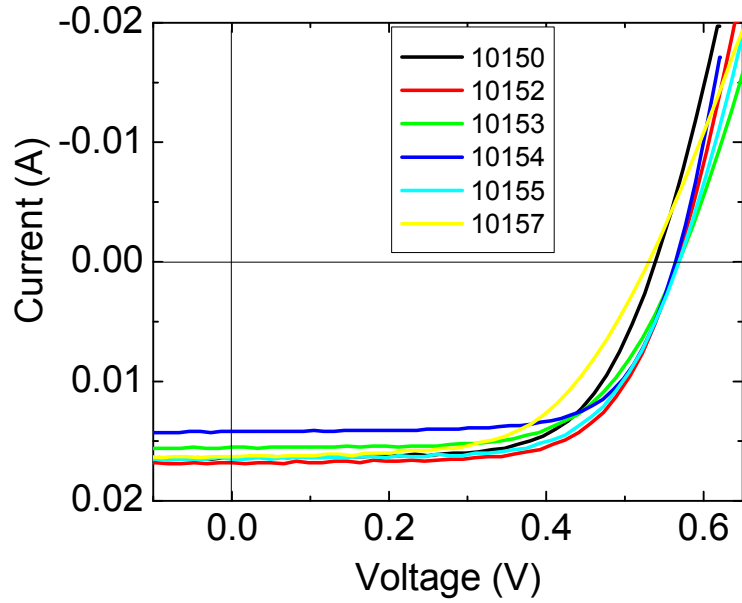


Figure 5-2. Comparison of the J-V curves for the six types of samples deposited

The QE measurements of the devices are summarized in Fig. 3 – Fig. 6. The shape of these curves are similar to those obtained for CIGS, due to the same chalcopyrite structure, and can be interpreted similarly as such. For example, the gradient seen on the left side of Fig. 3 and Fig. 4 (and magnified in Fig. 6), is due to the variation in the CdS thicknesses between the samples. These variations arise out of the nature of the chemical bath deposition method used to deposit CdS, whereby a small change of concentration of one of the three solutions, in time in each of the steps or in temperature of any solution as an effect on thickness. The change on the left side of Fig. 3 and Fig. 4 (as magnified in Fig. 5) is due to the variation of the band gap between the different absorber layers. If the linear line from the top of Fig. 5 is extended to the wavelength axis, the bandgap can be found by the relation $E_g = 1240 \text{ eV nm} / \lambda \text{ (nm)}$.

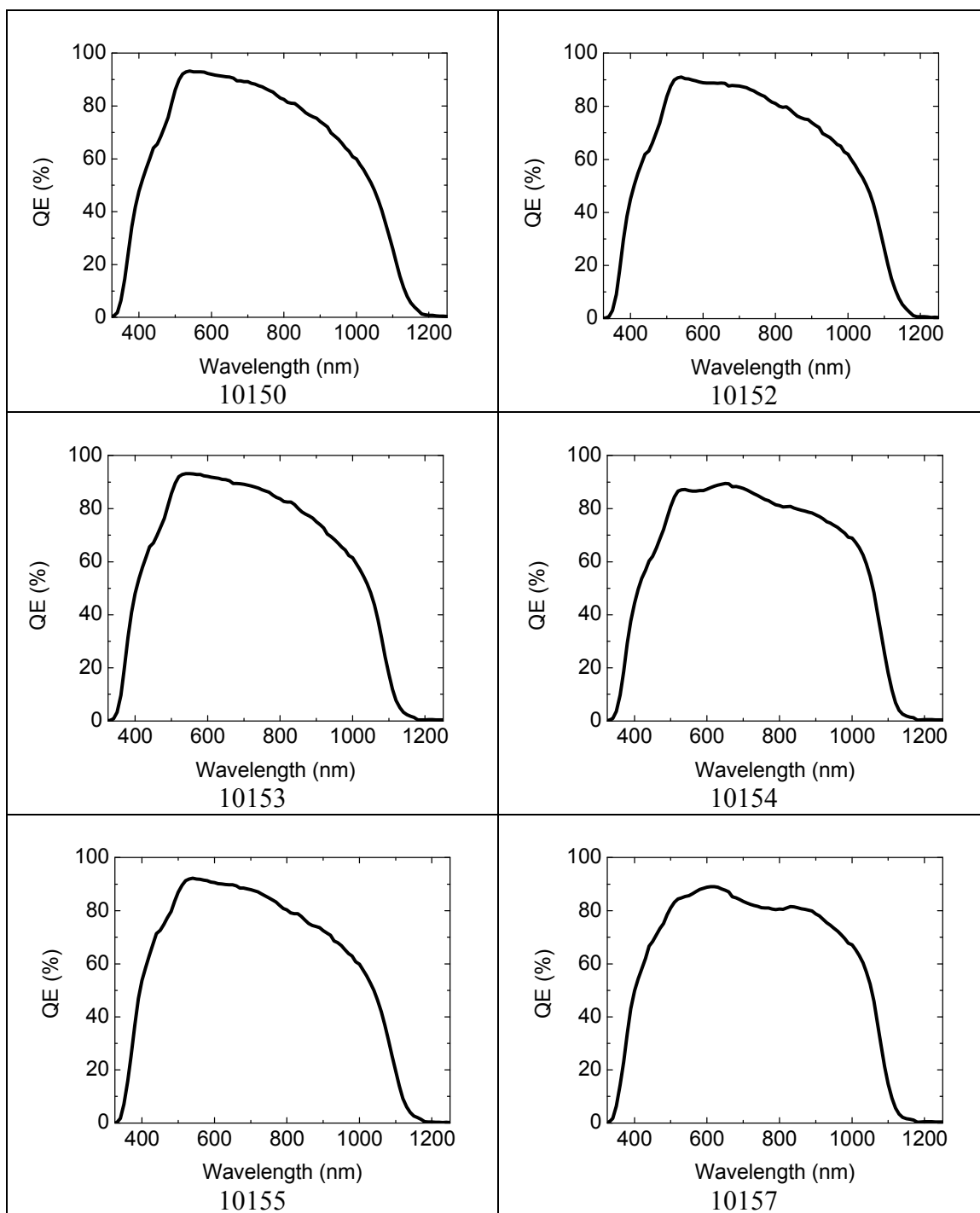


Figure 5-3. Quantum Efficiency measurements for the 6 types of samples deposited.

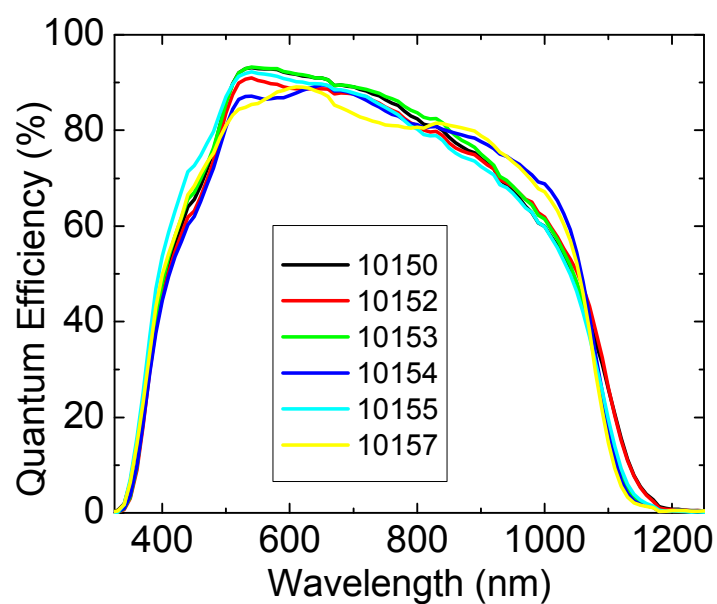


Figure 5-4. Comparison of the QE curves for the six types of samples deposited

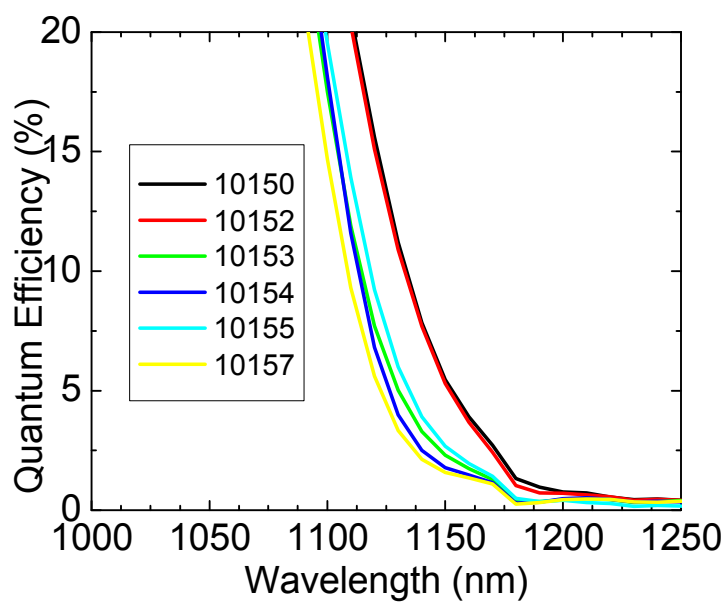


Figure 5-5. Comparison of the high wavelength range for the QE curves for the six types of samples deposited

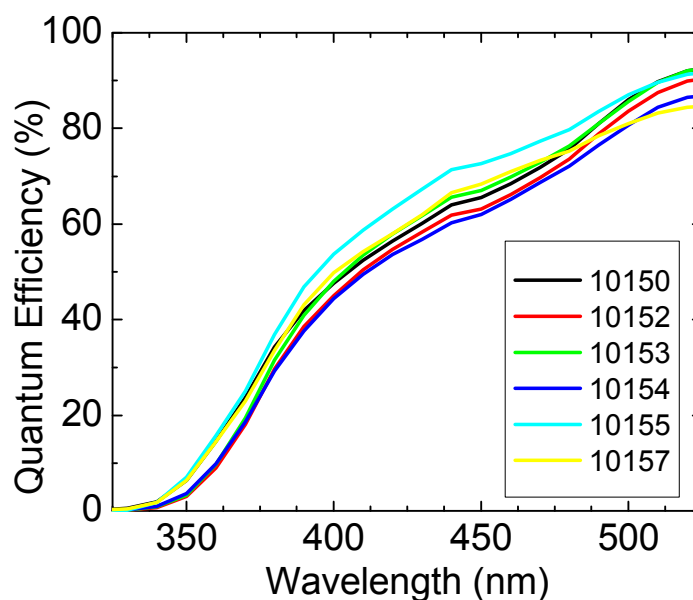


Figure 5-6. Comparison of the low wavelength for the QE curves for the six types of samples deposited

The band gap was extracted from Fig. 5 and plotted in Table 1. This value allows for a better understanding of the variation of V_{oc} and J_{sc} as explained previously.

Finally, the integration of QE over the solar spectrum (usually at AM 1.5) gives the value of J_{sc} . For these devices, a good correlation between J_{sc} reported from the current vs. voltage measurement and integrated value from QE was observed.

5.2.3. Material Characterization

The same devices that we studied in the previous section were also characterized by XRD, SEM and SIMS to correlate their electrical properties with structural and chemical analysis.

5.2.3.1. XRD Results

XRD measurements were done in a theta-2 theta mode for the 6 samples. The results are summarized in Table 3 and 4, and in Figure 7. In Table 3, the position, height, full width at half maximum and area of the (112) peak (also named 1st P), and of the (220) peak (also named 2nd P) are reported. In Table 4, the ratio of the height of the (112) peak to the (220) peak, the ratio of the area of the (112) peak to the (220) peak as well as the efficiency of the corresponding solar cells are reported. In Figure 7, the efficiency of the solar cell as a function of the ratio of area of the (112) peak to the (220) peak is plotted.

Table 5.3. Comparison of the position, height, full width at half maximum and area for the (112) and (220) peak of our six samples.

Sample	1 st P Pos	1 st P Height	1 st P FWHM	1 st P AREA	2 nd P Pos	2 nd P Height	2 nd P FWHM	2 nd P AREA
10150	26.71	6754	0.18	1242	44.30	5183	0.33	1715
10152	26.72	4800	0.08	384	44.38	5533	0.27	1493
10153	26.72	6129	0.09	551	44.33	1831	0.19	347
10154	26.67	6602	0.07	462	44.25	1349	0.08	107
10155	26.80	6142	0.10	614	44.50	3085	0.19	586
10157	26.60	4098	0.08	327	44.25	2128	0.05	106

Table 5.4. Comparison of the ratio of the height and area of the (112) and (220) peaks for our six samples with the efficiency of the solar cells.

Sample	Height (112)/(220)	Area (112)/(220)	Eff (%)
10150	1.30	0.72	11.6
10152	0.86	0.25	12.6
10153	3.34	1.58	11.3
10154	4.89	4.28	11.1
10155	1.99	1.04	12.3
10157	1.92	3.08	10.3

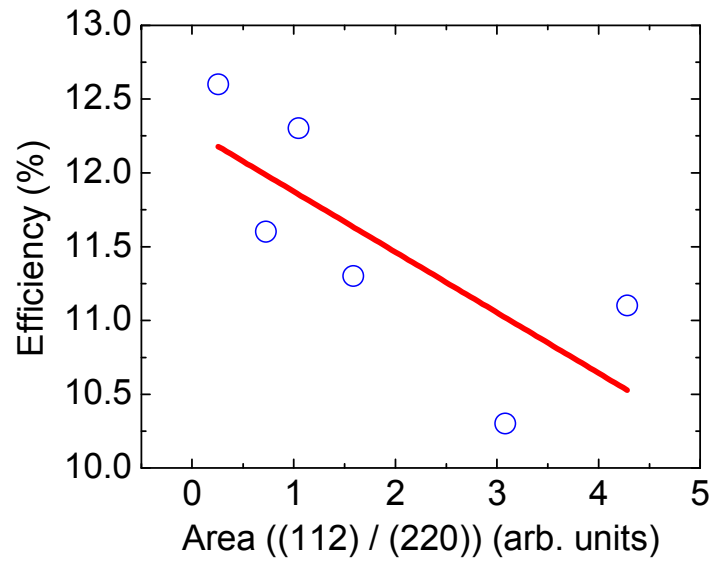


Figure 5-7. Plot of the efficiency of the solar cell as a function of the ratio of the area of the (112) to the (220) peaks for the six types of samples deposited

ACIGS films have a chalcopyrite structures that share the $I-42d$ space group.

The lattice parameters between CIS, CGS and AIS can be related in a plane as an extension to Vegard's law. The lattice parameters of CIS are $a = 5.78 \text{ \AA}$ and $c = 11.6 \text{ \AA}$,

while the lattice parameters of CGS is $a = 5.61 \text{ \AA}$ and $c = 11.02 \text{ \AA}$. This leads to the relations for CIGS of: $a (\text{in \AA}) = 5.78 - 0.17 x$ and $c (\text{in \AA}) = 11.6 - 0.58 x$, where x is as defined previously as the Ga:In content. Similarly, AIS has lattice constants of $a = 6.10 \text{ \AA}$ and $c = 11.7 \text{ \AA}$, which leads for ACIS to $a (\text{in \AA}) = 5.78 + 0.32 (1 - z)$ and $c (\text{in \AA}) = 11.6 + 0.14 (1 - z)$, where z is defined as the Ag:Cu content. Combining these equations leads to the relationship for ACIGS: $a (\text{in \AA}) = 5.78 - 0.17 x + 0.32 (1 - z)$ and $c (\text{in \AA}) = 11.6 - 0.58 x + 0.14 (1 - z)$. So, starting with CIS, substituting Ga decreases both lattice constants and substituting Ag increases both the lattice constants. Lattice constants usually are inversely proportional to the band gap, but in the case of the substitution of Ag with Cu, the band gap increases even though the lattice constant also increases. By knowing the lattice parameters, it is therefore possible to calculate the peak positions from x and z .

As can be seen in Fig. 7, in which the data is related in Fig. 3 and Fig. 4, a correlation between the efficiency and peak area ratio is established where the efficiency increases for lower $[112]/[220]$ ratios. This has been observed previously in CIGS by other authors [Chaisitsak 2002]. The reason given by Chaisitsak et al. was that cells with lower $[112]/[220]$ ratios had more Cd that diffused into the absorber layer at the interface, which allowed for the formation of a better homojunction. Excess Cd-doping, however decreased this favorable behavior as was seen in a loss of V_{oc} . In the case of ACIGS, an optimum value of (x, z) may be found by maximizing this ratio using XRD simulation software. In this way, the Ag content may be used as an optimization parameter in maximizing the efficiency of ACIGS beyond what is possible for CIGS.

5.2.3.2. x-SEM

Cross section SEM (x-SEM) was performed on the series of solar cells by cleaving the sample and executing SEM on the profile of the cell. The x-SEM images are shown in Fig. 8. Fig 8 – 10155 is what is typically seen in a high efficiency solar cell – large, vertically aligned grains that appear to go from the molybdenum surface to the top of the sample. However, the efficiency in sample 10155 is only second best of the series with 12.3% efficiency. The champion solar cell of this series, 10152 with an efficiency of 12.6%, appears to have smaller grains that do not appear to be as vertically aligned. It is interesting to note that the XRD FWHM (112 peak), which is inversely proportional to the grain size (Chapter 2 and Chapter 4), is the smallest in this champion cell, suggesting that the grain size is the largest in this sample. Larger grain sizes are usually beneficial to device properties since the defect states are reduced in the entire volume of the absorber layer. Another cell, 10157, that is tied with the champion cell for the smallest (112) XRD FWHM, has what appears to be the largest grain size of the series. This cell, however, only has an efficiency of 10.3%. So, why is this cell not as efficient as the champion? By comparing the V_{oc} of the two cells, 10157 has a higher band gap than 10152, but has a lower V_{oc} . This suggests that while the absorber layer appears to have large grains in 10157, the junction quality or material quality is creating defect states that lower V_{oc} . While the grain size can be correlated to the FWHM of any peak in the XRD spectra, the largest peak is usually chosen to maximize the signal to noise ratio.

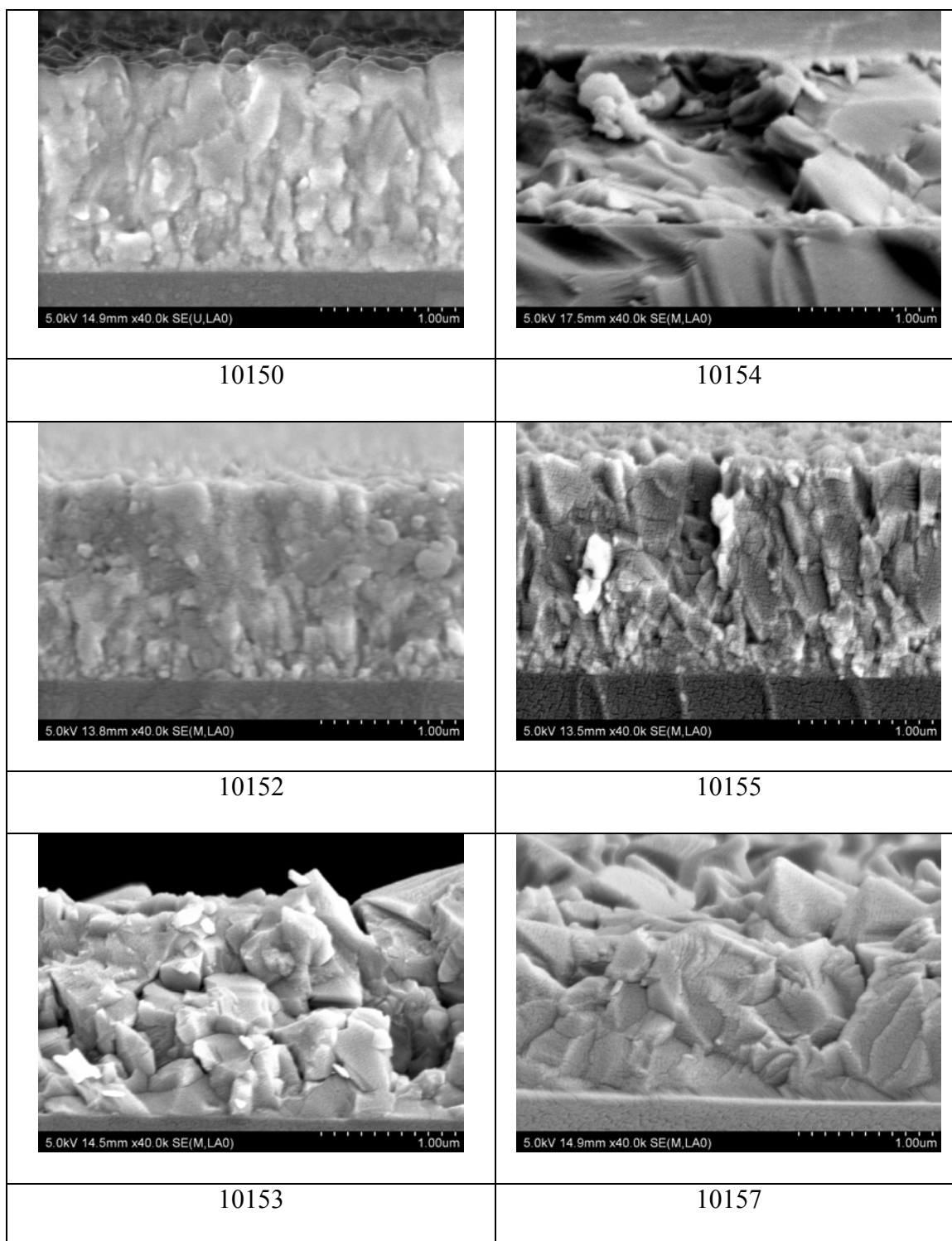


Figure 5-8. Cross section SEM of ACIGS samples

In this case, looking at the inverse of the FWHM of the (220) peak corresponds very well with the apparent grain size in Fig. 8.

Also observed in Fig. 8, is the top surface of the solar cell. It has been observed that sometimes more specularly reflective films (less rough) have a higher efficiency. This may be due to the complications that arise if CdS is not thick enough. Looking at cell 10157, we see that the surface of the cell appears very rough. Also looking at the QE around CdS absorption (Fig. 6) of this particular cell compared to the other cells, reveals that this cell might have had a thin layer of CdS deposited on the surface. If this conclusion is true, it corroborates well with the previous statement that V_{oc} is low due to a contact issue. Also from the QE of 10157 in the 600 – 800 nm region, a dip occurs. This dip may be caused by undesired optical effects caused by the diffuse surface of this cell.

5.2.3.3. SIMS measurements

Secondary ion mass spectroscopy was performed on some selected samples to further understand the difference between our ACIGS samples deposited by the hybrid process and regular CIGS samples deposited by evaporation. The results of these SIMS analysis are reported Figure 9 for a typical CIGS sample and Figure 10 for the ACIGS sample 10155. This ACIGS sample was selected for its relatively high efficiency (12.3%) but smaller grain size. Only selected ions are represented on both figures as a function of time, which is equivalent to a depth profile of the sample. The surface of these samples is on the left side of the figures and the substrate is on the right side.

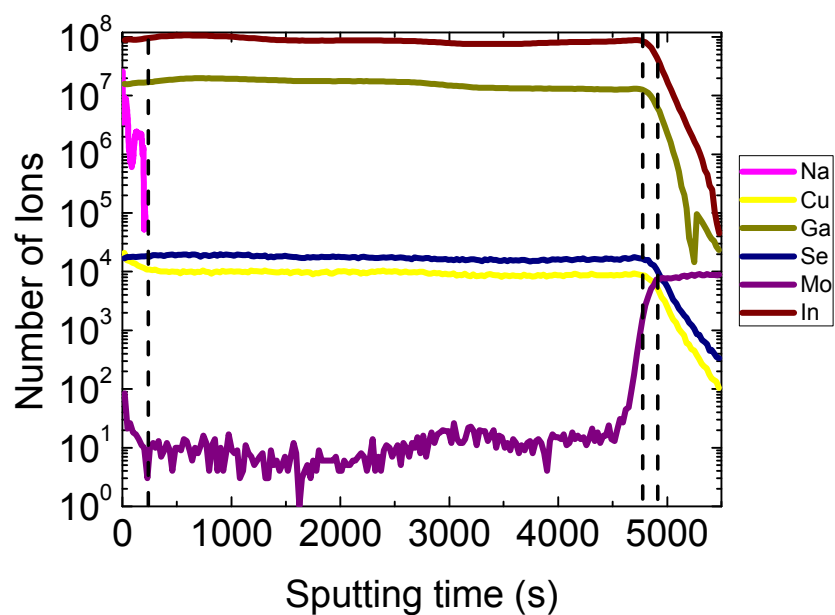


Figure 5-9. SIMS depth profile for a typical CIGS film deposited by evaporation

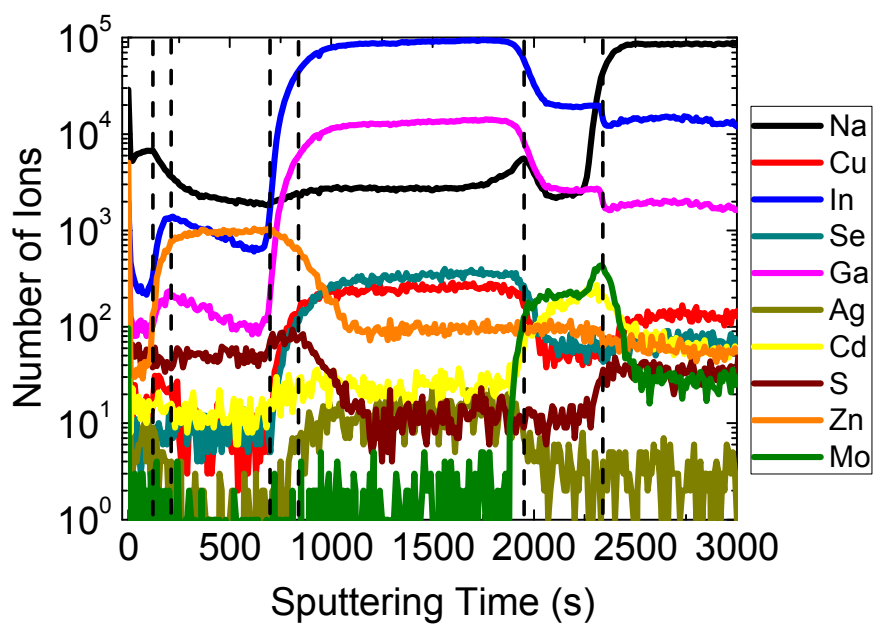


Figure 5-10. SIMS depth profile for sample 10155

Fig. 5.9 includes from the left, the CdS layer, the absorber layer and the substrate, whereas Figure 5.10 represents the completed solar cell of 10155. While Fig. 5.9 appears to have a fairly uniform distribution of constituent elements within the absorber layer, in Fig. 5.10 it appears that the amount of these elements drops towards the ACIGS – CdS interface (fourth dashed line from the left).

This uneven gradient may cause a problem at this interface – especially if the x, y, or z change in a way that is not favorable to a good junction. Also, in Fig. 5.10, there is a build up of Na near the Mo surface that is not observed for the CIGS sample.

5.3. Conclusion

We have successfully deposited ACIGS solar cells by a one stage hybrid process with efficiency as high as 12.6%, without MgF_2 AR coating. The efficiency seems to be mainly limited by a low V_{oc} associated with a low FF , compared to an evaporated CIGS solar cell with equivalent band gap. XRD, SEM and SIMS analysis seems to indicate a strong influence of the crystal orientation on the efficiency, a grain size and grain distribution different from the standard one observed in CIGS and a compositional distribution of the elements (with lower Cu and Ag at the interface with CdS) that might lead to a lower quality junction, and therefore enhanced recombination. However, this is still the highest efficiency obtained with the hybrid process to our knowledge and shows therefore the potential that both the process and the material has.

Chapter 6

ACIGS materials and devices deposited by 2-stage hybrid deposition method

6.1. Background

Up unto this point, the depositions reported have been done using a one-stage process. The one-stage process is simply keeping the deposition rates constant throughout the entire length of the deposition. This is accomplished in the hybrid system by keeping the powers of the targets constant. The evaporated Se rate is maintained in excess of the stoichiometric amount to create a Se environment for the reacted elements on the substrate. Even though the Se is kept three or four times higher than stoichiometric, the final film composition shows 50% Se in every experiment.

The 2- and 3-stage processes were developed by Boeing, Bell Labs, etc. [Shafarman 2003] to increase the grain size or create band gap gradient and, in effect, increase the conversion efficiency. The highest efficiency solar cells that have been reported were deposited by a 3-stage process with an efficiency of 19.6% [Green, 2011]. During the 1-stage process, the film is always Cu-poor whereas during the 2-stage and 3-stage processes, the film becomes Cu-poor only at the end of the deposition. Cu-poor

Cu(In,Ga)Se₂ absorber layers grown by 2-stage and 3-stage processes are best suited for high efficiency solar cells. During these processes, there are compositional changes during the film growth as well as Cu-rich to Cu-poor transitions. Due to these changes, the electrical and optical properties of the films also change during the growth. To grow better quality Cu(In,Ga)Se₂ films and to improve the device efficiency, it is necessary to understand these evolution of material properties. Since the properties of Cu(In,Ga)Se₂ evolve during growth i.e. at temperature of around 550 °C, it is also of interest to study the changes in the properties at deposition temperature and then correlate these properties after the growth with other measurements.

Multiple stage processes may yield higher grain size and efficiencies, but there are consequences in terms of the increased complexity. Yet, solar cell manufacturers would be willing to incorporate this into their process as long as the throughput is not significantly decreased. Conventionally, multiple stage processes employ a technique called “end-point detection” to identify the end or status of the stage. This is accomplished by monitoring the temperature of the substrate (via thermocouple, pyrometer, etc.) or power necessary to maintain a temperature set-point to identify the phase transition between Cu-rich and Cu-poor or vice-versa [Ranjan, 2011]. For example, in the case of the 2-stage process, the substrate transitions from Cu-rich to Cu-poor after the Cu source or target is turned off or diminished. With the end-point detection, the person or machine monitoring the deposition is able to tell when the transition is complete. Recent advances in ellipsometry [Ranjan, 2011] have allowed for end point detection via ellipsometry.

6.2. Experimental results on the thin films

To investigate the effects of the two stage process for the hybrid sputtering process, a set of four depositions were performed at 510 °C: AIS 1-stage, AIS 2-stage, CIS 1-stage and CIS 2-stage. Samples were deposited at 510 °C to prevent cracking of the Mo-coated soda lime glass substrate during the deposition. In this set of experiments, Ga was not used due to physical limitations of the sputtering machine. Since we wanted the second stage of this set of experiments to be completely without Cu or Ag, Ga could not be used because it is coupled with Cu and Ag in this hybrid deposition system.

6.2.1. XRD Results

The four types of films (CIS and AIS, 1 and 2 stage process) were characterized using x-ray diffraction in theta-2 theta mode. The results of the scans are reported in Figure 1 for the individual scans and figure 2 for a comparative scan. A summary of the results for the two main peaks (the (112) and the (220) peaks) are reported in Table 1 and 2. One can see that (see Figure 3-5 for details):

- the intensity of the main peak is higher for CIS than for AIS
- CIS 1-stage and 2-stage process only have 3 peaks corresponding to the (112), (220) and (313) orientation.
- AIS 1-stage process has 4 peaks corresponding to the (112), (220), (312) and (313) orientation
- AIS 2-stage process XRD spectrum has a very different shape. Even though the (112) and (220) peaks are still present, there is also other peaks corresponding to another phase $\text{Ag}_3\text{In}_5\text{Se}_9$.

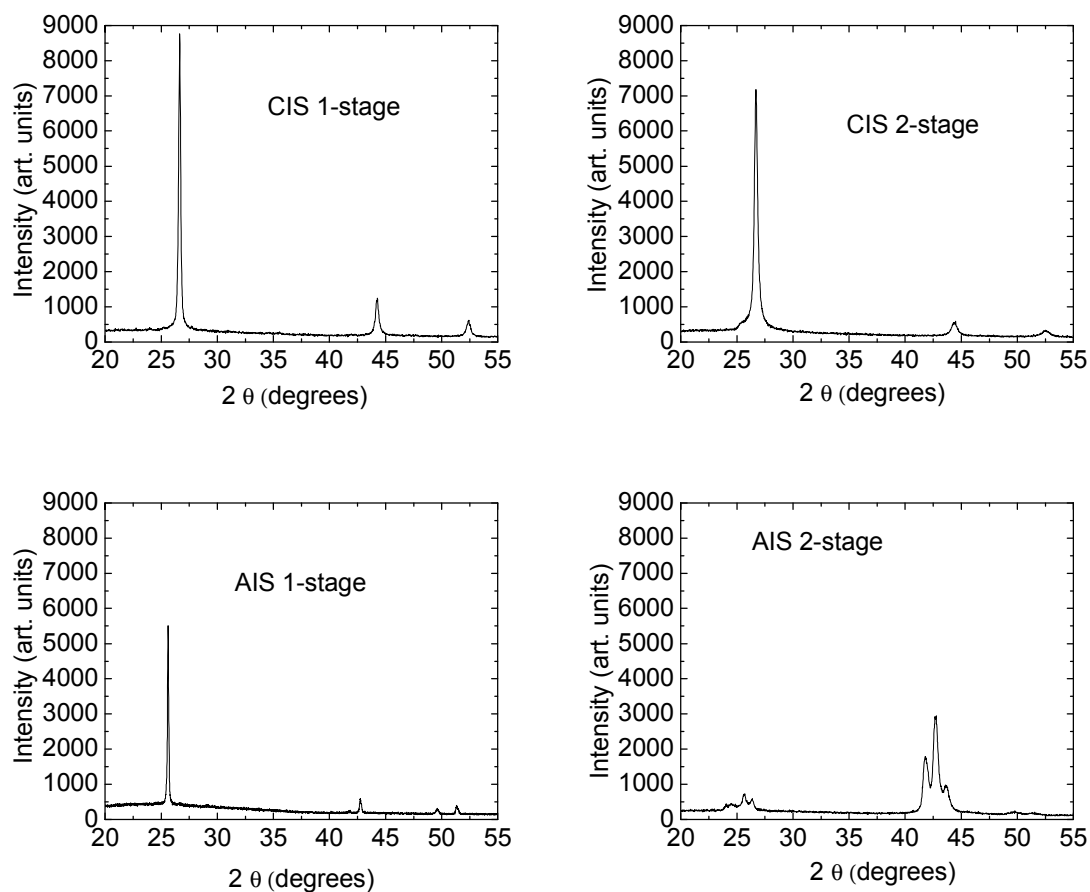


Figure 6-1. XRD results for CIS and AIS 1-stage and 2-stage processes.

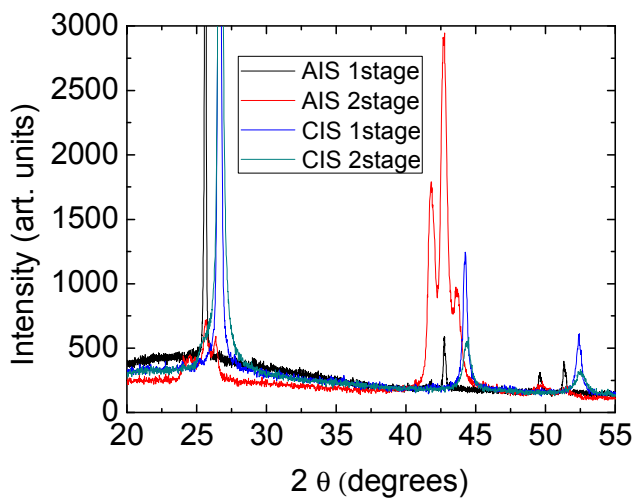


Figure 6-2. Comparison of the XRD patterns for the CIS and AIS films deposited by 1-stage and 2-stage processes

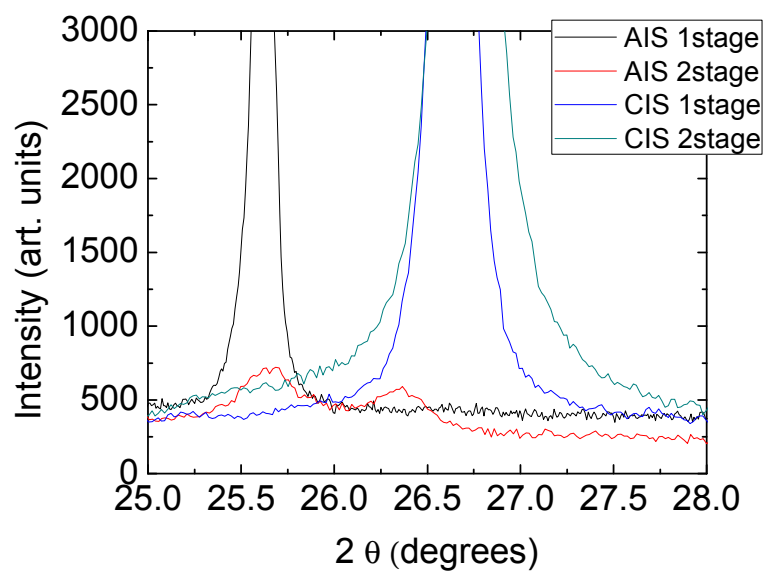


Figure 6-3. Detail of the (112) peak for the CIS and AIS films deposited by 1-stage and 2-stage processes

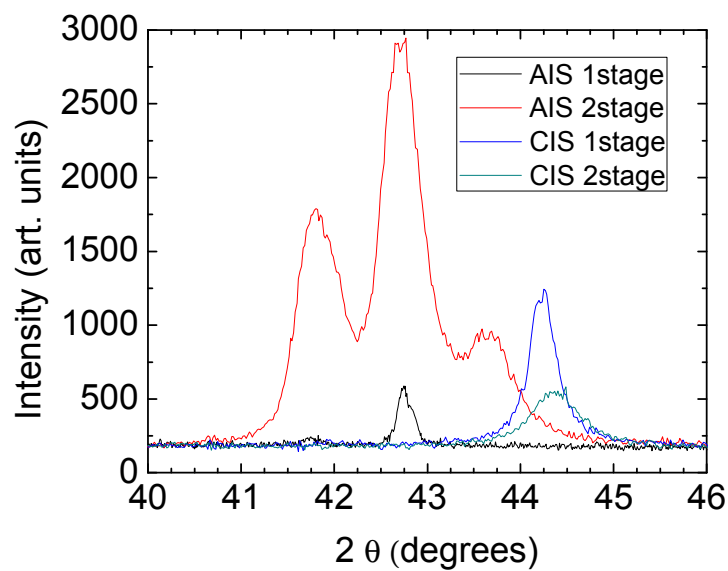


Figure 6-4. Detail of the (220) peak for the CIS and AIS films deposited by 1-stage and 2-stage processes

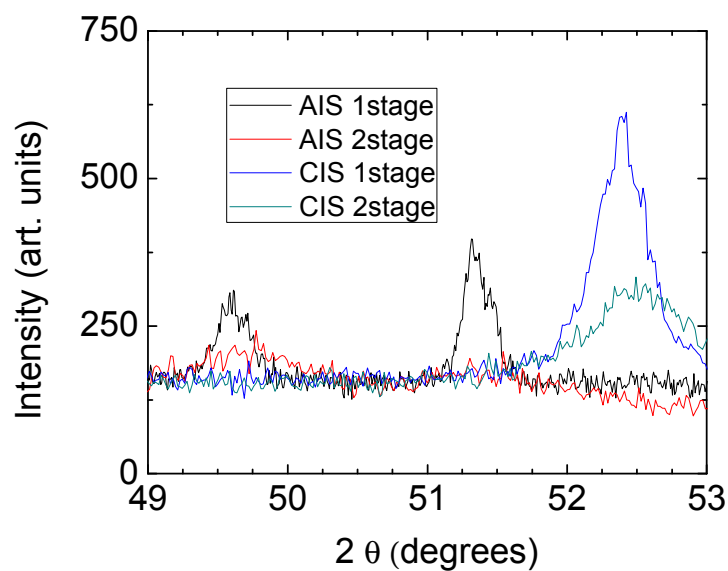


Figure 6-5. Detail of the (312) peak for the CIS and AIS films deposited by 1-stage and 2-stage processes

Table 6.1. Position, Height, FWHM and Area for the (112) and (200) peaks for the CIS and AIS films deposited by 1-stage and 2-stage processes

Sample	1 st P Pos	1 st P Ht	1 st p FWHM	1 st P AREA	2 nd P Pos	2 nd P Ht	2 nd P FWHM	2 nd P AREA
CIS 1-stage	26.64	8386	0.117	981	44.27	1030	0.067	69
CIS 2-stage	26.67	6754	0.184	1242	44.31	346	0.234	80
AIS 1-stage	25.60	5085	0.076	390	42.75	401	0.086	34
AIS 2-stage	25.72	418	0.117	25	42.81	1078	0.167	180

Table 6.2. Comparison of the height and the area of the (112) and (200) peaks for the CIS and AIS films deposited by 1-stage and 2-stage processes

Sample	Height [112]/[220]	Area [112]/[220]
CIS 1-stage	8.1	14.2
CIS 2-stage	19.5	15.3
AIS 1-stage	12.6	11.2
AIS 2-stage	0.20	0.146

The presence of this 2nd phase for the AIS 2-stage process is a problem, since secondary phase tends to deteriorate electrical and optical properties, and therefore devices properties.

The shift in the peak position observed for the AIS compared to the CIS is due to Vegard's law, where the peak position is directly related to lattice constants.

The ratio of the height and area of the (112) peak to the (220) peak is roughly the same for the CIS 1-stage and 2-stage processes, as well as for the AIS 1-stage process indicating no specific influence of the deposition process or material on the preferred orientation of the crystallites for these films.

As was previously mentioned, the main intent behind using a two-stage process is to enhance the grain size. However, the FWHM of these data tend to increase when going from 1-stage to 2-stage for both AIS and CIS; it therefore seems that the 2-stage process is not beneficial for the grain size for these 2 compounds when using the hybrid process.

6.2.2. SEM

Surface scanning electron microscopy images of the four samples (CIS and AIS, 1-stage and 2-stage) were taken and are presented in Figure 6. As one can see, the surface of the CIS 1-stage process seems to have the larger grains, while the one of the CIS 2-stage process seems to be rougher. Comparing the two CIS images, CIS 1-stage appears to have larger grains than the CIS 2-stage, corroborating with the XRD results.

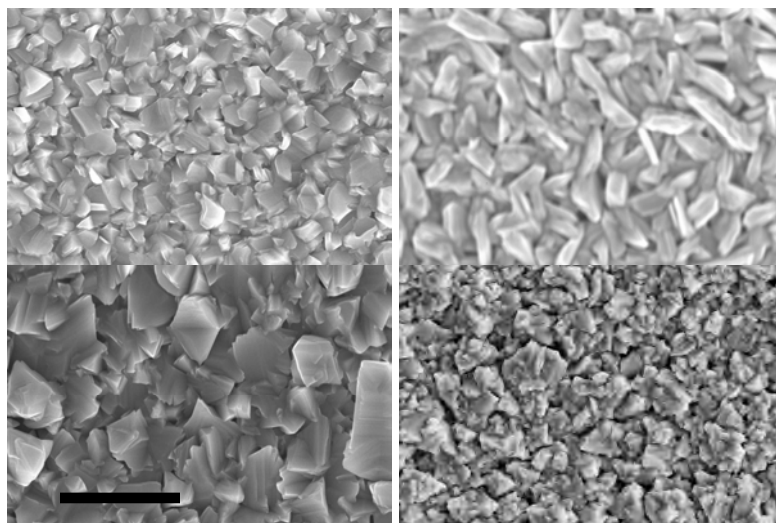


Figure 6-6. SEM surface image for the four different types of samples (scale bar is 2 μm)
 Top: AIS 1-stage (left), AIS 2-stage (right)
 Bottom: CIS 1-stage (left), CIS 2-stage (right)

XRD suggested that the grain size of AIS 1-stage is larger than that of AIS 2-stage. In the SEM image of Fig. 6, the AIS 2-stage appears to be more elongated than AIS 1-stage. The length of this elongation appears to be larger than the AIS 1-stage grains, but the width appears smaller.

6.2.3. Ellipsometry analysis

Ellipsometry as an analysis tool for measuring optical constants (or the dielectric function) has become more standard than extracting optical constants from Kramers-Kronig relations. Ellipsometry, with its ability to measure at multiple angles of incidence and multiple wavelength collection over a short period of time, makes it a perfect tool to measure and monitor the evolution of films grown in a deposition chamber *in situ* and in real time. The typical ellipsometer used is the M-2000 rotating compensator ellipsometer from the Woollam Company, which is capable of measuring 706 pairs of (ψ, Δ) data in a

short period of time (1-12 seconds). The amount of data largely outnumbers the amount of variables desired, so a least squared regression analysis is preferred. In the case of industrial application of ellipsometry, it would be preferred to have a real-time model from a previous analysis monitor the behavior of the desired measurement. However, sometimes this may not be possible or practical in an industrial setup, or may be used in conjunction with another *in situ* measurement, such as pyrometry.

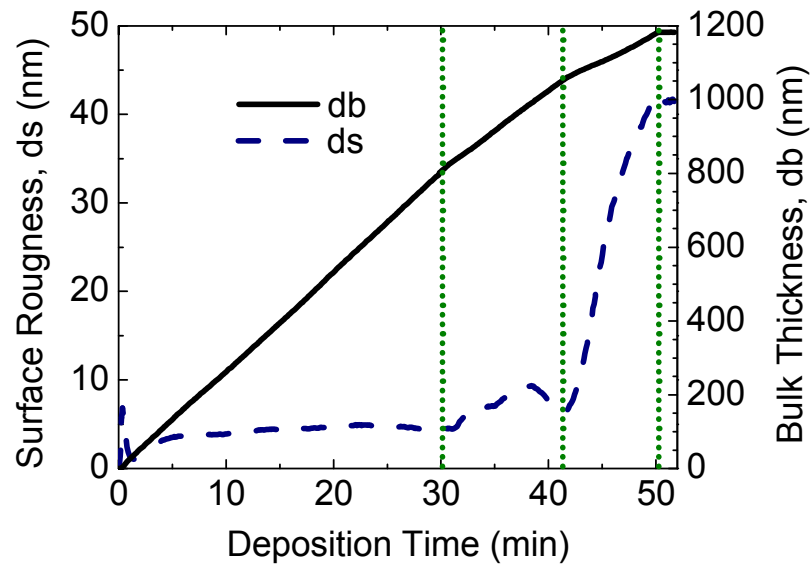


Figure 6-7: Bulk thickness (db) and surface roughness (ds) of AIS thin film deposited by a two stage hybrid process as a function of time for the full stage of deposition.

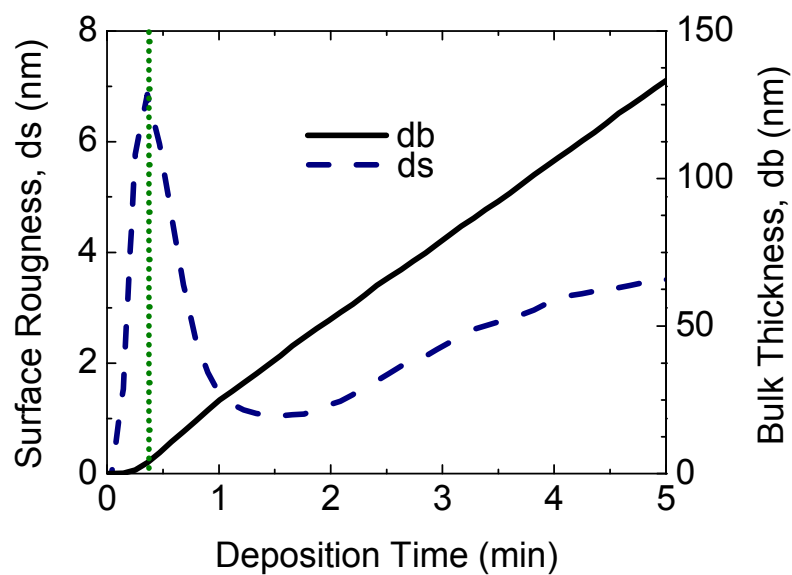


Figure 6-8. Detail of bulk thickness (db) and surface roughness (ds) of AIS thin film deposited by a two stage hybrid process as a function of time for the initial stage of deposition

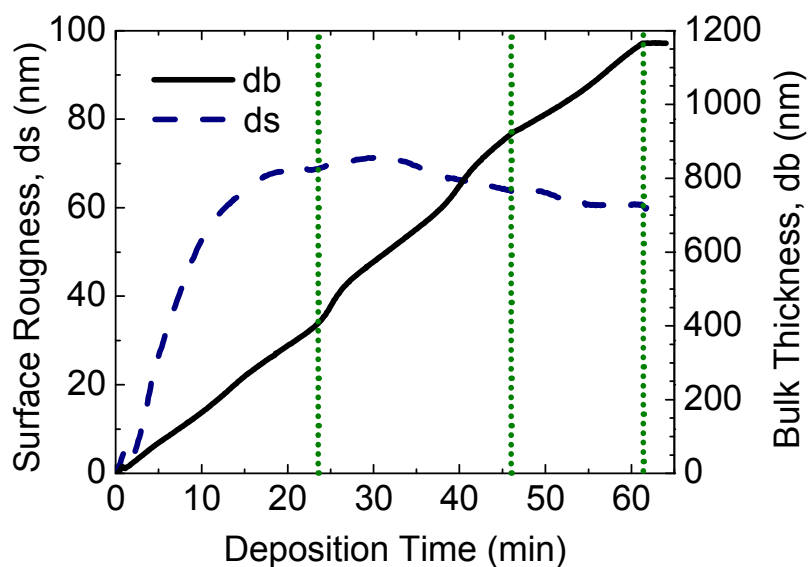


Figure 6-9. Bulk thickness (db) and surface roughness (ds) of CIS thin film deposited by a two stage hybrid process as a function of time for the full stage of deposition

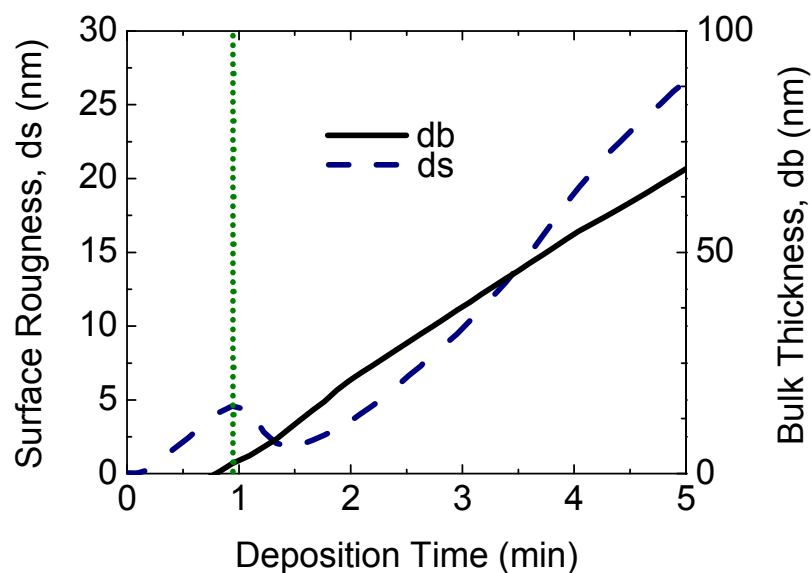


Figure 6-10. Detail of bulk thickness (db) and surface roughness (ds) of CIS thin film deposited by a 2-stage hybrid process as a function of time for the initial stage of deposition

From the beginning of the deposition (0 min.) to 30 min., as depicted in Fig. 7 (and detailed in Fig. 8), Ag-rich material $\text{Ag/In} = 1.42$ was deposited. From 30 min. to the end of the deposition (50 min.), Ag-poor material $\text{Ag/In} = 0$ was deposited.

Calculated end composition was $\text{Ag/In} = 0.85$. A sudden increase in surface roughness, as denoted by the second dashed line around 41 min., could lead one to believe that a major structural change has occurred, thus possibly indicating a phase change. Because this phase is unwanted, it would have been ideal to stop the deposition soon after this occurred. It is interesting to note that this change occurs precisely where composition Ag/In becomes less than one. This indicates that it may be possible to detect non-stoichiometric materials in real-time. Similar analyses were applied for CIS, as depicted in Fig. 9 and Fig. 10. In section 6.4, this method was used to detect the transition point for reasonable efficiency solar cell devices.

6.3. ACIGS Devices deposited by 2 stage hybrid process

6.3.1. Solar cells results

Solar cell devices were produced by a 2 stage hybrid evaporation and sputtering process. Three targets were used in the deposition: Ag, In, and an alloy of Cu/Ga. The powers of the targets were calibrated so that the individual sputtering rates of the targets produced the desired composition. The “x” used to describe the Cu to Ag ratio is redefined in this chapter to be “z”: $z = \text{Cu}/(\text{Cu}+\text{Ag})$. This was done because “x” is conventionally used to denote the Ga to In ratio in CIGS films, as it is here: $x = \text{Ga}/(\text{Ga}+\text{In})$. As an expansion of the conventionally used “y” ratio used in CIGS, “y” is used to denote the Group I elements to Group III elements: $y = (\text{Ag}+\text{Cu})/(\text{Ga}+\text{In})$.

Solar cells were deposited on soda-lime glass covered with molybdenum. The molybdenum was deposited in 5 mTorr of Argon at 50 W. The final thickness of the layer was between 0.8 and 1 μm . After the ACIGS deposition, a CdS layer was deposited by chemical bath deposition at 60°C, following a standard solution containing 0.0015 M thiourea, 0.1 M cadmium acetate and 1M ammonium hydroxide. Following the deposition of this 50-60 nm layer, an intrinsic ZnO layer was deposited in 5 mTorr of Argon at 50 W, followed by a ZnO:Al layer in the same conditions, using a 99.999% pure ZnO target and a 99.995% pure ZnO:Al target respectively.

Eight types of samples were deposited. They have the following x, y, and z values are given in Table 3. The Ga content (x) was held within values of ~ 0.3 eV, as in champion solar cells, the Group I/Group III (y) content was held between the constraints of the desired phase, and the Ag content (1-z) was held at less than 10% when added.

The results for the devices are reported in Table 4 below as well as in Figure 11.

Table 6.3. Samples grown at different compositions.

Run number	x	y	z
10272	0.21	0.75	1.00
10274	0.28	0.95	1.00
10275	0.23	0.92	1.00
10276	0.30	0.91	0.95
10277	0.28	0.96	0.96
10278	0.35	0.90	0.91
10282	0.27	0.86	1.00
10284	0.24	0.81	1.00

Table 6.4. Results of the J-V measurements for the various samples, with Voc, Jsc, FF, Rs, Rsh and efficiency.

Sample	Type	Efficiency (%)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)
10272	CIGS	9.6	0.52	36.0	51.6
10274	CIGS	6.2	0.45	34.1	40.0
10275	CIGS	8.9	0.52	34.4	50.0
10276	ACIGS	0.3	0.14	10.0	26.2
10277	ACIGS	0.3	0.16	6.6	27.0
10278	ACIGS	0.01	0.03	1.9	16.1
10282	CIGS	1.6	0.30	17.2	31.8
10284	CIGS	7.9	0.46	58.5	58.5

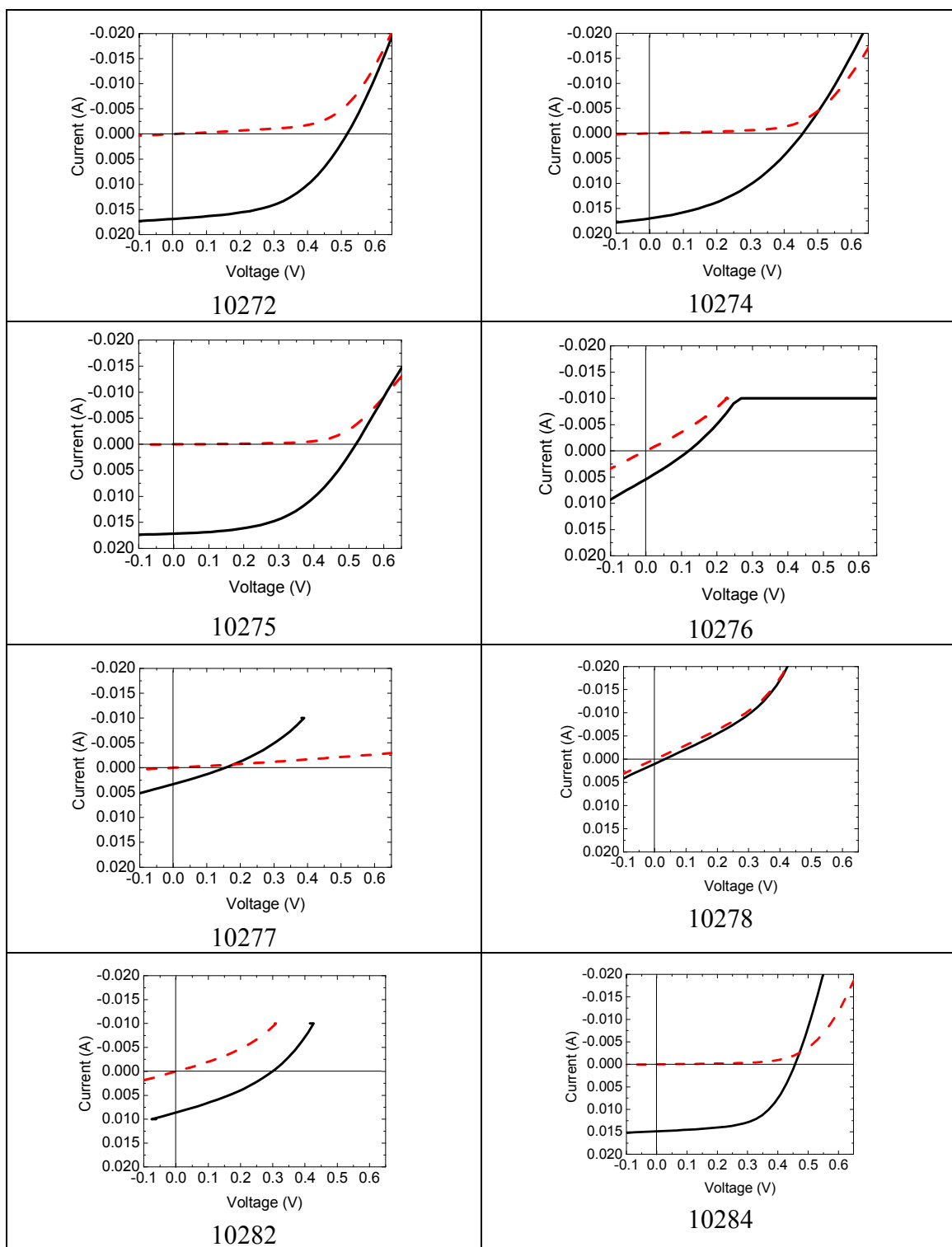


Figure 6-11. J-V curves for the eight types of ACIGS samples deposited by 2-stage hybrid process.

As can be seen by the results in Fig. 11 and Table 4, the devices fabricated with CIGS yielded reasonable efficiencies with low Voc and FF, while the current is in the range expected for this band gap. However, the cells fabricated with ACIGS systematically had a low efficiency mostly due to shunting. This correlates well with the observation made by XRD where a secondary phase was observed for the AIS 2-stage process, phase is probably at the origin of the shunts.

6.3.2. Comparison with 1-stage hybrid process

Since the 2-stage hybrid process is a novel approach in exploring ACIGS materials and devices, there is much to learn from these runs. Several devices were selected from the 2-stage ACIGS runs above (10275: CIGS; 10276: ACIGS) and the 1-stage ACIGS from the previous chapter and are presented in Table 5 and Table 6.

Table 6.5. XRD information for selected devices

Sample	Type	1st P Pos	1st P Ht	1st P FWHM	1st P AREA	2 nd P Pos	2 nd P Ht	2 nd P FWHM	2 nd P AREA
10155	1-stage	26.9	7385	0.041	302	44.4	2847	0.080	227
10275	2-stage	25.7	3329	0.167	556	43.5	629	0.110	68
10276	2-stage	25.7	1125	0.133	149	43.4	813	0.135	109

Table 6.6. XRD information for selected devices

Sample	Height [112]/[220]	Area [112]/[220]	Eff (%)
10155	2.59	1.32	12.3
10275	5.28	8.02	8.9
10276	1.38	1.36	0.3

Table 6.5 and Table 6.6 compare the 1-stage process to 2-stage process. According to the FWHM, which is inversely proportional to the grain size, the 1-stage ACIGS solar cell appears to have larger grain size than both of the 2-stage devices. Also, the efficiency appears to follow the same trend as the grain size. Thus, it may be concluded that the

formation of larger grain sizes is important for better efficiency devices for the hybrid deposition process.

SIMS analyses were performed on the devices for comparison of 1-stage and 2-stage processes, as seen in Fig. 12 - 14. It is seen, in Fig. 12, that there is a buildup of Na near the Mo/CIGS interface. However, in Fig. 13 and Fig. 14, there is no such buildup but the Na concentration diminishes rapidly when compared to that of Fig. 12. Na is important to the functioning of high-performance devices [Shafarman, 2003] and is needed to passivate defects in the device.

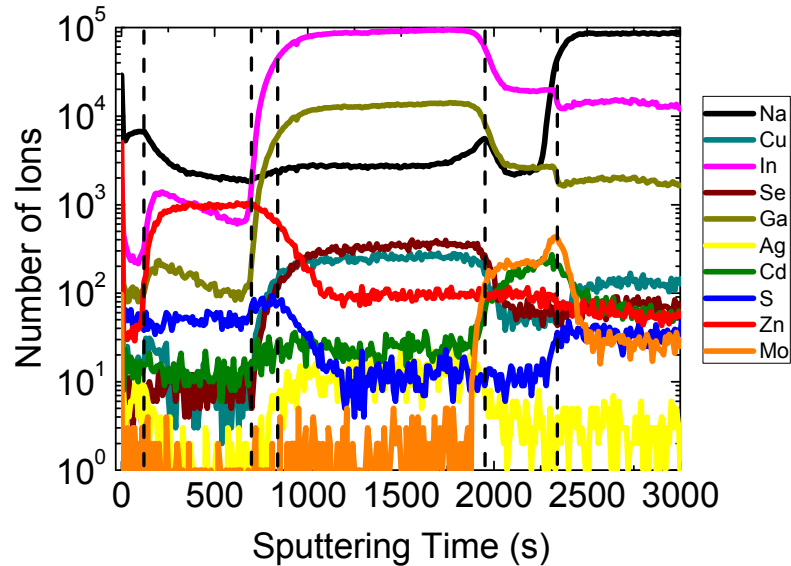


Figure 6-12. SIMS analysis on ACIGS device 10276 deposited by 1-stage process. From the left, the first vertical line separates the window layers; the second line separates the window layer and CdS; the third line separates CdS and the absorber layer; the fourth line separates the absorber layer and Mo; and the fifth line separates Mo and the soda lime glass substrate.

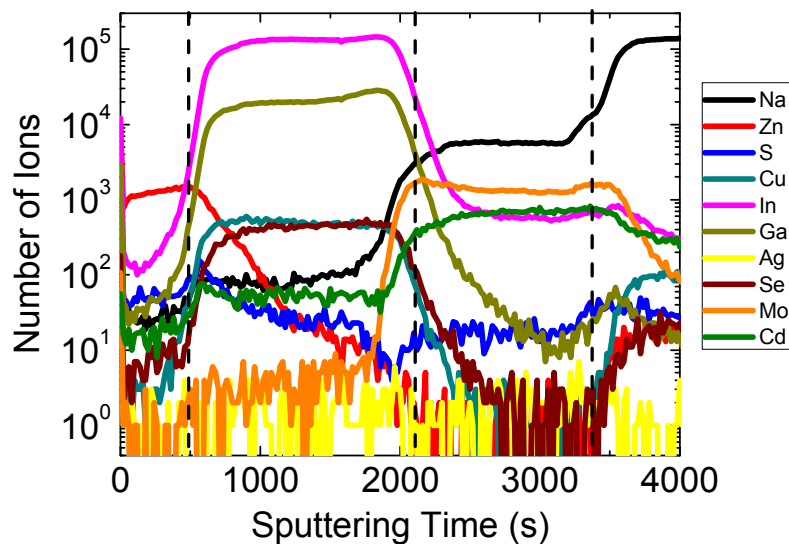


Figure 6-13. SIMS analysis on CIGS device 10275 deposited by 2-stage process. From the left, the first line separates CdS and the absorber layer; the second line separates the absorber layer and Mo; and the third line separates Mo and the soda lime glass substrate.

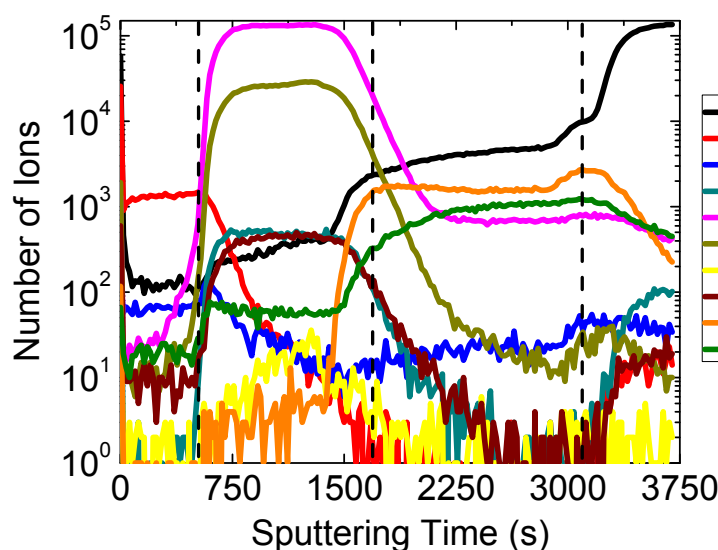


Figure 6-14. SIMS analysis on ACIGS device 10276 deposited by 2-stage process. From the left, the first line separates CdS and the absorber layer; the second line separates the absorber layer and Mo; and the third line separates Mo and the soda lime glass substrate.

XRD (112)/(220) preference has been associated with Na diffusion [Rudmann, 2003], but this is not evidenced by Table 6. Perhaps this barricading of Na as seen in the 2-stage process in Fig. 13 and Fig. 14 can be overcome by the addition of NaF on Mo

before the deposition. Also, in the 2-stage devices, Ag appears to rise and fall within the absorber layer, especially as seen in Fig. 14. This gradient of Ag will cause a band gap gradient that could affect the cell performance. S is another element that may be migrating too far into the absorber layer of the 2-stage devices. S helps passivate Se deficiencies, but too much S could cause effects that were not accounted for in pre-fabrication calculations.

Devices 10155, 10275, and 10276 were cleaved for x-SEM analysis as seen in Fig. 15. The window layer is more visible in 10155 (Fig. 15a), meaning that the surface is smoother so that it can be seen, as compared to Fig. 15b, or that it was not removed in the cleaving process, as suggested in Fig. 15c. The grains of Fig. 15c appear built on each other, whereas the grains in Fig. 15a and Fig. 15b appear to extend from the substrate to the top or window layer. This structure probably has a detrimental effect on solar cell efficiency.

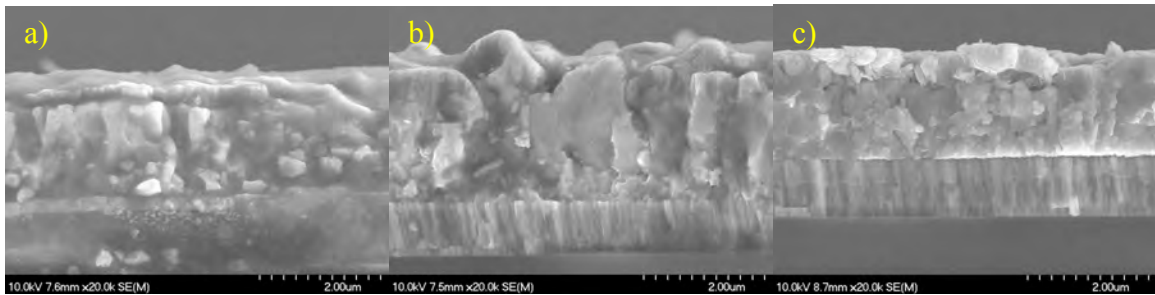


Figure 6-15. a) 10155 1-stage ACIGS, b) 10275 2-stage CIGS, c) 10276 2-stage ACIGS

6.4. Comparison of Two-stage process by Evaporation and Sputtering

High performance solar cell devices with efficiencies over 15% are routinely deposited by the co-evaporation method. However, for scalability, the hybrid method is favored for larger area devices. Ellipsometry is a powerful tool to gain real-time and *in situ* knowledge about the deposition of the absorber layer. As a first approximation analysis, ellipsometry analysis gives insight into structural changes, such as the evolving thicknesses d_b , the bulk layer thickness, and d_s , the surface roughness layer, and optical changes, such as the dielectric functions or optical constants (OC). Further analysis can provide more information about electrical properties and the electronic structure.

In the following figures, the co-evaporation process and the hybrid deposition process are compared, specifically as it pertains to the so called Cu-rich to Cu-poor transitions.

For the co-evaporation process, we have plotted (d_b, d_s) versus time close to the transition point (Fig. 16), the Real part of the dielectric function as a function of energy for specific points (Fig. 17), the Imaginary part of the dielectric function as a function of energy for specific points (Fig. 18).

For the hybrid process, we have plotted (d_b, d_s) versus time close to the transition point (Fig. 19), the Real part of the dielectric function as a function of energy for specific points (Fig. 20), the Imaginary part of the dielectric function as a function of energy for specific points (Fig. 21), a close up of the imaginary part of the dielectric function as a function of energy for specific points (Fig. 22).

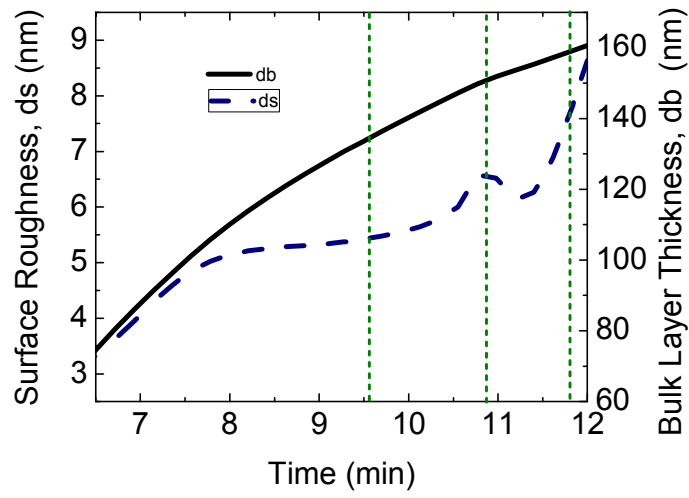


Figure 6-16. Selected d_b and d_s for 2-stage evaporation method with vertical dashed lines denoting before, during, and after transition point.

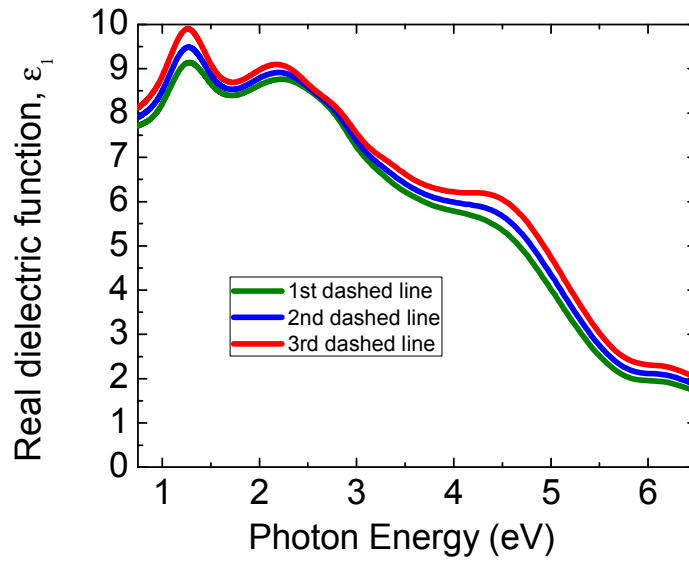


Figure 6-17. Real part of dielectric function for evaporation method at high temperature with references to dashed lines corresponding to Fig. 16.

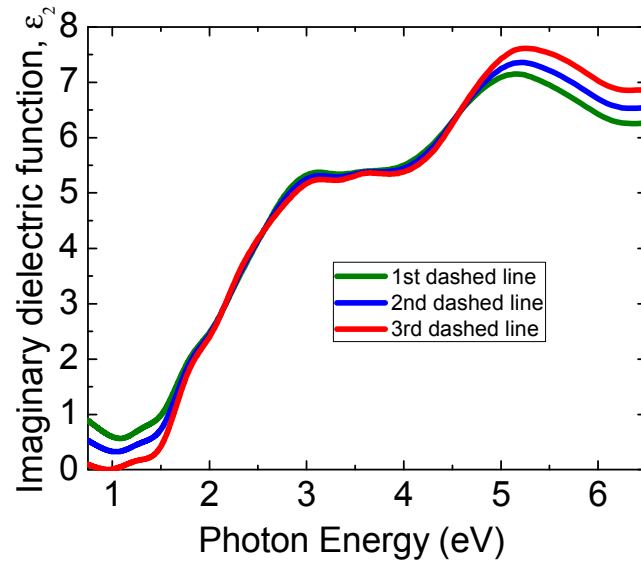


Figure 6-18. Imaginary part of dielectric function for evaporation method at high temperature with references to dashed lines corresponding to Fig. 16.

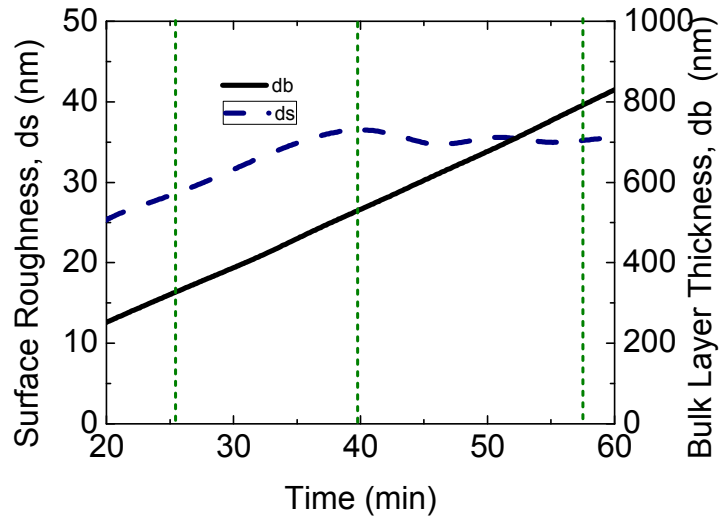


Figure 6-19. Selected d_b , d_s vs time (min) around transition for hybrid deposition method with vertical dashed lines denoting before, during, and after transition point.

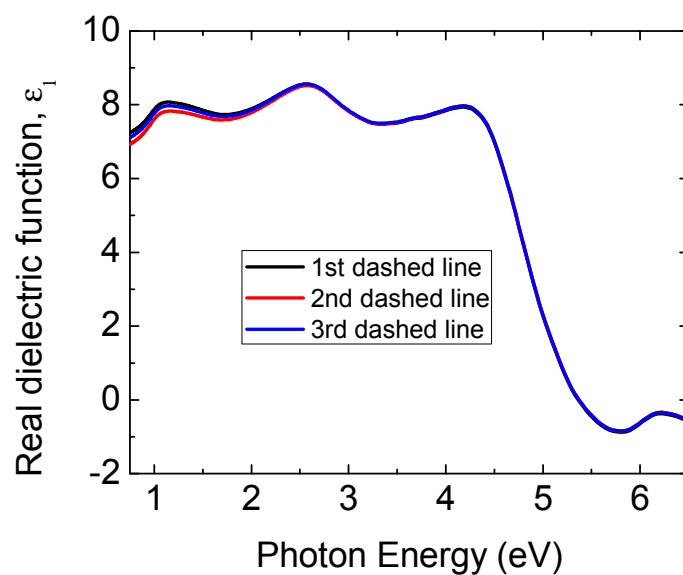


Figure 6-20. Real part of dielectric function for hybrid deposition method at high temperature with references to dashed lines corresponding to Fig. 19.

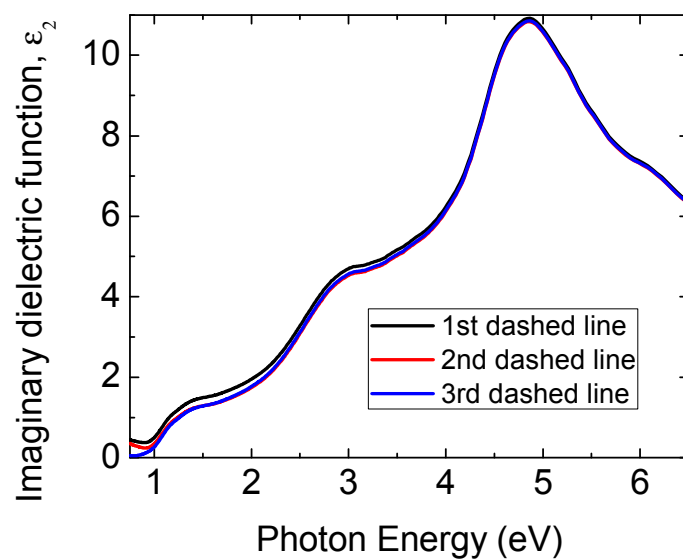


Figure 6-21. Imaginary part of dielectric function for hybrid deposition method at high temperature with references to dashed lines corresponding to Fig. 19.

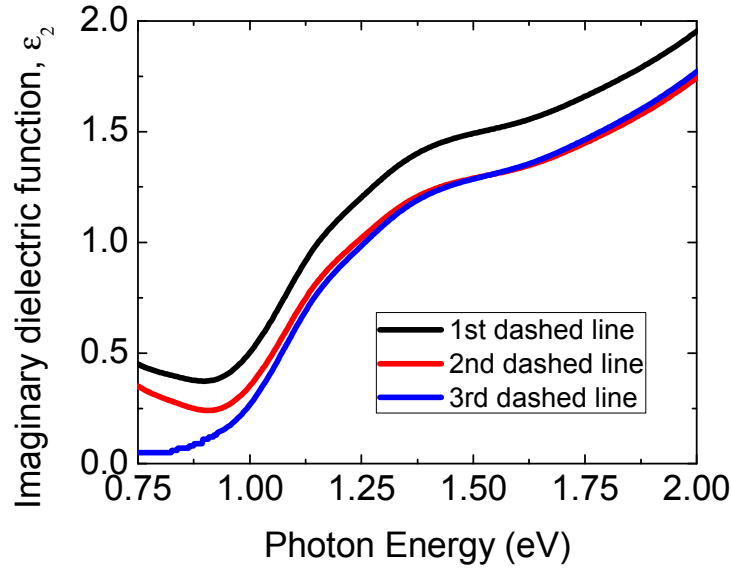


Figure 6-22. Detail of imaginary part of dielectric function for hybrid deposition method at high temperature with references to dashed lines corresponding to Fig. 19.

The analyses revealed that a real time change in the dielectric function—especially in the imaginary part of the dielectric function—and structural properties—especially d_s —can indicate when the Cu-rich to Cu-poor transition occurs for both hybrid and evaporation deposition methods. Fig. 16 shows the window of time where the transition occurs for the evaporation process as a function of the physical parameters d_b and d_s . A large peak in d_s corresponds to the transition point, as corroborated by the dielectric functions in Fig. 17 and Fig. 18. The transition is confirmed by the lowering of the free electron part of the imaginary dielectric function (Drude component) becoming zero at below the band gap of CIGS. The decrease in the Drude component denotes the disappearance of the secondary phase Cu_{2-x}Se in the absorber layer, after which y becomes less than one. The same ellipsometric analysis was applied to the hybrid deposition method, as seen in Fig. 19 – Fig. 22. The transition point is more subtle for d_s in the hybrid deposition case because the Cu source for the hybrid deposition

was not completely turned off in the Cu-poor phase of the deposition due to the limitations of sputtering Ga mentioned earlier.

Finally, x-SEM was performed on evaporated and hybrid deposition materials. The grains in Fig. 23 left are more pronounced and appear larger than the ones in Fig. 23 right. Yet, the surfaces in both figures appear to be similar. In general, the samples in Fig. 23 left and right suggest that CIGS deposited by evaporation and hybrid method are relatively similar. A TEM analysis would however be necessary to study in more detail the difference between the two deposition processes.

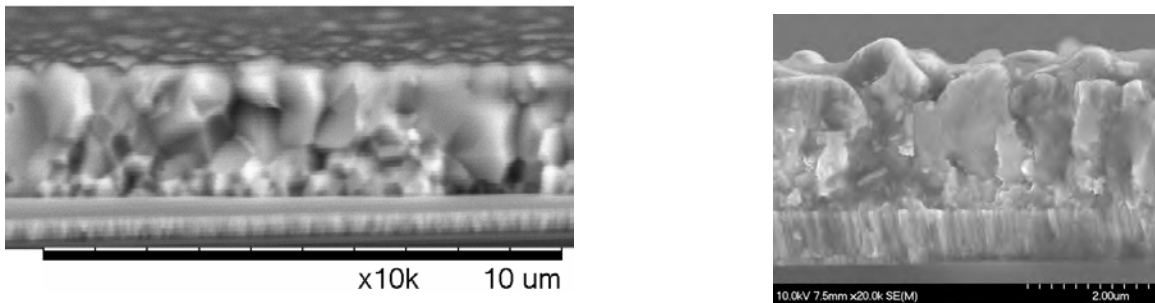


Figure 6-23. x-SEM of evaporated deposition material (left) and hybrid deposition material (right)

6.5. Conclusions

In conclusion, materials and devices with and without Ag and deposited via different methods were characterized by various techniques and analyzed using spectroscopic ellipsometry. There is still much to be learned about the dynamics of the multiple stage process with respect to the hybrid deposition, as seen in the decrease in grain size and decrease in overall efficiency. However, it was seen that spectroscopic ellipsometry was successful in analyzing the structural and optical properties of both deposition methods, allowing for promising insights as both deposition methods are analyzed in parallel.

Chapter 7

Conclusion

As the CIGS technology has proven itself to be a worthy solar cell technology, research efforts have redoubled to explore ways to enrich the already mature technology or create spin-offs of the technology with specific goals for manufacturing in mind. CIGS technology is now up to an efficiency and production level to compete with other second generation solar cell devices and c-Si. Further extended research in CIGS allows for a toolbox for new ideas to try in the technology. This thesis aims at that goal by generating and presenting many ideas on how that may be possible. Not as an exhaustive list, this thesis contained information on how to improve the manufacturing process using a sputter deposition chamber for scaling up and allowing for easy in situ monitoring using ellipsometry, it explores the possibility of the addition of Ag to enhance and control device behavior and properties, and the idea of a two-stage process with a co-sputtering deposition chamber is also explored. The monitoring of Ag in situ and in real time was explored to possibly improve the back contact of solar cells that use Ag as a back contact (not necessarily CIGS) and as potential precursors for nanocrystals.

In chapter 1, an introduction to solar cell technology and an outline of this work was given.

In chapter 2, material and device characterization methods to explore solar cell materials and performance were discussed. Characterization techniques ranging in measurement settings from *in situ* growth monitoring to the characterization of the final film device have been presented. Use of more than one technique is encouraged to develop a holistic idea of what is happening with a particular specimen or device.

In chapter 3, noble metals, with special interest in Ag nanoparticles, were explored by *in situ* spectroscopic ellipsometry via the real time monitoring of the dielectric functions, the thickness and the roughness. Three studies of silver nanoparticles were presented in this chapter. In the first study, a broadband analysis of the optical properties of silver nanoparticle films over the range from 0.75 to 6.5 eV was performed by applying *in situ* real-time spectroscopic ellipsometry (RTSE) during the nucleation, coalescence, and bulk thin film growth regimes. The dielectric functions of the particulate films were found to depend strongly on the particle size and film thickness from the nucleation regime throughout coalescence. These dependences were analyzed by separately characterizing the three types of transitions evident in the dielectric function: intraband, particle plasmon polariton, and interband. Throughout the film growth regimes, the thickness evolution of the amplitude, energy, and broadening parameter for each type of transition was discussed in view of the structural characteristics of the films, and corroborated by *ex situ* atomic force microscopy for films deposited over different time durations. In the second study, the dielectric function of Ag nanoparticle films, deduced by *in situ* real-time spectroscopic ellipsometry (RTSE), was found to evolve with time in close consistency with the film structure, also deduced by RTSE. In the nucleation regime, the intraband component is absent and

plasmon polariton behavior dominates. Only at nuclei contact, does the intraband amplitude increase above zero. Both intraband and plasmon amplitudes coexist during surface smoothening associated with coalescence. The evolution of the relaxation times for the interband, intraband, and plasmon dielectric function components shows trends that are similarly consistent with the Ag film structure. In the final study, the temperature dependence of these oscillators was analyzed via RTSE and a melting point depression was detected via an abrupt change in the generalized oscillator broadening, allowing for the surface energy to be calculated. After annealing, permanent structural changes, such as the reduction in crystallinity and change in size, were observed in the nanoparticles via ex-situ measurements, thereby confirming that the nanoparticles had melted.

In chapter 4, the basic properties of (Ag,Cu)InSe₂ thin film materials by 1-stage process were discussed. The observations in section 4.3 corroborate with those found in section 4.2. The lack of surface defects found in the AIS sample in section 4.3 could add an explanation for the different growth mode of AIS seen in section 4.2. A lowered surface defect condition can be attributed to the S-K growth method through relieving the surface tension via elastic undulations to the substrate in what is known as the Grinfeld instability [Markov 1995]. In general, corroborations of the conclusions pertaining to structural and optical features described in section 4.2 with the conclusions about structural and electrical features described in section 4.3, aid greatly in the complete understanding of the opto-electronic nature of a ACIS thin film material. This full characterization is part of an exploration of how Ag can be used to optimize this chalcopyrite family.

Part of the solution to figuring out the dynamics of how Ag helps in the ACIS system is to study other phases that may exist in the production of these films due to the conditions in which they were grown. Phases such as Ag_{2-x}Se , much like Cu_{2-x}Se were studied in the past [Khatri 2009]. A simple understanding of the reaction pathways and possible phases of a system can also be insightful. A study by Nichols et al. found that films at higher deposition temperatures than 120 °C were metallic while those deposited lower than this temperature are semiconducting [Nichols 2008].

The melting point of copper is 1068 °C while silver is 962 °C. Similarly, the melting point of Ag_2Se is lower than Cu_2Se according to Miyatani [Miyatani 1973]. Likewise, CIS and AIS have a melting point of 987 °C and 782 °C respectively. Since the deposition temperature is much closer to the melting point of the sample, this could mean the elimination of some of the defects as the composition of Ag increases in ACIS [Ehrhart 1991].

Future studies will include epitaxial growth of ACIS thin films to determine the single crystal properties—allowing for the direct comparison of the polycrystalline samples grown here. In the next chapter, we will explore ACIS thin films in solar cell devices—including the addition of Ga and growth by the two-stage process.

In chapter 5, the properties of $(\text{Ag,Cu})(\text{In,Ga})\text{Se}_2$ thin films deposited by 1-stage process and devices fabricated from these films were presented. We have successfully deposited ACIGS solar cells by a one stage hybrid process with efficiency as high as 12.6%, without MgF_2 AR coating. The efficiency seems to be mainly limited by a low V_{oc} associated with a low FF , compared to an evaporated CIGS solar cell with equivalent band gap. XRD, SEM and SIMS analysis seems to indicate a strong influence of the

crystal orientation on the efficiency, a grain size and grain distribution different from the standard one observed in CIGS and a compositional distribution of the elements (with lower Cu and Ag at the interface with CdS) that might lead to a lower quality junction, and therefore enhanced recombination. However, this is still the highest efficiency obtained with the hybrid process to our knowledge and shows therefore the potential that both the process and the material has.

In chapter 6, the properties of (Ag,Cu)(In,Ga)Se₂ thin films deposited by 2-stage process and devices fabricated from these films were presented. Materials and devices with and without Ag and deposited via different methods were characterized by various techniques and analyzed using spectroscopic ellipsometry. There is still much to be learned about the dynamics of the multiple stage process with respect to the hybrid deposition, as seen in the decrease in grain size and decrease in overall efficiency. However, it was seen that spectroscopic ellipsometry was successful in analyzing the structural and optical properties of both deposition methods, allowing for promising insights as both deposition methods are analyzed in parallel.

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