Synthesis and Characterization of CdSe-Coated ZnO Nanowires for Extremely Thin Absorber Solar Cells

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Dedications

To my parents, Ari and Orly
And to my sisters, Talia and Ella
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Abstract
Synthesis and Characterization of CdSe-Coated ZnO Nanowires for Extremely Thin Absorber Solar Cells
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Extremely thin absorber (eta) solar cells are new and promising solid-state photovoltaic devices. eta solar cells use a nanostructured interpenetrating heterojunction featuring a thin light-absorbing layer at the interface between an n-type semiconductor and a p-type semiconductor. As a first step towards the realization of a ZnO nanowire/CdSe/CuSCN eta solar cell, I report a proof-of-concept that the successive ionic layer adsorption and reaction (SILAR) technique can be used to sensitize ZnO nanowire arrays with a thin CdSe absorber layer. Scanning electron micrographs show that CdSe conformally and uniformly coats the ZnO nanowires, leaving open interstices between nanowires to be filled with CuSCN. Coating thickness depends on the number of SILAR cycles, and a thickness of ~10 nm is achieved with 150 cycles. Solar cells utilizing the CdSe-coated ZnO nanowires, but which use liquid electrolyte as the hole transport material instead of CuSCN, exhibited light harvesting efficiencies of 40-50% and incident-photon-to-electron-conversion efficiencies of 1-5% in the visible light range (400-600 nm). Response of those solar cells to visible light confirms the sensitization of ZnO nanowires with CdSe, as compared to bare ZnO nanowires which show only UV response. Effects of different sample treatments such as ZnO seeding technique, O_2 plasma cleaning, and annealing on the resulting ZnO nanowires/CdSe structure are discussed.
CHAPTER 1: INTRODUCTION

1.1 Background and Motivation

In the last two decades there have been major efforts to address the overwhelming growth of both the worldwide energy demand and the emissions of green house gases (GHG) that are due to human activities. The Energy Information Administration (EIA) of the U.S. Department of Energy reported in its International Energy Outlook for 2008 that the world energy consumption is projected to expand by 50% from 2005 (462 Quadrillion Btu) to 2030 (projected 695 Quadrillion Btu) [1]. To satisfy the growing demand, the EIA predicts a sharp increase in the utilization of coal over the next 20 years, as well as a steep increase in the development of renewable energy sources as viable solutions to the demand. Figure 1.1 shows the projected trend from the EIA’s International Energy Outlook for 2008.

Coupled with the increasing energy demand is the issue of climate change and global warming, made worse by the burning of fossil fuels. The United Nations’ Intergovernmental Panel on Climate Change (IPCC) report “Climate Change 2007:
Synthesis Report” identified long-lived green-house gases (GHGs) as the main factor affecting global warming and the radiative forcing of the climate system, and pointed out that global GHGs emissions by human related activities have increased 70% between 1970-2004 [2]. Some of the observed effects of the ongoing climate change include alterations in disturbances of forests due to fires and pests, excess heat-related mortality in Europe, changes in infectious diseases vectors, earlier “greening” of vegetation in the spring, and others. Greater negative impacts, such as decreases in the productivity of crops, increase in risk for coastal erosion due to sea-level rise, and an increase in malnutrition are projected if the current GHG emissions trends (and as a result, the trend in globally increasing temperature) continue in the next 50-100 years [2].

In order to curb the constant rise in GHG emissions and avoid the morbid projections, energy sources that are carbon-neutral and renewable must be researched and developed to a point where they can become a viable alternative to fossil fuels. The EIA report shows that renewable energy is projected to be the fastest growing energy consumption source at a growth rate of 2.1%/yr [1]. Many reasons exist for this rising interest in renewable energy. The previously discussed identification of carbon dioxide as a leading cause of climate change and global warming, the postulated peak oil theory, and rising oil prices are all current scientific and political topics of investigation that are directly related to the recent surge in interest. The overall effect of those factors and others is a major academic and legislative push for new sustainable solutions to the world’s growing energy demands, and there are many different avenues to pursue these solutions. Much of the research currently underway in the renewable energy sources field is concentrated on the development and applications of photovoltaic (PV) cells.
Out of the four different significant renewable energy sources (hydropower, biomass, wind, and solar), solar PV energy is the fastest growing field with an average annual growth rate of about 60% in recent years. Figure 1.2 shows the recent growth rate comparison between the different renewable energy sources.

![Figure 1.2: Average Annual Growth Rate of Renewable Energy Capacity, 2002-2006 [3].](image)

In his 2003 essay “Motivation for Photovoltaic Application and Development”, Joachim Luther explains that the attractiveness of PV technology stems from two sources: (1) the technical potential of solar energy (i.e. taking into account a small percentage of land area utilization and assuming conservative overall efficiencies) is very high, ranking first among renewable energy sources at 1575 exajouls/annum, enough to produce more than twice the projected world energy demand for 2030, and (2) PV energy conversion meets the requirement of a sustainable energy source as it produces no harmful emissions during operation [4]. Photovoltaic cells can provide clean, renewable, zero-emission electricity production that is scalable and flexible.
1.2 Photovoltaic Cells

A photovoltaic (PV) cell, or solar cell, is a device that converts light energy to electrical energy by the photovoltaic effect. In a solar cell, light (photons) is absorbed by the cell and converted to electron-hole pairs, which must be separated in order for the electrons to do work on a connected load.

Three distinctively different types of solar cells are in existence. The so-called “first generation” photovoltaics include the traditional single band-gap, monocrystalline silicon wafer solar cells, and have a 31% efficiency limit (for $E_g \sim 1.1-1.5 \text{ eV}$) under 1 sun illumination known as the Shockley-Queisser limit. These solar cells were developed beginning in the 1970s and today have a mature market and established production and electricity generation costs that are not likely to change significantly, except for minor on-going improvements. A “second generation” of devices began developing in the 1980s, based on thin-film technology. Thin-film solar cells offer a large reduction in material costs (and therefore costs per unit area of the cell) due to the elimination of the high purity silicon wafer, as they employ materials such as polycrystalline or amorphous silicon, direct band gap materials like Cadmium Telluride (CdTe) and Gallium Arsenide (GaAs), but do not present the potential for efficiencies higher than the Shockley-Queisser limit as they are still based on the conventional single band gap p-n junction.

“Third generation” solar cells, where the most recent developments in solar cell technology are implemented, uses “second generation” materials but foregoes the use of the single band-gap junction. Fundamentally different underlying concepts are used in the design and development of “third generation” photovoltaic cells, and new methods such as thin-film stacking, p-i-n and n-i-p junctions, and quantum dots have been utilized in
devices like the dye-sensitized solar cell (DSSC), multijunction cell, organic polymer cell, and extremely thin absorber (eta). These types of photovoltaic devices can have theoretical efficiency limits that approach the carnot thermodynamic limit of 66% at 1 Sun irradiation, much higher than the single-band device limit of 31% [5]. Figure 1.3 shows a good representation of the economics of the three solar cell generations, based both on electricity generation cost (given in $/W) and material cost (given in $/m^2). In order to even begin being competitive with fossil fuel electricity generation costs, solar energy costs must be decreased to about $1.0/peak W (or ~5¢/kW-hr).

![Figure 1.3: Solar electricity cost as a function of efficiency and material cost. The three solar cell generations are labeled in the areas as I, II, and III. Taken from [6], originally from [5].](image1)

Many different types of cells have been developed, and some of the more important types are presented here.
1.2.1 First Generation Solar Cells

In a conventional PV cell, a semiconductor (generally high purity silicon) is used as the cell material. The electron-hole charge separation occurs in a p-n junction: a contact area between a p-type semiconductor and an n-type semiconductor sets-up an electric field in the junction, and generates a built-in potential in the cell between the two extrinsic semiconductors. At the junction itself, a depletion region free of mobile carriers is formed, in which the electric field is present. When light photons with energy greater than the material’s band gap \((E>E_g)\) are absorbed by the cell, electron-hole pairs with energy greater or equal to the material band gap are generated in the depletion region. Due to the electric field in the depletion region, the electrons generated drift towards the n-type side and the holes drift towards the p-type side. This charge separation results in current flow, and in the possibility of the electrons to do work on a connected load [7].

Figure 1.4(a) shows a schematic of a p-n junction in a traditional silicon solar cell during thermal equilibrium, which illustrates the main principle upon which a conventional solar cell is based. Figure 1.4(b) presents the general, macro-size operation of a crystalline silicon solar cell, highlighting the way that the charge separation is achieved in the cell.

Many types of traditional monocrystalline p-n junction silicon (c-Si) solar cells exist; most of them utilize similar principles but new technologies in fabrication. Some of the different types include the crystalline silicon concentrator cell (as presented in figure 1.4(b)), the bifacial cell, and the buried contact cell, with the highest efficiency reported for crystalline silicon solar cells as 25.0\%±0.5\% [8]. The average module cost for c-Si solar cells is currently around $4.0/peak Watt.
1.2.2 Second Generation Solar Cells

The basic principle behind “second generation” photovoltaic devices is using thin films of direct semiconductor materials (such as GaAs and CdTe) instead of single-crystal silicon, which is an indirect band-gap semiconductor and therefore less efficient at absorbing light. As an example, for a 90% light absorption it takes only 1µm of GaAs as opposed to 100µm of c-Si [11]. The significant decrease of required material makes the so-called “second generation” materials much more cost effective, as only a very thin layer of material is needed to produce a cell with efficiencies that are comparable to Si cell efficiencies. In this section I will give as an example the Cadmium Telluride photovoltaic cell to illustrate the benefits of thin-film materials in solar energy application research.
1.2.2.1 Cadmium Telluride (CdTe) Solar Cell

In general, most CdTe photovoltaic devices are based on the p-n junction between CdTe and CdS. The attractiveness of this type of cell arises from two factors: (1) CdTe has nearly ideal optoelectronic properties and (2) the ease with which thin films of the materials used can be deposited. The schematic structure of the CdTe-CdS solar cell is presented in Figure 1.5, which illustrates a cell not much thicker than 4 µm.

![Schematic structure of the CdTe-CdS solar cell](image)

Figure 1.5: Schematic structure of the CdTe-CdS solar cell [12].

The basic mechanism upon which the cell is based on is similar to that of a conventional Si cell: photons pass through the glass substrate, transparent conductive oxide layer (TCO), and CdS, and are absorbed by the CdTe. Those photons with energies above or equal to the CdTe band gap (1.4-1.5 eV) excite electrons out of their valence band and into the CdTe conduction band. Once the electrons become mobile, the electric field in the p-n junction drives the electrons in the direction of the n-type material, CdS. The band structure of the CdTe-CdS heterojunction is very similar to that of a c-Si p-n junction.
CdTe solar cells have recently become the first feasible, economically viable alternative to traditional c-Si solar cells. The highest reported efficiency as of January 2009 for a CdTe thin film cell was 16.7%±0.5%, and the best commercial module efficiency was reported as 10.9%±0.5% [8]. Companies like First Solar, LLC currently sell CdTe-CdS based PV modules to residential, commercial, and utility companies. The National Renewable Energy Laboratory (NREL), in its 2005 annual report, announced that First Solar sold about 20 MW of CdTe PV modules in 2005, with plans to expand production five fold in three years [13]. As can be seen from Figure 1.3, second generation photovoltaics are limited by low efficiencies, even though their application lowers the module cost to around $1.0/peak W. Although the CdTe-CdS cell is becoming more and more attractive, low efficiencies and the use of perceivably toxic (Cd-containing) materials are still considered disadvantageous.

### 1.2.3 Third Generation Solar Cells

As second generation photovoltaics become more economically viable and begin replacing conventional cells, the solar cell industry turns to new methods and concepts in order to improve the efficiencies of thin-film cells while keeping the module cost low enough to stay competitive with first generation cells and even fossil fuels. Research into third generation PV aims to minimize the processes that lead to efficiency losses that occur in a standard first generation cell. Some of these processes are: (1) thermalization loss, (2) junction and contact voltage loss, and (3) recombination loss [14].

In order to minimize those losses, increase efficiency, and minimize cost, new types of cells were and are still being developed; examples include multijunction devices...
known as tandem cells and hot-carrier cells. In addition to novel types of cells, new technologies are also being developed that can increase solar cell efficiencies. Those technologies include the concentration of incident spectrum (which can raise the Shockley-Queisser limit to about 41% in single junction cells), making use of thermophotonics, and making use of infrared radiation to produce electricity at night. Since “third generation” photovoltaics are still mostly theoretical, new, nanostructured “second generation” cells are currently being developed which show promise for reducing module and electricity generation costs (even compared with more traditional planar thin-film solar cells), but are still limited to 15-20% efficiency.

1.2.4 Nanostructured Second Generation Solar Cells

Nanostructured “second generation” solar cells use sophisticated fabrication techniques and to manipulate the solar cell’s geometry in order to reduce the amount or cost of raw materials needed for the construction of the cell.

To illustrate the new concepts upon which nanostructured “second generation” PV are based, I will explore in the rest of this chapter three of these new types of cells: the dye-sensitized solar cell (DSSC), the organic solar cell, and the extremely thin absorber (eta).
1.2.4.1 The Dye-Sensitized Solar Cell (DSSC)

1.2.4.1.1 TiO$_2$ nanoparticle-based DSSC

The dye-sensitized solar cell (DSSC) was first developed by Michael Grätzel and Brian O’Regan in 1991, at the École Polytechnique Fédérale de Lausanne in Switzerland [15]. The novelty of the DSSC is that it separates the processes usually achieved in a first- or second-generation cell by using two materials (p-type and n-type Si or CdTe and CdS, respectively) into three materials. The most studied cell is made up of two heterojunctions: one between TiO$_2$ nanoparticles and a visible light absorbing dye, and another between the absorbing dye and a liquid, hole-conducting electrolyte. In this cell, charge separation occurs at the interface between the conducting dye (which is not a doped material) and the wide band gap material, TiO$_2$. A schematic representation of the general operation of that kind of cell is given in Figure 1.6. In the classical DSSC, a photon passes through the transparent conductive oxide glass anode and through the TiO$_2$ nanoparticle layer, and is then absorbed by the sensitizing dye. An electron is excited by the photon to the excited state of the dye (S$^*$ in Figure 1.6), from which it can be injected into the conduction band of the TiO$_2$ layer. Since this electron now has a high potential, it diffuses through the nanoparticle layer by a hopping mechanism and eventually reaches the anode, where it can be directed to flow across an external load and do work. At the same time, the dye is returned to its ground state (S$^0$/S$^+$) by an electron donation from an I$^-$ ion in the electrolyte, forming I$_3^-$. The redox cycle is completed at the cathode where triiodide is reduced by an electron that was originally injected into the TiO$_2$ layer [16]. This electron-flow mechanism is appropriate for most types of DSSCs, and is very similar to the extremely thin absorber cell mechanism.
The main advantage of the DSSC is its expected very-low module cost, based on the extremely low cost of its constituent materials and simplicity of fabrication. Forecasts made about the dye-sensitized module project a cost estimate of $0.6/peak W and a payback period of one year [17, 18]. Currently, the highest reported efficiency of a DSSC is $10.4\%\pm0.3\%$ [8], however 8\% efficiency is currently more likely for a DSSC-based PV module that can be produced on a large scale.

![Figure 1.6: Schematic of TiO2 nanoparticle/Dye/Electrolyte dye-sensitized solar cell. The green arrows represent the closed circuit electron flow from the dye ground state. The red arrow represents an unwanted electron-hole recombination. Light source is incident from the left. Adapted from [16] by Jason Baxter and Ishai Padawer.](image)

One of the main issues and disadvantages hindering the development of the classical DSSC is the redox electrolyte’s instability: the traditionally used liquid electrolyte degrades over time under UV radiation and may leak if the cell is not perfectly sealed, rendering the device inefficient for long-term use [16]. A half-year study by the Division of Energy Engineering, SEIKI Co. and Toyota Central R&D Laboratory, showed that poor sealing causes the electrolyte to leak, which impedes the outdoor performance of the cell [19]. Another ~2.5 year study by the same group which utilized
better sealants identified electrolyte degradation as the main factor affecting the decreasing stability of the cell [20]. Another theoretical disadvantage of the original DSSC is the hopping diffusion mechanism by which electrons migrate through the TiO$_2$ nanoparticle layer- the relatively long diffusion length is theorized to be a leading cause for recombination in the cell. One recently proposed design that aims to eliminate efficiency losses in the TiO$_2$-nanoparticle DSSC is the ZnO nanowire-based cell. This design will be briefly explained in the next section.

1.2.4.1.2 ZnO nanowire-based DSSC

In order to minimize the efficiency losses in the dye-sensitized solar cell, several groups [21, 22] have utilized ZnO nanowire arrays as the wide band-gap material, substituting for the TiO$_2$ nanoparticle layer. ZnO has a band gap of ~3.3 eV, compared with the ~3.2 eV band-gap of TiO$_2$, and a wurtzite (hexagonal) crystal structure with inherent anisotropy which makes it ideal for nanowire formation. Kopidakis, et al. explain that in a TiO$_2$ nanoparticle cell, an electron must cross approximately $10^3$-$10^6$ particles before reaching the back contact, but that decreasing the nanoparticle layer thickness also decreases the surface area of dye-semiconductor contact [23]. The reasoning for applying the nanowire structure in the cell is that it provides a direct conduction path for electrons injected from the sensitizing dye, thereby reducing electron diffusion time from the point of injection to the back contact, and indirectly reducing electron-hole recombination events that occur in the TiO$_2$ nanoparticle-based cell. Figure 1.7 presents a schematic of the nanowire-based cell, emphasizing the importance of ZnO morphology, as well as a ZnO nanowire micrograph taken by SEM. Dense arrays of nanowires can have a high
surface area; in fact, a close packed array of 40nm diameter wires, which are 10µm in length, produces an equivalent roughness factor to a typical nanoparticle film. Another advantage of the nanowire configuration is the low temperature fabrication of the production of the cells: generally, high temperature techniques are required to produce high-quality, dispersed TiO$_2$ nanoparticle layers, driving the energy cost for traditional DSSCs up. So far,

![Figure 1.7: (a) SEM image of ZnO nanowire array grown in the NEAT lab. (b) Schematic of ZnO nanowire-based DSSC [22].](image)

reported efficiencies for the ZnO nanowire efficiencies are between 0.5% [22] to 1.5% [21] under 1 sun irradiation. The nanowire cell still utilizes a liquid electrolyte, and therefore still faces stability issues from leakage and UV degradation.

### 1.2.4.2 Organic Solar Cell

Organic solar cells originated in the end of the 1950s, when Kearns and Calvin reported on the photovoltaic effect and photoconductivity in a laminated two-layer
organic system [24]. The principles for organic photovoltaics were laid out, and in 1986 Tang attempted to explain the charge carrier mechanism by exciton diffusion [25]. The discovery of the photoinduced electron transfer from a conducting polymer to a buckminsterfullerene ($C_{60}$) in 1992 [26] has inspired much research into semiconducting-polymer based photovoltaics. The main processes in an organic solar cell as well as a general schematic of the different layers in the cell are depicted in Figure 1.8.

![Figure 1.8: (a) The operation of an organic solar cell: light is absorbed (A), excitons are generated (G), and carriers are collected (C). (b) A general schematic of an organic solar cell [27, 28].](image)

The most important difference between organic solar cells and first generation, single junction solar cells, is the mechanism of charge transport. In the organic solar cell, two layers form a heterojunction that acts in a similar to a p-n junction, with the exception that the charge carriers (electrons and holes) are not separated immediately. The light conversion process is as follows: light is absorbed in the active layer (as seen in Figure 1.8b)- a photon is absorbed by an electron donor polymer, such as polyphenylene vinylene (PPV), where it excites an electron into the conjugated polymer’s conduction
band. The electron is injected into the conduction band of an acceptor polymer such as C$_{60}$, which leaves the PPV with a hole. In this manner, an exciton (electron-hole pair) is generated in the material [28]. A gradient in the chemical potentials of electrons and holes, which depends on the difference between the highest occupied molecular (HOMO) level of the donor and the lowest unoccupied molecular (LUMO) level of the acceptor, is built up in the donor-acceptor junction, and contributes to the field induced drift of the excitons. The excitons then migrate to a dissociation site, where they are separated by local electric fields generated at the interface. Current flow on the external load is therefore dependent on exciton diffusion to the dissociation site, which means that the cell’s optimal operation depends on the thickness of the active layer. The interface is distributed by blending the two components (C$_{60}$ and PPV) to create a “bulk heterojunction” in the cell. A typical diffusion length in polymers is around 10 nm [27].

Polymer-based solar cells are advantageous for their low-cost (based on the materials they are made of), ease of fabrication (compared to inorganic cells), and range of structural properties. One of the novel concepts currently being developed is that of the mechanically flexible cell, with prototypes based on the layered structure described in Figure 1.8b already in existence [29]. Although very attractive, organic PV cells are currently limited by low efficiencies, and at their present state do not offer a viable alternative to silicon or even thin-film solar cells. The highest reported efficiency of an organic polymer cell is 5.15%±0.3% [8], and that of an organic PV module is 1.1±0.3% [8], considerably less than other alternatives currently developed.
1.2.4.3 Extremely Thin Absorber (eta) Solar Cell

In an extremely thin absorber (eta) solar cell, a thin layer of an intrinsic absorber material is “sandwiched” between two transparent layers, an n-type material and a p-type material, in a way that maximizes the contact surface area and creates a p-i-n junction. A highly structured configuration allows for a substantial reduction in the local thickness of the absorber, while the total thickness of the absorber ensures maximal absorption of light. Many different types of materials are currently being investigated as possible alternatives for the eta-cell, including TiO$_2$ and ZnO as n-type materials; CdSe, CdTe, and CuInS$_2$ as intrinsic absorbers; and CuSCN and ZnTe as p-type materials [30,31].

In Chapter 2 I will discuss in detail the history of development, as well as the physical governing principles of the eta-cell. I will also detail the techniques required to characterize the eta-cell, and explain the goals of the investigation undertaken in this thesis.
CHAPTER 2: EXTREMELY THIN ABSORBER SOLAR CELLS

2.1 Historical Development

Research into extremely thin absorber solar cells began accelerating soon after the early developments in dye-sensitized solar cells. This is not surprising, considering that the concept underlying eta-solar cells—electron injection from an absorber layer to an n-type semiconductor—is very similar to that of the dye-sensitized solar cell. In 1994 Green and Wenham proposed a silicon solar cell based on parallel multijunctions [32], aimed at increasing the charge carrier collection probability by utilizing thin, parallel p-n junctions—a concept which may be seen as the foundation to extremely thin absorber cells. Many similar type cells, such as the solid state DSSC [33], developed shortly after DSSC stability issues became known, yet they were all still based on organic and inorganic materials. In 1996 Konenkamp et al. proposed the extremely thin absorber concept as a quantum dot heterojunction in the paper “Heterojunction and devices of colloidal semiconductor films and quantum dots”, where they presented a PbS-sensitized TiO$_2$ photovoltaic device that is effectively an eta-cell [34]. The explicit eta technology itself is still relatively new, gaining notice in 1997 when Siebentritt et al. presented the concept of fully-inorganic heterojunction solar cells in the 14th European Photovoltaic Solar Energy Conference and Exhibition [35].

One of the earliest, fully inorganic eta-solar cells was reported in 1998 by Tennakone, et al. as a nanoporous n-TiO$_2$/Selenium/p-CuSCN photovoltaic cell [36], basing the design of the cell on that of a DSSC, where elemental Se was used as a sensitizer for the wide band gap TiO$_2$. The authors explained the carrier injection into the n-TiO$_2$ and p-CuSCN with a band-position diagram of the three materials, after
calculating the band positions of Se and CuSCN. With an average Se layer thickness of \(~23\) nm, the cell’s reported efficiency was \(0.13\)% \([36]\).

Two papers published in 2001 marked a significant step forward in eta-solar cell technology. The first, by Kaiser, \emph{et al.} investigated the use of CuInS\(_2\) as the absorber material in a TiO\(_2\)/CuInS\(_2\)/CuSCN cell, specifically studying what effect the absorber thickness has on photocurrent density \([37]\). The second paper, by Ernst, \emph{et al.} of Hahn-Meitner-Institut Berlin, presented research done on a TiO\(_2\)/CdTe eta-cell, providing one of the earliest schematics explaining the interpenetrating heterojunction upon which the device is based \([31]\). The schematic will be presented and discussed in detail in section 2.2, to help illustrate the physical operation of an eta-cell. The paper by the Hahn-Meitner-Institut group led by Ernst also reported a reduction in absorber thickness from the typical 3-8 µm (for a CdTe/CdS thin-film cell) to around 200 nm, while still achieving about 90% absorbance of light \([31]\).

Since 2001 there have been serious efforts by many groups (mainly in Western Europe) to develop, characterize, and model different types of eta-cells \([38, 39, 40]\). The focus has mainly been on exploring new materials and their potential applications in the cell, and working towards a highly structured geometry in the cell to improve charge transport. Among the materials explored as absorbers are Cu\(_2\)S \([41]\), CuInS\(_2\) \([37]\), CdS \([35]\), CdTe \([35]\), CdSe \([42]\), a-Si, and Cu(In,Ga)S\(_2\) \([43]\). The main candidates for the n-type material are nanoporous-TiO\(_2\) \([39]\) and ZnO nanoarrays \([30]\), and those for the p-type material are ZnTe \([44]\), CuSCN \([42]\), and the organic hole conductor PEDOT:PSS \([43]\).
Work presented in this thesis is focused on the ZnO/CdSe/CuSCN structure of the *eta*-solar cell for reasons explained in detail in section 2.5. The Tena-Zaera group did much work on this structure (and variations of it), its fabrication, and characterization [42, 45, 30, 46], and reported a relatively high overall conversion efficiency of 2.3%, showing the specific structure as a very promising one.

The following section (2.2) is intended to provide a detailed mathematical and physical foundation for understanding the important processes that occur in an *eta*-cell. Section 2.3 is an overview of the different techniques that are used to deposit the materials in the ZnO/CdSe/CuSCN cell, and in Section 2.4 the important characterization techniques are reviewed. Finally, Section 2.5 details the specific structure of the ZnO/CdSe/CuSCN *eta*-cell, including an overview of important parameters and material characteristics.

### 2.2 Physical and Mathematical Description

#### 2.2.1 General Physical Description

In an *eta*-solar cell, an absorber material forms and interpenetrating heterojunction with a transparent n-type material and a transparent p-type material, so that the absorber is “sandwiched” between the two materials (see Figure 2.1a). Generally, the n-type material is deposited on a transparent conductive oxide (TCO) which is deposited on transparent glass, and a thin metallic layer serves as the back contact on the p-type material.
Photons enter the cell from the transparent glass side, pass through the TCO and the n-type layers, and absorb in the intrinsic absorber layer. An absorbed photon excites an electron from the valence band to the conduction band in the extremely thin absorber, which leaves a hole in the valence band. The charge carriers created are now inside the electric field created between the n-type and p-type semiconductors, and due to the short transport path length in the absorber and band alignment between the three materials, inject the electrons into the n-type and the hole into the p-type layers, respectively. This process is illustrated by considering the band diagram, as presented in Figure 2.1b, and is very similar to the carrier transport in a dye-sensitized solar cell (discussed in section 1.2.3.1.1). Once the charges are separated, they are transported to their respective contacts and flow across an external load.

A key feature of the device is extreme surface enlargement: using a highly structured, high effective surface area n-type layer allows for direct deposition of the absorber material and a surface enlargement factor of 10-100 relative to planar thin films [30]. Due to the non-planar arrangement in the device, the local thickness of the absorber layer can be significantly reduced while keeping the overall thickness of the absorber similar to that in a thin-film cell [47]. This reduction in local thickness leads to an
improved charge collection probability, as it shortens the transport path for the charges in
the absorber, limiting the probability of electron-hole recombination in the absorber
itself. Another important aspect of the cell is the optical scattering that occurs at the
interfaces of the absorber, which increases the optical path of photons in the device, and
therefore enhances photon absorption, a process known as light-trapping [48]. In order to
be a good light-trapping layer, the n-type material should be structured so that it has a
typical length scale in the range of solar light wavelengths.

2.2.2 Physical and Mathematical Model

2.2.2.1 Criteria for High Efficiency

In a traditional p-n junction solar cell two important criteria must be met for the
cell to be efficient. The first criterion is that the carrier collection length $L_C$ be larger than
the absorber thickness $W$, stated as $L_C/W > 1$. This criterion must be satisfied to ensure that
separated charges do not recombine before they are collected. The second criterion states
that the absorber thickness must approach the inverse of the light absorption coefficient
$\alpha$, and is stated mathematically as $L_C/\alpha > 1$. Satisfying the second criterion ensures that the
majority of light which passes through the cell is absorbed by it. Satisfying both criteria
requires that the material has a high electronic quality [40].

The most important feature of an eta cell is that the condition $L_C/\alpha > 1$ is relaxed.
Due to folded, highly-structured absorber morphology, the eta cell can absorb the same
amount of light as a traditional PV cell. By utilizing what can be described as extremely
thin, parallel ‘nanojunctions’, the cell’s constraints become $L_C/W > 1$ and $W_{tot}/\alpha > 1$, where
$W_{tot}$ is the total thickness of the absorber film, calculated as the product of the local
thickness (W) times the number of parallel ‘nanojunctions’ (N), or $W_{\text{tot}} = NW$ [40]. By relaxing the high electronic quality condition for the cell, a wider range of lower electronic quality materials can be explored. These materials can have other potentially desirable characteristics, for example transparency to light and lower cost.

### 2.2.2.2 Recombination Processes

There are two major recombination processes in the *eta* cell, described schematically in Figure 2.2. The first, bulk recombination, occurs when an electron and a hole recombine in the bulk absorber material before the separated charges can reach the n-type semiconductor and p-type semiconductor, respectively (See Figure 2.2a). Bulk recombination competes with charge separation, the process which generates charge carriers in the cell. The second type of recombination process is known as interfacial recombination, where charges that were separated and reached the semiconducting materials recombine before they can be transported to their respective contacts and contribute to the photocurrent.

![Bulk Recombination and Interfacial Recombination](image)

Figure 2.2: Charge recombination in an extremely thin absorber cell. (a) bulk recombination, and (b) interfacial recombination [49].
Two major types of interfacial recombination processes can occur: (1) the absorber can be reduced by an injected electron in the n-type material before the compound is regenerated by the hole conductor (the p-type material), and (2) an electron in the n-type material can recombine with a hole in the p-type material via tunneling-enhanced recombination [50]. These processes are illustrated in Figure 2.3:

![Figure 2.3: Interfacial recombination processes (shown as red arrows) in an eta cell. Adapted from [50].](image)

Under a strong electric field, interfacial recombination in the eta-cell between the n-type and p-type materials is postulated to be both trap-assisted and direct (Zener tunneling). Direct recombination due to tunneling is a well-known phenomenon in pn-junctions [51], as is the trap-assisted mechanism of recombination [52]. Traps in the middle of the absorber band gap may lead to the tunneling of electrons which enhance the recombination processes described earlier. Although it may seem at first that the absorber should be as thin as possible to minimize bulk recombination, it has been shown [40] by modeling the complex PV system that there is an optimal thickness (which is a function of the roughness factor) of the absorber layer which minimizes tunneling-enhanced recombination as well as bulk recombination.
2.2.2.3 Light-Trapping

The concept of applying light-trapping in a solar cell in order to increase its efficiency was proposed in 1974 by David Redfield in his paper *Multiple-pass thin-film silicon solar cell* [53]. Light-trapping makes use of internal reflection within the light absorbing material to increase the pathway of light through the sample.

![Light trapping in the eta cell. The green arrows represent the possible path of a photon.](image)

A highly structured and convoluted absorber layer can increase the light harvesting efficiency of an *eta*-cell due to multiple reflections. A longer photon pathway (see Figure 2.4) increases the chances of its absorbance by the absorber layer and increases the probability of converting the photon to an electron-hole pair.

2.2.2.4 The *pin*-junction Model

Limited research has been conducted on the mathematical modeling of extremely thin absorber solar cells. Some early work by Grasso *et al.* modeled an *eta*-cell using the SCAPS program developed at Ghent University for “second generation” photovoltaic modeling [54], however, the model is not general enough to apply to a range of cells as
the program requires specific material-dependent parameters. Although some work has been done to model the cells either as a \( \text{pn}^+ \)- or a \( \text{p}^+\text{n} \)-junction [55], most of the work on theoretical models of current density \( (J) \)/voltage \( (V) \) characteristics of \( \text{eta} \) cells have been based on the \( \text{pin} \)-junction structure of the cell, which assumes a three-layer structure of a p-type hole conductor, an intrinsic light absorber, and an n-type electron conductor [40,56]. Both papers are based on preliminary work by the same group [57], where the authors developed a full model for the J-V characteristics of a solar cell based on a \( \text{pin} \)-junction, and the work by Burgelman and Grasso. The modified \( \text{pin} \)-junction model as presented by Taretto \textit{et al.} in [57] and [40] gives a good physical/mathematical description of the ZnO nanowires/CdSe/CuSCN solar cell, as it considers enhanced tunneling recombination as well as light trapping in the cell, both of which have been shown to be relevant in the cell [30]. The model developed by Taretto \textit{et al.} is therefore the most complete theoretical model of an \( \text{eta} \)-cell to date.

Taretto’s model [40] is based on solving the continuity equations for the carrier concentrations \( (n(x) \) for electrons and \( p(x) \) for holes) in the intrinsic absorber layer. The equation for electrons is given as:

\[
G - \frac{n(x) - n_g(x)}{\tau} + D \frac{d^2 n(x)}{dx^2} + \mu F \frac{dn(x)}{dx} = 0
\]  

(2.1)

Where \( G \) is the photogeneration rate, \( \frac{n(x) - n_g(x)}{\tau} \) is the recombination rate (\( \tau \) is the carriers’ lifetimes), \( D \) is the diffusion coefficient, \( \mu \) is the charge mobility, and \( F \) is the electric field.

The following assumptions are made in the model:

(i) The electric field in the intrinsic absorber is not a function of position, and therefore depends only on the applied voltage and the absorber thickness \( (W) \):
\[ |F| = \left| \frac{V - V_{\text{bi}}}{W} \right| \]  \hspace{1cm} (2.2)

Where \( V \) is the applied voltage and \( V_{\text{bi}} \) is the built-in voltage.

(ii) The current density \( (j) \) satisfies the condition \( j < j_{\text{CR}} \), where \( j_{\text{CR}} \) is the critical current density defined as:

\[ j_{\text{CR}} = \frac{q \mu N_d F}{\exp \left( \frac{F W}{V_t} \right) - 1} \]  \hspace{1cm} (2.3)

Where \( q \) is the elementary charge, \( \mu \) is the carrier mobility, \( N_d \) is the doping density of the p- and n-layers, calculated as \( N_d = n_i \exp \left( V_{\text{bi}}/2V_t \right) \), where \( n_i \) is the intrinsic carrier concentration in the absorber, and \( V_t \) is the thermal voltage given as \( V_t = kT/q \), where \( k \) is Boltzmann’s constant, and \( T \) is the absolute temperature of the system.

(iii) The photogeneration rate \( (G) \) is spatially constant in the absorber. The mean generation rate is calculated using the following equation:

\[ \bar{G} = \frac{1}{NW} \int_{E_g}^{h\nu_{\text{max}}} \Phi_{\text{Sun}}(h\nu) A(h\nu) d(h\nu) \]  \hspace{1cm} (2.4)

Where \( N \) and \( W \) have been defined earlier, \( E_g \) is the absorber band gap, \( h\nu_{\text{max}} \) is the maximum solar flux energy, \( \Phi_{\text{Sun}} \) is the solar photon flux, and \( A \) is the wavelength dependent absorbance.

(iv) The carrier mobilities \( (\mu) \) and lifetimes \( (\tau) \) are equal for electrons and holes. Carrier lifetimes (recombination times) which occur via defect levels in the band gap are given by:

\[ \tau = \frac{\tau_0}{1 + \Gamma} \]  \hspace{1cm} (2.5)

Where \( \tau_0 \) is the nominal lifetime describing the carrier trapping properties of the defect level, related to the nominal diffusion length \( L_0 \) by \( L_0 = (D\tau_0)^{1/2} \), where \( D \) is
the diffusion coefficient of the charge carriers, and $\Gamma$ is the field-effect function, given by:

$$
\Gamma = \frac{\Delta E_{n,p}}{kT} \int_0^1 \exp \left( \frac{\Delta E_{n,p}}{kT} u - K_{n,p} u^{3/2} \right) du 
$$

(2.6)

Where $\Delta E_{n,p}$ is the energy difference between the defect level and either the valence or conduction band (for holes and electrons, respectively), and $K_{n,p}$ is given by the following equation:

$$
K_{n,p} = \frac{3}{4} \sqrt{\frac{2m_{\text{tun}} \Delta E_{n,p}^3}{q\hbar |F|}}
$$

(2.7)

Where $m_{\text{tun}}$ is the effective tunneling mass and $\hbar$ is the reduced Planck’s constant. Equations (2.6) and (2.7) were originally developed by Hurkx et al [52] for the modeling of trap-assisted tunneling in a pn-junction device.

Using these 4 assumptions, a model for $j(D, \tau, W, S, G, V_{b_i}, V)$ was developed by Taretto, where $S$ is the recombination velocity of minority carriers at the absorber interfaces and all other variables have been previously defined. Equation (2.1) can be nondimensionalized to the following form:

$$
G_s + \exp(-V_{s0} x_s) - n_s(x_s) + L_s^2 V_s \frac{dn_s}{dx_s} + L_s^2 \frac{d^2 n_s}{dx_s^2} = 0
$$

(2.8)

Which can be solved analytically to produce the following expression:

$$
n_s(x_s) = G_s + n_{p0} \exp(-V_{s0} x_s) + C_1 \exp(\lambda_1 x_s) + C_2 \exp(\lambda_2 x_s)
$$

(2.9)

Where $G_s$ is the scaled photogeneration rate given by $G_s = \frac{G_s}{n_{p0}}$, $n_{p0}$ is the thermal equilibrium electron concentration in the p-type layer, $V_{s0} = \frac{-V_{b_i}}{V_t}$ and $V_s$ is the scaled potential drop related as $V_s = \frac{V - V_{b_i}}{V_t}$, $x_s$ is the scaled distance given by $x_s = \frac{x}{W}$, $n_s$ is the
scaled electron concentration given by \( n_s = \frac{n}{n_{p0}} \), \( L_s \) is the scaled diffusion length given by \( L_s = \frac{L}{W} \), \( n^0_s \) is given by \( n^0_s = \frac{1}{1 + (V_{zh}^2 - V_{zh})L_s^2 V_{zh}} \), the eigenvalues \( \lambda_1 \) and \( \lambda_2 \) are related as 
\[
\lambda_{1,2} = \pm \sqrt{\left(\frac{W}{L_0}\right)^2 + \left(\frac{V - V_{zh}}{2V_t}\right)^2 - \frac{V - V_{zh}}{2V_t}},
\]
and \( C_1 \) and \( C_2 \) are constants determined by the boundary conditions.

The first nondimensionalized boundary condition for the charge transport in the \textit{pin}-junction is as follows:

\[
S_s(n_s(0) - 1) = V_s n_s(0) + \left. \frac{dn_s}{dx_s}\right|_{x_s=0} \tag{2.10}
\]
Equation (10) equates the scaled surface recombination current generated by the scaled surface recombination velocity \( S_s = \frac{S_W}{D} \) with the scaled drift and diffusion currents at \( x_s=0 \). The second nondimensionalized boundary condition required to solve the second order ordinary differential equation uses assumption (iv) to estimate a point-symmetric profile for the charge carriers around the center line of the intrinsic absorber (at \( x=W/2 \), or \( x_i=1/2 \)). The second boundary condition is expressed in the following form:

\[
n_s \left(\frac{1}{2}\right) = \left(\frac{n_s}{n_{p0}}\right) \exp \left(\frac{V}{2V_t}\right) \tag{2.11}
\]
Solving for the constants \( C_1 \) and \( C_2 \) by using equations (2.10) and (2.11) yields the following expressions:

\[
C_1 = \frac{-\exp(-\lambda_{2}/2)}{A_s} \left[A_1(\lambda_2 + S_s) + A_2 \exp\left(\frac{\lambda_2}{2}\right)\right] \tag{2.12}
\]
and

\[
C_2 = \frac{\exp(-\lambda_{2}/2)}{A_1} \left[A_1(\lambda_1 + S_s) + A_2 \exp\left(\frac{\lambda_1}{2}\right)\right] \tag{2.13}
\]
where
\[
A_1 = n_s \left(\frac{1}{2}\right) - G_s - n_{s0} \exp(-V_{s0}/2),
\]
\[
A_2 = n_{s0}(S_s - V_s + V_{s0}) - S_s + G_s(S_s - V_s),
\]
and
The equation for the scaled current density, which is an integration of the generation-recombination term from $x_s=0$ to $x_s=1/2$ multiplied by two to account for both electrons and hole currents, and added to the surface recombination can now be solved. The nondimensionalized current equation is

$$I_s = 2S_s (n_s(0) - 1) + 2 \int_0^{1/2} n_s(x_s) \exp \left( \frac{-V_{gs} x_s}{L_g} \right) d(x_s)$$  \hspace{1cm} (2.14)

Equation (2.9) for $n_s(x_s)$ can now be incorporated in equation (2.14), which is subsequently integrated to give a complete expression for the scaled current density $J_s$

$$J_s = 2S_s (C_1 + C_2 + G_s + n_s^2 - 1) + \frac{1}{2} \left[ \frac{C_1 \exp \left( \frac{A_s}{2} \right)}{\frac{A_s}{2}} - 1 - \frac{C_2 \exp \left( \frac{A_s}{2} \right)}{\frac{A_s}{2}} - \frac{(n_s^2 - 1)(1 - \exp \left( -\frac{V_{gs}}{L_g} \right))}{\frac{L_g}{2}} \right]$$ \hspace{1cm} (2.15)

The current density can then be determined from the scaled current density through the following equation:

$$j = \frac{a \eta p \rho D}{w} J_s$$ \hspace{1cm} (2.16)

Equation (2.16), when combined with equation (2.15) gives a full theoretical description of the current in the $pin$-junction $eta$-cell. The different assumptions can be invoked to calculate specific terms in the current density equation, which can help develop hypothetical limits for the cell, such as minimum absorber thickness.

An important aspect of the model as presented is that different conditions can be imposed. The scattering of light in the material (which would lead to increased absorption) can be modeled simply by modifying the expression for the absorbance $A(h\nu)$ in equation (2.4). Taretto et al. explore two models for the absorbance and show their effect on the current density equation and the maximum absorber thickness. The first
model for absorbance considers a cell with no light-trapping with a non-reflecting front contact and a perfectly reflecting back contact. The absorbance is given by Beer’s law as

\[ A_{BL}(h\nu) = 1 - \exp \left[ -2\alpha(h\nu)NW \right] \]  

(2.17)

Where \( \alpha(h\nu) \) is the absorption coefficient of the absorber as a function of photon energy, which can be expressed in many ways, \( N \) is the number of nanojunctions, and \( W \) is the local width. The second absorbance model studied by Taretto et al. assumes light-trapping in the cell, which results in the following equation for absorbance:

\[ A_{LT}(h\nu) = \frac{1 - \exp \left[ -4\alpha(h\nu)NW \right]}{1 - (1 - n^{-2})\exp \left[ -4\alpha(h\nu)NW \right]} \]  

(2.18)

Where \( n \) is the refractive index of the absorber material.

For photon energies not much higher than the absorber band gap \( E_g \), and direct band gap materials, the absorption coefficient can be related as

\[ \alpha(h\nu) = \alpha_0 \left( \frac{h\nu - E_g}{kT} \right)^{1/2} \]  

(2.19)

Where \( \alpha_0 \) is the characteristic absorption coefficient defined as \( \alpha_0 = \alpha(h\nu = E_g + kT) \).

Equation (2.19) is not valid for light in the visible spectrum; however, it is useful for modeling purposes and helps in the illustration of important concepts. The model for absorbance given in equation (2.17) or (2.18), when used with equation (2.19) or any other suitable equation for the absorption coefficient, can be used in the current density/voltage model to predict important parameters in the eta-solar cell, such as the overall cell efficiency, \( \eta \):

\[ \eta = \frac{V_{mpp}/J_{mpp}}{P_{Sun}} \]  

(2.20)

Where \( V_{mpp} \) is the voltage at the maximum power point, \( J_{mpp} \) is the current density at the maximum power point, and \( P_{Sun} \) is the power density of the sun’s radiation (a standard value for \( P_{Sun} \) is 0.1 W/cm\(^2\)).
2.3 Thin Film Deposition Techniques

The concept and physical principles of the *eta*-cell allow for the use of low-quality and inexpensive semiconducting materials. The importance of nanoscale structure of all layers in the cell results in a need for highly sensitive and skilful synthesis methods. In general, the n-type material is deposited first, a convention that leads to the dominance of the n-type structure geometry in the cell; however, theoretically, the p-type semiconductor could be synthesized first [43].

Many different deposition techniques have been developed for the various layers in the *eta*-cell, with varying complexities and varying qualities of film formation. In this section I will present a few of those techniques, focusing mainly on the techniques pertinent to this work.

2.3.1 Chemical Bath Deposition (CBD)

Chemical bath deposition (CBD) has been used as synthesis method for over 130 years [43], and in the recent two decades has been widely applied successfully, reproducibly, and at a low cost, to the synthesis of thin-films and other morphologies for PV cells [58]. Many different types of chalcogenide (CdS, CdSe, ZnS, PbS), chalcopyrite (CuInS₂, CuInSe₂), and oxide (ZnO, TiO₂) materials have been successfully deposited by CBD [43, 59, 60]. The deposition process in CBD uses a controlled (generally temperature activated) chemical reaction or reactions which result in the deposition of a thin-film by precipitation.

In a typical procedure, a soluble salt of the desired metal which serves as the cations source is dissolved in an aqueous solution. The nonmetallic part of the desired
semiconductor is provided by a suitable source compound which decomposes in the presence of hydroxide ions to produce the anions; an example of this is hexamethylenetetramine (HMT), which has been used as a source of hydroxide ions in ZnO deposition [61]. The anions and cations react in solution to form precipitate in the bulk (homogeneously) or on an exposed surface (heterogeneously). Often times complexing agents are used to form metal complexes which limit the hydrolysis rates, and by that give some stability to a system that would otherwise rapidly hydrolyze. The homogeneity and stoichiometry of the deposited semiconductor usually depends on the solubility product ($K_{sp}$) of the material in the solution.

In this work, CBD was mainly used to deposit zinc oxide (ZnO) nanowire arrays on a ZnO seed film. The exact deposition technique, including the seeding step, is described in Section 3.1.3. Terminal nanowire length for one cycle of growth (“batch”) is around 1 µm, however, longer wires can be deposited by running multiple cycles. CBD is useful as it is simple and does not require large amounts of energy (it is usually performed at temperatures lower than 100°C). The technique does, however, have two important disadvantages: (1) homogeneous (bulk) precipitation in solution depletes the ion source and limits the yield of the method. Low terminal nanowire length or film thickness is a direct result of this disadvantage. (2) Bulk precipitation can clog the pores in the material and lead the voids in the nanostructure [43]. Recent work on those limiting drawbacks of the CBD method has led to the development of microreactors that minimize bulk-precipitation, resulting in efficient deposition of longer nanowires or thicker films [62].
2.3.2 Successive Ion-Layer Adsorption and Reaction (SILAR)

The successive Ion-Layer Adsorption and Reaction (SILAR) deposition method, sometimes called the sequential CBD method, was invented in 1985 by Yann F. Nicolau [63]. The method has been used to deposit sulfides (ZnS [64], CdS [64], Cu₆S [65], NiS [66], etc), iodides (CuI [67], etc), thiocyanates (CuSCN [67,68], etc), selenides (CdSe [69], ZnSe [70], etc), and many other metal chalcogenides [70].

The SILAR technique consists of the sequential immersion of a substrate in two separate ionic solutions; the first solution contains a cationic, usually metallic salt (Cd⁺², Zn⁺², or Cu⁺²), while the second solution contains an anion compound (such as S⁻², Se⁻², I⁻, or SCN⁻). Usually, a rinse step in de-ionized water is added between each immersion in the ionic solutions to remove any excess ions and limit the deposition rate to one layer per immersion. A schematic of a general SILAR method is given below:

![Figure 2.5: SILAR method for thin film deposition. (a) Cationic precursor (white circles represent metal cations), (b) 1st rinse, (c) anionic precursor (black circles represent anions), and (d) 2nd rinse. [70].](image-url)
The scheme described in Figure 2.5 represents one cycle (in this case the first cycle) of deposition which results in one layer of the thin film. To achieve a required film thickness, the process is repeated typically between 5-20 cycles [43], although as many cycles as needed can be repeated. The paper by Pathan and Lokhande from 2003 [70] gives a good overview of SILAR deposition and a wide range of the different semiconductors that have been successfully deposited using the method. The SILAR method has been mainly applied to the deposition of the absorber and the p-type material.

2.3.3 Electrochemical deposition (ECD)

Electrochemical deposition has been used to deposit all the different components of the eta-solar cell. ZnO as an n-type material [71,72]; CdTe [73], ZnTe [74], and CdSe [75] as absorbers; and CuSCN [76,77] as a p-type material have all been successfully electrodeposited. In electrochemical deposition, a conducting substrate must be used as an electrode in an electrochemical cell. The deposition occurs by the reduction or oxidation of dissolved species, depending on the desired film composition [43]. The general electrodeposition reaction that takes place is of the type:

$$M^{+n} + X + n\bar{e} = MX$$

(2.21)

Where M is a metal atom, X is an oxidizing agent, ē is an electron and n is the formal charge of the metal ion. Equation (21) may need to be modified to fit the stoichiometry of a particular reaction (for example, when ZnO is electrodeposited the reaction is Zn$^{+2}$ +0.5O$_2$+2$\bar{e}$=ZnO [43]). The successful deposition of each material is highly dependent on precursor concentration, solution temperature and pH, the applied electrochemical cell potential and current density. ECD parameters must be optimized for each material.
individually as they affect both the morphology and thickness (or length) of the final film (or nanowires).

### 2.3.4 Solution Casting: Deposition of CuSCN

The method of solution casting was developed particularly for the deposition of copper thiocyanate (CuSCN) on porous materials [36, 78,79]. The deposition process is based on a solution of CuSCN powder dissolved in n-propylsulfide ((CH₃CH₂CH₂)₂S). CuSCN dissolves slowly in n-propylsulfide, and the initial mixture must be stirred for a long time for all of the CuSCN to dissolve. Deposition is done in a drop-coat manner on a preheated substrate (the commonly used temperature is ~80°C). The deposition solution is allowed to flow slowly from a pipette while the pipette is moved in a rectangular pattern over the substrate, creating a uniform thickness layer [43]. The organic solvent then evaporates due to the high temperature, completing one coating cycle. Generally, several cycles are needed to completely coat a TiO₂ film or ZnO nanowires. Tena-Zaera et al. used the solution casting method as described by O’Regan and Lenzmann to deposit CuSCN on CdSe-coated ZnO nanowires [30].

### 2.3.4 Other Deposition Techniques

In addition to CBD, SILAR, and ECD, many other deposition techniques have been developed. These other techniques include the sol-gel method [80,81], spray pyrolysis [82, 83], ion-layer gas reaction (ILGAR) [84,85], and gas-phase atomic layer deposition [86]. All of the above mentioned techniques have been used, with varying
degrees of success, to deposit semiconductors as thin films and in other morphologies for use in solar cells.

2.4 The ZnO nanowires/CdSe/CuSCN Structure

The structure explored in this work is made of three inorganic semiconductors: (1) zinc oxide, (2) cadmium selenide, and (3) copper thiocyanate. These three materials were chosen based on their optoelectronic properties, which are described in the following sections. The complete heterostructure itself has been shown to be a viable configuration for an extremely thin absorber solar cell by Tena-Zaera et al [45,30].

The photovoltaic device structure is similar to that of a DSSC (see Section 1.2.3.1, Figure 1.6), with ZnO nanowires taking the place of TiO$_2$ nanoparticles, CdSe taking the place of the dye absorber, and CuSCN taking the place of the iodide/triiodide electrolyte. The estimated band diagram of the complete *eta*-cell structure is presented in Figure 2.6.

![Figure 2.6: The band diagram of ZnO/CdSe/CuSCN. VB, CB, e, and p represent the valence band, conduction band, electron, and hole, respectively [30].](image)
2.4.1 Zinc Oxide (ZnO)

The n-type semiconductor used in this work is zinc oxide (ZnO). Zinc oxide is a II-VI binary oxide semiconductor, naturally occurring as zincite, a rare mineral with the hexagonal wurtzite crystal structure [87], which is also the most common crystallographic phase of synthetically grown zinc oxide. The general structure of a wurtzite crystal, as well as the common growth configuration of zinc oxide, are given in Figure 2.7 below.

![Figure 2.7: (a) The general wurtzite structure, consisting of two interpenetrating hcp structures (black and white circles). (b) The high surface energy plane, the (002) plane, leads to favorable crystal growth in the [0001] direction (along the c-axis) in the ZnO wurtzite structure [88].](image)

The ZnO hexagonal unit cell has the parameters \( a=0.325 \) nm and \( c=0.52066 \) nm, with two molecules in the unit cell [87]. Zinc oxide is a wide direct band gap with a reported band gap \( E_g=3.2-3.4 \) eV [87,89], depending on temperature. The wide band gap corresponds to a light transparency for wavelengths >360nm, ideal for solar cells where the absorption of light is designed to take place in the absorber material and not in the
electron conductor. Compared to pure silicon, zinc oxide can be synthesized inexpensively at high purities and low temperatures (below 100°C) and is generally an environmentally friendly material [43]. Another benefit of ZnO is that it can be synthesized with different morphologies, from flat films to nanowire arrays, depending on the growth conditions.

As an n-type material, zinc oxide’s electrical properties are of great importance. Since this work is focused mainly on the application of ZnO nanowires in the eta-solar cell, the electrical properties of the nanowire morphology is considered here, as opposed to the bulk single crystal or polycrystalline properties. The electron mobility in ZnO nanowires has been reported as 23 cm$^2$/Vs at room temperature [71], much higher than another popular n-type semiconductor, mesoporous TiO$_2$, which has electron mobility on the order of 10$^{-2}$ cm$^2$/Vs at room temperature [90]. The high electron mobility makes ZnO nanowires a promising candidate for the electron conducting material in extremely thin absorber solar cells. The prospect is limited by the lower roughness (surface enlargement) factor nanowire arrays generally have, as compared to mesoporous films: a large contact surface area between the absorber material and the n-type material is required in a DSSC or eta-cell in order to have a high light harvesting efficiency. This can be potentially mitigated by careful engineering of the nanowire arrays to have higher surface areas.

2.4.2 Cadmium Selenide (CdSe)

Cadmium selenide (CdSe) was chosen as the absorber material, and much of this thesis is focused on the deposition of CdSe on ZnO nanowires via the SILAR method. The wurtzite structure configuration of CdSe is a II-VI binary semiconductor composed
of the Cd$^{+2}$ and Se$^{-2}$ ions. Cadmium selenide has been studied extensively as a candidate material for use in a wide variety of solar cells [91, 92, 93, 94].

The most important properties absorbers in eta-cells must have are the ability to absorb light in the visible range (1.1 eV<$E_g$<1.8 eV, with optimal $E_g$~1.5 eV), and the ability to transfer electrons and holes to wide band-gap semiconductors [43]. Both of these requirements have been shown to be fulfilled by CdSe in a study conducted by Liu and Kamat [95]. Cadmium selenide has a measured optical band gap ($E_g$) of ~1.7 eV at 300K [96], placing it in the ideal range for extremely thin optical absorbers. The electron and hole mobilities in nanocrystalline CdSe have been shown to depend on nanoparticle size [97]. By applying the correlation developed by Beard et al., the electron and hole mobilities in a CdSe particle 10 nm in diameter are predicted to be around 200 cm$^2$/Vs and 60 cm$^2$/Vs, respectively. These values indicate good charge transport in nanocrystalline CdSe, and reveal that charge transport in the absorber layer does not limit cell performance.

Cadmium telluride (CdTe) has a measured optical band gap of ~1.4 at 300K [96] which is closer to the optimal absorber band gap for the eta-cell applications. Recent work on the ZnO/CdTe/CuSCN heterostructure has shown that the structure produces poor photocurrent [45], however, a more concentrated research effort may improve the performance of that specific structure.

2.4.3 Copper Thiocyanate (CuSCN)

The p-type semiconductor chosen to complete the eta solar cell heterostructure in this work is copper (I) thiocyanate (CuSCN), a pseudohalide cuprous semiconductor
composed of the Cu$^+$ and SCN$^-$ ions. Copper thiocyanate can be synthesized in two polymorphic crystal structures: (1) $\alpha$-CuSCN, which is an orthorhombic crystal, and (2) $\beta$-CuSCN, which contains closely packed networks of cylindrical CuSCN units in trigonal pyramid configuration with adjacent layers bonded by Cu-S bonds [98,99].

CuSCN is a p-type semiconductor (i.e. a hole conductor) with a wide band gap of $\sim$3.6 eV [100,101], making it transparent to visible light. The optoelectrical band locations of CuSCN, as well as the availability of the method for its deposition, make it an ideal void filling hole-conductor in solid-state solar cells, and therefore the material of choice in many eta cell applications [102, 37,36,30], as well as in dye-based photovoltaic devices [103, 78,104]. The positive charge (hole) mobility in CuSCN has been reported to be around 10-20 cm$^2$/Vs [105].

2.5 Novel Research in this Thesis

The focus in this thesis is the application of the SILAR method (described in Section 2.3.2) to the conformal deposition of CdSe on ZnO nanowire arrays for the purpose of eta solar cell fabrication. Kale et al. have grown and characterized CdSe films deposited on glass by SILAR [69], and Tena-Zaera et al. have deposited CdSe on ZnO nanowire arrays by electrodeposition for applications in an eta solar cell [30,42], however, the SILAR method has not been used explicitly for CdSe deposition on ZnO nanowires. The effects of the deposition conditions, as well as post-deposition treatment (such as substrate annealing), on the resulting ZnO nanowire/CdSe structure are investigated here.
A proof-of-concept that the SILAR method can be used instead of ECD for the deposition of CdSe in the fabrication of the ZnO NW/CdSe/CuSCN 
eta solar cell is presented here, and a semi-solid state cell is constructed from the ZnO NW/CdSe heterojunction and characterized. The following chapters present the experimental methods employed, followed by the results, discussion, and conclusions of this investigation.
CHAPTER 3: EXPERIMENTAL AND CHARACTERIZATION METHODS

3.1 General Description of Experimental Methods

Fluorine-doped tin oxide (F:SnO$_2$) coated transparent glass was used as the substrate for zinc oxide (ZnO) seeding, growth of zinc oxide nanowires (ZnO NW), and cadmium selenide (CdSe) deposition. Semi-solid state solar cells (ZnO NW as the electron conductor n-type material, CdSe as the solid semiconducting absorber and I$^+$/I$^-^3$ liquid electrolyte as the hole conductor) were constructed.

3.1.1 Substrate Cleaning

F:SnO$_2$ (FTO) coated transparent glass (25-40mm x 20mm x 2.5mm TEC15, Hartford Glass Co., Inc.) was used. The substrates were blown with nitrogen prior to cleaning to remove packaging dust. The conductive side of the glass was identified (using an OMEGA HHM29 multimeter) and marked. Each individual substrate was then placed in a cleaning solution (1/3 acetone, 1/3 isopropanol, 1/3 deionized water) and ultrasonicated (CREST Ultrasonics Tru-Sweep Ultrasonic Cleaner) for ~15 minutes at 60°C. The substrates were then rinsed with water and blown dry with nitrogen.

3.1.2 Substrate Seeding

Substrates were seeded with zinc oxide films by zinc acetate (ZnAc) solutions using two primary methods: (1) the drop coating method, and (2) the dip coating method.
3.1.2.1 Seeding by the Drop Coating Method

The drop coating method is based on the procedure described by Greene *et al.* in the paper “General Route to Vertical ZnO Nanowire Arrays Using Textured ZnO Seeds” [106]. In a typical procedure, the conductive side of the substrates was coated with 100 µL of 0.005M zinc acetate (Aldrich, 99.99% metals basis) in ethanol solution. After 25 s, the seeding solution was rinsed with ethanol and allowed to dry in air for 2.5 min. This coating step was repeated 5 times for each substrate. The substrates, which were now covered with zinc acetate crystallites, were placed on a hotplate (Fisher Scientific Isotemp) and heated in air at 350°C for 20 minutes, yielding layers of ZnO nanocrystals with their (0001) planes parallel to the substrate surface [106].

3.1.2.2 Seeding by the Dip Coating Method

The dip coating method is based on a procedure developed by Ohyama, *et al.* [107] and the investigation by Sagar, *et al.* [108] on the influence of pH on the quality of ZnO films. The exact method was developed by Kevin McPeak and Jason Baxter [62]. In a typical procedure, clean FTO substrates were dipped by a mechanical dipper at a rate of 120 mm/min into an ethanol solution containing 0.375M zinc acetate (Aldrich, 99.99% metals basis) and 0.375M monoethanolamine (J.T. Baker, 99.6%). The withdrawal rate used was 56 mm/min. After one such dip, substrates were placed on a hotplate (Fisher Scientific Isotemp) and annealed at 450°C for 20 minutes, yielding ZnO seeded substrates.
3.1.3 Zinc Oxide Nanowire Array Growth

The general procedures for zinc oxide nanowire growth by hydrothermal aqueous solution have been described and studied by several groups [109, 110, 111]. In this thesis, procedure for one growth cycle of ZnO nanowire arrays was as follows: (1) ZnO-seeded substrates were placed with seeded side angled down in 30 mL vials containing 0.025M zinc nitrate hexahydrate (Fluka, >99.0%) and 0.025M hexamethylenetetramine (SigmaUltra) in water, (2) the vials were placed in an oven (Fisher Scientific Isotemp Oven) at 90°C for 4 hours, (3) each substrate was rinsed with deionized water and blown dry with nitrogen, and finally (4) the back (non-conductive) side of each substrate was wiped with 5% nitric acid solution in water, dried, and then wiped with deionized water and dried again in order to remove settled precipitate.

In general, each growth cycle corresponds to ~1µm in length of nanowires. In this work, substrates with one and two growth cycles were tested to determine the effect nanowire length have on CdSe deposition.

3.1.4 Zinc Oxide Nanowire Array Pretreatment

Some substrates with ZnO NW were annealed prior to CdSe deposition to test the effect of pre-annealing on CdSe adhesion to the ZnO nanowire arrays. The substrates were annealed on the hotplate (Fisher Scientific Isotemp) in air at 450°C for 30 minutes and were cooled by natural convection on the hotplate.

Some substrates were treated for 10 minutes immediately before CdSe deposition in an O₂ plasma cleaner (Harrick Plasma, PDC-001). This procedure has been shown to enhance the short circuit current (J_SC) in ZnO NW/CdSe quantum dots solar cells [112].
3.1.5 Cadmium Selenide Deposition

Cadmium selenide was deposited by the SILAR method (see Section 2.3.2) from solutions of sodium selenosulfate (Na$_2$SeSO$_3$) and cadmium acetate (CdAc+TA+TEA) following the general method described by Kale et al. [69].

3.1.5.1 Solution Preparation

**Sodium selenosulfate (Na$_2$SeSO$_3$):** 50.0 g of sodium sulfite (Sigma-Aldrich, 98%) were dissolved in 250 mL of deionized water until the solution became clear. 2.50 g of elemental Se (Aldrich, 100 mesh, 99.5%) were added to the solution and the resulting mixture was stirred on a hotplate (IKA Werke or Fisher Scientific Isotemp) at 60°C and 1100 rpm for 6.5 hours. The resulting sodium selenosulfate solution is supersaturated with selenium and is left to cool and settle overnight. The solution was filtered the following day with a vacuum pump filtration apparatus (coarse filter paper) so that a clear, yellowish solution was obtained.

**Cadmium acetate (CdAc+TA+TEA):** 13.33 g of cadmium acetate dihydrate (Sigma-Aldrich, 98% reagent grade) were dissolved in 250 mL of deionized water until the solution becomes clear. The solution is then stirred and monitored with a pH probe (Thermo Orion 4 Star) until the end of the preparation. 1M tartaric acid (ACROS Organics, 99.5%) in water (TA) is added to the CdAc solution until it reaches a pH of ~5. Next, triethanolamine (TEA, Sigma-Aldrich, 98% reagent grade) is added to the CdAc+TA solution until it reaches a pH of ~8. The solution is then stirred for another minute, and then capped.
3.1.5.2 Robot-Assisted SILAR Deposition

The deposition was carried out using a StratoSequence VI robot and the corresponding StratoSmart operating software (nanoStrata, Inc.). One cycle of CdSe deposition consisted of the following: (1) the substrate was dipped in the CdAc+TA+TEA solution for 50 s, (2) transferred to a rinse beaker with deionized water for 25 s, then (3) the substrate was dipped in the Na$_2$SeSO$_3$ solution for 20 s, and finally (4) transferred to a second rinse beaker with deionized water for 25 s. Each cycle theoretically deposits one layer of the CdSe semiconductor on the contacting surface.

In a typical procedure, 150 mL beakers were used to hold the deposition solutions and rinse water. Since the robot stage holds up to 8 beakers, two deposition cycles were completed for every full robot cycle. The number of deposition cycles was varied from 75-300 and the number of times the deposition solutions and rinse water were changed in the middle of the run (due to contamination) was also varied.

3.1.6 Cadmium Selenide Annealing

Some substrates were annealed after the CdSe deposition to test the effect of annealing on CdSe adhesion and crystallographic orientation, as well as the resulting light harvesting efficiency of the CdSe layer. The substrates were annealed in air on a hotplate (Fisher Scientific Isotemp) at 350°C or 450°C for one hour and were cooled by natural convection on the hotplate.
3.1.7 Solar Cell Preparation

**Cell Construction:** Semi-solid state solar cells were constructed by clipping together an FTO/ZnO Seeds/ZnO NW/CdSe substrate with a Pt counter-electrode so that the CdSe layer is facing the platinum layer. The gap between the resulting two-substrate structure was infused with liquid iodide/triiodide electrolyte (SOLARONIX SA Iodolyte TG-50) so that both the CdSe layer and the Pt layer were in contact with the electrolyte, completing the solar cell.

The use of liquid electrolyte to prove the working principle of an otherwise solid-state solar cell was shown to be viable by Leschkies, *et al.* [112] in a similar cell consisting ZnO nanowires and CdSe quantum dots.

**Pt counter-electrode:** the solar cell counter electrode was prepared by dipping a clean FTO substrate in 0.005M chloroplatinic acid (Aldrich, 99.9%) in isopropanol at a rate of 120 mm/min. The withdrawal rate was 300 mm/min, and the dipped substrate was annealed in air at 350°C for 30 minutes. The result is a Pt-covered FTO substrate which serves as the counter electrode in the solar cell.

3.2 General Description of Characterization Methods

The FTO/ZnO Seeds/ZnO NW/CdSe substrates were characterized using UV-Vis absorption/transmittance, X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS). The solar cells were characterized using I-V curves and incident-photon-to-electron-conversion efficiency (IPCE) spectral response.
3.2.1 UV-Vis

Scans of the ZnO NW/CdSe structures in the UV-Vis energy range (380nm-700nm) were used to determine the Absorbance (A) and Transmittance (T), as well as the light harvesting efficiency of the deposited CdSe. For a typical scan, a 1/8 m Monochromator (Oriel Cornerstone 130) was used with a 30mm integrating sphere (Mikropack) and an OceanOptics spectrophotometer (USB4000). CdSe absorption was evaluated by measuring CdSe-coated ZnO NW arrays with ZnO NW arrays as references. The light harvesting efficiency (LHE) of the cell is determined by the following relationship:

\[ LHE = (1 - 10^{-4}) \times 100\% \]  

(3.1)

3.2.2 X-ray Diffraction

X-ray diffraction (XRD, Siemens model D500) with CuKα radiation (40kV, 30 mA) was used to determine the crystallographic orientation of the deposited CdSe as well as to provide another material identification source (i.e. verify that CdSe has indeed been deposited on the substrates). A typical 2θ scan was between 20°-60°, where the peaks for the (111), (220), and (311) CdSe planes (cubic crystal) are expected at ~25.5°, ~42°, and ~49.5°, respectively [30, 69]. Scan parameters included a 0.03° step size and a 1.0 s dwell time.

3.2.3 Scanning Electron Microscopy

The CdSe-coated nanowires were imaged using scanning electron microscopy (SEM, Zeiss model Supra 50VP). SEM was used to investigate the degree of uniformity
of the deposited CdSe films, the effect of CdSe annealing on the grain structure of the deposited films, and the general morphology of the coated nanowires. For some samples, the SEM images were also analyzed to estimate the thickness of the deposited CdSe film by comparing diameters of coated and uncoated nanowires.

### 3.2.4 Energy Dispersive Spectroscopy

Energy dispersive spectroscopy (EDS, Oxford Instruments INCAx-Sight) was used in conjunction with SEM to identify the presence of Cadmium and Selenium atoms on the zinc oxide nanowire arrays. A typical scan was 300s at 15kV on a selected section of the substrate (top down view) usually at 30,000x magnification.

### 3.2.5 Transmission Electron Microscopy

The CdSe-coated ZnO NW substrates were characterized by Transmission Electron Microscopy (TEM, Tecnai F30, Sandia National Laboratories). Both transmission images and diffraction patterns of the coated nanowires were taken. The thickness of the deposited CdSe layer was estimated based on the high magnification TEM images, while the d-spacing for the different materials (ZnO, CdSe) could be determined based on the TEM diffraction patterns.

### 3.2.6 I-V Curves

The overall conversion efficiency of the solar cells constructed by the methods described in Section 3.1.7 was determined based on I-V curves generated with the
OceanOptics spectrophotometer (USB4000). Variable bias was applied to the cells by a potentiostat (Gamry Instruments, Reference 600) and the resulting current was measured and plotted. An illumination of white light at 0.1 W/cm² and 1.5 AM (air mass), usually known as “1 sun”, was used on the substrates. A typical I-V curve for a solar cell is given in Figure 3.1, with the important cell parameters highlighted.

![I-V curve with cell parameters highlighted](image)

Figure 3.1: Typical dark and illuminated I-V curves of a solar cell. The short-circuit current (I\textsubscript{SC}), open-current voltage (V\textsubscript{OC}), shunt resistance (R\textsubscript{sh}), series resistance (R\textsubscript{s}), and maximum power (P\textsubscript{max}) are shown [113].

The overall cell efficiency (\(\eta\)) is:

\[ \eta = \frac{P_{\text{max}}}{P_{\text{light}}} \]  \hspace{1cm} (2.20)

The cell’s fill factor, which measures the actual maximum power compared to the hypothetical maximum power for a given I\textsubscript{SC} and V\textsubscript{OC}, is given by:

\[ FF = \frac{P_{\text{max}}}{I_{\text{SC}} \times V_{\text{OC}}} \]  \hspace{1cm} (3.2)
3.2.7 Incident Photon-to-electron Conversion Efficiency

The incident-photon-to-electron conversion efficiency (IPCE) at different wavelengths, which compares the number of incident photons to the number of electrons produced, is calculated by generating chronoamperometric curves for the tested cells (current vs. time) while varying the incident photon wavelengths. The cells’ IPCE at different wavelengths were calculated based on the following relationship:

\[
IPCE = \frac{(I_{\text{light}} - I_{\text{dark}}) \times 1240^{\text{nm}/\text{eV}}}{\lambda \times P_{\text{light}}}
\]  

(3.3)

Where \(I_{\text{light}}\) and \(I_{\text{dark}}\) are the currents generated by the cell under illumination and under dark conditions at a specific wavelength, respectively, \(\lambda\) is the photon wavelength, and \(P_{\text{light}}\) is the power of incident light. For a typical IPCE scan, wavelengths in increments of 20nm between 300nm and 700nm, with a 10 s pause time between intervals, were used. A monochromator (Oriel 130 1/8 m) was used to generate the different wavelengths, while the potentiostat (Gamry Instruments, Reference 600) was used to measure the output current at each wavelength. Finally, the cell’s internal quantum efficiency (IQE), a measure of the absorbed photons which are converted to electric current is calculated by the following relationship:

\[
IQE = \frac{IPCE}{LHE} = \varphi_{\text{inj}} \times \varphi_{\text{sep}}
\]  

(3.4)

where \(\varphi_{\text{inj}}\) and \(\varphi_{\text{sep}}\) are the cell’s injection efficiency and charge separation efficiency, respectively (which are not calculated directly.)
CHAPTER 4: RESULTS AND DISCUSSION

The extremely thin absorber (eta) solar cells reported in this thesis utilized an array of ZnO nanowires which are coated by CdSe using the SILAR method, with a liquid electrolyte as the hole-conducting material. In the cell, visible light is absorbed by the CdSe layer, and photons with \( h\nu \geq E_g \) are able to excite electrons into the absorber’s conduction band. The excited electrons can then be injected into the electron-conductor (ZnO NW), and can contribute to the generated photocurrent. In Section 4.1, I will present and discuss the results of the materials characterization of the CdSe-coated ZnO NW structure. In Section 4.2, I will present and discuss the results of the characterization of solar cells fabricated from the CdSe-coated ZnO NW.

4.1 Materials Characterization

The standard sample used as-grown CdSe deposited using 150 SILAR cycles (see Section 3.1.5.2) on ZnO nanowires. The nanowires were grown using 2 growth cycles (see Section 3.1.3) from seeds deposited by the dip-coating method (see Section 3.1.2.2) on FTO glass. During SILAR deposition, the deposition solutions remained clear for \( \sim 75 \) cycles. After \( \sim 60 \) deposition cycles, white precipitate began to appear toward the top of the CdAc deposition solution beaker, presumably due to cross-contamination from the beaker containing the anion. No observable color change took place in the \( \text{Na}_2\text{SeSO}_3 \) solution after 75 cycles. In order to avoid precipitation in solution which may cause large crystals to deposit on top of the ZnO NW, the deposition solutions and rinses were changed after 75 cycles. After SILAR deposition, the dipped area of the substrate showed
a color change from white (ZnO) to red/yellow, detectible by the naked eye. Figure 4.1 shows digital images comparing the bare nanowires with the CdSe@ZnO (CdSe-coated ZnO nanowires) standard sample, indicating a significant color change. The UV-Visible absorption spectrum for the CdSe@ZnO sample is given in Figure 4.2. The absorption spectrum is taken relative to bare ZnO nanowires and therefore represents the absorption of only the CdSe coating. The standard CdSe@ZnO sample shows absorbance onset at ~700 nm, with increasing absorbance of about 40% between 400 and 550 nm. This is expected from CdSe, which has a band gap of ~1.7 eV (or ~700 nm) The shape of the transmittance vs. wavelength curve is similar to that reported by Kale, et al. [69] for CdSe transmittance, as well as that reported by Tena-Zaera, et al. [30], suggesting the presence of CdSe.

![Figure 4.1: digital images of (a) bare ZnO NW grown by two growth cycles, and (b) the standard CdSe@ZnO sample](image)
Figure 4.2: Absorbance and transmittance as a function of incident light wavelength for the standard CdSe@ZnO sample with bare ZnO NW of similar length as a reference.

The standard CdSe@ZnO sample was characterized by SEM, showing that a CdSe layer has indeed coated the ZnO nanowires conformally and uniformly. Micrographs of bare ZnO nanowires are shown next to those of the standard CdSe@ZnO sample in Figure 4.3. The SEM images of the bare nanowires show the expected well-faceted hexagonal structure of ZnO with smooth surfaces. The bare nanowires are ~2 µm long relatively well aligned, considering the rough FTO substrate. Increased alignment could be obtained with faster dip-coating withdrawal rate during seed film formation. The SEM images of the standard CdSe@ZnO sample reveal the coating pattern produced by the SILAR technique, and show a conformal coating all the way to the base of the high aspect ratio nanowires. From the micrographs in Figure 4.3, it is apparent that CdSe deposits conformally, in a continuous, but cluster-like pattern on the ZnO nanowires. The micrographs show that CdSe does not form a film on top of the ZnO layer, but rather it
penetrates all the way down the pores between the nanowires. It is difficult to determine the amount of CdSe deposited on ZnO nanowires and the thickness of the absorber layer by comparing treated and untreated nanowire diameters due to initial high variability in nanowire diameters, however, the thickness of the deposited CdSe layer is approximated to be ~10 nm.

The presence of cadmium and selenium atoms was verified by EDS scans of the substrate, and EDS results for the standard CdSe@ZnO sample are given in Figure 4.4. Quantitative elemental analysis (Table 4.1) shows an atomic ratio between Cd and Se atoms of roughly 1:1, indicating almost theoretical stoichiometry in deposited CdSe. This result should be evaluated with caution, as there is usually a high error associated with quantitative elemental analysis. The EDS spectrum also shows the presence of sulfur atoms, most likely from the sulfite ion present in the Se precursor.
Figure 4.3: SEM micrographs of reference bare nanowire grown by 2 growth cycles (a-d) and the standard CdSe@ZnO sample (e-h). (a), (b), (e), and (f) show a planar view, while (c), (d), (g), and (h) show a cross-sectional view. Conformal deposition of CdSe is apparent in the CdSe@ZnO sample.
Figure 4.4: EDS Spectrum of the standard CdSe@ZnO sample. (Unlabeled peaks are those of C and Sn from substrate).

<table>
<thead>
<tr>
<th>Element</th>
<th>App Conc.</th>
<th>Intensity</th>
<th>Weight%</th>
<th>Weight%</th>
<th>Atomic%</th>
</tr>
</thead>
<tbody>
<tr>
<td>O K</td>
<td>8.43</td>
<td>1.0854</td>
<td>18.00</td>
<td>0.28</td>
<td>48.52</td>
</tr>
<tr>
<td>S K</td>
<td>0.40</td>
<td>0.9033</td>
<td>1.02</td>
<td>0.07</td>
<td>1.37</td>
</tr>
<tr>
<td>Zn K</td>
<td>26.96</td>
<td>0.9511</td>
<td>65.65</td>
<td>0.42</td>
<td>43.30</td>
</tr>
<tr>
<td>Se L</td>
<td>0.97</td>
<td>0.3952</td>
<td>5.70</td>
<td>0.20</td>
<td>3.11</td>
</tr>
<tr>
<td>Cd L</td>
<td>3.35</td>
<td>0.8066</td>
<td>9.62</td>
<td>0.26</td>
<td>3.69</td>
</tr>
</tbody>
</table>

| Totals  |           |           | 100.00  |         |         |

Table 4.1: EDS elemental analysis for the standard CdSe@ZnO sample.

TEM imaging was performed on bare ZnO nanowires and on the CdSe@ZnO sample. Figure 4.5 shows a comparison of wires before and after deposition, illustrating the pronounced morphology change that is due to SILAR deposition. Figure 4.5c shows
two individual nanowires coated with CdSe after annealing, demonstrating a continuous absorber layer along the wire. The thickness of the CdSe layer can be estimated from the TEM image to be roughly ~12 nm, similar to the approximation based on SEM images.

Figure 4.5: TEM images of (a) bare ZnO nanowires, (b) the CdSe@ZnO sample and (c) two nanowires of the annealed CdSe@ZnO sample.

The XRD 2-theta scan of the standard CdSe@ZnO sample is presented in Figure 4.6, where it is compared to a scan of bare ZnO nanowires on FTO. CdSe peaks are not distinguishable in the XRD spectrum of as-deposited sample. The XRD data does not show evidence for crystalline CdSe, suggesting that the deposited CdSe may be
amorphous. Other possibilities for the absence of the CdSe peaks are that the small amount of CdSe deposited by SILAR is not detectible by the machine, or that it was not CdSe that was deposited. UV-vis and EDS suggest that the material deposited is indeed CdSe, indicating that it is much more likely that CdSe is amorphous or in amounts too small to detect in XRD. The CdSe@ZnO sample was annealed at 350°C for 60 minutes in an attempt to crystallize any amorphous CdSe deposits. While this procedure induced crystallization in [30], there was no significant change to the XRD pattern here, as is evident in Figure 4.7. Two explanations for this are: (1) annealing did not improve the deposited crystalline structure of the deposited CdSe, or (2) the amount of post-annealing crystalline CdSe is still too small to detect in X-ray diffraction.

![Figure 4.6: XRD patterns of bare ZnO NW (red) and the standard CdSe@ZnO sample (blue). The black bars indicate the location of the expected CdSe peaks.](image)
In order to have a better understanding of the crystalline structure of the deposited CdSe, diffraction patterns of the standard CdSe@ZnO sample and the annealed CdSe@ZnO sample (A1) were taken in the TEM. Figure 4.8 shows TEM diffraction patterns for the as-deposited and annealed samples. The ring formation in Figure 4.8 confirms the presence of amorphous or nanocrystalline CdSe: a d-spacing of ~3.5 Å was determined for the first ring, corresponding to the (100) reflection of cubic crystalline CdSe. Figure 4.8 also shows the rectangular diffraction pattern expected from ZnO single crystal which is oriented along its c-axis. The lack of CdSe peaks in the XRD spectrum shown earlier is therefore probably due to small nanocrystals embedded in an amorphous matrix. It should be noted that the diffraction pattern presented for the as-deposited standard sample was taken for multiple coated nanowires, while the pattern taken for the annealed sample included only two wires.
The effect of the ZnO seeding method on the material properties was also investigated, and substrates seeded by the drop-coating method were compared to the standard CdSe@ZnO sample with seeds from dip-coating. The relatively misaligned ZnO nanowires that result from dip coating with a withdrawal rate of 56 mm/min appear very similar to the nanowires grown from seeds that were drop coated. Figure 4.9 is a side-by-side comparison of coated wires grown from dip coated seeds (standard CdSe@ZnO sample) and coated wires grown from drop coated seeds.

Figure 4.8: TEM diffraction patterns for (a) the standard CdSe@ZnO sample, and (b) the annealed CdSe@ZnO standard sample (A1).

Figure 4.9: Planar view of (a) the sample seeded by the drop-coating method, and (b) the standard CdSe@ZnO sample.
Since the ZnO nanowire orientation and length were similar, other characterizations of the CdSe-coated nanowires produced results similar to those described in the standard CdSe@ZnO sample section: the EDS scan produced similar peaks for Cd and Se, while the XRD spectrum lacked the expected CdSe peaks.

4.2 Solar Cells Characterization

4.2.1 Standard CdSe@ZnO Sample Solar Cell

Table 4.2 shows the different samples that were prepared in this thesis. A (+) sign signifies that the respective treatment applies to the sample, while a (-) sign signifies that the treatment was not done to the sample. The effects of the seeding technique, the nanowires length, the O₂ plasma treatment, and the annealing of the substrate after CdSe SILAR deposition were investigated.

Table 4.2: Experimental Samples Breakdown

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Seeding Technique</th>
<th>ZnO Nanowires Length</th>
<th>O₂ Plasma Treatment</th>
<th>CdSe Anneal (350°C for 1 hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dip Coat</td>
<td>Drop Coat</td>
<td>1 Growth Cycle (≈1 µm)</td>
<td>2 Growth Cycles (≈2 µm)</td>
</tr>
<tr>
<td>Standard: CdSe@ZnO</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>A</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>S1</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>S2</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>D1</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>D2</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>P1</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>P2</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
</tbody>
</table>
Solar cells (ZnO NW/CdSe/Liquid Electrolyte) were constructed from standard CdSe@ZnO samples, as well as from the samples described in Table 4.2. The dark and light (100 mW/cm², AM 1.5 simulated sunlight) J-V curves for the standard CdSe@ZnO solar cell are shown in Figure 4.10. The light curve shows a $J_{SC}$ of ~0.20 mA/cm² and a $V_{OC}$ of ~0.45 V. The offset between the ZnO conduction band and the I-/I3- redox potential is ~1.0 eV. Overpotentials and losses result in a reported $V_{OC}$ which is about 0.5 V below this value. The fill factor (FF) of the standard CdSe@ZnO sample solar cell was found to be 0.22, while the overall power conversion efficiency was found to be 0.02%. The dark curve exhibits diode-like rectifying behavior as expected. $J_{SC}$ is not exactly zero due to stray light incident upon the cell.

![J-V Curves](image)

Figure 4.10: J-V curves for the illuminated (blue) and dark (red) standard CdSe@ZnO sample solar cell.
Although the solar cell showed a low overall efficiency, the standard CdSe@ZnO solar cells exhibited photocurrent generation in the visible light range (400-600 nm). This visible response confirms that the CdSe absorber layer absorbed photons and was able to inject electrons into the ZnO NW layer. Figure 4.11 shows the generated photocurrent for the standard CdSe@ZnO sample as a function of wavelength. The photocurrent versus wavelength curves depend on the light spectrum produced by the lamp; however, since both curves were generated using the same lamp intensities, the high increase in photocurrent generation in the CdSe@ZnO sample confirms the functionality of the solar cell.

Figure 4.11: Room-temperature photocurrent response spectrum of solar cells constructed from the standard CdSe@ZnO sample (blue) and from bare ZnO nanowires grown by 2 growth cycles (red).
Based on the photogeneration curve (Figure 4.11) and the light harvesting efficiencies (based on Figure 4.2), the IPCE and IQE can be calculated. Figure 4.12 shows a positive IPCE and IQE response for the CdSe@ZnO sample in the visible light range between 400-500 nm. Electrons in the visible light energy range are injected from the CdSe absorber layer into the n-type ZnO nanowires, showing that the SILAR method was used successfully to deposit CdSe on ZnO nanowires for a solar cell application. The fabricated solar cells were not stable, as the liquid electrolyte degraded the CdSe layer shortly after testing. It has been observed that the electrical current caused accelerated degradation to the CdSe layer. CuSCN is expected to be a stable hole-conducting replacement for the liquid electrolyte.

Figure 4.12: IPCE (blue), LHE (red), and IQE (green) curves for the standard CdSe@ZnO sample solar cell.
The shape of the IPCE and IQE curves in Figure 4.12, and particularly the high photoresponse in the UV range, indicate that electrons photoexcited in the ZnO are collected more efficiently than those photoexcited within the CdSe absorber layer. The fact that LHE>>IPCE, and that UV photocurrent is lower in CdSe@ZnO than bare ZnO despite higher absorption, indicates that low currents are a result of low electron injection efficiencies (low IQE) rather than from low absorption. Low IQEs may be a result of the amorphous structure of CdSe in the cell or the presence of defects at the CdSe/ZnO interface, either of which may lead to less efficient electron injection due to trapping and recombination of photoexcited charges.

4.2.2 Nanowire Length Effects

The deposition of CdSe on ~1 μm nanowires (sample S1) was compared to that of the standard CdSe@ZnO sample (~2 μm long nanowires) and to uncoated nanowires ~1μm in length. Figure 4.11 shows SEM micrograph images of these three samples. Figure 4.13(a) shows that bare nanowires have smooth surfaces, while the CdSe-coated nanowires in Figure 4.13(b) appear rough, confirming that they are coated by CdSe. The comparison to the standard CdSe@ZnO sample shows that the shorter coated wires appear to have a similar morphology to that of the standard CdSe@ZnO sample. EDS of S1 showed evidence of Cd and Se atoms, similar to the standard CdSe@ZnO sample, while XRD scans done on S1 showed no change from the standard CdSe@ZnO sample, and none of the expected CdSe peaks were present.
Figure 4.13: SEM images of (a) uncoated ~1 µm long nanowires, (b) CdSe-coated ~1 µm long nanowires, (c) standard CdSe@ZnO sample.

The absorbance and LHE of the shorter nanowires solar cells were compared to those of the CdSe@ZnO sample. Figure 4.14 shows LHE versus wavelength for sample S1 and the standard CdSe@ZnO sample, with a reference of bare ZnO NW grown by one growth cycle for S1.
Figure 4.14: LHE as a function of wavelength for the standard CdSe@ZnO sample (blue) and for sample S1 (red), where CdSe was deposited on ~1µm long nanowires.

Figure 4.14 shows slightly more visible absorption in the CdSe@ZnO for 2 µm long nanowires than for 1 µm long wires. However, the difference in magnitude of the LHE is significantly less than a factor of two, suggesting that absorbance does not strongly depend on the length of the wires. Since we expect the absorber thickness to depend only on the number of SILAR deposition cycles, and therefore longer coated wires to absorb more light (due to a larger volume of CdSe deposited), the results are not entirely consistent with our expectations. Two possible explanations are offered for this anomalous light harvesting behavior: (1) the amount of CdSe deposited is the same for S1 and the standard CdSe@ZnO sample, or (2) large CdSe clusters that lie on top of the wires absorb most of the light for both samples, causing the percentage of light absorbed by CdSe that actually coats the wires to be statistically insignificant. Further discussion of
this behavior will be presented later, with reasoning as to why explanation (1) is more plausible in this case.

The solar cell constructed from sample S1 showed an overall cell efficiency of 0.01%, with a fill factor of 0.27. $V_{OC}$ and $J_{SC}$ for the S1 solar cell were found to be 0.39 V and 0.1 mA/cm$^2$, and the J-V curves for the cell are shown below in Figure 4.15. The lower $J_{SC}$ (as compared to the standard CdSe@ZnO sample) is expected for solar cells made with shorter nanowires since the light harvesting efficiency is lower for shorter wires. The slope of the light curve near $J_{SC}$ indicates significant shunting in the cell, the source of which will be the subject of further investigation.

![Figure 4.15: J-V curves for the illuminated (blue) and dark (red) S1 sample solar cell, made up of ~1µm long ZnO nanowires.](image)

Since the light harvesting efficiency is similar for short and long wires in this case, the two explanations given above for the light harvesting behavior lead to two different descriptions for why shorter wires produced lower photocurrents. The first description, based on the assumption that the same volume of CdSe has been deposited
on the standard CdSe@ZnO sample and S1, asserts that the thicker absorber layer on S1 leads to more electron-hole recombination in the bulk absorber, which would lower the generated photocurrent. The second description, based on the assumption that large CdSe clusters on top of the nanowires absorb most of the light, asserts that CdSe clusters absorb photons but cannot inject electrons into the ZnO nanowires. Instead, only photons absorbed by CdSe in direct contact with ZnO NW can contribute to the photocurrent. Both descriptions are compatible with the photocurrent versus wavelength curves presented in Figure 4.16, which shows the photocurrent generation as a function of wavelength for bare nanowires ~2 µm long, the standard CdSe@ZnO sample solar cell, and the S1 solar cell. As expected for shorter nanowires, the photocurrent generation in the UV is lower than that of longer wires since there is much less ZnO, which also absorbs light in that range. The S1 solar cell exhibited photocurrent generation in the visible range, although the current generated was lower than that of the standard CdSe@ZnO sample.

Figure 4.16: Room-temperature photocurrent response spectrum of solar cells constructed from the standard CdSe@ZnO sample (blue), bare ZnO nanowires grown by 2 growth cycles (red), and S1 (green).
4.2.3 $O_2$ Plasma Treatment Effects

Substrates treated with $O_2$ plasma (sample P1) prior to CdSe deposition by SILAR were compared to the standard CdSe@ZnO sample. The rationale behind $O_2$ plasma treatment was to clean the ZnO NW thoroughly prior to SILAR deposition in order to provide a more consistent, smoother surface for CdSe adsorption, and as a result more crystalline CdSe. $O_2$ plasma treatment have in the past lead to a more efficient, higher power CdSe quantum dots/ZnO NW solar cell [112], and, given the similarity in materials, plasma treatment was thought to be potentially viable for this study.

XRD results, however, do not show CdSe peaks in this case either. Furthermore, Figure 4.17 shows the J-V curves for the standard CdSe@ZnO sample and the as-deposited $O_2$ plasma treated sample (P1), showing that no improvement in the cell’s performance is obtained by treating the nanowires with $O_2$ plasma. No evidence has been produced to support the fact that $O_2$ plasma treatment leads to more efficient solar cells. However, further investigation is required to determine the complete effects of $O_2$ plasma treatment on the ZnO NW/CdSe heterostructure. Possible improvements in solar cell performance are yet to be determined for the fully solid-state cell (ZnO NW/CdSe/CuSCN).
4.2.4 Annealing Effects

Every solar cell sample described up to this point was characterized as-deposited, without any post deposition treatment. Substrate annealing has been shown to enhance the photoresponse in ZnO NW/CdSe/CuSCN solar cells [30]. To investigate the effects of annealing after the deposition of CdSe, every as-deposited sample was compared to another sample prepared under the same conditions which was then annealed at 350°C in air for one hour.

Annealing does appear to have a minor effect on solar cell performance. Figure 4.18 shows illuminated J-V curves for the different sample pairs (S1 and S2, D1 and D2, and P1 and P2) which show a relatively consistent trend where annealing increases the
short circuit current and lowers the cell’s fill factor (makes the J-V curve less square). The fill factors for the solar cells made of samples S2, D2, and P2 were 0.25, 0.23, and 0.25, respectively, while the fill factors for the solar cells made of S1, D1, and P1 were 0.28, 0.31, and 0.28, respectively. Figure 4.19 shows the photocurrent generation of the same sample pairs in Figure 4.18 as a function of wavelength. It should be noted that sample pairs should only be compared to each other, as different light intensity was used for each pair.

It is difficult to determine why annealing causes an increase in the short circuit current, however, it appears from Figure 4.16 that the increase in photogeneration by ZnO NW (in the UV range) is the major contributor to the higher short circuit currents. Although it appears that some additional photocurrent is generated in the visible range in the different samples as a result of annealing, more experimentation is needed to determine whether this effect is a result of a higher degree of crystallinity of the deposited CdSe or whether another factor is causing the apparent change.
Figure 4.18: Illuminated J-V curves for solar cells made of (a) S1 (blue) and S2 (red) samples, (b) D1 (blue) and D2 (red) samples, and (c) P1 (blue) and P2 (red) samples.
Figure 4.19: Room-temperature photocurrent generation as a function of wavelength for (a) S1 (blue) and S2 (red) samples, (b) D1 (blue) and D2 (red) samples, and (c) P1 (blue) and P2 (red) samples.
CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

A proof-of-concept that ZnO nanowires grown on F:SnO$_2$-coated glass can be successfully sensitized with thin layers of CdSe deposited by SILAR has been demonstrated. Solar cells were constructed from CdSe-sensitized ZnO NW using a liquid I$^+/I_3^-$ electrolyte as the cell’s p-type hole conductor, achieving a maximum overall cell efficiency of 0.02% and an average fill factor of 0.25. The solar cells exhibited relatively high light harvesting efficiencies in the 400-600 nm range (about 45% absorption) and low incident-photon-to-electron-conversion efficiencies in the same range (under 5%). The high LHE and low IPCE indicate that while photons are absorbed by the CdSe layer, most electrons generated by the excited photons do not contribute to the photocurrent, but rather recombine with holes either in the absorber layer itself, in the ZnO NW layer, or in the liquid electrolyte. In order to improve IPCE in the CdSe-coated ZnO NW solar cells, the cells’ architecture must be modified.

Scanning electron microscopy imaging, as well as energy dispersive spectroscopy, was used to verify the presence of a deposited CdSe layer. A study of the effects that ZnO nanowires length, the ZnO seeding technique, O$_2$ plasma treatment, and post-CdSe deposition substrate annealing have on the ZnO NW/CdSe heterostructure characteristics was carried out. While the nanowires length, seeding technique, and O$_2$ plasma treatment effects were inconclusive based on the obtained results, it is evident that substrate annealing causes an increase in the resulting solar cells’ short circuit current densities while lowering the cell’s fill factor. A photoamperometry study of annealed
cells shows that a significant amount of the additionally generated current originates in the UV light range, and is therefore attributed to changes in the ZnO layer in the cell, and no the CdSe absorber layer.

A comprehensive study of the effects that the SILAR deposition procedure have on the thickness of the deposited CdSe layer is required to further understand the behavior of the resulting photovoltaic devices. Transmission electron microscopy (TEM) analysis is required for accurate determination of the crystalline structure, composition, and thickness of the absorber film, as well as optoelectronic characterization of the different layers in the proposed solar cell. Further experimentation is required for complete understanding of the absorber layer crystalline structure. X-ray diffraction results from this thesis were inconclusive in regards to the structure of the deposited CdSe, and different deposition conditions (pH, deposition solutions’ concentrations, and perhaps even temperature) must be studied in order to try and achieve better control on the characteristics (thickness, absorbance, etc) of the absorber film. A study of the effect of ZnO morphology on those characteristics of the deposited CdSe, as well as on charge transport in the eta solar cells, is also recommended. Future work must include the incorporation of CuSCN into the solar cell structure, as the ultimate goal of the project is to synthesize fully solid-state solar cells.
LIST OF REFERENCES


62. McPeak KM, Baxter JB. Microreactor for high-yield chemical bath deposition of semiconductor nanowires: ZnO nanowire case study. Ind Eng Chem Res 0;0(0).


