Optical metrology for CIGS solar cell manufacturing and its cost implications

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A Dissertation
Submitted to the University at Albany, State University of New York
in Partial Fulfillment of
the Requirements for the Degree of
Doctor of Philosophy

College of Nanoscale Science and Engineering
2016
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Dedicated to my loving parents, Sudhakar and Gurumala

and to my brother, Srujan, for his endless love and support
Acknowledgements

I have been very fortunate to have Prof. Pradeep Haldar as my advisor. I am extremely grateful for his encouraging guidance, care and secured funding to make this work possible. He has inspired me to be an independent thinker and instilled confidence to achieve new heights in my career. He has given me freedom to explore, diversify, and develop my own ideas. I am very thankful to him for taking time out of his busy schedule to listen to my ideas and appropriately advising me during the course of my research. I feel privileged to have memorable discussions with him regarding career pathways and life in general.

I am extremely grateful to my co-advisor, Dr. Sandra Schujman (US PVMC), who has been guiding me all along my PhD. Since the beginning of my PhD, she has been extremely supportive and friendly while encouraging me and giving me freedom to explore my ideas. I cannot thank her enough for her insightful comments and constructive criticism during our thought provoking discussions without which I would not have been able to widen my research from various perspectives and learn new concepts. I owe my gratitude and sincere thanks for her immense patience in reading my manuscripts and this thesis. I am extremely privileged to have been able to appreciate the practical, theoretical, and engineering aspects of my research and would like to thank Dr. Sandra Schujman for all her efforts.

I would like to express sincere gratitude towards my dissertation committee members; Prof. Alain C. Diebold, Prof. Harry Efstathiadis, and Prof. Unnikrishnan Sadasivan Pillai for their cooperation and their constructive feedback on the research. I am deeply grateful to Prof. Alain C. Diebold for granting me access to his tools without which this research would not have been possible. I am honored by the opportunity to conduct my research with his help. I express my
sincere thanks to Prof. Unnikrishnan Sadasivan Pillai for his guidance in the cost modeling work. I sincerely appreciate his patience in teaching me the nuances of economics. I would also like to thank Prof. Harry Efstathiades for his encouragement, support and valuable suggestions which helped me to finish my PhD on time.

I gratefully acknowledge the engineering support of US PVMC members; Dr. Dave Metacarpa, Dr. David Fobare, Dr. Rajalakshmi Sundaramoorthy and Dr. Daniel Dwyer. Also, I would like to thank John Wax, Crispin Rice and Amara Conteh for helping me out with sample fabrication and in-line measurements. I also thank my fellow CNSE graduate student, Graeme Housser, for his valuable discussions and help in sample fabrication.

I am extremely thankful to Dr. Raja Muthinti, Dr. Manasa Medikonda, Dr. Dharya Dixit, Dr. Sam O’Mullane and Avery Green, members of Optical Metrology group for their valuable and insightful suggestions and discussions in regards to ellipsometry measurements and Critical Point analysis. I thank Dr. Thomas Laursen and Dr. Steve Novak for their help in SIMS measurements. I would especially like to thank, Miguel Rodriguez for training me on various characterization tools. I am deeply appreciative of his constant effort to keep the tools in good shape for the benefit of the students.

I express my sincere thanks Dr. Praneeth Adusumilli (IBM), Sridhar Mahendrakar (GlobalFoundries), Dr. Ravi Kumar Bonam (IBM), Alex Varghese (IBM), Dr. Brown Peethala (IBM) and Dr. Pavan Chintamanipeta (IBM) for their constant support and advice. I am grateful to Abhishek Gottipati and Pratik Agnihotri for their encouragement and practical advice. I am also thankful to them for reading my manuscripts, commenting on my views and helping me understand and enrich my ideas. I am extremely thankful to CNSE graduate students especially,
Avyay Narsimham, Girish Malladi, Gnanaprakash Dharmalingam, Adarsh Basavalingappa, and Vijay Jain for their immense help and support.

This thesis might not have been possible without utilizing the excellent facilities at the College of Nanoscale science and engineering, SUNY Polytechnic Institute. Also, I am very grateful to the application engineers at J.A. Woollam and Accustrata, especially Dr. Christopher Metting, for their support. I am thankful to the administrative staff of CNSE; Krista Thompson, Dr. Daniel White and Taryn Whittaker for keeping my paperwork in check.

I would like to thank my friends with whom I have shared many memorable events here in US. I can’t thank them enough for all the good times we shared during my stay at Albany and making my PhD years go so easy.

Finally, and most importantly, I am extremely grateful to my family for their blessings and for giving me the opportunity to pursue my dreams. I would like to thank my parents, Gurumala and Sudhakar, and my brother, Srujan, to whom this thesis is dedicated, for every sacrifice they have made for my education and for all their prayers and unconditional love. Without the constant encouragement, support and love of my brother, this thesis would not have been possible. I can’t thank him enough for believing in me and being there for me whenever I needed him.
Solar energy is a promising source of renewable energy which can meet the demand for clean energy in near future with advances in research in the field of photovoltaics and cost reduction by commercialization. Availability of a non-contact, in-line, real time robust process control strategies can greatly aid in reducing the gap between cell and module efficiencies, thereby leading to cost-effective large-scale manufacturing of high efficiency CIGS solar cells. In order to achieve proper process monitoring and control for the deposition of the functional layers of CuIn$_{1-x}$Ga$_x$Se$_2$ (CIGS) based thin film solar cell, optical techniques such as spectroscopic reflectometry and polarimetry are advantageous because they can be set up in an unobtrusive manner in the manufacturing line, and collect data in-line and in-situ. The use of these techniques requires accurate optical models that correctly represent the properties of the layers being deposited. In this study, Spectroscopic ellipsometry (SE) has been applied for the characterization of each individual stage of CIGS layers deposited using the 3-stage co-evaporation process along with the other functional layers. Dielectric functions have been determined for the energy range from 0.7 eV to 5.1 eV. Critical-point line-shape analysis was used in this study to determine the critical point energies of the CIGS based layers. To control the compositional and thickness uniformity of all the functional layers during the fabrication of CIGS solar cells over large areas, multilayer photovoltaics (PV) stack optical models were developed with the help of extracted dielectric functions. In this study, mapping capability of RC2 spectroscopic ellipsometer was used to map all the functional layer thicknesses of a CIGS solar cell in order to probe the spatial non-uniformities that can affect the performance of a cell. The optical functions for each of the stages of CIGS 3-stage deposition process along with buffer layer and transparent conducting oxide (TCO) bi-layer, thus derived were used in a fiber opti-
based spectroscopic reflectometry optical monitoring system installed in the pilot line at the PVMC’s Halfmoon facility. Results obtained from this study show that the use of regular fiber optics, instead of polarization-maintaining fiber optics, is sufficient for the purpose of process monitoring. Also, the technique does not need to be used “in-situ”, but the measurements can be taken in-line, and are applicable to a variety of deposition techniques used for different functional layers deposited on rigid or flexible substrates.

In addition, effect of Cu concentration on the CIGS optical properties has been studied. Mixed CIGS/Cu$_{2-x}$Se phase was observed at the surface at the end of the second stage of 3-stage deposition process, under Cu-rich conditions. A significant change in optical behavior of CIGS due to Cu$_{2-x}$Se at the surface was observed under Cu-rich conditions, which can be used as end-point detection method to move from 2$^{\text{nd}}$ stage to 3$^{\text{rd}}$ stage in the deposition process. Developed optical functions were applied to in-line reflectance measurements not only to identify the Cu$_{2-x}$Se phase at the surface but also to measure the thickness of the mixed CIGS/Cu$_{2-x}$Se layer. This spectroscopic reflectometry based in-line process control technique can be used for end-point detection as well as to control thickness during the preparation of large area CIGS films.

These results can assist in the development of optical process-control tools for the manufacturing of high quality CIGS based photovoltaic cells, increasing the uptime and yield of the production line.

Finally, to understand the cost implications, low cost potential of two different deposition technologies has been studied on both rigid and flexible substrates with the help of cost analysis. Cost advantages of employing a contactless optics based process control technique have been investigated in order to achieve a low cost of < 0.5 $/W for CIGS module production. Based on
cost analysis, one of the best strategies for achieving the low cost targets would be increasing manufacturing throughput, using roll-to-roll thin-film module manufacturing, with co-evaporation and chemical bath deposition processes for absorber and buffer layer respectively, while applying a low-cost process control technique such as spectroscopic reflectometry to improve module efficiencies and maintain high yield.
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1. Introduction

1.1 Summary and Motivation

World’s energy consumption is increasing at a rapid pace with the growth in the human population and technological progress. To meet this worldwide energy demand, humanity is primarily dependent on fossil fuels. As reported in the Fig. 1.1, worldwide primary energy consumption in 2014 made up of fossil fuels (Oil, Natural gas, and Coal) was 86.3 % while the non-conventional renewables other than hydro-power represent only 2.5 %. With increasing energy consumption and demand, we cannot rely on fossil fuels anymore as the reserves are being depleted rapidly\(^1\).

\[\text{Figure 1.1: World primary energy consumption from 1987 until 2014. Non-conventional renewable energy sources reached a record share of the global primary energy consumption of 2.5 % in 2014}^2.\]

Since the beginning of the industrial revolution, the majority of world’s energy needs are met by the rapid consumption of fossil fuels, which has led to climate change adversely affecting the
environment and posing significant challenges to human civilization. Due to the limited non-renewable energy resources and their adverse effects on the environment, the development of an environmentally friendly renewable energy source is inevitable. Wind, geothermal, solar thermal, and photovoltaics are some of the renewable energy sources with comparatively lesser impact on environment, which are promising alternatives to replace the conventional fossil fuels.

![Graph showing renewable energy share](image)

**Figure 1.2:** Estimated renewable energy share of global electricity production at the end of 2014.

Estimated renewable energy share of global electricity production for 2014 is shown in Fig. 1.2. As seen in the Fig. 1.2, non-conventional renewable energy share has increased from 5.8% (End-2013) to 6.2% (End-2014) and Photovoltaic (PV) solar energy has increased from 0.7% (End-2013) to 0.9% (End-2014) of the worldwide electricity production while fossil fuels and nuclear energy share has dropped from 77.9% in 2013 to 77.2% in 2014.
Solar energy is considered to be the most promising among all renewable energy sources as it is readily available globally and has a huge potential to be the primary source of clean energy in the near future. From Fig. 1.3, every year, 23,000 TW of solar power is incident on the Earth's surface which corresponds to 15,000 times the existing annual demand of energy by the world's population. Recently, with advances in research in the field of photovoltaics for generation of electricity, high efficiency solar cells have been developed. PV efficiency gains and cost reduction by commercialization will achieve convergence with fossil fuel grid costs ($/W) in near future. In contrast to non-renewable energy, which is slowly declining, the production capacity of solar energy sources has been growing rapidly in the last decade. As seen in Fig. 1.4, the global solar PV capacity has grown from only 3.7 GW in 2004 to 177 GW in ten years.
Figure 1.4: Global photovoltaic capacity from 2004 to 2014.

The photovoltaic technologies commercially available today can be divided into two distinct technologies: Wafer based bulk crystalline silicon (c-Si) or multi-crystalline silicon, often referred to as the 1st generation PV technology. Solar modules based on c-Si technology occupy 85% of current market share. Even though Crystalline-Si has good photovoltaic properties, it is abundantly available and utilized vastly in the semi-conductor industry, production and fabrication of monocrystalline Si solar cells involves Czochralski process, which is expensive and has huge energy requirements. Although they are expensive to fabricate, with record efficiencies for single-crystalline and multi-crystalline Si modules reaching up to 22.9 % and 19.2 % respectively, they can still compete to reach a grid parity with conventional sources of energy in near future.

In order to reduce the solar module costs, second generation PV technology based on thin films containing light-absorbing semi-conductor with significantly higher absorption coefficients than Crystalline-Si have been introduced. Thin film PV absorber materials exhibit high absorption...
coefficients as they either have direct band gaps or their indirect gap behavior is suppressed by the amorphous and nano-crystalline structures. Due to high absorption coefficient, much thinner absorber layer is required compared to bulk Crystalline-Si solar modules. Also, instead of using rigid substrates, low cost flexible substrates can be used with deposition processes like sputtering and thermal co-evaporation for high throughput thin film production. With similar lifetimes as that of Crystalline-Si, use of flexible substrates allows high automation in roll to roll fabrication which lowers the costs further. Cheaper fabrication costs and higher flexibility regarding shape, size and color compensates thin film modules’ lower efficiencies compared to Crystalline-Si.

Low-cost thin-film PV absorber materials currently in the market are amorphous silicon (Si:H), cadmium telluride (CdTe), copper indium diselenide (CuInSe$_2$; CIS), and its alloys with Ga and/or sulphur (CIGS). Si:H solar cells have low efficiency ($\sim$10 %) due to light induced degradation leading to long term stability issues$^7$. Even though CdTe lab-scale cells show high efficiency ($\sim$21 %)$^6$, the toxicity of Cd and strict environmental regulations make them less attractive. CIGS cells with reported laboratory scale cell efficiency exceeding 22 % are promising$^6$ due to their very high absorption coefficient ($\sim 1 \times 10^5 /\text{cm}$) in the visible wavelength range and the fact that they can be deposited on a variety of substrates, both rigid and flexible$^{8,9}$. CIGS lab-scale cells made on flexible metal substrates reported efficiencies above 20 %$^{10}$.

Cu(In,Ga)Se$_2$ (CIGS) is a I-III-VI$_2$ semiconductor compound that crystallizes in the tetragonal chalcopyrite phase which can be described as zinc-blende structure with an ordered replacement of the group II atoms (Zn or Fe in zinc-blende) by group I (Cu) and group III (In, Ga) atoms where In and Ga atoms are interchangeable without disturbing the crystal structure. A unit cell of CIGS in the chalcopyrite phase is shown in Fig. 1.5.
Figure 1.5: A unit cell of CIGS chalcopyrite structure (phase). Each Se atom is the center of a tetrahedral bond with 2 Cu and 2 group III atoms\textsuperscript{11}.

Depending on the type of intrinsic defects, CIGS can be either an n-type or a p-type semiconductor. Cu can either occupy interstitial sites or induce Se vacancies, when CIGS is deposited under a Cu-rich flux in a low Se pressure. This leads to n-type conductivity\textsuperscript{12} with the selenium vacancy (V\textsubscript{Se}) as the dominant donor. Conversely, Cu vacancies (V\textsubscript{Cu}) are created if CIGS is deposited under a Cu-poor flux and a high Se vapor pressure. This leads to p-type conductivity, where V\textsubscript{Cu} acts as the dominant acceptor and V\textsubscript{Se} as a compensating donor\textsuperscript{13}. CIGS solar cells use Cu-poor p-type material as an absorber layer. This device quality p-type material has a carrier concentration of \(\sim 10^{16} - 10^{17}\) cm\(^{-3}\), minority carrier lifetime of \(\sim 1\) ns and the diffusion length of \(\sim 1\) \(\mu\)m \textsuperscript{14}. 

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\textsuperscript{11} Se is the dominant donor in CIGS solar cells.

\textsuperscript{12} CIGS has n-type conductivity when Cu occupies interstitial sites.

\textsuperscript{13} CIGS has p-type conductivity when Cu vacancies are created.

\textsuperscript{14} carrier concentration, lifetime, and diffusion length values vary between different studies.
Figure 1.6: a) Thin film composition is close to the pseudobinary Cu$_2$Se – In$_2$Se$_3$ tie-line in the ternary phase diagram of the Cu–In–Se system$^{15}$ b) Pseudobinary In$_2$Se$_3$ – Cu$_2$Se equilibrium phase diagram for compositions around the CuInSe$_2$ chalcopyrite phase, denoted $\alpha$. The $\delta$ phase is the high-temperature sphalerite phase, and the $\beta$ phase is an ordered defect phase. Cu$_2$Se exists as a room-temperature (RT) or high-temperature (HT) phase$^{15}$.

The Cu–In–Se phase diagram has been studied extensively$^{15}$. The ternary phase diagram in Fig. 1.6 shows the possible phases in the Cu–In–Se system. Thin films of Cu–In–Se prepared under an excess supply of Se (normal conditions for thin film growth of Cu(In,Ga)Se$_2$) have compositions that are close to the tie-line between Cu$_2$Se and In$_2$Se$_3$. Chalcopyrite CuInSe$_2$ falls on this line. A pseudobinary phase diagram of the Cu$_2$Se–In$_2$Se$_3$ tie-line near CuInSe$_2$ is shown in Fig. 1.6 (b)$^{15}$. Here $\alpha$ is the chalcopyrite CuInSe$_2$ phase, $\delta$ is a high-temperature (HT) phase with the sphalerite structure, and $\beta$ is an Ordered Defect Compound (ODC) phase, which includes a number of compounds such as Cu$_2$In$_4$Se$_7$, CuIn$_3$Se$_5$, and CuIn$_5$Se$_8$. It is interesting to note that the single phase field for CuInSe$_2$ at room temperatures is in the relatively narrow range of $\sim$ 24.0 – 24.9 at. % of Cu. The phase field widens toward the In-rich side, at higher temperatures, around 500°C, where thin films for photovoltaic applications are typically grown. Device-quality films have typical average compositions of 22 – 24 at. % Cu, which fall within the single-phase region at growth temperature.
In 1953, Hahn et al.\textsuperscript{16} first reported the synthesis of chalcopyrite CuInSe\textsubscript{2}. Later in 1975, a CIGS solar cell was fabricated at Bell Laboratories, with an efficiency of 12 \% by evaporating n-type CdS onto a p-type single crystal of CuInSe\textsubscript{2}\textsuperscript{17}. The first thin film CuInSe\textsubscript{2} solar cells were fabricated by evaporating a powder of CuInSe\textsubscript{2} with excess Se in 1976 at the university of Maine\textsuperscript{18} and from then CIGS solar cells were developed by different companies. Researchers at Boeing Corporation achieved an efficiency of 11 \% in 1984 by co-evaporation of Cu, In and Se to deposit CuInSe\textsubscript{2} absorber layer on Mo-coated ceramic substrates with CdZnS as buffer layer\textsuperscript{19}. These cells were fabricated with a bilayer of evaporated CdS or (Cd,Zn)S, where one layer was undoped while the following layer, heavily doped, served as a transparent front contact. At Boeing, efficiency was improved significantly by incorporating Ga into the absorber layer which increased the band-gap from 1.02 eV to 1.1-1.2 eV\textsuperscript{20}. The photocurrent was increased by \~25 \% by using a thin (< 500 Å) undoped CdS layer and a 1 \( \mu \)m thick conductive ZnO layer instead of CdS or (Cd,Zn)S bilayer\textsuperscript{21}. Use of soda-lime float glass as a substrate was introduced in 1993 by Hedström et al\textsuperscript{22} to replace the conventionally used ceramic or borosilicate substrate. CIGS crystallites showed a preferential orientation on soda-lime glass and resulted in highest solar cell conversion efficiency. Na from the soda lime glass substrates was found to diffuse into the CIGS absorber layer deposited by co-evaporation processes acting as a beneficial dopant. In 1994, NREL developed a 3-stage co-evaporation process which was later adopted at ZSW (Center for solar and hydrogen research, Stuttgart, Germany) to fabricate CIGS solar cells with efficiencies of up to 20.3 \% in 2011\textsuperscript{23}. By the help of post-deposition treatments (PDT), 20.4 \% efficient CIGS solar cells were fabricated on a flexible polyimide substrate with a low-temperature process (<500 °C) in 2013\textsuperscript{24}. Using potassium PDT on glass substrate the ZSW research group has reached a record efficiency of 21.7 \%\textsuperscript{6}. They have also shown that with K PDT the range of
possible Ga concentrations in the absorber layer for very high efficiency cells (> 20 %) increases from GGI\(\leq 0.35\) to GGI \(\leq 0.45\), where GGI is atomic concentration ratio \([\text{Ga}]/([\text{Ga}]+[\text{In}])\). In December 2015, Japanese CIGS thin film solar cell manufacturer, Solar Frontier, reported an efficiency of 22.3 % on a 0.5 cm \(\times\) 0.5 cm cell\(^{26}\).

One of the great advantages of CIGS is its ability to tolerate large variations in composition without significant differences in optoelectronic properties, which makes it an ideal material for efficient low-cost PV modules. Solar cells with high performance can be fabricated with \([\text{Cu}]/([\text{In}] + [\text{Ga}])\) (CGI) ratios from 0.7 to 0.95 and \([\text{Ga}]/([\text{Ga}]+[\text{In}])\) (GGI) ratios ranging from 0.25 to 0.45\(^{25}\). Today, in all high efficiency CIGS solar cells, the absorber layer is Cu-deficient. The deviation of the CGI from unity can be understood as Cu vacancies (V\(_{\text{Cu}}\)) and In on Cu antisite defects (In\(_{\text{Cu}}\)) that form a defect complex (2V\(_{\text{Cu}}\) + In\(_{\text{Cu}}\)) which results in a net doping, usually p-type for slightly Cu-poor CIGS\(^{27}\). Wei et al.\(^{28}\) calculated the effect of Na in the CuInSe\(_2\) structure. It was found that Na replaces In\(_{\text{Cu}}\) antisite defects, reducing the density of compensating donors. Na in polycrystalline CIGS films, is found to strongly reduce the concentration of compensating donors\(^{29}\) and also to increase the net acceptor density\(^{30}\). The tendency of Na to occupy Cu vacancies and suppress the formation of antisite defects, increases the conductivity and the compositional range in which single-phase chalcopyrite exists, by checking the formation of the ordered defect compounds\(^{28,31}\).

The optical and the electrical properties of the layers of a CIGS solar cell are greatly influenced by the deposition process. Additionally, the deposition parameters such as vapor fluxes and substrate temperatures during the deposition of CIGS absorber layer, can vary over the deposition area, leading to non-uniformities in the properties of the film across the sample surface.
High-efficiency CIGS solar cells can be achieved if the composition and thickness of CIGS absorbers can be controlled within the range of each desired value. Advancements at the cell level will have an influence on large-scale module efficiencies. The module efficiency seems to follow the cell-level performance with few years of time lag.

Even though co-evaporation of CIGS via 3-stage process produces high efficiency devices there exists a significant gap between the champion and average device efficiencies. In order to improve the average device efficiency and reduce the gap between cell and module efficiency substantial reduction in process variations responsible for such inconsistencies is required. In-line, real time robust process control strategies can greatly aid in reducing these discrepancies. With availability of such process control techniques cost-effective large-scale manufacturing of high efficiency CIGS-based photovoltaics can be achieved easily.

One of the most critical aspects of 3-stage co-evaporation of CIGS is controlling the CGI ratio. Mildly Cu-rich conditions (CGI>1) during the deposition process lead to increased grain size and device quality\textsuperscript{32–35}. Cu-rich growth period which is dependent on deposition time and temperature has a direct impact on throughput and cost of manufacturing\textsuperscript{36}. Also, high efficiency CIGS solar cells are always Cu-deficient, hence it is critical to control and maintain final CGI ratio within acceptable range\textsuperscript{35}.

Sensor technologies currently available are not suitable for controlling CGI ratio to desired accuracy as flux control during CIGS co-evaporation process is rigorous and it is difficult for rate sensors to operate in high temperature and high Se pressure environment to monitor the flux rates of multiple species simultaneously. Rate control methods currently used such as electron impact emission spectroscopy (EIES)\textsuperscript{37,38}, mass spectrometry\textsuperscript{39}, and atomic absorption
spectroscopy\textsuperscript{38,40} and effusion source temperature control\textsuperscript{40} are not suitable to control CGI ratio to a desired accuracy. However, contact thermocouple method\textsuperscript{41} based on the change in emissivity due to CGI transition\textsuperscript{42–44} during the deposition process has successfully demonstrated fine control of CGI ratio leading to world record CIGS devices\textsuperscript{45}. Increase in emissivity can not only be detected as a drop in sample temperature\textsuperscript{45} but also as increase in heater power required to keep the sample at same temperature\textsuperscript{46}.

Even though contact thermocouple method offers fine control over CGI ratio, but from a manufacturing perspective sensing CGI transition can be problematic as change in temperature during CGI transition may be a very small, masked by power and temperature fluctuations and therefore, undetectable. Also, in case of roll-to-roll manufacturing, thermal contact between moving substrates and thermocouples is not possible.

Hence, a non-contact, robust in-line optical based technique for probing and controlling the deposition of different functional layers of CIGS-based solar cells have gained a lot of interest. Studied optical techniques use in-situ measurements of reflected\textsuperscript{44,47,48}, transmitted\textsuperscript{44} and emitted\textsuperscript{43,44} light. Of these optical approaches, scattered light measurements provide information on surface roughness, transmitted measurements require a transparent substrate but provide very high sensitivity to low-emissivity films, specularly reflected light measurements require precise optical alignments and emission measurements require no light source with simple setup.

PVMC has compared different techniques that could be used for process monitoring or process control based both on published data and internal work. In Fig. 1.7, the main conclusions are summarized.
Figure 1.7: Comparison of possible process monitoring techniques that could be used for in-line/in-situ process control.

From this comparison, it is clear that the optical techniques have several advantages over other techniques. Optical reflectance techniques, such as spectroscopic reflectometry and ellipsometry, are both reliable methods for the characterization of the different layers that compose a photovoltaic stack. They are useful at high temperatures and sensitive to layer thickness, composition and compositional gradients. When used to monitor the CIGS deposition process in an evaporation chamber, spectroscopic ellipsometry has shown superior results to the more common metrology carried out by pyrometers and elemental rate monitors. Spectroscopic reflectometry is a new technique which can be applied to different deposition techniques and installed at various geometries. These advantages of spectroscopic reflectometry over ellipsometry makes this technique best suited for in-line or in-situ data collection.
The main objective of this research is to develop a methodology based on optical techniques to study and control the variations in film properties, which affect the performance of the device posing a challenge to scale-up of laboratory processes. The critical need for measuring, monitoring, and controlling the thickness, structure, phase, and composition of these solar cell component layers in real time, during their deposition can be fulfilled by real time spectroscopic reflectometry which offers rapid and relatively low cost in-line process control but it requires accurate optical models which represent the main properties (e.g. thickness and composition) of the photovoltaic layers.50 Proper optical models developed using off-line spectroscopic ellipsometry could then be used to relate the reflectometry signals to material properties of the layers.

Spectroscopic Ellipsometry (SE) is a non-destructive linear optical technique that uses polarized light to characterize thin film and bulk materials that can provide information about structural properties (e.g., thicknesses) and optical properties (e.g., $n$ and $k$ spectra). The light undergoes a change in polarization as it interacts with the sample structure. Ellipsometry measures the change in polarization as light reflects or transmits from a material structure. The optical constants (complex refractive index) and film thickness of the sample are extracted from the change in the polarization state by light reflection or transmission with the help of appropriate optical models. Ellipsometry can provide the multilayer structure of thin film material stacks, such as solar cell devices, which are fabricated using a series of several different deposition methods. Spectroscopic Ellipsometry is a very useful technique in thin film photovoltaics technology as it allows for characterization of film thicknesses and band-gap of the material. By modeling the raw SE spectra, we can calculate the index of refraction $n$ and extinction coefficient $k$ for the
materials that make up the layers. To further understand the nature of the materials used we can use other techniques in conjunction with SE.

Spectroscopic reflectometry (SR), if implemented with fiber optics, is a metrology technique that allows determination of material properties for an assortment of deposition geometries and conditions. Given the variety of deposition technologies used by the different manufacturers, the PVMC Pilot Line offers the advantage of using both sputtering and co-evaporation chambers where the monitoring units were installed.

Coupled with appropriate optical models, spectroscopic reflectometry can be used to monitor thickness and composition of the layers, both in-situ and real time, as well as in-line, after the layers are grown. In the case of the CIGS absorbers, spectroscopic reflectometry may be sensitive to the compositional gradients that are purposefully set up during the layer growth, for example, when using two- or 3-stage co-evaporation method, or when running the selenization process after deposition of the metal precursors.

Reported production costs for CIGS modules fabricated in a production line with an annual capacity of 200 MW is 0.55 $/W or 0.40 $/W for a 1000 MW production line, while crystalline Si manufacturing costs are close to 1 $/W on average\textsuperscript{51}. Compared to c-Si technology, thin film CIGS technology is at an early stage on the experience-curve, hence it has a good potential for further cost-reductions. Low cost potential (< 0.5 $/W) can be achieved by increasing the solar cell/solar module conversion efficiency, throughput and yield with help of robust and cheap in-line process control techniques while producing high quality devices.
1.2 Thesis Content

This thesis focuses on spectroscopic ellipsometry studies of the change in optical properties of CIGS at different stages of the co-evaporation deposition process having various compositions in the range that is often encountered in large area depositions. Based on this study, robust optical models were developed that can be utilized to control the CIGS deposition process on different substrates. Similarly, optical models for the rest of the functional layers in CIGS solar cell stack were developed. The resulting set of developed optical models has been utilized in ex-situ mapping of CIGS thin films and solar cells to identify the non-uniformities across the cell surface area. A novel process control method based on spectroscopic reflectometry (SR) has been investigated. SR measurements have been analyzed with the help of optical models developed using SE. Results from the SR measurements show very good agreement with SE results, as well as ancillary characterization methods. The potential of this process control technique to lower the cost of production of CIGS solar cell has been analyzed with help of cost modeling based on manufacturing metrics of a pilot plant installed at Halfmoon, NY. Also an analysis of most cost effective deposition process for CIGS solar cell manufacturing has been performed. Mapping applications of spectroscopic ellipsometry and in-line process control method based on spectroscopic reflectometry have also been explored in this nanomaterials research due to their potential for improving the efficiency and lowering the cost of production of CIGS solar cells respectively.
1.3 References

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2. Experimental Techniques

2.1 The Classic CIGS Solar Cell Structure

A typical CIGS solar cell structure is shown in Fig. 2.1. Generally, the most studied and used structure is Substrate/Mo/CIGS/CdS/i-ZnO/ZnO:Al, where i-ZnO is intrinsic Zinc oxide and ZnO:Al is Aluminum doped Zinc oxide. Various alternative materials have been studied by different research groups, in particular for the substrate, such as stainless steel, which are nowadays even used by CIGS manufacturing companies. In this section, materials used for each of the functional layers and their fabrication techniques are discussed.

![Typical CIGS Solar Cell Structure](image)

**Figure 2.1**: A typical CIGS solar cell structure.

2.1.1 The Substrate

The substrate gives mechanical stability to the solar cell/module structure. Soda-lime glass (SLG) has replaced borosilicate glass substrates as it is cheaper, has better thermal expansion coefficient match with CIGS and, mostly, because the diffusion of sodium from the glass to the CIGS absorber layer has proven to be beneficial to the performance of the cell. CIGS films grown on SLG are found to be preferentially oriented towards (112). The solar cell open circuit
voltage and efficiency are higher, although it is not clear if the strong orientation is a precondition for the good cell performance\(^1\). Wei \textit{et al.}\(^2\) found theoretically that a reason for good performance is the increase in the hole density and decrease in the stability of the \((2\text{V}_{\text{Cu}} + \text{In}^{2+}_{\text{Cu}})\) defect complex, often referred as “ordered vacancy compound” (OVC) in the absorber layer.

A record efficiency of 20.4 \(\%\) achieved by EMPA for a CIGS solar cell on a flexible polyimide substrate has garnered much interest in flexible substrates\(^3\). Other flexible substrate materials being investigated are stainless, mild, and enameled steel as well as molybdenum, aluminum, and titanium. Flexible substrates are cost effective as they can be used in roll-to-roll production with high throughput. Incorporation of alkaline metals such as sodium and potassium\(^3\)–\(^7\) as well as the suppression of impurity diffusion from these substrates into the functional layers\(^7,\!^8\) is essential for high solar cell performances.

\textbf{2.1.2 The Back Contact}

The back contact collects charge carriers generated in the absorber layer and separated at the p-n junction in a solar cell. Requirements for a back contact layer are a) high lateral conductivity, to obtain as low a series resistance as possible, b) form an ohmic contact with the CIGS absorber layer without any electrostatic barrier at the interface and c) provide a good adhesion between the CIGS layer and the substrate.

Molybdenum deposited by DC-sputtering is the most commonly used back contact. Depending on the solar cell/module design, thickness of Mo and conductivity are configured. If a different substrate is used instead of soda-lime glass, sodium is added to the back contact to enable its diffusion into the CIGS absorber layer. An increase in plasma pressure during deposition lowers
the Mo layer density and forms a porous structure thereby increasing the sodium (or potassium) concentration in the CIGS absorber layer\(^9\) while a decrease in the DC power leads to increase in the Na and K concentration in both Mo and CIGS absorber layer\(^10\). A thin MoSe\(_2\) layer forms at the interface during the CIGS deposition on molybdenum which is responsible for an ohmic instead of Schottky-contact with the absorber layer\(^{11,12}\). Many other metals have been tried such as gold which shows good electrical behavior but only molybdenum was feasible as a good low-cost back-contact\(^13\).

### 2.1.3 CIGS Thin Film Deposition

CIGS thin films can be prepared using a wide variety of deposition methods. The factors that determine the best deposition method for the commercial manufacture of modules are low cost and fast processing rate with high yield and reproducibility. High yield necessitates compositional uniformity over large areas. A thick CIGS layer (> 0.7 µm) is needed to fully absorb incident light, while keeping the relative composition of the constituents within bounds as per the phase diagram (Fig. 1.6). The CIGS is deposited on a molybdenum-coated glass or flexible substrate for solar cell fabrication. The structural and optical properties of CIGS thin films depend sensitively on the deposition process.

Deposition methods commercially used for manufacture of modules that demonstrate high device efficiencies are divided into two categories. In the first approach, Cu, In, Ga, and Se constituents are simultaneously delivered to a substrate heated to 450 – 600 °C by physical vapor deposition and the CIGS film is formed in a single growth process. To achieve this, the elemental sources Cu, In, and Ga are thermally evaporated simultaneously at temperatures greater than 1000 °C. In the second approach, a two-step process is used where the delivered metals react to
form device-quality films. First step involves depositing a precursor with uniform composition containing the Cu, Ga, and In using low-cost and low-temperature methods. The film deposited is annealed at 450 – 600 °C in a Se atmosphere. The co-evaporation process is faster than the two-step process as reaction and anneal steps may take longer time than the formation of films due to reaction and diffusion kinetics, which limits the throughput and is not suitable for roll-to-roll manufacturing. High process rate can be achieved by moving continuously through sequential process steps using a roll-to-roll substrate.

![Figure 2.2: An illustration of a laboratory CIGS co-evaporation system](image)

The highest efficiency CIGS devices have been deposited from elemental sources by thermal co-evaporation process\textsuperscript{14}. An illustration of the CIGS co-evaporation system used in this research is shown in Fig. 2.2. In the process Cu, In, Ga, and Se constituents are deposited using line-of-sight delivery from Knudsen-type effusion cells or open-boat sources to the heated substrate\textsuperscript{16}. While the evaporation temperatures for each metal depend on the specific source design, typical ranges for Cu are 1300 – 1400 °C, for In are 1000 – 1100 °C, for Ga are 1150 – 1250 °C, and for Se are 250 – 350 °C. The vapor flux rates of Cu, In, and Ga are monitored and controlled by electron impact emission spectroscopy (EIES). A thermocouple connected to the backside of the substrate
is used to measure the substrate temperature. The flux distribution and effusion rate from each source determines the film composition and growth rate as the sticking coefficients of Cu, In, and Ga are very high. According to the relative concentration of Cu compared with In and Ga, the film’s composition tends to follow the pseudo-binary tie-line between (InGa)\(_2\)Se\(_3\) and Cu\(_2\)Se when there is sufficient Se availability (see Fig. 1.6). Se is always evaporated in excess as it has a much higher vapor pressure and lower sticking coefficient. Insufficient Se results in the formation In\(_2\)Se or Ga\(_2\)Se leading to loss of In and Ga\(^{17}\). To change the film’s composition through its thickness during the deposition, elemental flux rates can be varied. The bandgap can be varied by changing the relative concentrations of In and Ga.

The co-evaporation process has been explored extensively for different sequential depositions by varying elemental fluxes. CIGS devices with efficiencies greater than 16 % are fabricated by four different sequences as shown in Fig. 2.2. The targeted final composition in each case is Cu-deficient with Cu/(In + Ga) = 0.8 ∼ 0.9. For a 2 µm thick film, the total deposition time varies from 10 – 90 minutes with typical deposition rates of 20 to 200 nm/min, depending on the effusion rates from the elemental sources.

In a modality called “one-stage evaporation process,” Cu, In, Ga, and Se are evaporated simultaneously and the flux rates of individual elements are kept constant throughout the deposition process\(^{18}\). CIGS films grown by this process show constant composition along the depth of the film.

In a different modality called “two-stage evaporation process” as shown in the Fig. 2.3, elemental flux rates are kept constant so that the bulk of the film is grown with Cu-rich overall composition during the first stage of the process. In Cu-rich CIGS, a semi-metallic Cu\(_{2-x}\)Se phase
coexists along with the CIGS phase\textsuperscript{19}. In the 2\textsuperscript{nd} stage of the deposition process, the Cu flux is terminated while maintaining In and Ga flux in order to make the final film composition Cu-deficient. Deposition of the film is terminated as soon as the excess Cu, in the form of Cu\textsubscript{2-x}Se, is consumed and the film becomes Cu-poor.

\textbf{Figure 2.3}: (a) Different types of co-evaporation processes with relative metal fluxes and substrate temperatures\textsuperscript{14}. (b) Schematics showing typical substrate temperatures, deposition rates of individual sources during the 3-stage process used in this research.

The 3-stage process as shown in the Fig. 2.3, was developed by NREL. During the first-stage, only In, Ga and Se are co-evaporated to form (In,Ga)\textsubscript{2}Se\textsubscript{3} precursor which is followed by the deposition of Cu and Se in the absence of In and Ga fluxes at a higher substrate temperature until the precursor is completely consumed. During the second-stage, Cu atoms diffuse into the
precursor \((\text{In,Ga})_2\text{Se}_3\) film and convert it into CIGS. When the precursor is completely consumed, the material becomes stoichiometric and the excess Cu starts accumulating on the surface as \(\text{Cu}_{2-\delta}\text{Se}\). The second stage is terminated with this Cu-poor to Cu-rich transition and the third stage is started. In this stage, the Cu source power is turned off and In and Ga are evaporated again in the presence of excess Se at the same substrate temperature, to bring the composition back to Cu-deficient. During this process the metals diffuse to form a ternary chalcopyrite film. This 3–stage deposition process has been used to produce the highest-efficiency devices\(^20\). The improved device performance has been attributed to a bandgap gradient which is a result of a double graded profile of Ga concentration, and to larger grain size of the films\(^21,22\). The double grading profile results from a Ga concentration decrease starting from the Mo back-contact into the bulk of the film and then increasing towards the film’s free surface. A constant Se flux rate is maintained by setting the Se source at a constant temperature throughout the deposition process. The main advantage of depositing CIGS using elemental co-evaporation is the flexibility to control the bandgap and film composition. Because of this, many high efficiency devices have been produced using variations of this process. The primary disadvantage of this process arises from the difficulty in controlling the source flux rate, especially Cu-evaporation source. Hence, there is a need for better diagnostics and control of the deposition process over large areas.

The structural, optical, and electronic properties of CIGS thin films vary depending on the the film’s composition i.e. the atomic percentages (at. %) of Cu, In, Ga, and Se. One-stage, two-stage, and 3-stage processes mentioned before are the most common among different variations of co-evaporation process used for CIGS growth. However, 3-stage deposition process is the most successful method yielding world record efficiencies. In all the high efficiency CIGS solar
cells irrespective of the deposition process used, the Cu at. % falls within the narrow range of 22% – 24% \(^{14}\).

### 2.1.4 Buffer Layer

The buffer layer is the n-type material which forms a p-n junction with the p-type CIGS. Energy band discontinuities may arise at the p-n junction due to this heterojunction nature. Hence, the choice of the buffer layer will play an important role in the junction formation mechanism. A more detailed review of buffer layer technologies was prepared by Naghavi et al. \(^{23}\).

CdS is the most common and widely used buffer layer material that is known for best solar cell performance. The best deposition method for CdS that has demonstrated highest cell efficiencies (up to 22.3 %) is chemical bath deposition (CBD) \(^{24}\). One of the possible reasons for high performance of CBD buffer layers is that they act as protective layer for the p-type CIGS absorber layer from the the plasma deposition of the \(i\)-ZnO/ZnO:Al layers, which prevents detrimental shunt paths and passivates the absorber forming a conformal layer without pinholes \(^{23}\). Precursors usually used are a cadmium salt such as CdSO\(_4\), CdCl\(_2\), CdI\(_2\) or Cd(CH\(_3\)COO)\(_2\), ammonia as complexing agent and a sulfur precursor such as SC(NH\(_2\))\(_2\) (thiourea) \(^{14}\).

Even though CdS is known for its performance, the material is toxic and has relatively small bandgap of 2.4 eV that leads to detrimental absorption in the blue spectral range and thus decreases the cells short circuit current, which are its two main disadvantages.

### 2.1.5 Transparent Conductive Oxide Layers

For TCO, generally a highly resistive intrinsic ZnO \((i\)-ZnO\) is deposited first, followed by
ZnO:Al to form the front contact. $i$-ZnO is known to improve cell efficiency due to the passivation of pinholes in the CdS layer which lead to local CIGS/ZnO junctions\textsuperscript{14}. This passivation effect is confirmed by the observation that for thick CdS layers, the $i$-ZnO layer has no effect\textsuperscript{25}. Rau \textit{et al.}\textsuperscript{26} proposed that $i$-ZnO layer reduces the local recombination current due to the varying electronic quality (defects, non-uniformity) of the absorber layer, leading to a significant improvement in total solar cell performance.

Both layers are typically deposited by radio frequency (RF) magnetron sputtering. The thickness of the TCO layers is determined based on the cell or module design. A thicker ZnO:Al layer is used on modules with no metal current collection grid to keep the resistive losses low.

### 2.2 Fabrication of CIGS Solar Cells

The structure of a standard CIGS solar cell deposited on a soda lime glass/stainless steel substrate is shown in Fig. 2.1. The various steps involved in the fabrication process are listed below.

- **Substrate cleaning:** Before the deposition the substrates were cleaned in an ultrasonic bath of isopropyl alcohol for 15 minutes followed by an ultrasonic bath of deionized (DI) water for 15 minutes. The clean substrates were subsequently dried in a nitrogen atmosphere and placed in the load lock of the sputtering chamber.

- **Back contact deposition:** Molybdenum (Mo) is the metal back contact in all the samples used in this research. Commercially available Mo-coated SLG substrates were used in this research. For stainless steel substrates, Cr/Mo metal stack has been sputter deposited by DC-magnetron sputtering from their targets under Ar flow. The thicknesses of the
layers are 300 – 500 nm.

- **Absorber layer deposition**: The deposition process for CIGS films has already been discussed in Section 2.1. For all the samples prepared, the absorber layer was deposited by the 3-stage process.

- **Buffer layer deposition**: A 50 – 60 nm thick n-type CdS layer was deposited on top of the CIGS layer by chemical bath deposition, in order to form a p-n junction with p-type CIGS. Before the deposition, the temperature of the solution was raised slowly, with the help of a heated exterior water bath. Samples were immersed into a solution containing DI water, cadmium sulfate \([\text{Cd}(\text{SO}_4)]\), thiourea \([\text{CS} (\text{NH}_2)_2]\), and ammonium hydroxide \((\text{NH}_4\text{OH})\). In this solution, cadmium sulfate acts as a source of \(\text{Cd}^{2+}\) ions, thiourea acts as a source of \(\text{S}^{2-}\), and ammonium hydroxide acts as a catalyst. The samples were then washed with DI water and dried with nitrogen.

![Figure 2.4: Setup for chemical bath deposition of CdS.](image)

- **TCO layer deposition**: After the buffer layer, a bi-layer of \(i\)-ZnO/ZnO:Al is deposited by RF-sputtering. A 50 – 100 nm layer of \(i\)-ZnO was deposited at room temperature from ZnO target. Then, 200 – 250 nm of ZnO:Al was deposited on top of the \(i\)-ZnO layer by the same process under Ar pressure.
2.3 Materials Characterization Techniques

2.3.1 Secondary Ion Mass Spectrometry (SIMS)

Secondary Ion Mass Spectroscopy (SIMS) uses a high energy (25 keV) pulse ion beam (primary ions) incident on the sample that causes surface atoms and molecules to be ejected out of the sample\textsuperscript{27}. These ejected atoms consist of both secondary ions and neutral atoms. In SIMS, only the secondary ions are analyzed using a mass/charge analyzer (mass spectrometer). O\textsubscript{2}\textsuperscript{+} and Cs\textsuperscript{+} are two types of primary ion sources, which are usually used for sputtering. O\textsubscript{2}\textsuperscript{+} is used to sputter positively charged ions while Cs\textsuperscript{+} is used for negatively charged ions. SIMS has the ability to detect elements present down to parts per billion (ppb) and this high sensitivity is advantageous in tracing impurities or presence of small quantity of elements. SIMS can also be used for depth profiling when the primary ions are bombarded on the surface at a sufficiently high rate\textsuperscript{28} and the signal output or counts corresponding to particular mass/charge is recorded as a function of time\textsuperscript{27}. The primary ion beam sputters a crater while the secondary ion beam (Bi\textsuperscript{+}) analyses the crater bottom. This depth profiling mode can provide elemental depth profiles over a range from a few angstroms (Å) to tens of microns (µm). Static SIMS has been employed to analyze the compositions of solar cell stacks in this research.

2.3.2 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) uses a focused beam of high-energy electrons to obtain topographical and morphological information of the samples. In this technique, the incident electrons are bombarded on to the sample generating signals derived from electron-sample interactions. The incident electron can excite another electron (secondary electron) or it can be
scattered (back-scattered electron). SEM images are produced by detecting secondary and backscattered electrons. Secondary electrons are used for morphology and topography while backscattered electrons are valuable for showing contrast in multiphase samples. A Leo 1550 Schottky source scanning electron microscope was used to image top-view and cross-sections at an accelerating voltage of 10 or 15 kV. Cross-sectional images were used to determine film thickness.

2.3.3 Energy Dispersive X-ray Spectroscopy (EDS)

Energy Dispersive X-ray Spectroscopy (EDS) is a technique that uses the X-ray spectrum emitted when a focused beam of highly energetic electrons is bombarded on a solid sample, to obtain a localized quantitative compositional analysis of a specimen. When this high-energy beam of electrons interacts with a solid specimen, it excites electrons from a low energy state to an excited state. An electron from the higher energy state decays occupying the vacant lower state, by emitting a characteristic X-ray with energy equivalent to the difference between the two states. As the atomic structure of each element is unique, these emitted X-ray photons are characteristic of the element. Qualitative analysis of the X-ray spectrum involves identification of elements present in the sample by detecting the lines in the spectrum. Quantitative analysis involves measuring the elemental composition using known calibration spectra for these elements. A typical EDS spectrum of a 2.2 µm thick CIGS film is shown in Fig. 2.5. A Zeiss 1550 FE-SEM with in-lens and secondary electron detector integrated with a Bruker Quantax energy-dispersive X-ray spectrometer was used in this research. A secondary electron detector (Everhart-Thornley) using an acceleration voltage of 20 kV, at a working distance of 15 mm was used to capture images. The Bruker Quantax energy-dispersive X-ray spectrometer was used to
confirm the elemental composition of CIGS samples. EDS-based elemental distribution maps of the regions of interest (ROI) were overlaid on the corresponding SEM images.

**Figure 2.5**: EDS spectrum of a typical 2 µm thick CIGS thin film on Mo substrate.

### 2.3.4 X-ray fluorescence

For this work, a commercially available system, Solar Metrology XRF SMX-BEN, has been used. It consists of an energy-dispersive x-ray spectrometer, a micro-focus x-ray tube with tungsten anode and beryllium window and a Peltier-cooled Si-drift X-ray detector. The setup has been calibrated using a set of CIGS samples (multipoint calibration) with various thicknesses and composition, in particular analyzing samples with different atomic concentration ratios of Cu/(Ga+In).
2.3.5 Spectroscopic Ellipsometry

Spectroscopic Ellipsometry (SE) is a fast, non-destructive, highly precise optical metrology technique commonly used for the characterization of thin film materials. A beam with known polarization impinges on the sample, and the polarization change of the reflected beam is measured. By modeling the change, the thickness ($t$) and optical properties of bulk materials and thin films can be obtained\(^{29}\). Parameters $\psi$ and $\Delta$ are defined by the relationship $\tan\psi \exp(i\Delta) = r_p/r_s$, where $r_p$ and $r_s$ are the complex amplitude reflection coefficients of the sample for $p$ (parallel) and $s$ (perpendicular) linear polarization states. A brief review of the physics of the amplitude ratio ($\psi$) and the phase difference ($\Delta$) from the parallel ($r_p$) and perpendicular ($r_s$) Fresnel reflection coefficients along with the relationship between dielectric function, refractive index and absorption coefficient is presented in the next section. Furthermore, SE instrumentation used to collect the spectra, and the modeling and data analysis performed to extract the optical properties and thickness will be covered.

2.3.5.1 Propagation of Light in Thin Films

(i) Maxwell’s Equations

The propagation of electromagnetic radiation in free space and its interaction with a medium can be described by Maxwell’s Equations (SI units):

\[
\nabla \cdot E = \frac{\rho}{\varepsilon_0} \quad (2.1)
\]

\[
\nabla \times E = -\frac{\partial B}{\partial t} \quad (2.2)
\]
\[ \nabla \cdot \mathbf{B} = 0 \quad (2.3) \]
\[ \nabla \times \mathbf{B} = \mu_0 \left( \varepsilon_0 \frac{\partial \mathbf{B}}{\partial t} + \mathbf{J} \right) \frac{\rho}{\varepsilon_0} \quad (2.4) \]

where \( \mathbf{E} \), \( \mathbf{B} \), \( \mathbf{J} \), and \( \rho \) represent the electric field vector, magnetic induction vector, current density vector, and charge density, respectively. \( \varepsilon_0 \) and \( \mu_0 \) are the permittivity and permeability of free space, respectively \(^{30,31}\).

Two additional vectors are introduced, the displacement vector \( \mathbf{D} \) and the magnetic field intensity vector \( \mathbf{H} \), to describe the propagation of electromagnetic radiation in matter\(^{32}\)

\[ \mathbf{D} = \varepsilon_0 \varepsilon \mathbf{E} \quad (2.5) \]
\[ \mathbf{B} = \mu_0 \mu \mathbf{H} \quad (2.6) \]

where \( \varepsilon \) and \( \mu \) are in general tensors, called the relative dielectric permittivity and the magnetic permeability of the material, respectively. These tensors, which are functions of the frequency of the radiation, describe the material’s response to propagating electromagnetic radiation. Hence, \( \varepsilon(\omega) \) and \( \mu(\omega) \) are called “optical functions” of the material\(^{33}\). In an isotropic medium, these tensors reduce to scalar functions \( \varepsilon(\omega) \) and \( \mu(\omega) \).

From the Maxwell’s equation and the relations described in Equations 2.1 to 2.6, we can obtain the following wave equation for the electric field\(^{32,34}\):

\[ \nabla^2 \mathbf{E} = \frac{\varepsilon \mu}{c^2} \left( \frac{\partial^2 \mathbf{B}}{\partial t^2} + \frac{4 \pi \sigma \mu}{c^2} \frac{\partial \mathbf{E}}{\partial t} \right) \quad (2.7) \]
where \( c \) is the speed of light and \( \sigma \) is the electrical conductivity in the medium. If the electromagnetic radiation is travelling through a homogeneous and non-magnetic medium, then there is no spatial dependence of \( \varepsilon \) and \( \mu \), which further simplifies the Equation 2.7. Finally, when the material is electrically neutral, then the solution to Equation 2.7, yields a polarized transverse electromagnetic wave propagating at phase speed \( v = c/\text{Re}(N) \) in the medium, where \( N = \varepsilon^{1/2} \) is the complex index of refraction of the material, and damping in accordance with an absorption coefficient \( \alpha \), given by \( \alpha = (2/c)[\text{Im}(N)] \). If the propagation direction of the electromagnetic wave is considered as the \( z \)-axis of a Cartesian coordinate system, then the electric field of the electromagnetic plane wave can be represented by:

\[
E(z,t) = E_0 e^{i\omega \left(\frac{Nz}{c}\right) - t}
\]

where \( \omega \) is the frequency of light. The complex refractive index \( N \) can be written as \( N = n + ik \), where the real part \( n \) is the real index of refraction and the imaginary part \( k \) is the extinction coefficient of the material. \( N \) is related to \( \varepsilon \), the complex dielectric function of the material as:

\[
\varepsilon = \varepsilon_1 + i\varepsilon_2 = N^2 = (n + ik)^2
\]

From the above equation, we can derive

\[
\varepsilon_1 = n^2 - k^2
\]

\[
\varepsilon_2 = 2nk
\]

The complex vector \( \mathbf{E}_0 \) in Equation 2.8, in a Cartesian coordinate system with orthogonal unit vectors \( \hat{x} \) and \( \hat{y} \), can be written as:
\[ E_0 = E_{0x}(e^{i\varphi_x})x + E_{0y}(e^{i\varphi_y})y \]  

(2.12)

where \( \varphi_x \) and \( \varphi_y \) represent the absolute phases of the electric field components \( E_x \) and \( E_y \), respectively, at \( z = 0 \) and \( t = 0 \).

(ii) **Ellipsometry and Reflectance of Polarized Light**

The path traced by the electric field of a plane light wave propagating along the \( z \)-direction at a fixed point in space, \( z = z_0 \), as given by Equation 2.12, is an ellipse in the \( x-y \) plane, as a function of time \( t \), as shown in Fig. 2.6. The two special cases of polarization are:

(a) linear polarization with \( \varphi_x = \varphi_y \), and

(b) circular polarization with \( \varphi_x = \varphi_y \pm \pi/2 \) and \( E_{0x} = E_{0y} \).

In a general case, the polarization can be described by an ellipse having the tilt angle \( Q (-90^\circ \leq Q \leq 90^\circ) \) between its major axis and the \( x \)-axis, and the ellipticity angle, \( \chi = \arctan (b/a) \), which is the inverse tangent of the ratio of the minor axis (b) to the major axis (a). \((-45^\circ \leq \chi \leq 45^\circ)^{29}\).
Figure 2.6: Schematic representation of the electric field vector \( E(z_0, t) \) for an elliptically polarized light wave at a given \( z = z_0 \). \( E \) traces out an ellipse over time. The sense of rotation determines whether the light wave exhibits left or right handed polarization. \( Q \) is the tilt angle between the ellipse major axis ‘a’ and the x-axis, measured in counterclockwise-positive sense when facing the light beam source. \( \chi \) is the ellipticity angle given by \( \tan^{-1}(b/a) \), where \( \chi > 0 \) corresponds to right handed polarization and \( \chi < 0 \) corresponds to left handed polarization.

Figure 2.7: Reflection of light showing the p and s electric field components in the incident (i), transmitted (t), and reflected (r) waves with the propagation vectors \( k_i \) (incident), \( k_t \) (transmitted), and \( k_r \) (reflected).

Conventionally, in ellipsometry the arbitrary orthogonal coordinates “x” and “y” are redefined to those based on the plane of incidence in a reflection measurement. As shown in Fig. 2.7, the electric field is then resolved into two components; p-component, parallel to the plane of
incidence and an s-component, perpendicular to the plane of incidence. The complex amplitude
reflection coefficients are defined in this new p-s coordinate system as:

\[ r_p = |r_p| e^{i\varphi_p} = \frac{E^r_p}{E^i_p} \]  

\[ r_s = |r_s| e^{i\varphi_s} = \frac{E^r_s}{E^i_s} \]  

where \( E \) represents the complex electric field components and \( \varphi \) represents the phase shifts due
to reflection. The superscripts “i” is for incident fields while “r” is for reflected fields of the
corresponding waves. In reflection ellipsometry the ratio of the p and s reflection coefficients are
of interest, rather than their individual values. The complex amplitude reflection ratio \( \rho_r \) is
defined as:

\[ \rho_r \equiv \frac{r_p}{r_s} = \frac{|r_p|}{|r_s|} e^{i(\varphi_p - \varphi_s)} \]  

The complex quantity \( \rho_r \) can be expressed in terms of the ellipsometric angles (\( \psi, \Delta \)) as:

\[ \rho_r = \tan \psi e^{i\Delta} \]  

where

\[ \tan \psi = \left| \frac{r_p}{r_s} \right| \]  

\[ \Delta = \varphi_p - \varphi_s \]
**Optical Interference in Thin Films**

Consider a simple example of reflection from a single interface between a semi-infinite ambient and a semi-infinite isotropic, homogeneous, and uniform medium as an example of the application of ellipsometry to determine $N_s$, the complex index of refraction of the medium. Here, the complex-amplitude reflection coefficients for $p$ and $s$ polarized light are given by the Fresnel coefficients as:

$$r_p = \frac{N_s \cos \theta_i - n_a \cos \theta_t}{N_s \cos \theta_i + n_a \cos \theta_t}$$  \hspace{0.5cm} (2.19)$$

$$r_s = \frac{n_a \cos \theta_i - N_s \cos \theta_t}{n_a \cos \theta_i + N_s \cos \theta_t}$$  \hspace{0.5cm} (2.20)$$

where $n_a$ is the real index of refraction of the ambient; $N_s$ is given by $N_s = n_s - ik_s$, where $n_s$ is the real index of refraction of the substrate (medium) and $k_s$ is its extinction coefficient; $\theta_i$ is the angle of incidence; and $\theta_t$ is the angle of transmission. Snell’s Law can be applied to eliminate $\theta_t$. Hence, we have three unknown values, $n_s$, $k_s$, and $\theta_t$. Also, the two ellipsometric angles $\psi$ and $\Delta$ can be expressed in terms of $N_s$, $n_a$, and $\theta_i$ through the defining equation:

$$\tan \psi e^{i\Delta} = \frac{r_p}{r_s} = \rho$$  \hspace{0.5cm} (2.21)$$

$N_s$ can be determined from the ellipsometry data values by substitution of Equations 2.19 and 2.20 into Equation 2.21 and (or complex $\rho$) using the known quantities $n_a$ and $\theta_i$. By expressing optical functions $n_a$ and $N_s$ as the corresponding complex dielectric functions, the resulting equation becomes simpler in form:
\[ \varepsilon_s = N_s^2 \quad \text{and} \quad \varepsilon_a = N_a^2 \]  

where \( s \) is the complex dielectric function of the reflecting substrate medium, and \( a \) is the complex dielectric function of the ambient. The result, which relates the measured ellipsometry parameters to the complex dielectric function of the substrate medium, is given as:

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

(2.23)

For a single interface, the requirements on \( \varepsilon_s \), i.e., that the imaginary part be positive, implies that \( 0^\circ \leq \psi \leq 45^\circ \) and \( 0^\circ \leq \Delta \leq 180^\circ \).

If we substitute \( \theta_i = \theta_t = 0 \) and \( N_s = 1 - i0 \) into Fresnel equations, we obtain the reflectance at normal incidence:

\[ R_s = R_p = \frac{\left( n_s - 1 \right)^2 + k_s^2}{\left( n_s - 1 \right)^2 - k_s^2} \]  

(2.24)

(iv) **Multilayers**

In most practical cases, a general sample structure consists of \( m \) layers on a substrate and \( m+1 \) interfaces. In the case of multiple layers as shown in Fig. 2.8, the 2x2 scattering matrix given by \( S \) should be determined, where \( S_v \) designates either \( p \) or \( s \) polarization.

\[ S_{v,m+1} = l_{v,01}l_{11}l_{v,12}l_{22} \ldots l_j \times l_{v,j+1} \ldots l_m l_{v,m} l_{m+1} \]  

(2.25)
The above matrix is a product of \(m+1\) interface matrices (I) and \(m\) layer matrices (L), where the index 0 represents the semi-infinite ambient, and the index \(m+1\) represents the semi-infinite substrate. The interface and layer matrices for both polarizations are given below:

\[
I_{v,j+1} = \frac{1}{t_{v,j+1}} \times \begin{pmatrix} 1 & r_{v,j+1} \\ r_{v,j+1} & 1 \end{pmatrix} \tag{2.26a}
\]

\[
L_j = \begin{pmatrix} Z_j & 0 \\ 0 & Z_j^{-1} \end{pmatrix} \tag{2.26b}
\]

Fig. 2.8 shows the schematics of a multilayer stack. \(N_a\) is the complex index of refraction of the ambient, \(N_j\) is the complex index of refraction of the \(j\)th layer, and \(N_{m+1}\) is the complex index of refraction of the substrate. \(\theta_0\) is the angle of incidence that the light makes with the first layer, \(\theta_j\) is the angle of incidence at the interface between the \(j\)th and the \((j+1)\)st layer, and \(\theta_{m+1}\) is the angle of transmission into the substrate.

In Equation 2.26a, \(r_{v,j+1}\) and \(t_{v,j+1}\), can be determined from the following formulae given below through the substitution \(j \rightarrow j+1\). These are the reflection and transmission coefficients, respectively, for the interface between layers’ \(j\) and \(j+1\).
Figure 2.8: Schematic of a multi-layer thin film stack.

\[
\begin{align*}
(r_{j-1,j})_p &= \frac{N_j \cos \theta_{j-1} - N_{j-1} \cos \theta_j}{N_j \cos \theta_{j-1} + N_{j-1} \cos \theta_j} \\
(r_{j-1,j})_s &= \frac{N_{j-1} \cos \theta_{j-1} - N_j \cos \theta_j}{N_{j-1} \cos \theta_{j-1} + N_j \cos \theta_j} \\
(t_{j-1,j})_p &= \frac{2N_{j-1} \cos \theta_{j-1}}{N_j \cos \theta_{j-1} + N_{j-1} \cos \theta_j} \\
(t_{j-1,j})_s &= \frac{2N_{j-1} \cos \theta_{j-1}}{N_{j-1} \cos \theta_{j-1} + N_j \cos \theta_j}
\end{align*}
\]  

(2.27a)  

(2.27b)  

(2.27c)  

(2.27d)

In addition, \( Z_j \) in the layer matrix of Equation 2.26b is given by,

\[
Z_j = e^{\left(\frac{2\pi d_j}{\lambda}N_j \cos \theta_j\right)}
\]  

(2.28)

where \( d_j \) is the thickness of layer \( j \). The incidence angle for the interface between layer \( j \) and layer \( j+1, j \), is obtained from successive applications of Snell’s Law:

\[
N_0 \sin \theta_0 = N_1 \sin \theta_1 = N_j \sin \theta_j = N_{j+1} \sin \theta_{j+1} = N_m \sin \theta_m = N_{m+1} \sin \theta_{m+1}
\]  

(2.29)

After determining the scattering matrix, the complex reflection coefficients for the entire stack
can be determined by:

\[ r_{m,p+1} = \frac{[S_{p,m+1}]_{21}}{[S_{p,m+1}]_{11}} \quad (2.30a) \]

\[ r_{s,p+1} = \frac{[S_{s,m+1}]_{21}}{[S_{s,m+1}]_{11}} \quad (2.30b) \]

Once these reflection coefficients are determined, the \((\psi, \Delta)\) values corresponding to this stack can also be found, using the following equation:

\[ \rho_r = \frac{r_{m,p+1}}{r_{s,p+1}} = \tan \psi e^{i\Delta} \quad (2.31) \]

This equation relates the measured quantities \((\psi, \Delta)\) to \(\lambda, \theta_0, N_0, ..., N_{m+1},\) and \(d_1, ..., d_m\) and must be solved for the useful information on the film stack using a computer program. Solutions can be obtained either numerically from a single pair of \((\psi, \Delta)\) values, for example, with the user providing \(d_j\) values to extract a single \(N_j\) at a given wavelength, or by fitting spectra in the \((\psi, \Delta)\) values, for example, with the user providing spectra in \(N_j\) to extract multiple \(d_j\).

### 2.3.5.2 History of Spectroscopic Ellipsometry

In the late 19th century, the first ellipsometric measurements were performed by Paul Drude. Drude measured film thicknesses using the phase shift induced between mutually perpendicular components of polarized light. The light is said to be elliptically polarized when the mutually perpendicular components of polarized light \((E_x\) and \(E_y\)) are out of phase, hence the technique that evolved from Drude’s early measurements came to be known as ellipsometry.
Even though the fundamentals behind ellipsometry have been known for some time, due to the unavailability of computers, the use of ellipsometry as an important surface and thin film characterization technique did not occur until last quarter of the 20th century when SE evolved significantly. Until the early 1970s, most ellipsometry measurements were very time consuming as they were carried out only at a single wavelength and operated manually. Developments in the field of SE not only improved the measurement time but also the measurement precision significantly. Aspnes et al. in 1975, first demonstrated the use of completely automated SE measurements and Muller and Farmer in 1984 reported the use of ellipsometry for real-time monitoring.

Recently, the incorporation of improved optics and use of compensators, development of variable angle of incidence, increases in spectral range, development of imaging ellipsometry, and improvement of spectroscopic ellipsometry for real time applications have been reported. Several books on SE have been published recently which provide comprehensive information about its concepts and applications.

Ellipsometric systems integrated with several other instruments such as gas adsorption systems, deposition chambers, cryogenic stages, high-temperature stages, liquid cells, etc., provide the capability to characterize a wide variety of samples using appropriate optical models. Fitting these optical models to the ellipsometric data can determine the optical properties and thickness of the thin films from the as well as the band gap of materials, carrier concentration, evolution of microstructure, alloy compositions, growth processes, phase, and grain size, optical conductivity, mobility, porosity, pore size, coefficient of thermal expansion, glass transition temperature, Young’s modulus, and anisotropic properties.
2.3.5.3 Instrumentation

In the present work, SE data was collected using a dual rotating compensator ellipsometer (RC2®) of J. A. Woollam shown in the Fig. 2.9. The optical configurations of the RC2® ellipsometer are shown in Fig. 2.10. The RC2® is configured with two rotating compensators, a polarizer, and an analyzer that measure the change in polarization of light. The tool is equipped with a xenon (Xe) arc lamp and a quartz tungsten halogen (QTH) lamp to cover a spectroscopic optical range of 245 – 1700 nm. InGaAs and Si charge-coupled device (CCD) detectors are used to detect the UV/visible and near IR wavelengths, respectively. Complete EASE®, a computer-controlled software is used to align, calibrate, and collect data from the ellipsometer. Typically, the data acquisition time for a single spectrum at one angle of incidence is 5 – 15 seconds. The spot size of the incident beam is ~ 3 mm × 5 mm depending upon the selected angle of incidence. However, focusing optics can be used to reduce the spot size of the incident beam to ~200 µm × 450 µm. This instrument is capable of mapping samples with dimensions up to 20 cm × 20 cm in various spatial patterns, such as rectangular, circular, or hexagonal at various incidence angles.

Figure 2.9: J.A. Woollam’s RC2: a dual rotating compensator variable angle ellipsometer.
2.3.5.4 Experimental Methods in Spectroscopic Ellipsometry

In a reflection-type ellipsometry experiment, a polarized beam of light is incident at an oblique angle onto the surface of the sample under investigation, and the reflected beam of light is collected. As the polarized light interacts with the material its polarization state changes. The reflected beam has a different polarization state than the incident beam, and contains information about the optical and structural properties of the sample. These sample properties are obtained by analyzing the change in the polarization state of the light wave induced by the interaction with the sample upon reflection.

General steps in a spectroscopic ellipsometry procedure, from data collection to analysis, are described sequentially as follows:

- Polarization of un-polarized light by passing the incident light beam through a polarizer and optional compensators
- Collection of the reflected beam and analysis of its polarization state
- Determination of the spectra ($\psi$, $\Delta$) from the change in polarization caused by reflection and from the ellipsometry calibration parameters
- Construction of a realistic optical model that accurately represents the sample’s optical behavior such that model parameters can agree between the simulated and the measured spectra.

The parameters in the model such as

(i) Surface and interface roughness-layer thicknesses
(ii) Composition that define any composite layer dielectric functions from known components
(iii) Analytical expression’s parameters for unknown dielectric functions can be varied in computational program.

The objective is to match the experimental ($\psi$, $\Delta$) spectra with the simulated spectra through a least squares regression analysis. Fig. 2.11 shows a flow chart of above mentioned steps from measurement to data analysis, which will be discussed in detail in the next section.

**Figure 2.11:** Characterization of physical properties by spectroscopic ellipsometry.
2.3.5.5 Data Analysis in Spectroscopic Ellipsometry

In spectroscopic ellipsometry, the physical and optical properties of the sample are not obtained directly but are deduced from the measured spectra ($\psi$, $\Delta$) that carry information about the changes in the polarization state of the light beam upon reflection. As described in Section 2.3.9, the spectroscopic ellipsometry data must be analyzed with mathematical computational programs in order to extract physical information from the data such as complex dielectric functions and component layer thicknesses. Several data analysis methods such as least squares regression (LSR) and mathematical inversion have been developed that can be applied to determine layer thicknesses, dielectric functions and compositions of single-phase bulk materials and thin films\textsuperscript{32,34}.

Spectroscopic ellipsometry measurements may be carried out in a wide spectral range, from ultraviolet (UV) to the infrared (IR) region. Generally, SE Data in the UV/visible region is used to determine film thickness, electronic transitions (inter-band transitions) and band structure of the material\textsuperscript{40,46,48}. Properties such as alloy composition, phase structure, and crystal grain size affect the band structure hence these properties can also be determined from the spectral analysis of optical constants. For example, the absorption shape of silicon films in the UV region can be used to determine the layer crystallinity as seen in Fig. 2.12. If the film is amorphous, the absorption is broadened with no critical point features and as crystallinity increases, the absorption features in the ultraviolet become more distinct.
Figure 2.12: Real and imaginary part of dielectric functions ($\varepsilon_1$ and $\varepsilon_2$) for amorphous, polycrystalline, and crystalline Si\textsuperscript{47}.

Figure 2.13: Calculated optical spectra of $\Psi$ and $\Delta$ for 50 nm, 100 nm, 150 nm, 200 nm, and 250 nm thick SiO\textsubscript{2} thin film on Si substrate\textsuperscript{47}.

Free carrier absorption in the IR wavelength region is induced by free electrons (or holes) in solids (only for metals and solids with a metallic character or heavily doped semiconductors). Electrical properties such as carrier mobility, carrier concentration, and conductivity can be obtained\textsuperscript{42} when the carrier concentration is high. SE is very sensitive to the film thickness measurements up to $\sim$0.1 Å and is typically used for films whose thickness ranges from angstroms to microns. Path length of light traveling through the film is affected by the film thickness, while the light waves’ velocity and refracted angle are affected by optical properties of the material. In order to deduce the thickness accurately from data analysis, measurements must be carried out in the spectral region with lower absorption. For example, thickness determination...
should be carried out using visible wavelengths, if a film strongly absorbs UV and IR light, but remain transparent in the visible region.

The position and number of interference oscillations in the SE data provide information about the thickness as seen in Fig. 2.13. Thicker films produce large number of oscillations, which are better resolved at longer wavelengths than shorter wavelengths. Hence, probing wavelength and the samples’ optical properties determine the upper thickness limit measurable by SE. For example, the maximum thickness determination of metal films using SE is typically in the range of 100 nm which has been one of the major challenges in optical metrology. When looking at optical properties of thin film alloys, changes in concentration lead to change in real and imaginary part of the dielectric functions as well as the optical band gap of the material which can be measured using SE analysis. SE can be used as the inline metrology tool for accurate process control to characterize composition, thickness, and optical properties during the deposition process in order to improve the efficiency of solar cells and product yield.

Consider a multilayer stack with m number of layers, as shown in Fig. 2.9, to describe a general data analysis problem. The variables $d_1$, $d_2$, $d_3$, ..., $d_m$ represent the thicknesses of the layers while $(\varepsilon_1, \varepsilon_2)_1$, $(\varepsilon_1, \varepsilon_2)_2$, $(\varepsilon_1, \varepsilon_2)_3$, ..., $(\varepsilon_1, \varepsilon_2)_m$ represent their corresponding dielectric functions. Subscript 0 represents the ambient and the subscript $(m+1)$ represents the substrate with the corresponding dielectric functions $(\varepsilon_1, \varepsilon_2)_0$ and $(\varepsilon_1, \varepsilon_2)_{m+1}$, respectively. The $(\psi, \Delta)$ spectra of the sample can be uniquely determined using Equations 2.30 and 2.31, if all the layer thicknesses $(d_1, d_2, ..., d_m)$, the dielectric functions $(\varepsilon_1, \varepsilon_2)_0$, $(\varepsilon_1, \varepsilon_2)_1$, $(\varepsilon_1, \varepsilon_2)_2$, ..., $(\varepsilon_1, \varepsilon_2)_m$, $(\varepsilon_1, \varepsilon_2)_{m+1}$ and the angle of incidence $\theta_0$ are all known. If all the above mentioned quantities are known except the thickness and dielectric function of the $j^{th}$ layer ($1 \leq j \leq m$) (to be determined in the analysis), then
a single measured pair of \((\psi, \Delta)\) from spectroscopic ellipsometry is insufficient because the number of unknowns to be determined, \(2n+1\) are greater than the number of measured knowns, \(2n\). The unknowns include thickness, \(d_j\) and \(2n\) dielectric function values \((\varepsilon_1, \varepsilon_2)_j\) at the \(n\) different wavelengths. Many methods have been proposed in spectroscopic ellipsometry to address this problem.

In one such method called “artifact minimization”, the thickness of the unknown layer \(d_j\) is fixed at an approximate value (determined by ancillary techniques) so that the number of unknown parameters is then equal to the number of known parameters. Then, it becomes possible by solving the corresponding non-linear equations through successive approximations, to invert numerically the \(n\) pairs of \((\psi, \Delta)\) to obtain the \(n\) pairs of \((\varepsilon_1, \varepsilon_2)\). This method known as “mathematical inversion” describes the transformation of \(n\) pairs of measured quantities \((\psi, \Delta)\) to the \(n\) pairs of unknown quantities \((\varepsilon_1, \varepsilon_2)_j\) through the scattering matrix expressions given in Equations 2.30 and 2.31. If the estimated value of thickness \(d_j\) deviates from the true thickness of the layer, then the inverted \(n\) pairs of dielectric function values will be incorrect. Due to such deviations, artifacts will be observed in the inverted dielectric function of the unknown layer. The artifacts may be categorized depending on the source as:

(i) **Substrate Artifacts**: Arise when features of the substrate or any other layer in the stack appear erroneously in the inverted dielectric function of the unknown layer;

(ii) **Interference Artifacts**: Arise due to the coupling of interference oscillations versus wavelength to the inverted dielectric function of the \(j^{th}\) layer; and

(iii) **Sub-Gap Absorption Artifacts**: Arise in semiconductors, when \(\varepsilon_2\) from the inversion is non-zero below a known band gap of the material of layer \(j\).
More on the artifact minimization approach and examples showing identification of the correct thickness $d_j$ of the unknown layer can be found here\textsuperscript{34}. The final thickness $d_j$ and the dielectric function $(\varepsilon_1, \varepsilon_2)_j$ obtained from a mathematical inversion method with minimum artifacts are considered as the correct parameters of the unknown layer.

<table>
<thead>
<tr>
<th>Optical Constant (symbol)</th>
<th>Real part</th>
<th>Imaginary part</th>
</tr>
</thead>
<tbody>
<tr>
<td>conductivity ((\sigma = \sigma_1 + i\sigma_2))</td>
<td>$\sigma_1 = \omega\varepsilon_1\varepsilon_2$</td>
<td>$\sigma_2 = -i\omega\varepsilon_2(\varepsilon_1 - 1)$</td>
</tr>
<tr>
<td>dielectric function ((\varepsilon = \varepsilon_1 + i\varepsilon_2))</td>
<td>$\varepsilon_1 = 1 - \varepsilon_{rj}/(\omega\varepsilon_0)$</td>
<td>$\varepsilon_2 = \varepsilon_{rj}/(\omega\varepsilon_0)$</td>
</tr>
<tr>
<td>refractive index ((N = n + ik))</td>
<td>$n = \sqrt{(\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2})/2}$</td>
<td>$k = \sqrt{(-\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2})/2}$</td>
</tr>
</tbody>
</table>

Figure 2.14: Interdependency of optical constants\textsuperscript{34}.

The real and imaginary parts of the complex dielectric constant depend on each other according to the Kramers-Kronig (KK) relation. Absorption \(k\) in the material also affects the refractive index \(n\). Most oscillator models use KK consistency to maintain a physical relationship between the optical constants. A KK consistent dispersion model produces KK consistent optical constants and reduces the number of unknown parameters, such that thickness can be fit simultaneously with optical constants. KK consistency can help us in verifying a model when transparent region is not sensitive to the actual sample structure (layer thickness, number of layers).

The optical constants of a material vary with wavelength (dispersion). Common dispersion models include the Cauchy and Sellmeier relationships for transparent materials and oscillator models (Lorentz, Drude, Gaussian, Tauc-Lorentz, Herzinger-Johs) for absorbing materials\textsuperscript{32}.  

53
The index of refraction, \( n(\lambda) \), for transparent materials can be described with the Cauchy dispersion model and is described with an equation given in the Fig. 2.15, where \( A_n, B_n, \) and \( C_n \), are Cauchy parameters and \( \lambda \) is the wavelength in nm. The Sellmeier dispersion model is shown on the right of Fig. 2.15. The real part of the dielectric constant, \( \epsilon_1(\lambda) \), for transparent materials can be described using zero-broadened oscillators outside the measured spectral range, based on Kramers-Kronig consistency, where \( E_a \) and \( A_a \) are Sellmeier coefficients while \( E \) is photon energy in eV.

**Figure 2.15:** Cauchy and Sellmeier models for the dependence of the index of refraction on wavelength.

Various absorbing oscillator models are available, including Drude, Lorentz, Gaussian, Harmonic, Tauc-Lorentz, and more. While each is different, they function in a similar manner. The \( \epsilon_2 \) shape is described using oscillators with center energy, \( E_c \), amplitude, \( A \), and broadening, \( B \). The \( \epsilon_1 \) shape is linked to the \( \epsilon_2 \) values through KK consistency. There is also an \( \epsilon_1 \) offset to account for absorption outside of the measured spectral range. \( e1 \) and \( e2 \) in the plots refer to \( \epsilon_1 \) and \( \epsilon_2 \) respectively.
The Lorentz oscillator model is based on the assumption that electrons respond to a driving electric field (light beam) in a manner similar to a mass on a spring subject to a dissipative force. This classical representation of materials is often adequate for resonant absorptive processes. The dielectric response is given where $A$ is amplitude, $E_0$ is center energy, $\gamma$ is broadening and $E$ represents probe beam energy. The Tauc-Lorentz oscillator was developed by Jellison and Modine. It is based on the Tauc joint density of states and the Lorentz oscillator with four parameters to describe $\varepsilon_2$: $\gamma$, $A$, $E_0$ and $E_g$. The additional parameter, $E_g$, (over 3-term oscillator models) is band gap.

**Figure 2.16:** Parameters of an absorbing oscillator.

**Figure 2.17:** Comparison of Lorentz and Tauc-Lorentz oscillator line shape.
Fig. 2.17 compares a Tauc-Lorentz line shape with that of a simple Lorentz oscillator. This model works particularly well for amorphous materials and will ensure $k = 0$ below the band gap.

The Drude model is a Lorentz oscillator centered at zero energy. It is typically used to describe free carrier absorption present in metals, conductive oxides and heavily doped semiconductors. A comprehensive overview of the oscillators can be found here$^{33,42,51-53}$.

The B-Spline layer describes the optical constant dispersion using a series of control points, which are equally spaced in photon energy (eV). The appropriate spacing is controlled depending on the sample and optical features to be described. The B-Spline layer uses b-spline (also known as basis-spline) curves to represent the dielectric function ($\varepsilon_1$ and $\varepsilon_2$) versus photon energy. Basis spline curves are smooth and continuous in the 0th, 1st, and 2nd derivatives$^{54}$. A B-spline basis function $B_i^k(x)$ is defined by:

![Drude Optical Constants](image)

**Figure 2.18:** Drude oscillator model’s line shape with its governing equation.
The superscript on the function denotes the degree $k$ of the B-spline, and the subscript $i$ indexes the knot locations $t_i$ (‘knots’ are nodes on the x-axis where the curve transitions from one polynomial segment to another). Eq. 2.32 defines the degree 0 B-spline basis function; higher degree B-spline basis functions are constructed using the recursion relation in Eq. 2.33. A spline curve $S(x)$ is then constructed as a linear sum of $n$ basis functions (Eq. 2.34), in which $c_i$ are the spline coefficients for the $i$-th basis function:

$$B_i^0(x) = \begin{cases} 1 & t_i \leq x < t_{i+1} \\ 0 & \text{otherwise} \end{cases} \quad (2.32)$$

$$B_i^k(x) = \left( \frac{x - t_i}{t_{i+k} - t_i} \right) B_i^{k-1}(x) + \left( \frac{t_{i+k+1} - x}{t_{i+k+1} - t_{i+1}} \right) B_{i+1}^{k-1}(x) \quad (2.33)$$

B-spline curves have many desirable properties for modeling dielectric functions:

- B-Spline curves and their derivatives (up to the spline order minus one) are continuous.
- Since the basic functions depend only on the node positions, the node amplitudes which define the resulting curve are linearly independent, which greatly increases computation efficiency.
- The Kramers-Kronig (KK) integral can be applied to the b-spline recursion formula to generate KK consistent basis functions (i.e., the $\varepsilon_1$ curve is defined by the KK transform of $\varepsilon_2$).
Dielectric function spectra can be constrained to follow the analytical forms as a function of wavelength or photon energy, when the nature of the material is well understood. For example, it is possible to assume that the real part of the dielectric function of the material follows the Sellmeier/Cauchy function (and that the imaginary part of the dielectric function is zero) if the jth layer under consideration is a transparent material with a band gap higher than the upper limit of the measured (ψ, Δ) spectra. The Sellmeier/Cauchy function uses only a few photon energy independent parameters to describe the dispersion of the real part of the dielectric function as shown in the Fig. 2.15.

By fitting the simulated spectra to the measured (ψ, Δ) spectra, the Cauchy/Sellmeier parameters along with unknown thicknesses can be determined. Layer thicknesses and other parameters such as interfacial roughness can be fitted together with the dielectric function parameters, since the number of unknown fitting parameters in this case is much smaller than the number of known values of (ψ, Δ). In this approach, the analysis is based on least squares regression and does not rely on exact inversion, hence, there is not a one-to-one correspondence between the analytical function parameter values and the measured (ψ, Δ) values. The quality of the fit is evaluated
based on the root-mean square error (RMSE). A commonly used form of RMSE from the CompleteEASE® software package (reference) used here is given by:

$$\text{RMSE} = \sqrt{\frac{1}{3n-m} \sum_{i=1}^{n} \left[ (N_i^{(\text{exp})} - N_i^{(\text{cal})})^2 + (S_i^{(\text{exp})} - S_i^{(\text{cal})})^2 + (C_i^{(\text{exp})} - C_i^{(\text{cal})})^2 \right]} \times 1000 \quad (2.35)$$

where $N = \cos^2 \psi$, $S = \sin^2 \psi \sin \Delta$, $C = \sin^2 \psi \cos \Delta$, $n$ is the number of data points versus wavelength or photon energy, and $m$ is the number of fit parameters. The subscript “cal” denotes the generated value and “exp” denotes the experimental value of the identified parameters. The RMSE is minimized through least squares regression during data analysis.

**Figure 2.20**: Variation of MSE as the film thickness is varied.

Ellipsometry measurements use polarized light. If the sample is isotropic and ideal, this measurement can be described by the two values $\psi$ and $\Delta$. However, if a sample is partially depolarizing (due to roughness and thickness inhomogeneity), these two parameters are insufficient to fully describe the change in polarization. The Rotating Compensator technology used in the RC2 system permits measurements of three reported quantities: $\psi$, $\Delta$, and %depolarization. The “%depolarization” should remain zero for ideal sample conditions. If the film thickness varies across the spot, the phase difference generated by optical interference also
changes. Thus, thickness inhomogeneity induces the depolarization of reflected light. If the film thickness is uniform over the illuminated spot, then all the N’s will be the same. However, if this is not the case, then N, S, and C will each be different, and the intensity reaching the detector will be best represented by the integral of the light intensity times the probability distribution over the sample thickness.

\[
w(d) = \begin{cases} 
  \frac{1}{2\sigma} & \text{for } |d - d_{av}| \leq \sigma \\
  0 & \text{for } |d - d_{av}| > \sigma 
\end{cases}
\]

(2.36)

Here, \(w(d)\) represents the probability of finding the thickness \(d\). The \(d_{av}\) and \(\sigma\) show the average film thickness and width of the distribution function, respectively, and \(\sigma\) becomes smaller when a thin film is uniform\(^56\).

Generally, in ex-situ experiments ellipsometry data are collected at multiple angles of incidence so that the number of known parameters is multiplied whereas the number of unknown parameters remains the same. Hence, with the angle of incidence as an additional known parameter it becomes possible to find the dielectric function \((\varepsilon_1, \varepsilon_2)\) and the layer thickness \(d_j\) of the unknown layer simultaneously through least squares regression.

In this research, SE data analysis was performed to obtain the dielectric function following the steps shown in the Fig. 2.21. The model is fit to the data by regression analysis. The modeling is performed assuming that the dielectric function of an analyzed layer is independent of thickness.
Figure 2.21: Steps involved in the regression analysis used in this research.

In this method, a simple model such as Cauchy model, was fit to the measured \((\psi, \Delta)\) to define the dielectric function in the wavelength region where the material of interest is transparent. This simple model was used as a starting point in the Kramers-Kronig-consistent B-Spline function, which was fit to the experimental spectra \((\psi, \Delta)\) by regression analysis to obtain the dielectric function. The thickness of the material of interest obtained by ancillary experimental techniques was used as a fixed parameter in the regression analysis. In the final step, the extracted dielectric
function was parameterized using absorbing oscillators (e.g. Tauc-Lorentz) to provide physically meaningful parameters such as energies, broadening parameters, and resonance exponents related to the band structure and excited state relaxation times of the CIGS material under study. From the parameterized dielectric function, we performed the fitting again, to determine the dielectric function more accurately\(^{32}\).

### 2.3.5.6 Effective Medium Theory in Spectroscopic Ellipsometry

It is necessary to incorporate surface and interface structures into an optical model in data analysis as spectroscopic ellipsometry is quite sensitive to these structures. With the application of effective medium theory (EMT), the complex refractive indices of surface roughness and interface layers can be calculated relatively easily and also, characterize volume fractions in composite materials. Effective medium approximation (EMA) methods can be applied when the scale of the inhomogeneity of the composite structure is much smaller than the wavelength of the probe beam, but sufficiently large so that the optical response is independent of the size of the structure.

![Figure 2.22: EMA approximation for surface roughness and interfacial roughness\(^{49}\).](image)

Microscopic surface roughness on top of a thin film and typical composite structures such as amorphous or polycrystalline materials with void inclusions at grain boundaries can be successfully handled with an effective medium theory. In modeling surface roughness, a 50 vol.%/50 vol.% mixture of underlying material and free space is often used. By fixing the
volume fraction, one reduces the number of unknown parameter associated with the roughness layer. A classic example of a composite occurs when an overlying layer is deposited on top of a previously deposited rough film. The voids in the roughness layer of the underlying film are filled by the overlying material, forming an interface roughness layer. When the void volume in the surface roughness of the underlying material is not completely filled by the overlying material, a three component EMT, including the two materials and void, is employed to obtain the interface layer optical functions.

EMT’s general expression suitable for the situation in which an inclusion is embedded within a host material, can be written as:

\[
\frac{\varepsilon_{\text{eff}} - \varepsilon_h}{\varepsilon_{\text{eff}} + \kappa \varepsilon_h} = \sum f_i \frac{\varepsilon_i - \varepsilon_h}{\varepsilon_i + \kappa \varepsilon_h}
\]  

(2.37)

where \(\varepsilon_{\text{eff}}, \varepsilon_h, \varepsilon_i,\) and \(f_i\) are the effective medium dielectric function, the host dielectric function, and the dielectric function and volume fraction of the \(i^{\text{th}}\) component, respectively. The quantity \(\kappa\) is given by \(\kappa = (1/q) - 1\), where \(q (0 \leq q \leq 1)\) is the screening parameter which describes the shape of the inclusions. In fact, the shape of each inclusion must be the same in order to apply Equation 2.37. In addition, Equation 2.37 describes an isotropic effective dielectric function for which the inclusions must be spherical in shape. Then, \(q = 1/3\) and hence the screening parameter is given by \(\kappa = 2\). Based on this assumed shape and the choice of the host material, Equation 2.37 can be simplified in different ways, resulting in different EMTs. There are three EMTs appropriate for the isotropic composites, depending upon the choice of the host material, as follows:

(i) Lorentz-Lorentz effective medium theory with air as the host (\(\varepsilon_h = 1\));

(ii) Maxwell-Garnett effective medium theory with the dominant component as the host
\[ \varepsilon_h = \varepsilon_k \text{ where index } k \text{ is selected such that } f_i < f_k \text{ for all } i \]; and

(iii) Bruggeman effective medium approximation (EMA) with the mixture itself as the host \( \varepsilon_h = \varepsilon_{\text{eff}} \).

These effective medium theories are applicable when the sizes of the phases (dielectrics) in a composite material are greater than atomic sizes, but smaller than \( 1/10 \) of the wavelength\(^{57,58} \) and their dielectric functions are independent of size and shape. In this research, EMA models were employed for modelling surface and interfacial roughness.

### 2.3.6 Spectroscopic Reflectometry

An in-line process monitoring system based on spectroscopic reflectometry was installed in the 100kW CIGS-based pilot line at the Photovoltaic Manufacturing Consortium (PVMC) Halfmoon facility. This system was used to monitor preparation of layers by sputtering and co-evaporation. Film analysis software was developed as a part of the system. This software is tied to an internal database that relates in-line and off-line process conditions and characterization. Off-line spectroscopic ellipsometry was used in order to obtain proper optical models for reflectometry calibration. The schematics of the system is provided in the Fig. 2.23.

In this work, two separate optical monitoring terminals (OMT) based on spectroscopic reflectometry were used. One is located in the CIGS co-evaporation chamber and the other is located in the sputtering line.
2.3.6.1 Sputtering Line Optical Probe

A fiber optic based OMT is mounted in the load lock chamber of one of the sputtering lines used for the deposition of back contacts and transparent conductive oxides. A series of three optical probes were installed that allows measurement of three substrates at a time. The substrates are mounted in a \((4 \times 3)\) matrix and the probes measure one substrate per row. Each optical probe consists of three optic fibers: one illumination fiber and two light collection fibers. One of the collection fibers connects to the visible (Vis) detector and the other to the near-infrared (NIR) detector. More optical fibers can be added to improve the signal-to-noise ratio.

2.3.6.2 Evaporation Chamber Optical Probe

The evaporation chamber in the pilot line at the Halfmoon facility holds one substrate at a time, but allows for movement that resembles a roll-to-roll configuration. The OMT installed in the evaporation chamber uses a single optical probe configured to withstand the high temperature and the Se atmosphere. Metal-clad fibers are bundled in a steel sheath. A purging line was included with the fibers if clogging affects the signal-to-noise ratio.
2.3.6.3 Optical Monitoring Terminals

Each optical monitoring terminal includes a light source (halogen lamp), a visible unit and a near-infrared unit. Each OMT is attached to a computer. The particular specifications of the light source and detector units are listed in Tables 2.1 through 2.3.

**Table 2.1: Specifications for the OMT light source**

<table>
<thead>
<tr>
<th>Type</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength range:</td>
<td>360 – 2400 nm</td>
</tr>
<tr>
<td>Stability: Drift: Time to stabilize:</td>
<td>0.5% &lt;0.3% per hour ~ 5 minutes</td>
</tr>
<tr>
<td>Bulb lifetime:</td>
<td>2,000 (typical), 10,000 hours (extended lifetime)</td>
</tr>
<tr>
<td>Bulb color temperature:</td>
<td>3,000 K</td>
</tr>
<tr>
<td>Optical interface:</td>
<td>SMA</td>
</tr>
<tr>
<td>Operating temperature:</td>
<td>5 °C – 35 °C 5 – 95% at 40°C</td>
</tr>
<tr>
<td>Humidity:</td>
<td></td>
</tr>
<tr>
<td>Computer interface: Air cooling:</td>
<td>None, on/off by power button  Fan internally integrated into light source body</td>
</tr>
</tbody>
</table>

**Table 2.2: Infrared unit specifications**

<table>
<thead>
<tr>
<th>Detector: Detector range:</th>
<th>InGaAs linear CCD array 900 – 2200 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grating-limited range:</td>
<td>900 – 2150 nm</td>
</tr>
<tr>
<td>Pixels:</td>
<td>512</td>
</tr>
<tr>
<td>Entrance aperture:</td>
<td>25µm wide slit</td>
</tr>
<tr>
<td>Fiber optic connector:</td>
<td>SMA 905</td>
</tr>
<tr>
<td>Grating:</td>
<td>NIR-2: 100 l/nm</td>
</tr>
<tr>
<td>Optical resolution (FWHM)</td>
<td>~ 4.6 nm w/25µm slit</td>
</tr>
<tr>
<td>OSNR</td>
<td>&gt;10000:1 @100 ms int.</td>
</tr>
<tr>
<td>Dynamic range:</td>
<td>1000:1</td>
</tr>
<tr>
<td>Integration time:</td>
<td>1 ms to 2 s</td>
</tr>
<tr>
<td>Computer interface:</td>
<td>USB</td>
</tr>
</tbody>
</table>
**Table 2.3:** Visible unit specifications.

<table>
<thead>
<tr>
<th>Detector: Detector range</th>
<th>Linear Si CCD array 200 – 1100 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pixels:</td>
<td>2048</td>
</tr>
<tr>
<td>Wavelength range: Groove density:</td>
<td>Grating #4 500 – 1100 nm (detector limited) 600 mm⁻¹</td>
</tr>
<tr>
<td>Optical resolution (FWHM):</td>
<td>&lt; 1.3 nm (25μm slit)</td>
</tr>
<tr>
<td>Signal-to-noise ratio: Dynamic range:</td>
<td>250:1 (at full signal) 1300:1 (for a single acquisition)</td>
</tr>
<tr>
<td>Integration time:</td>
<td>&gt; 1 ms to 65 seconds</td>
</tr>
<tr>
<td>Stray light: Corrected linearity:</td>
<td>&lt;0.05% at 600 nm; &lt;0.10% at 435 nm Yes</td>
</tr>
<tr>
<td>Computer interface: Optical interface:</td>
<td>USB SMA</td>
</tr>
</tbody>
</table>

### 2.4 References


42. Tiwald, T. E. *et al.* Carrier concentration and lattice absorption in bulk and epitaxial


3. Optical Metrology for CIGS solar Cell Manufacturing

3.1 Introduction

In this chapter, development of optical metrology technique for CIGS solar cell manufacturing will be presented. Some of the results and interpretation that will be presented here are published elsewhere by the author\textsuperscript{1,2}. The dielectric function of the CIGS absorber layer and other functional layers were derived using offline spectroscopic ellipsometry (SE) in this research. Thicknesses and surface roughness used in SE analysis were measured using other characterization techniques. Spectroscopic reflectometry (SR), an optical reflectance technique has been investigated as a reliable method for the characterization of the different layers that compose a photovoltaic (PV) stack. SR and SE results were compared in order to validate reflectometry technique as a reliable process control method for CIGS solar cell manufacturing.

3.2 Motivation

CIGS lab-scale cells made on both rigid and flexible\textsuperscript{3-5} substrates reported efficiencies above 20.4 \textpercent\textsuperscript{6,7}. A typical CIGS solar cell structure consists of a molybdenum back contact, a CIGS absorber layer, a thin buffer layer (CdS, ZnS or In\textsubscript{2}S\textsubscript{3}), and a transparent conducting oxide (TCO) bi-layer made up of intrinsic and aluminum doped zinc oxide which acts as a front contact. This photovoltaic stack is traditionally deposited on a rigid substrate (soda-lime glass), but recent trends show that flexible substrates such as stainless steel and polymer-based materials are also being used. Many applications such as light photovoltaic (LPV), building integrated photovoltaics (BIPV) and space power generation can be achieved using these flexible substrates which allow roll-to-roll manufacturing leading to substantial cost reductions\textsuperscript{8}. 
CIGS absorber layer can be deposited using various deposition techniques such as co-evaporation\textsuperscript{9}, two-step selenization\textsuperscript{10}, sputtering\textsuperscript{11}, spray pyrolysis\textsuperscript{12}, and electro-deposition\textsuperscript{13}. Laboratory scale CIGS solar cells produced using 3-stage co-evaporation process have demonstrated high efficiencies in the order of $\eta > 21\%$\textsuperscript{14}, while commercial modules achieved efficiencies varying between $11\% < \eta < 17\%$. CIGS modules with high efficiency can be achieved if the composition and thickness of the absorber layer are controlled within a particular range.

The efficiency of CIGS solar cells is strongly influenced by the alloy composition. The molar ratio $[Ga]/([In]+[Ga])$, referred to as GGI, is optimized to $\sim 0.3$ for high efficiency\textsuperscript{15–18}. For devices with GGI $> 0.3$ the efficiency falls sharply. This is associated with a reduction in fill factor due to the voltage dependent current collection\textsuperscript{19}. Also, high efficiency CIGS solar cells are slightly Cu poor, having $\sim 23.5 – 24.5$ at.$\%$ Cu. A decrease in absorption coefficient has been reported with an increase in Cu deficiency\textsuperscript{3}. Hence, controlling the composition of the CIGS absorber films within this range is critical for achieving high efficiency.

Transition from Cu-poor to Cu-rich and then back from Cu-rich to Cu-poor stoichiometry is the key-element of the 3-stage co-evaporation process which can be achieved by control of the Cu, In, and Ga deposition rates. During the first stage, In, Ga, and Se are co-evaporated. The sample is Cu-free (CGI = 0) until the beginning of the second stage. Here CGI stands for $[Cu]/([In]+[Ga])$ atomic concentration ratio. In the 2$^{\text{nd}}$ stage, during evaporation of Cu and Se, at a certain point the sample reaches stoichiometry (CGI = 1). Immediately after this point $\text{Cu}_{2-x}\text{Se}$ starts forming at the surface\textsuperscript{20,21} leading to a change in the thermal behavior of the sample. A $\text{Cu}_{2-x}\text{Se}$ surface layer (CGI $> 1$) has a higher emissivity than pure CIGS (CGI $< 1$). This change
in emissivity can be used to detect the stoichiometric transitions based on the measurement of the substrate temperature by a thermocouple and/or the substrate heating power\textsuperscript{22-25}. From a manufacturing perspective, for flexible substrates that allow low-cost, roll-to-roll processing, sensing the CGI transition must be done in a non-contact manner.

The presence of even a small amount of Cu excess changes the properties of Cu–III–VI\textsubscript{2} materials, which according to pseudo-binary phase diagrams\textsuperscript{26-28}, can be attributed to the formation of copper–chalcogenide secondary phases, such as Cu\textsubscript{2-x}Se. Cu\textsubscript{2-x}Se is conductive with typical hole concentrations\textsuperscript{21,29,30} of $p > 10^{19}$ cm\textsuperscript{-3} and its presence in a solar cell absorber is detrimental to device performance as it dominates the opto-electronic and surface properties of the Cu-rich CIGS films\textsuperscript{31}. Previously, optical properties of CIGS and Cu\textsubscript{2-x}Se in the far-infrared (IR) region have been studied by Schöldström, \textit{et al.}\textsuperscript{32}. Based on the theoretical calculations\textsuperscript{33-36} of the band structure of Cu-poor CIGS (CGI < 1) and experimental results\textsuperscript{37}, the density of states (DOS) near the valence band maximum (VBM) at the grain boundaries (GBs) effectively produces a charge-neutral barrier to holes. This leads to passivation of GBs, thereby reducing non-radiative recombination resulting in high-efficiency CIGS solar cells. Hence, a final Cu-poor composition is crucial in order to prevent the segregation of Cu\textsubscript{2-x}Se phases for a high quality device.

Deposition of CIGS films over large areas can lead to compositional gradients across the surface due to the location of elemental sources needed for the evaporation process within the deposition system. High-efficiency CIGS modules can be achieved if the composition and thickness of CIGS absorbers can be controlled within the range of each desired value\textsuperscript{38}. SEM along with EDX are most commonly used technique for micro-scale compositional analysis and hence is not
suitable for checking the uniformity of large areas\textsuperscript{37}. X-ray florescence is a powerful tool for compositional analysis, which also provides thickness point-by-point over large areas under atmospheric conditions\textsuperscript{39,40}. For large area analysis needed for CIGS scale, XRF has been the most successfully applied technique\textsuperscript{41}.

The critical need for measuring, monitoring, and controlling the thickness, structure, phase, and composition of these solar cell component layers in real time during their deposition can be fulfilled by optical techniques, such as spectroscopic ellipsometry (SE) and spectroscopic reflectometry (SR). These techniques offer rapid in-line process control but require accurate optical models which represent the main properties (e.g. thickness and composition) of the photovoltaic layers\textsuperscript{42}. In this research, spectroscopic ellipsometry is used to develop optical models and extract dielectric functions for all functional layers of CIGS thin film solar cells. These optical models can determine composition, surface and interfacial roughness layer thicknesses, and along with other parameters, such as grain size, that influence the complex dielectric function ($\varepsilon = \varepsilon_1 + i\varepsilon_2$).

Spectroscopic ellipsometry and reflectometry are non-contact optical techniques which require modeling to obtain a result. Both are indirect measurement methods, where a model of the measured film stack is created and physical parameters (thicknesses and optical constants) are inferred from the best fit of the model to the measured data. Both techniques use Fresnel equations to analyze interaction of the light with the film stack. Spectroscopic ellipsometry measures the change in the polarization state of light whereas, a reflectometer, however, measures an intensity ratio of light. Ellipsometry is very sensitive to ultrathin films whereas, reflectometry is not sensitive to small changes in thin film thickness, so it is generally used on thicker (> 100 nm) samples. Changes in the source lamp intensity can alter results in case of
reflectometry as it is intensity-based whereas ellipsometry is polarization-based, hence, in this case lamp intensity is required only to maintain good signal to noise ratio. An ellipsometer can measure reflectance and transmittance, as well.

The optical constants (complex refractive index) and film thickness of the sample are extracted from the change in the polarization state by light reflection or transmission with the help of appropriate optical models. By least-squares regression analysis, complex dielectric functions of the component layers can be effectively extracted from the SE data, with the help of which we can find the multilayer thicknesses as well\(^4^2\). Parameterization of the complex dielectric function yields parameters of amplitude, bandgap energy, and broadening for each of the multiple oscillators equation versus photon energy for \(\varepsilon = \varepsilon_1 + i\varepsilon_2\) of the layer. The optical models for the PV stack can be built from these parameterized complex dielectric functions of each individual functional component layers in the CIGS solar cell.

Optical models developed for thin CIGS films (< 700 nm) can be found in the literature\(^4^3\)–\(^4^5\). These models are very successful at describing not only the thin CIGS layers, but when combined with models for the full photovoltaic stack, they can very accurately predict the quantum efficiency of the device. However, these models do not properly describe thick samples (between about 1.5 and 2.5 \(\mu m\)) or compositional gradients across the layer thickness. Spectroscopic Ellipsometry is a powerful tool to develop proper optical models for thick samples, as it is quite sensitive to surfaces/interfaces to characterize the complex dielectric functions precisely\(^4^2\). From this dielectric function, characteristics of the bulk layer such as the composition and phase can be determined. All this information can assist in understanding the fabrication process as well as more realistic quantum efficiency modeling\(^4^6\).
In order to develop the optical models for thick CIGS-based polycrystalline layers, samples grown by the 3-stage evaporation process were analyzed using SE, and the thicknesses, roughness and complex dielectric functions were determined. The thickness and surface roughness thus obtained were compared with values measured by other techniques. Optical models developed for samples prepared by stopping the deposition after each stage, took into consideration thickness non-uniformity and surface roughness. Standard line-shape analysis has been used in this study to determine the critical point energies in the complex dielectric functions of the CIGS layers. In this analysis, the theoretical formulas of the dielectric function are fitted to the second derivative of the dielectric functions obtained from the SE data modeling. This method relies upon the observation that prominent features in the optical response are due to inter-band transitions near critical points in the joint density of states. Thus, inter-band transitions at the critical points were characterized from these dielectric functions by this analysis. To confirm the validity of resulting SE analysis, optical models developed for CIGS on a glass substrate were applied to the characterization of CIGS on a flexible substrate (stainless steel).

In order to understand the effect of CGI on optical properties of CIGS, samples were prepared by stopping the CIGS deposition process during the 2\textsuperscript{nd} stage before and after the stoichiometric transition (CGI=1). The difference in optical properties of CIGS with and without a Cu\textsubscript{2-x}Se surface layer has been studied. The use of this change in optical behavior of CIGS due to the Cu\textsubscript{2-x}Se surface layer as a non-contact, optical end-point detector has been investigated.

Dielectric functions were extracted for the rest of the functional layers in the CIGS PV stack i.e. buffer layer (CdS) and TCO layers, by depositing each of the functional layers separately on Mo-coated SLG substrates. These dielectric functions along with the CIGS optical functions were
used to develop optical models for PV stack of the CIGS solar cell. By obtaining the dielectric functions of functional layers separately first, SE analysis of the complex PV stack becomes significantly accurate and less challenging. With the help of the RC2, spatially resolved measurements were taken over an area of 100 cm² of PV stack of a CIGS solar cell in order to reveal the non-uniformity of basic properties across the surface area. Identifying these non-uniformities across the cell’s surface is critically important to reduce the efficiency gap that exists between the research cells and production modules\textsuperscript{16}, which ultimately results in lowering the CIGS solar cell manufacturing costs (See Chapter 4).

In order to lower manufacturing costs for thin film photovoltaics it is essential to control the production yield and line uptime. For this purpose, a reliable process control or at least, process monitoring technique is essential. Optical reflectance techniques, such as spectroscopic reflectometry (SR), have been demonstrated as reliable methods for the characterization of the different layers that compose a photovoltaic stack, as long as the proper optical functions are used for each layer. These techniques are useful at high temperatures and sensitive to layer thickness, composition and compositional gradients. In this research, the dielectric functions extracted for each functional layer in the PV stack of the CIGS solar cell has been applied to the spectroscopic reflectometry measurements and results from SR and SE are compared, in order to evaluate the SR technique as a novel low cost in-line process control method for CIGS solar cell manufacturing. In addition, the change in optical properties due to the presence of Cu\textsubscript{2-x}Se has been investigated for developing an end-point detection of the 2\textsuperscript{nd} stage in 3-stage deposition process.
3.3 Experimental Details

The 3-stage process, originally developed by researchers at the National Renewable Energy Laboratory (NREL), was used to deposit CIGS. In the first stage In, Ga, and Se are co-evaporated. After an \((\text{In},\text{Ga})_2\text{Se}_3\) (IGS) precursor film of a prescribed thickness is deposited, the second stage is initiated where the substrate temperature is increased to a higher temperature, and Cu and Se are evaporated in the absence of In and Ga fluxes. CIGS is formed as Cu atoms diffuse into the precursor \((\text{In},\text{Ga})_2\text{Se}_3\) film. Excess Cu starts accumulating on the surface forming \(\text{Cu}_{2-x}\text{Se}\) as the material becomes stoichiometric. After this Cu-poor to Cu-rich transition, the third stage is initiated. In this stage In and Ga are evaporated in absence of Cu flux. A Cu-rich to Cu-poor transition marks the end of third stage when the source temperatures of In and Ga are reduced to stop co-evaporation. 3-stage CIGS was co-evaporated in a chamber fitted with Indium, Gallium, Copper, and Selenium sources. Soda-lime glass coated with a 300 nm layer of molybdenum, and stainless steel with a metal stack capped by a 500 nm layer of molybdenum, were used as substrates.

A similar process was used to deposit CIGS samples on stainless steel substrates. These samples had the same nominal composition as the samples prepared on glass substrates. For the rest of this work, samples will be referred as 1\(^{st}\) stage, 2\(^{nd}\) stage and 3\(^{rd}\) stage samples respectively, depending on the stage they were stopped at, for both glass and stainless steel substrates, indicating the substrate nature wherever it is relevant as shown in Fig. 3.1. These samples were used to develop optical models for each individual stage of 3-stage deposition process.
A CdS buffer layer with an intended thickness of ~50 nm was deposited by the chemical bath deposition (CBD) process on top of the CIGS layer. Layers of $i$-ZnO (intended thickness 70 nm) and ZnO:Al (intended thickness 170 nm) were deposited by RF magnetron sputtering on top of the buffer layer. Finally, Ni-Al-Ni grids were deposited on top of ZnO:Al (AZO) followed by anti-reflection (AR) coating. The intended thicknesses of Ni and Al layers were 50 nm and 2.5 µm, respectively. Cells were scribed with a mechanical scribe such that the area of each cell was 1.1 cm$^2$. The structure of the solar cells is shown in Fig. 3.3. Similar solar cells were fabricated on both SLG and SS substrates. Samples were prepared by stopping the fabrication at each functional layer step, as shown in the Fig. 3.2.
To derive the dielectric functions of the buffer (CdS) and TCO layers (i-ZnO and ZnO:Al), these individual functional layers were deposited separately on Mo-coated soda-lime glass substrates. 50 nm (intended thickness) of CdS layer was deposited using chemical bath deposition process while TCO layers (70 nm of i-ZnO and 170 nm of ZnO:Al) were deposited using RF magnetron sputtering. In order to maintain similar optical properties, these individual functional layers were deposited using same deposition conditions and thicknesses as for solar cell fabrication as shown in Fig. 3.4.

For studying the effect of Cu$_{2-x}$Se on optical properties of CIGS, samples were grown using 3-stage deposition process on a molybdenum-coated soda-lime glass. Electron-impact emission
spectroscopy (EIES) was used to monitor and control the flux rates of these metals. Samples were prepared by stopping the deposition process before the end of 2\textsuperscript{nd} stage when CGI < 1 and immediately after the transition where CGI > 1. Focused ion beam (FIB) was used to cut cross-sections of the samples and energy dispersive X-ray spectroscopy (EDS) analysis was performed to understand the distribution of Cu over the surface.

Depth profiles of the concentration of Cu, In, Ga and Se across the thickness of the samples were obtained by secondary ion mass spectroscopy (SIMS) in “Time-of-flight” (TOF) mode. Samples were analyzed using an ION-TOF V TOF-SIMS instrument in static mode. A 25 keV Bi\textsuperscript{+} beam was used for analysis while in-situ Cs\textsuperscript{+} beam was used for sputtering with a 300 µm raster area and a 50 µm detection area. The thickness of each sample was determined using a stylus profilometer (Dektak M150), and was used for TOF-SIMS depth calibration. X-ray fluorescence spectroscopy (XRF), FIB cross sections and stylus profilometer were used to determine the thickness of the samples. Samples’ roughness was determined using a Zygo Newview 5000 optical profilometer. J.A. Woollam RC2 variable-angle spectroscopic ellipsometer was used to take measurements at angles of incidence of 65°, 70°, and 75°, in the 0.7 eV to 5.1 eV range, with an acquisition time of 5 seconds. SE analysis was performed to model the dielectric function and thickness of the material layers, and surface roughness layer with help of the results obtained from SIMS, FIB and EDS. The data collected at all three angles were analyzed simultaneously. These derived optical models were applied to in-line spectroscopic reflectometry (SR) measurements using a setup installed at the US PVMC pilot plant facility in Halfmoon, NY.
3.4 Results and Discussion

3.4.1 Spectroscopic Ellipsometry Studies of 3-stage Deposition of CIGS on Glass and Stainless Steel Substrates

Fig. 3.5 (a), (c) and (e) show scanning electron microscope (SEM) images of the surface morphology of layers deposited after 1st stage, 2nd stage and 3rd stage on SLG substrates respectively while (b), (d) and (f) show the surface morphology of layers deposited after 1st stage, 2nd stage and 3rd stage on SS substrates respectively. Fig. 3.5 (g) and (h) show the cross section and thickness of CIGS layers on top of Mo after the 3-stage deposition process on SLG and SS substrates, respectively.

When compared to IGS on SLG, IGS on SS has more defects due to the inherent surface roughness of the SS substrate. During the 2nd stage of the 3-stage deposition process, morphological re-organization takes place. The Cu-rich film at the end of the second stage consists of large-grain mixed phase of CIGS and Cu$_{2-x}$Se. Cu-rich conditions lead to increased grain size and higher conversion efficiency. 1st stage and 2nd stage SLG samples have densely packed grains with lower defect density compared to SS samples. In the 3rd stage, the addition of 10 % – 20 % (vol.) of In and Ga at the end aids in the formation of a smooth surface as seen the Fig. 3.5 (e) and (f). In general, samples on SS have more defects and SLG samples are smoother due to substrate temperature effects. The samples on different substrates were prepared in separate batches, and the thickness of the CIGS layers on glass were on average 0.5 µm thicker than those on stainless steel.
Figure 3.5: (a), (c) and (e) show the surface morphology of 1st stage, 2nd stage and 3rd stage samples on SLG substrate respectively while (b), (d) and (f) show the surface morphology of 1st stage, 2nd stage and 3rd stage samples on SS substrate respectively, (g) and (h) show the cross section and thicknesses of CIGS layer in 3rd stage samples on SLG and SS substrates respectively.
Figure 3.6: Depth profiles determined by SIMS (a) 1st stage sample (stopped after first stage) shows uniform In, Ga and Se profiles, (b) 2nd stage sample (stopped after second stage) shows that the concentration of Ga dips as soon as the second stage starts. (c) 3rd stage sample (stopped after third stage) shows that the concentration of Ga increases once the third-stage deposition begins. The bottom pictures show the structure of (d) 1st stage sample consisting of Mo layer topped with IGS layer, (e) 2nd stage sample with Cu-rich CIGS layer on top Mo, and (f) 3rd stage sample with Mo layer and CIGS layer.

The results of the TOF-SIMS depth profiles are shown in Fig. 3.6 for each of the stages of the deposition. The 1st stage sample, stopped after the 1st stage exhibits a uniform concentration of In, Ga and Se along the thickness. Cu is added in the 2nd stage, which reacts with IGS and forms CIGS. As Ga diffusion is slower than that of Cu, the Ga depth profile dips moving towards the surface in the 2nd stage sample. In the 3rd stage sample, the Ga concentration rises moving towards the surface as in this stage Ga and In are co-evaporated under Se flux. It is also noticeable that once Cu is introduced in the second stage, it diffuses to the back of the absorber layer. Samples grown on glass and stainless steel showed similar concentration profiles with minor differences.
3.4.1.1 Spectroscopic Ellipsometry Analysis

Spectroscopic Ellipsometry (SE) data from all three sample types was analyzed to understand the way the dielectric function changes while stepping from one stage of deposition to another in the 3-stage deposition process.

SE data analysis was performed on the measurements collected at multiple angles (65°, 70°, 75°) to obtain the dielectric function. When there are unknown dielectric functions in a sample, dielectric function modeling for layers is carried out with the help of regression analysis where it is assumed that the dielectric function of an analyzed layer is independent of thickness. In this analysis, we have used a Cauchy model to define the dielectric function in the wavelength region where the CIGS material is transparent i.e < 1 eV. This Cauchy model was used as a starting point in the Kramers-Kronig-consistent B-Spline function which was fit to the experimental spectra (ψ, ∆) by regression analysis. This fit is based on the Levenberg-Marquardt algorithm to reduce the least-squares difference between experimental and model-generated data. Thickness of the material of interest obtained by ancillary experimental techniques was used as a fixed parameter in the regression analysis while the surface roughness is modeled with Bruggeman Effective Medium Approximation (EMA) where it is assumed a 50 vol.% / 50 vol.% mixture of underlying material and free space.

Thickness non-uniformity across the spot size and angle offset due to thick CIGS layers were considered in this analysis. The extracted dielectric function was further parameterized using Tauc-Lorentz oscillators to provide physically meaningful parameters such as energies, broadening parameters, and resonance exponents related to the band structure and excited state
relaxation times of the CIGS material under study. From the parameterized dielectric function, we performed the fitting again, to determine the dielectric function more accurately\textsuperscript{42}.

For the 1\textsuperscript{st} stage the model is based on an IGS bulk layer with surface roughness. For 2\textsuperscript{nd} and 3\textsuperscript{rd} stages the model considers a full CIGS bulk layer, which is formed after the first stage, along with surface roughness. As the Mo layer is opaque in the the wavelength range analyzed here, it was treated as a substrate for every sample using the dielectric functions developed by the U. Toledo group\textsuperscript{44}. In order to model the IGS and CIGS layers, the optical models incorporated surface roughness and thickness non-uniformity across the spot size. In 2\textsuperscript{nd} and 3\textsuperscript{rd} stage samples the Ga concentration varies as a function of thickness, as can be seen in the SIMS plot in the Fig. 3.6. The complex dielectric function obtained for these samples are affected by this variation. An excellent result was obtained when simultaneously fitting the experimental spectra (\(\psi\) and \(\Delta\)) collected at various incident angles to the optical model, indicating that the SE analysis is valid and appropriate. As an example, Fig. 3.7 shows the optical models fit quality for one incident angle for the 1\textsuperscript{st} stage and 3\textsuperscript{rd} stage samples on glass substrate.

Fig. 3.8 (a) shows the imaginary part of the complex dielectric function of IGS on a glass substrate. Similarly, Fig. 3.8 (b) and (c) show the corresponding dielectric functions of the CIGS layer in the 2\textsuperscript{nd} and 3\textsuperscript{rd} stage samples. As the deposition process progresses from one stage to the next, the imaginary part of the complex dielectric function evolves with higher number of critical points. The CIGS material formed in the second stage has few differences with respect to the CIGS formed in the third stage. Given the similarity in the Cu distribution measured by SIMS for both samples, the differences can be attributed to the change in the concentration of Ga.
Figure 3.7: (a) and (b) show the fit quality of the optical models shown on the top right corner to the SE spectra for the 1st stage and 3rd stage SLG samples respectively. Inset in (a) and (b) shows the fit quality of the optical models in the transparent region of each material.
3.4.1.2 Critical Point (CP) Analysis

A standard CP analysis has been performed for the dielectric functions of the CIGS-based layers in order to determine the CP energies of the optical transitions in the energy range 0.7 eV to 5.1 eV. In this analysis, the second derivative spectra of the modeled complex dielectric function are used and the theoretical formulas for second derivative of the dielectric function expressed by:

\[
\frac{d^2\varepsilon}{dE^2} = n(n - 1)A\exp(i\phi)(E - E_p + i\Gamma)^{(n-2)}; \quad n \neq 0
\]

\[
\frac{d^2\varepsilon}{dE^2} = A\exp(i\phi)(E - E_p + i\Gamma)^{-2}; \quad n = 0
\]

Where A, \(\phi\), \(E_p\) and \(\Gamma\) show the amplitude, phase, position, and width of the peak. CP is classified into one-dimension (\(n = -1/2\)), two-dimension (\(n = 0\)), and three-dimension (\(n = 1/2\)) according to the wave vector involved in the optical transition. The joint density of states (DOS) around the CP depends on the band structure. Furthermore, when an optical transition exhibits excitonic behavior \(n = -1\) is employed in the equation. From the CP analysis using the second derivative spectra, the specific features of the CP were characterized selectively. Since the
dielectric functions obtained by the analysis were based on B-spline polynomials there was no need to perform smoothing for the differentiation.

For accurate CP analysis, from the modeled dielectric functions ($\varepsilon_1$ and $\varepsilon_2$) obtained from SE analysis, the second derivative spectra were calculated for the energy range between 0.7 eV and 5.1 eV with uniform data spacing. Fig. 3.9 (a), (c), (e) show the second derivative of modeled $\varepsilon_2$ spectra (circles) for 1st stage, 2nd stage and 3rd stage samples (glass substrate) and the calculated fitted spectra (line) from the CP analysis. An excellent fitting between modeled and calculated spectra was observed when the excitonic transitions ($n = -1$) were assumed for all the critical points in all the samples. Earlier studies have been performed using 2D line shape ($n = 0$)\textsuperscript{38,48,49}. Fig. 3.9 (a), (c), (e) show the fitting procedure from where $A$, $\varnothing$, $E_p$ and $\Gamma$ values of each CP are extracted for each sample. In the case of IGS, CP analysis shows a band gap critical point ($E_0$) at 2.315 eV and another peak at 4.7 eV. From the Fig. 3.9 (b) it can be seen that the dielectric function is quite smooth over the measured region while dropping to zero below $E_g$. This result confirms that the SE analysis utilized produced reasonable dielectric functions. The transition peaks obtained for the IGS layer are in agreement with those reported by Pradhan \textit{et al.}\textsuperscript{50}. 
Figure 3.9: Second derivative $\varepsilon_2$ spectra calculated from the dielectric function shown in the Figure 3.7 (circles) and the fitted spectra calculated from the CP analysis for (a) 1st stage sample, (c) 2nd stage sample, (e) 3rd stage sample. (b), (d) and (f) show inter-band transitions in dielectric functions of IGS, CIGS 2nd stage, and CIGS 3rd stage layers.
Figure 3.10: Band structure of CIGS. The optical transitions in the chalcopyrite BZ are indicated by arrows. For the energy levels and the transitions, the notation used by Alonso et al. was adopted.

The band structure of CIGS is shown in the Fig. 3.10. The structure of the fundamental structure absorption edge of CIGS is well established. CIGS is a semiconductor with a direct band gap at the Brillouin-zone (BZ) center Γ. In this material, three transitions called \( E_0(A) \), \( E_0(B) \) and \( E_0(C) \) from lower to higher energy arise from a threefold valence-band maximum which is composed of three non-degenerate states. According to Alonso et al., the peak at the lowest energy seen in the \( \varepsilon_2 \) spectra of the 2\textsuperscript{nd} and 3\textsuperscript{rd} stage samples is composed by the two closer peaks \( E_0(A, B) \) and the following one corresponds to \( E_0(C) \). The ordinary polarization \( E \perp c \) is expected to dominate the spectra in polycrystals. Hence, the main contribution to the first observed peak comes from the component (A or B) with \( E \perp c \). Of the two components, \( E_0(A) \) corresponds to CIS and \( E_0(B) \) to CGS-like band of CIGS is shown. The structure of the fundamental arrangements. At room temperature A and B peaks are very close and not resolved in the Fig. 3.9 (d).
The $\varepsilon_2$ spectra from the 2nd and 3rd stage samples above the direct band gap ($E_0$) have very similar features. The main transitions that contribute to $\varepsilon_2$ have been assigned to critical points at the Brillouin-zone center $\Gamma$ and edge N and T points according to band-structure calculations by Jaffe and Zunger\textsuperscript{53} for ternary compounds (Cu-III-VI\textsubscript{2}) and correlating the observed transitions to those of binary zincblende analogues. The transitions are labelled according to the ref.\textsuperscript{48} and are related to the standard zincblende notation. The different observed transitions within the calculated band structure are listed in the table shown in Fig. 3.11 (b).

Figure 3.11: (a) shows the evolution of $\varepsilon_2$ as deposition process progresses from 1st to 3rd stage. Critical points in $\varepsilon_2$ are labelled according to the ref.\textsuperscript{38}. (b) shows the energy of the critical points seen in $\varepsilon_2$ as it evolves from 1st stage to 3rd stage.

$E_{\Gamma X}$ is an indirect transition from $\Gamma^{(1)}_3 v \rightarrow \Gamma_3 c$ at 2.2 eV which matches the calculated value. The prominent $E_{1A}$ transition observed in the 2nd and 3rd stage samples were very close to each other. $E_{1B}$, having a slightly larger broadening, is observed only in the 3rd stage sample. Crystal-field splitting of the valence band at the N point leads to the energy separation of about 0.8 eV between $E_{1(A)}$ and $E_{1(B)}$ as seen in the 3rd stage sample spectra. This effect is either small or non-existent in the 2nd stage sample where there is only one observed $E_1$ transition. The transitions

<table>
<thead>
<tr>
<th>Critical Point</th>
<th>IGS (1st Stage)</th>
<th>CIGS 2nd Stage</th>
<th>CIGS 3rd Stage</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_0$</td>
<td>2.315</td>
<td>1.315</td>
<td>1.265</td>
</tr>
<tr>
<td>$E_{\Gamma X}$</td>
<td>-</td>
<td>2.216</td>
<td>2.216</td>
</tr>
<tr>
<td>$E_{1A}$</td>
<td>4.782</td>
<td>3.073</td>
<td>3.131</td>
</tr>
<tr>
<td>$E_{1B}$</td>
<td>-</td>
<td>-</td>
<td>3.848</td>
</tr>
<tr>
<td>$E_{\Gamma X}'$</td>
<td>-</td>
<td>4.377</td>
<td>4.323</td>
</tr>
<tr>
<td>$E_{2B}$</td>
<td>-</td>
<td>5.044</td>
<td>5.136</td>
</tr>
</tbody>
</table>
observed around 4 eV in these two samples were identified as $E'_{\Gamma X}$, the gap at the $\Gamma$ point by comparing with previously calculated values$^{48,53}$. Transitions seen at higher energy, around 5 eV, correspond to $E_{2B}$ which is a T-point transition. All the energies observed are close to the theoretical values from ref.$^{48,53}$.

With the help of CP analysis, the dielectric functions extracted for 1$^{\text{st}}$ stage IGS, 2$^{\text{nd}}$ stage CIGS and 3$^{\text{rd}}$ stage CIGS on SLG substrates were confirmed to be valid and appropriate. The parameterized dielectric functions were used in the optical models for the IGS and CIGS layers deposited on Mo-coated SS substrates. IGS and CIGS layers deposited on Mo-coated SLG and SS differ in grain size and defect distribution due to substrate temperature effects. Changes in grain size or number of defects such as pinholes and micro-cracks have a significant effect on the complex dielectric function of the layers. Optical models using these parameterized dielectric functions were applied to fit SE measurements obtained from SS samples. By varying the oscillator parameters of the extracted dielectric functions and with the help of regression analysis, the optical models were fitted to the SE spectra. Fig. 3.12 shows the fit quality of the optical models to the SE spectra obtained from IGS and CIGS layers deposited on Mo-coated SS substrates. By varying the amplitude and lifetime broadening parameter of the parameterized complex dielectric functions for the layers, excellent fits were obtained for all the SS samples. Fig. 3.12 (a) shows the fit quality of the 1$^{\text{st}}$ stage SS sample while (b) shows the fit quality of the 3$^{\text{rd}}$ stage SS sample with the optical models used.
Figure 3.12: (a) and (b) show the fit quality of the optical models shown on the top right corner to the SE spectra for the 1st stage and 3rd stage SS samples respectively. Inset in (a) and (b) shows the fit quality of the optical models in the transparent region of each material.
Fig. 3.13 (a) shows $\varepsilon_2$ for the IGS layer on Mo-coated SS substrate while (b) shows $\varepsilon_2$ for the 3rd stage CIGS layer on Mo-coated on SS substrate. Differences in the $\varepsilon_2$ for IGS and CIGS layer on the SLG and SS substrates can be seen in the Fig. 3.14 (a) and (b) respectively. The fundamental absorption peak ($E_0$) in the IGS and CIGS layers are broader in SS substrates than SLG due to phonon scattering effects at the grain boundaries caused by the higher defect density. From Fig. 3.14, by comparison, the dielectric functions of CIGS on both glass and stainless steel substrates coincide, except for a slight difference at the $E_0$ peak.

![Figure 3.13](image)

**Figure 3.13:** (a) and (b) show the imaginary part of the complex dielectric function of 1st stage, and 3rd stage SS samples respectively which have been derived from the imaginary part of the complex dielectric functions shown in Figure 3.7.

The difference in $E_0$ peaks seen in Fig. 3.14 may be due to compositional fluctuations caused by the deposition tool leading to changes in the grain size distribution. Change in the grain size affects the lifetime broadening parameter. This sensitivity to the defect density and grain size distribution allows the optical models to be applied to CIGS of varying thicknesses and roughness over different substrates.
The next step in the development of these optical models for CIGS would be taking the effect of varying Ga concentration along the thickness into consideration. The compositional gradient of Ga across the thickness of the CIGS layer in 3rd stage sample, “double grading”, is a consequence of the 3-stage deposition process. Changes in the Ga concentration cause changes in the dielectric functions. The results shown here are an outcome of the cumulative effect of variation of the Ga concentration in the CIGS layer in the 2nd and 3rd stage samples. In order to determine the effect of Ga concentration on the dielectric function at each energy point, the CIGS layer model needs to be graded as per the Ga concentration variation. This will be a part of future studies.

3.4.2 Spectroscopic Ellipsometry Analysis of CIGS Solar Cell Film Stack

SE has been used to analyze a multilayer of CIGS-based PV stack. Fig. 3.2 shows the typical CIGS solar cell structure used for this analysis. As SE analysis of multilayered PV samples can be very challenging, hence, in order to simplify, a step wise approach has been employed. In
order to build optical models for multilayered samples shown in Fig. 3.2, the dielectric functions were first extracted for each functional layer using samples shown in Fig. 3.4. As shown in Fig. 3.4 each functional layer was deposited on Mo-coated SLG substrate. SE measurements were taken at multiple angles (65°, 70° and 75°) and the SE analysis was performed simultaneously at these angles using regression method to extract dielectric functions, followed by parameterization. The extracted dielectric functions for CdS, \textit{i}-ZnO (IZO), ZnO:Al (AZO) are shown in the Fig. 3.15.

The dielectric functions obtained for CdS show that the band-gap of the material is around ~2.5 eV, which is close to values reported in the literature. Similarly, the bandgap of IZO and AZO calculated from the dielectric functions is around ~3.2 eV, which matches the value measured in previous experiments\textsuperscript{56}. AZO shows high absorbance in the IR (infrared) region due to the Al doping. Al being a metal shows phonon absorption effects in the IR region. These dielectric functions along with the CIGS dielectric functions derived in Sec. 3.3.1 have been used in the multilayer PV stack SE analysis.

![Figure 3.15: Extracted dielectric functions for ZnO:Al (AZO), \textit{i}-ZnO (IZO) and CdS used for the analysis of PV stack of the CIGS solar cell.](image)

The samples were prepared by stopping the solar cell fabrication process after each layer is deposited as shown in the Fig. 3.2. The analysis approach consists of a step-by-step layer
modeling, where a number of fitting parameters are minimized. This makes it easier to develop full stack optical models that can be used on complete solar cell. Dielectric functions of individual layers previously extracted were used in the SE analysis of these samples. The dielectric function is strongly influenced by surface roughness, hence, it is included in the analysis.

![Cross sectional view of a complete CIGS PV stack on SLG substrate capped with Pt for protection from the ion beam source.](image)

**Figure 3.16:** Cross sectional view of a complete CIGS PV stack on SLG substrate capped with Pt for protection from the ion beam source.

SIMS analysis was carried out on a CIGS PV stack sample complete with absorber, buffer and TCO (transparent conducting oxide) on Mo-coated SLG substrate. Its cross section is shown in the Fig. 3.16. The IZO and AZO layers together constitute a TCO layer. Voids can be seen in the Fig. 3.16 at the Mo and CIGS interface as well as in the bulk close to the surface of the sample.

Fig. 3.17 shows the depth profile of a complete CIGS PV stack used in SE analysis. For Cu, In, Ga and Se, SIMS intensity counts have been converted to concentration (at. %) using a standard sample, which was ion-implanted with known concentration of Cu, In, Ga and Se at a particular depth. Cds, IZO, AZO and CIGS thicknesses can be seen in the figure. Ga double graded profile,
which is a characteristic feature of the 3-stage deposition process, can also be seen in the Fig. 3.17.

SE analysis of samples shown in Fig. 3.2 has been performed to obtain thicknesses and surface roughness. At first, a very simple model was considered with minimum number of fitting parameters for this sample’s SE analysis. Initially, only thickness fitting parameters were used. Surface roughness or interface roughness layers were not considered in this basic starting model.

**Figure 3.17:** SIMS depth profile of a CIGS PV stack showing thicknesses of AZO, IZO, CdS and CIGS layers on top of Mo coated SLG substrate. Calibrated concentration profiles of Cu, In, Ga and Se are shown while for the rest of the elements intensity counts are shown.

Using this basic starting model, the thicknesses of the CIGS and CdS layers were determined for the sample shown in Fig. 3.2 (a) in which the fabrication was stopped after the buffer layer
deposition. With these results, additional parameters were added to the model in order to improve the fit quality, given the known sample structure. In this step-by-step analysis approach, additional parameters were added to the model one at a time such as surface and interfacial roughness at each interface and the MSE is evaluated. The steps involved in the regression analysis are listed below:

- With thicknesses fixed, model parameters are fit one at a time until the MSE is minimized for each individual parameter.
- In the second step, two model parameters are fit simultaneously, and the regression analysis is carried out until the lowest MSE is achieved for the two parameters. In the selection of the two parameters, all possible set of pairs were considered and regression analysis was performed to improve the fit quality and lower the MSE.
- In the third step, three model parameters were considered at a time and regression analysis was performed.
- The process is continued until all the parameters are fit simultaneously and no further significant improvement in the MSE is obtained. In this process, oscillator parameters such as amplitude and lifetime broadening of the parameterized dielectric functions were also added to the model and dealt with extreme care and constraint, so that unrealistic and unphysical results are avoided while improving the fit quality. Some free parameters were discarded or otherwise fixed when there was not a significant improvement in MSE with their addition.
Figure 3.18: Experimental spectra in $\psi$ and $\Delta$ (points) along with the best fit (lines) for the PV stack measured from the film side at an angle of incidence of $65^\circ$ along with the optical models used for the analysis.
Bruggeman’s effective medium approximation (EMA) was used to model surface roughness and interface layers as a mixture of the overlying and underlying materials. Non-uniformity was modeled as a percentage depolarization caused due to change in optical interference of waves reflected from regions of different thickness\textsuperscript{57}.

Fig. 3.18 shows the fit quality obtained for the multilayered PV samples. SE analysis of these samples shows that the CdS clearly fills the voids in the surface of the CIGS absorber layer which helps in passivation and reduces the surface recombination effects. Hence, it forms an interfacial layer with a composition of voids, CdS and CIGS which is modelled with the help of EMA layer followed by a bulk CdS layer.

From SE analysis of the three samples shown in the Fig. 3.18, it is clear that the CdS surface is conformal and smooth while IZO and AZO layers had significant surface roughness. Due to the surface roughness of the IZO layer, an interfacial roughness layer was introduced in the model between the IZO and AZO layers. AZO passivated the IZO porous surface layer, which was modelled with help of an EMA layer. Excellent fits were obtained for the optical models used in the SE analysis as shown in the Fig. 3.18. The final optical model presented here for the complete CIGS PV stack is localized to its spot size. In order to understand the uniformity of the different layers of the PV stack, SE mapping analysis was performed with help of spatially resolved measurements. Thickness results obtained from the SE analysis matched the results obtained from other ancillary techniques. The error in the SE analysis is less than 2 % across the spot size which was calculated from the thickness non-uniformity by the Jellison model\textsuperscript{57}.

Spectroscopic ellipsometry (SE) has the capability to scan large areas and take measurements at high speed. This technique can generate detailed maps of properties such as thickness of
individual layers, composition, bandgap including bulk and surface roughness through data analysis of a CIGS PV stack structure. For producing high efficiency solar cells, composition should be tightly controlled within a narrow range near GGI ~ 0.3 while keeping the thickness uniform. At industrial scale, CIGS films are deposited over large areas, which lead to compositional and thickness gradients across the surface. SE mapping capability gives an opportunity to characterize these gradients in order to develop a suitable process control technique at production scale. Hence, for optimization over large areas, spatially resolved measurements that reveal such non-uniformities in basic properties are critically important.

![Figure 3.19](image)

**Figure 3.19**: Thickness map of CIGS absorber layer on top of 10 cm × 10 cm Mo-coated SLG substrate measured by (a) XRF and (b) SE over an area of 9 cm × 9 cm with 9×13 matrix.

Correlation between the thickness maps by XRF and SE as shown in Fig. 3.19 is 0.982. This shows that the SE and XRF results are in good agreement and optical models used for mapping thickness of CIGS absorber layer are accurate. Multilayer optical models were applied to spatially resolved measurements of complete CIGS PV stack taken over an area of 9 cm × 9 cm with a 7×11 grid size.
Figure 3.20: SE mapping analysis results shows the thickness variation of (a) CIGS (Thickness#1), (b) CdS (Thickness#2), (c) IZO (Thickness#3) and (d) AZO (Thickness#4) over an area of 8 cm × 8 cm. (e) % Thickness non-uniformity and (f) roughness variation are also shown.
Results obtained from the SE mapping analysis of a full stack sample as seen in the Fig. 3.20 (a) show that the thickness variation of the CIGS absorber layer over an area of 9 cm × 9 cm is about 12 % across the surface. The Ga distribution can vary across the surface leading to in alloy composition gradients which directly affects the band-gap and in turn the efficiency. Fig. 3.20 (b) shows that the thickness variations in the buffer layer is around 7 %, which is not very significant but noticeable. The buffer layer deposited by the CBD process is conformal and its thickness is comparable to the peak to valley ranges in the CIGS layer, and hence, it is difficult to control its thickness which deviates from the intended thickness quite often. Variation of TCO layers’ thickness is around 15 %, as seen in the Fig. 3.20 (c) and (d) which can be controlled to reduce the percentage non-uniformity to < 5 %.

In Fig. 3.20 (e), the roughness of the surface layer varies between 20 – 40 nm while the %thickness non-uniformity variation or the error in the thickness measurements at each grid point averages at 2 % as seen in Fig. 3.20 (f). SE mapping analysis was also performed for a CIGS PV stack on a SS substrate, which showed similar results.

### 3.4.3 Application of Derived Optical Models to an In-line Optical Monitoring System for CIGS Solar Cell Manufacturing

Spectroscopic Reflectometry (SR) has been investigated as a reliable process monitoring/control technique which is essential to maintain the production yield and line uptime and thus, lower manufacturing costs for thin film photovoltaics. A fiber optic-based SR monitoring system was installed in the TCO sputtering line and CIGS evaporation chamber, at the PVMC’s Pilot Line in Halfmoon, NY. Each optical monitoring terminal (OMT) includes a white light source (halogen lamp), a UV/visible and a near-infrared detection unit. Each OMT is attached to a computer. In
Fig. 3.21 a picture of the sputtering line OMT is shown, with the collected spectrum on the computer screen.

**Figure 3.21**: Optical Monitoring Terminal with probes installed in the load lock of the sputtering line, characterizing the deposition of the transparent conductive oxide on polished Si wafers.

In this section, preliminary in-line characterization is carried out on different single layers and PV stacks on different substrates to validate the use of reflectometry as a process monitoring tool. The dielectric functions derived for the different layers in the previous sections have been applied to the data analysis. As the primary focus of this analysis is to find the thickness of the different layers of the photovoltaic stack, roughness and interfacial roughness were not included in the optical models. In the sputtering line, magnetron sputtering deposition of Intrinsic Zinc Oxide (IZO) and Aluminum-doped Zinc Oxide (AZO) is carried out on CdS/CIGS/Mo/Substrate samples as part of the solar cell fabrication process. A fiber optic based OMT mounted in the load lock chamber of the sputtering line was used to monitor the deposition of transparent conductive oxides. The substrates mounted in a $4 \times 3$ matrix on to a sample holder through the load-lock chamber, were measured using a series of three optical probes that allow measurement of three substrates at the same time. The sputtering line consists of a series of vacuum chambers where the target is sputtered on to the substrate. The deposition on the substrate is a continual process as it moves along the series of deposition chambers till it reaches the end of the sputtering line in vacuum. After the substrate reaches the end of the line, it is withdrawn to the load lock chamber to take the reflectance measurements. After the measurements were taken, the
sample holder is sent back into the sputtering line to repeat the deposition process till the layer reaches a desired thickness. One passage of the substrates along the deposition chamber during the deposition process starting from the load-lock chamber till the end of the sputtering line is termed as a “pass”. “Pass” is used as a unit for these periodic measurements. Reflectance measurements were taken (before and after the deposition in one passage) at the end of each pass.

The in-situ optical monitoring system was configured to measure the deposited samples in reflection. It was used to ensure both accurate alignment and validation of its operation on the PVMC vacuum deposition (evaporation and sputtering) line as well as to ensure that sufficient material thickness was achieved for more accurate characterization of the optical properties of the films. The OMT in the sputtering line was used to monitor both the deposition of IZO and AZO at periodic instances (snapshots) during the process. A “pass” is used as the unit because the sputtering system uses a fixed deposition speed along the line, and each trip ensures only one passage through the deposition chamber.

Films deposited on quartz substrates and polysilicon wafers were supplied by AccuStrata Inc., manufacturer of the OMT. In order to observe the film growth, the sample holder has been periodically withdrawn from the deposition chamber and run into the load-lock chamber where the sample measurements took place.

Fig. 3.22 (a) shows the spectra of the IZO taken every four passes through the deposition chamber. The reflectance spectrum of the polished silicon wafer is also shown (green envelope line on top of the oscillations). The individual oscillations from the “passes” align well with the envelope of the bare Si substrate, which is the expected behavior for uniform and homogenous
films. Since the interference maxima touch very well the bare substrate, and the spectral minima go very well down to zero, it is a good evidence that the refractive index of the film is very close to \( n_{\text{film}} = \sqrt{n_{\text{sub}}} \). Fig. 3.22 (a) also demonstrates that there is no evidence of optical absorption in the films in the spectral region considered, down to below 500 nm, where very small optical absorption begins to appear (\( k < 10^{-5} \)).

The results for the AZO films are shown in Fig. 3.22 (b). Spectra were taken every 3 passes. In the case of AZO, the spectral maxima do not touch the bare substrate envelope. In addition, the gap between the bare substrate and interference maxima widens with wavelength. This is an evidence of optical absorption and/or film inhomogeneity. The widening gap can also evidence film porosity and presence of capillary absorbed water\(^{58,59}\). These results show the variations and change in the optical interference pattern for IZO and AZO as their thickness increases.

**Figure 3.22:** (a) IZO deposited on a polished silicon wafer with measurements taken every 4 passes (b) AZO deposited on a polished silicon wafer with measurements taken every 3 passes.
IZO and AZO layers deposited on Mo-coated SLG substrate were analyzed using this technique. The fit results obtained from the spectroscopic reflectometry (SR) analysis are shown in the Fig. 3.23. The thickness calculated from the SR results agrees well with SE models.

The OMT was used to monitor the growth of CIGS films in the evaporation chamber. Fig. 3.24 shows the spectra taken for a 1\textsuperscript{st} and 3\textsuperscript{rd} stages of a CIGS sample grown on SLG and SS substrate, respectively.

![Optical Model](image)

**Figure 3.23:** Reflectance spectra and model fit of (a) IZO sample (b) AZO sample along with the optical model is shown.

Good fits were obtained between the model and spectra for glass compared to SS samples. This is due to more scattering of light incident on the SS samples caused by higher defect density and surface roughness compared to glass samples. The table in Fig. 3.24 shows the results obtained for 1\textsuperscript{st} and 3\textsuperscript{rd} stage samples on SLG and SS substrates along with the measured values using
ancillary techniques. SR results with 5% error and SE results with 2% error have a very good overlap with the measured values.

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>Measured</th>
<th>SE Model (&lt;2% error)</th>
<th>SR Model (&lt;5% error)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IGS (G)</td>
<td>~1600</td>
<td>1643</td>
<td>1686</td>
</tr>
<tr>
<td>IGS (SS)</td>
<td>~1700</td>
<td>1756</td>
<td>1800</td>
</tr>
<tr>
<td>CIGS 3rd (G)</td>
<td>~2300</td>
<td>2297</td>
<td>2323</td>
</tr>
<tr>
<td>CIGS 3rd (SS)</td>
<td>~2200</td>
<td>2183</td>
<td>2227</td>
</tr>
</tbody>
</table>

Figure 3.24: Reflectance spectra fit plots of 1st stage of CIGS on Mo-coated (a) SLG and (c) SS substrates and 3rd stage of CIGS on Mo-coated (b) SLG and (d) SS substrates. The table shows the comparison of SR and SE results with the measured values using ancillary techniques.
Samples grown by stopping the fabrication process after deposition of each layer were also analyzed with this technique. Fit results for these samples are shown in the Fig. 3.25. Good fits were obtained for all the samples measured. As the layer bandgaps were above 1 eV, the reflectance spectrum shown was not affected by absorption due to inter-band transitions. Even though there is not a significant change in the reflectance spectra between samples with only buffer layer and samples with IZO and buffer layer, the change in reflectance spectra of the sample with all the functional layers as seen in the Fig. 3.25 (c), the Al metal doping in AZO (ZnO:Al) layer causes IR absorption. Optical absorbance in the IR region due to free carriers\textsuperscript{42,55} is a typical behavior seen in metals. The quality of the fit does not affect the thickness results as long as the peaks and valleys of measured and modeled spectra are in line. The difference seen between the modeled and measured spectra at the peaks and valleys, is due to scattering effects from roughness and other defects such pores and interfacial voids in the samples. The CIGS absorber layer thickness calculated by the monitoring software agrees very well with the
measured thickness in the film using X-ray fluorescence and a stylus profilometer. This implies that the optical functions used for its determination (hence, the sample composition) are well defined. The thicknesses of the other layers i.e. buffer and TCO layers, calculated from the SE agree well with SR results.

![SE/SR Model Correlation](image-url)

**Figure 3.26:** Correlation between SR and SE thickness results for all the functional layers.

Measurements carried out in the sputtering line and evaporation chamber with the optical monitoring systems resulted in the expected values for the layers deposited. As shown in the Fig. 3.26 there is a very good correlation between thickness results obtained from SE and SR. This means that the optical functions used are appropriate. Especially in case of CIGS, where the optical functions are dependent on the composition of the layer, this means that the models developed using SE are good, and that we can use the OMT in conjunction with those models to monitor the deposition of a sample of a certain composition. As the SE and SR results match the results obtained from the cross sectional analysis, the optical functions for the rest of the layers i.e. CdS, IZO and AZO are appropriate. There is good agreement between determinations done with the OMT software and the specified value. This confirms that the use of regular fiber optics as opposed to polarization-maintaining fibers (that is, using spectroscopic reflectometry instead of polarimetry), is sufficient for process monitoring for fabrication of a complete CIGS solar cell on both rigid and flexible substrates. As this technique can be applied at high temperatures and is
sensitive to layer thickness, composition and compositional gradients it can be used to monitor
the CIGS deposition process in an evaporation chamber, to give superior results to the more
common metrology carried out by pyrometers and elemental rate monitors. This technique does
not need to be applied truly in-situ, and can be used to monitor evaporation, selenization, reactive
sputtering, and other deposition types used for different layers.

3.4.4 Effect of Cu$_{2-x}$Se on the optical properties of CIGS

Fig. 3.27 (a) and (b) show the FIB cross-section of the samples that were used for energy
dispersive spectroscopy (EDS) analysis. For CGI < 1, the EDS map shows a uniform distribution
of Cu in CIGS across the surveyed region whereas for CGI > 1, there are clusters of high Cu
concentration regions near the surface of the sample. These regions are Cu$_{2-x}$Se phases formed
after the sample reaches stoichiometry (CGI = 1), which can be seen in the magnified cross
section images in Fig. 3.27 (f), whereas for CGI < 1 sample, no such regions were observed.
Also, SIMS depth profiles (Fig. 3.27 (g) and (h)) confirm that samples with Cu$_{2-x}$Se phases show
CGI > 1 near the surface while CGI < 1 for samples without Cu$_{2-x}$Se. This indicates that for CGI
> 1, Cu$_{2-x}$Se phases distributed across the sample’s surface form a mixed CIGS/Cu$_{2-x}$Se layer.
Figure 3.27: (a) and (d) show the FIB cross section of the CGI < 1 and CGI > 1 samples, where the marked boxes show the region where the EDS analysis was performed. (b) and (e) show the Cu signal intensity from EDS analysis. High concentrations of Cu can be seen near the surface of CGI > 1 sample in (e). (c) and (f) are the magnified cross section images of the samples. Cu clusters identified in (e) from EDS analysis of CGI > 1 sample can also be seen in (f). (g) and (h) show the CGI ratio variation along the depth obtained from SIMS depth profiles. Pt was deposited on CIGS to protect the layer from ion beam source.

SE optical models were created based on the EDS analysis as shown in the Fig. 3.28. Surface roughness is modeled assuming a dielectric function calculated from a Bruggeman Effective Medium Approximation (EMA) as a mixture of underlying and overlying materials\textsuperscript{42} and compared with actual optical profiler measurements. The quality of the optical model fit as seen in the Fig. 3.28 is good for both samples. For CGI < 1, the optical model included CIGS optical functions taken from Sunkoju \textit{et al.}\textsuperscript{1}. For CGI > 1, the optical model included an EMA layer used to define the mixed CIGS/Cu\textsubscript{2-x}Se surface region. Optical functions of Cu\textsubscript{2-x}Se were derived based on this EMA layer using regression analysis\textsuperscript{42}. As seen in the inset of Fig. 3.28 the optical model fit degrades between 1 – 1.2 eV for both samples as the band gap of CIGS deposited by 3-stage process varies depending on the Ga concentration, which is not uniform along the
thickness. Thickness results obtained from SE analysis were in quantitative agreement with the results obtained from ancillary techniques.

Figure 3.28: Optical model fit from the SE analysis for (a) CGI < 1 and (b) CGI > 1 sample. The inset shows the fit magnified in the transparent region below 1.2 eV. Optical models used for the analysis are shown in the upper right corner.
Fig. 3.29 (a) shows the CIGS optical functions while (b) shows the optical functions derived for Cu$_{2-x}$Se. The development of CIGS optical functions is explained in the Sec. 3.3.1. In Fig. 3.29 (c) and (d) equivalent SR measurements are shown. Below 1 eV, the magnitude of the extinction coefficient is shifted upward for Cu$_{2-x}$Se (Fig. 3.29 (b)). Such increase in absorbance in the NIR region is due to the free carrier absorption since it behaves as a semi–metallic material$^{44,60}$. The optical behavior of Cu$_{2-x}$Se is modeled as a Drude oscillator in conjunction with other absorbing oscillators$^{42}$. A fundamental inter-band transition is seen in the spectra close to ~2 eV with an onset of its absorption tail at ~1 eV below the transition along with a Drude tail below 1 eV in the NIR region due to high density of free charge carriers. The Cu$_{2-x}$Se derived dielectric function shows absorption beyond 1 eV in the UV/Vis region which is consistent with values reported from first principles calculations$^{61}$ and optical experiments$^{62,63}$.

![Figure 3.29](image.png)

**Figure 3.29:** (a) and (b) show the optical functions obtained for CIGS and Cu$_{2-x}$Se from the SE analysis. (c) and (d) show the fit quality between the reflectance spectra and the optical model.
From Fig. 3.29 (c) and (d), we can see that the reflectance for CGI > 1 decreases drastically in the region below 1 eV when compared to the CGI < 1 sample. This is due to the high free carrier absorption of Cu$_{2-x}$Se in the IR region. As soon as CIGS transitions from CGI < 1 to CGI > 1, Cu$_{2-x}$Se starts forming at the surface leading to a sharp fall in reflectance in the IR region. This change in reflectance can be used to detect CGI transitions with the reflectivity measurements. The optical functions obtained from the SE analysis were applied to fit the in-line reflectometry measurements. Fit results are shown in Fig. 3.29 (c) and (d). Thickness results obtained from reflectometry measurements matched SE results. This confirms that the in-line spectroscopic reflectometry tool can be used for thickness control and to control CGI transitions during the CIGS absorber deposition on different substrates.

The CIGS deposition process was stopped at CGI < 1 and CGI > 1 to study the effects of Cu$_{2-x}$Se on optical properties. The presence of Cu$_{2-x}$Se at the surface for CGI > 1 samples has been confirmed by SIMS, EDS and FIB cross section analysis. Spectroscopic ellipsometry was used to derive optical functions of Cu$_{2-x}$Se by modeling mixed CIGS/Cu$_{2-x}$Se region with help of an EMA layer. The successful modeling of the optical functions with Drude oscillator supports the hypothesis that Cu$_{2-x}$Se shows metallic behavior material in IR region. A drastic change in reflectance caused by high free carrier absorption after the transition to CGI > 1 due to the formation of Cu$_{2-x}$Se surface layer was reported. This change in reflectance measured with the help of an in-line spectroscopic reflectometry tool can be used to detect CGI transition and also, by fitting reflectivity measurements using derived optical functions, allows to monitor and control thickness during CIGS deposition process on flexible substrates in low-cost, roll-to-roll processing.
3.5 References


grown with a Cu-poor/rich/poor sequence: growth model and structural considerations. 


(2008).


4. Cost Analysis of CIGS Solar Cell Manufacturing

4.1 Introduction

Generally, the cost of photovoltaics (PV) module system is characterized into three subsystems; PV modules, power electronics, and balance of systems (BOS). Interconnected cells in PV modules convert sunlight into electricity. Solar cells are fabricated from semiconductor materials such as CIGS that generate direct-current (DC) electricity through “photoelectric effect”. In this effect, photons from sunlight knock electrons free out of a molecular lattice, generating an electron-hole pair that diffuse in an electric field to separate contacts, generating DC electricity. Alternating-current (AC) electricity is required by most of the electrical applications. Power electronics convert DC electricity generated by the PV module to AC electricity suitable for transmission and use. The remaining components and procedures such as installation, mounting and wiring hardware, land and permitting fees required to produce a complete PV system, comprise BOS. For cost comparison of different renewable energy technologies, the levelized cost of energy (LCOE) calculator is used. LCOE is the ratio of an electricity-generation system’s costs—installation costs plus lifetime operation and maintenance (O&M) costs—to the electricity generated by the system over its operational lifetime, given in units of dollars/kilowatt-hour (kWh).

The US Photovoltaic Manufacturing Consortium (PVMC) has reported that the high-volume manufacturing of Cu(In,Ga)Se$_2$ (CIGS) thin-film solar cells can achieve high efficiency with laboratory produced small area cells exceeding 18% efficiency$^1$. By 2020, the US Dept. of Energy (DOE) with help of the SunShot initiative, wants to achieve target installed costs of 1
$/W for utility-scale PV systems, 1.25 $/W for commercial rooftop PV, 1.50 $/W for residential rooftop PV. The SunShot target PV module prices as shown in Fig. 4.1 are 0.50 $/W for utility systems, 0.52 $/W for commercial systems, and 0.54 $/W for residential systems. These aggressively set module target prices can be reached by increasing module efficiency and reducing material and manufacturing costs. In this chapter, we discuss approaches and potential pathways to the advances needed to achieve these targets.

**Figure 4.1**: Estimated subsystem prices needed to achieve 2020 SunShot Targets

### 4.2 Cost comparison of deposition techniques

In this analysis, two types of deposition techniques generally used for depositing absorber and buffer layers in the PV industry were compared. Cost comparison is performed between, 3-stage co-evaporation and sputter deposition for CIGS absorber layer, and chemical bath deposition and sputter deposition for CdS buffer layer respectively. 3-stage co-evaporation and chemical bath deposition (CBD) processes are explained in chapter 2. Sputtering is a physical vapor deposition process, where atoms from the “target” material are ejected into a gaseous phase to form a vapor which condenses to form a thin film on the substrate in a high vacuum environment. Sputter deposition process can be used to deposit both absorber and buffer layers.
In an industrial setup, a typical CIGS solar module manufacturing line consists of surface preparation followed by deposition of back contact, absorber layer, buffer layer and the transparent conducting oxides (TCO) layers. After the deposition of these layers which constitute a PV stack, in case of SS substrate, Ag screen printing is performed which forms the front contact. Lamination, layup, and junction box assembly are part of packaging while high potential test, sun soak test, and final IV test are part of testing and qualifying the PV modules. During the lamination and layup, different modules are wired together which is called “module stringing” based on the voltage and current output specifications.

A comprehensive cost model application (Factory Analysis Tool) was developed based on the existing framework used by the PVMC for cost analysis of CIGS module production in order to identify the key aspects and driving factors of the manufacturing costs. The five main categories the cost is broken down in the analysis are manufacturing equipment cost and its maintenance cost, materials cost, utilities, direct and indirect labor, building and overhead depreciation. The equipment depreciation life of 7 years while the building depreciation life of 30 years is used in this cost analysis. Factors which affect production such as yield, uptime, substrate type and size, module design, and power performance along with operational efficiency of the modules, which are called “higher level” inputs, were also considered. Module design defined in terms of packing density (92 %) and grid coverage (5 %) were used in this analysis. Model inputs based on production capacity for each step in the fabrication process are divided into above mentioned five main categories. Two types of deposition techniques for depositing absorber and buffer layer on two different substrates were compared. Cost analysis was performed for determining and minimizing the production cost per module that does not include shipping, balance of system (BOS), installation, or other criteria used in levelized cost of electricity (LCOE) analysis. The
main objective of this work is to identify factors contributing towards the majority of the cost of production that can lead to technological pathway decisions from a financial sustainability perspective. Different configurations of the key components and deposition techniques have been worked out in order to reach a target of $< 0.5/W$ for this technology to meet grid parity in the near future. The projections mentioned in this analysis are based on the CIGS manufacturing development facility built at PVMC, Halfmoon, NY with a production capacity in excess of 10 MW which is being implemented through an industrial consortium including material suppliers, metrology, equipment manufacturers, module manufacturers, and end user installers.

Fig. 4.2 (a) shows the steps involved in the fabrication of a typical CIGS based solar cell on a substrate (rigid or flexible) along with the fabrication method used for each layer. The manufacturing cost components are based on this process flow which were used to determine the cost of a typical CIGS module on a glass substrate and roll-to-roll stainless steel substrate. Cost incurred during the junction box assembly, IV test, sun soak test, and final IV test, which come under packaging and testing part of manufacturing process flow, were also included in the analysis. Fig. 4.2 (b) shows different cost model scenarios with varying factory capacity and module efficiency. A modeled (“target CIGS” in the plot) CIGS factory has 300 MW capacity. It is clear from this plot that as throughput and efficiency increases, the module cost drastically decreases.
Figure 4.2: (a) Table shows the baseline process steps involved in CIGS module production (b) Different configurations of PVMC cost model to achieve < 0.5$/W operational production cost at 15% module efficiency with target CIGS factory capacity.

Fig. 4.3 (a) shows the cost breakdown for an example scenario of CIGS manufacturing via selenization while Fig. 4.3 (b) shows the breakdown of cost for each process involved in the fabrication of CIGS via selenization process into five different categories i.e. materials, labor, equipment depreciation, maintenance and utilities. Higher level inputs used in this example scenario cost analysis are module size (1.6 m × 0.6 m), module efficiency (13 %), annual production (600 MW) and type of substrate (rigid or flexible). Model inputs used in this cost analysis are different types of processes used for deposition of absorber, buffer and TCO layers along with depreciation schedules, cost of building, materials, labor, and utilities. Labor cost is calculated from working days per year, working hours per day and shifts per day for each labor.

The output of this is the module cost given in terms of $/Watt. This financial analysis tool was used to determine the relative impact of two different CIGS deposition techniques, namely co-evaporation and sputtering, coupled with buffer layer deposition techniques, namely chemical bath deposition and sputter deposition respectively, for two different substrates, i.e. glass and stainless steel on the total cost of the module ($/W).
Figure 4.3: Breakdown of (a) module cost and (b) cost of each process in the fabrication of a CIGS solar cell via selenization process.

For the comparative study, the higher-level inputs used in the analysis were module efficiency (fixed at 15%), annual production volume (at 600 MW), and module size (at 1.2 m × 0.6 m). Model inputs, such as equipment costs, materials costs and building and overhead components (which include building costs, utilities, labor, depreciation schedules and plant utilization) for each step in the fabrication process were determined by the facility size needs based upon production capacity. Operational and performance factors such as module efficiency, yield, system uptimes, and overall capacity inputs were incorporated in the factory power output calculations.

With these inputs, first the analysis was carried to figure out the cost differences between modules on glass and stainless steel with CIGS co-evaporation process and CdS CBD and then with CIGS sputtering and CdS sputtering process. Fig. 4.4 shows the module and process cost breakdown for (a) glass substrate and (b) stainless steel substrate for CIGS co-evaporation and CdS CBD process while Fig. 4.5 shows the module and process cost breakdown for (a) glass substrate and (b) stainless steel substrate for CIGS and CdS sputter deposition process.
Fig. 4.4 shows the cost breakdown of CIGS co-evaporation process and CdS CBD process on glass and stainless steel (roll-to-roll) substrate. From cost comparison, the main difference between these two substrates is in the equipment depreciation which has a life of 7 years. The module cost of manufacturing for CIGS cells using co-evaporation and CBD process is $0.57/W for glass substrates while it is $0.52/W for stainless steel substrates. The stainless steel substrate (roll-to-roll configuration) considered here is 2.5 km in length and 0.6m in width with an efficiency of 15% and yield of 95%. Note that these results are only for module fabrication and do not include shipping, BOS, or other PV system installation costs.
Similarly, in Fig. 4.5, the cost break-down of CIGS and CdS sputter deposition process on (a) glass and (b) stainless steel substrates are shown. From the cost comparison of the sputter deposition process on these two substrates, it can be seen that the difference is coming from material and labor costs. The module cost of manufacturing for CIGS solar cells using sputtering deposition process is 0.56 $/W for glass and 0.54 $/W for stainless steel substrates.

It is clear from cost comparison that manufacturing CIGS solar cells using co-evaporation and CBD process on roll-to-roll configuration would be more cost effective and bring down the module cost to 0.52 $/W. The main factors that affect cost significantly are substrate, module efficiency, yield, factory capacity, and packaging materials costs. Increasing the substrate width, length, and increasing the yield results in significant reduction in costs for a CIGS factory.

**Figure 4.5:** Module and process cost breakdown comparison of CIGS sputter and CdS sputter on (a) glass and (b) roll to roll substrate.
Factors such as factory capacity and depreciation schedules have very limited impact to the cost structure. To meet the target costs at high yield and high volume manufacturing scale, cell efficiency and module packaging costs are promising areas for improvement.

4.3 Advantages of a process control technique

![Figure 4.6: Distribution of efficiency obtained from a 10 cm × 10 cm CIGS solar cell (right) deposited using co-evaporation and CBD process on stainless steel substrate with 1.1 cm² grid size.](image)

To understand the spatial configuration of efficiency due to thickness non-uniformities and various other defect, individual cells of 1.1 cm² were fabricated on a 10 cm × 10 cm stainless steel substrate. With enough statistics effects of spatial configuration in the efficiency of cells can be figured out. Fig. 4.6 shows the distribution of efficiencies obtained from individual cells with an area of 1.1 cm² on a 10 cm × 10 cm stainless steel substrate deposited using co-evaporation and CBD process. The distribution curve shows that the average efficiency of the cells in one substrate is around 13.4 %. From the cost analysis, as shown in Fig. 4.4 and Fig. 4.5, a module cost of 0.52 $/W can be achieved by using a flexible substrate with co-evaporation and CBD process resulting in 15 % module efficiency, 95 % yield, and annual production capacity of
600 MW. In order to meet the SunShot target of $< 0.5 \$/W, critical components of the cost model were identified and the methods and criteria to achieve the target have been established.

A major strategy for reducing per-watt module price is increasing module efficiency and improving the mass-production efficiency. Cell-to-module losses during the scale up of laboratory cell PV technology to industrial scale module technology, should be minimized by improving the manufacturing processes. With higher best-cell efficiency and manufacturing technology improvements, higher module efficiencies can be achieved.

The main focus in reducing material costs is the active semiconductor material, which is a complex and expensive component of a CIGS PV module. CIGS absorber layers accounts for 22% of the module manufacturing cost. The optimum thickness for a CIGS absorber layer is around ~ 2.2 µm, hence, depositing a thicker layer would not contribute towards more efficiency and would be considered a waste of absorber material. The cost of CIGS modules could be reduced by depositing the absorber layers uniformly to their optimum thickness across the surface area thereby minimizing CIGS material losses during the deposition process.

Another way to reduce cost per watt is to increase yield and throughput. Yields can vary depending on the quality of the materials used in the fabrication process and on the minimum cell efficiency needed to qualify the product. A wide variation in cell efficiencies would lead to module-stringing losses later, which is unacceptable. Defective cells which are not identified until the end of the fabrication process increase the cost per watt compared to identifying them in the middle of the process. Hence, recognizing defective or low efficiency cells in the manufacturing process is critical to improve the yield. Maintaining interface quality, such as
device junction, back contact, front contact and other interfacial layers that affect the device behavior, is critical as defects in these regions lead to recombination effects.

The spectroscopic reflectometry tool analyzed in this work (developed by Accustrata Inc.) provides a low-cost process control solution for all the above-mentioned criteria. This optical method is fast, efficient, and can effectively be applied to in situ process controls and in-line metrology for manufacturing CIGS solar cells. Being a non-contact method, this can be easily applied to roll-to-roll configurations. This method can assist in correlation of the processing parameters with fundamental device physics which can accelerate the product development to achieve the price targets. By employing this technique, semiconductor materials can be deposited uniformly and more efficiently to reduce material costs in these technologies for lowering the module production costs. This method can help to improve the average cell efficiencies from 13.4 % to 15 % to lower the module cost. As this technique can be easily applied to large deposition areas, it can also help in reducing cell-to-module efficiency gap ensuring uniform properties such as thicknesses (interfacial, bulk) leading to less defects and dense packing of the material. There is growing need to control the processes for uniform deposition of layers and interfaces during the device scale-up from square inches to square meters and process scale-up to square miles of annual output at high yield. This cost effective optical technique gives an opportunity for existing thin-film-based modules for optimizing electronic and optical properties for improving the yield from existing 75 % to 95 % while maintaining a high throughput to achieve 600 MW annual capacity, which are key criteria based on the cost analysis to achieve < 0.5 $/W.
To reach the SunShot price targets, new technologies like spectroscopic reflectometry have to be brought quickly to commercial maturity. It is critical to scale up the technological innovations from the laboratory to commercial production quickly and efficiently. Based on the cost analysis, one of the best strategies for achieving the SunShot targets would be increasing manufacturing throughput, using roll-to-roll thin-film module manufacturing, with co-evaporation and CBD process for thin films, while applying a spectroscopic reflectometry based process control technique to reduce material wastage costs, improve module efficiencies, and maintain high yield.

4.4 References

5. Conclusions and Future Directions

In this study, the dielectric functions of polycrystalline Cu(In$_{1-x}$Ga$_x$)Se$_2$ layers formed after each stage of the CIGS 3-stage co-evaporation process have been determined by using spectroscopic ellipsometry. An initial model for the dielectric functions was extracted from ellipsometric data of CIGS layers on glass substrates, with a thickness in the order of 1.5 - 2.5 µm, incorporating the surface roughness observed layers. SE analysis was performed and an excellent fit between the model and the ellipsometric data was obtained for CIGS deposited both on glass and on stainless steel substrates. The thickness values obtained from SE have been verified by stylus profilometry, SEM, and SIMS measurements. To characterize the transition energies in the range between 1 and 5.1 eV, critical point line-shape analysis was performed. Inter-band transitions have been identified and verified by analogy with previously published work. Spectral dependency of CIGS’s optical functions on the Ga concentration needs to be investigated in order to understand the band structure evolution and identify the compositional fingerprints for real-time process control applications.

To address the need to monitor the deposition of the functional layers i.e. buffer and TCO layers for better yield and efficiency, dielectric functions of these layers have been derived using SE. These and CIGS dielectric functions were used to study the thickness and non-uniformity of all the layers during the fabrication of a complete CIGS solar cell. Optical models developed and used at each step of the fabrication process gave excellent fits and matching results. Similar results were obtained for samples fabricated on SS substrates.

With the help of PV stack optical models the large area compositional uniformity was studied. This is critical in reducing the efficiency gap between the high performance laboratory scale
CIGS solar cells and industrial scale modules. In this study, the RC2 spectroscopic ellipsometer was used to map all the layer thicknesses of a CIGS solar cell in order to probe the spatial non-uniformity that can affect the performance of a cell. In this chapter, SE proved to be an effective tool to study thickness non-uniformity in large area CIGS technology.

Optical functions thus derived for each of the stages of CIGS 3-stage deposition process along with CdS and TCO functional layers using spectroscopic ellipsometry, were used in an optical monitoring systems installed in the pilot line at the PVMC’s Halfmoon facility. Measurements carried out for full PV stack samples with the sputtering line optical monitoring system installed resulted in the expected values for the layers deposited. This means that the optical functions used are appropriate. Especially in the case of CIGS, where the optical functions are dependent on the composition of the layer, this means that the models developed using spectroscopic ellipsometry are good, and that we can use the OMT to monitor the deposition of a material of a given composition. There is good agreement between determinations done with the OMT software and the specified value. This confirms that the use of regular fiber optics as opposed to polarization-maintaining fibers is sufficient for process monitoring.

For high efficiency CIGS solar cells, controlling the CGI transition during the 3-stage deposition process is crucial. In this study, the effect of Cu on the optical properties of CIGS has been investigated using SE and SR techniques in order to control and detect the CGI transition. The CIGS deposition process was stopped at CGI < 1 and CGI > 1 to study the effects of Cu$_{2-x}$Se on optical properties. The presence of Cu$_{2-x}$Se at the surface for CGI > 1 samples has been confirmed by SIMS, EDS and FIB cross section analysis. Spectroscopic ellipsometry was used to derive optical functions of Cu$_{2-x}$Se by modeling mixed CIGS/Cu$_{2-x}$Se region with help of EMA layer. The successful modeling of the optical functions with Drude oscillator supports the
hypothesis that Cu$_{2-x}$Se shows metallic behavior material in IR region. A drastic change in reflectance caused by high free carrier absorption after the transition to CGI > 1 due to the formation of Cu$_{2-x}$Se surface layer was reported. This change in reflectance measured with the help of an in-line spectroscopic reflectometry tool can not only be used to detect CGI transition but also, by fitting reflectivity measurements using derived optical functions, allows to control and monitor thickness during CIGS deposition process on flexible substrates in low-cost, roll-to-roll processing.

In the cost analysis, key aspects and driving factors for the manufacturing were identified. Cost comparison of Sputtering and co-evaporation coupled with chemical bath deposition showed that latter was more cost effective than the former. Results show that manufacturing of CIGS solar cell using co-evaporation and CBD process on roll-to-roll substrate would be most cost effective and bring down the module cost to 0.52 $/W. Factors such as module efficiency, material cost, substrate, annual production capacity, yield and throughput had a significant impact on the final module cost ($/W). A low-cost process control solution to improve all the above mentioned factors is essential in order to achieve the target module cost of < 0.5 $/W.

Results obtained in this study prove that the critical need for measuring, monitoring, and controlling the thickness, structure, phase, and composition of these solar cell component layers in real time, during their deposition in high volume manufacturing can be fulfilled by optical techniques such as SE and SR. With accurate optical models developed for all the functional layers of a CIGS based solar cell using SE in this research, SR offers a rapid and relatively low cost in situ process control and in-line metrology for manufacturing CIGS solar cell. This non-contact control method was successfully applied to monitor thicknesses of layers deposited on both rigid and roll-to-roll substrates with excellent matching results unlike the conventional
contact based process control methods. Also, SR technique offers a novel method to detect the CGI transition during the 3-stage deposition process, which is very critical for manufacturing high efficiency solar cells. For applying this technique to monitor large-area depositions, multiple optical fiber probes connected to single monitoring unit can be used to scan over the full-width of a substrate in a roll-to-roll manufacturing setup. A low cost SR process control technique offers an opportunity to reduce material costs by depositing layers uniformly to their optimum thickness and can assist in reducing the cell-to-module efficiency gap, increase throughput and yield in a high volume manufacturing set up for producing high efficiency CIGS solar modules at the SunShot target of < 0.5 $/W.