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CuInSe₂ Nanowires and Earth-Abundant Nanocrystals for Low-Cost Photovoltaics

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CuInSe₂ Nanowires and Earth-Abundant Nanocrystals for Low-Cost Photovoltaics

by

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Dedication

For my family, and for Kelsey

Acknowledgements

I decided to leave industry in the summer of 2008 and enter graduate school at UT in the fall of that same year. Although I had a well paying job with a good company, and excellent future prospects of promotion, I wasn't happy. I had worked hard for four years during my undergraduate studies learning the many different areas of chemical engineering. There were many late nights of studying and preparing reports at the 'U.' However, at General Mills, I wasn't using much of what I had spent so much time studying and as a result the job just wasn't intellectually stimulating. I realized I missed the lab, doing experiments, and using my brain.

Although I was excited to go to grad school, I was somewhat apprehensive, and a little unsure if it was the right decision to leave industry at that point. After these past 4 plus years, I can safely say that it was certainly one of the best decisions of my life. I've met many great, intelligent, and motivated people, engaged in some very interesting research, and learned a lot about the fields of nanoscience and photovoltaics. I believe its been a productive few years, but I couldn't have done it without the help of many people, who I'd like to acknowledge here.

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CuInSe₂ Nanowires and Earth-Abundant Nanocrystals for Low-Cost Photovoltaics

Chet Reuben Steinhagen, Ph.D. The University of Texas at Austin, 2013

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Widespread commercialization of photovoltaics (PVs) requires both higher power conversion efficiencies and low-cost, high throughput manufacturing. High efficiencies have been achieved in devices made from materials such as CuIn_xGa_{1-x}Se₂ (CIGS). However, processing of these solar cells still requires high temperature and vacuum, driving up cost.

A reduction in manufacturing costs can be achieved by utilizing colloidal nanocrystals. Semiconductor nanocrystals can be dispersed in solvents and deposited via simple and scalable methods under ambient conditions to form the absorber layer in lowcost solar cells.

Efficiencies of ~3% have been achieved with CIGS nanocrystal PVs, but this must be improved substantially for commercialization. These devices suffer from poor charge transport in the nanocrystal layer.

Here, the synthesis of nanowires and their utilization in solar cells was explored as a way to improve charge transport. CuInSe₂ (CIS) nanowires were synthesized via the solution-liquid-solid method. PV devices were fabricated using the nanowires as the light absorbing layer, and were found to exhibit a measureable power output. Earth-abundant materials were also explored, motivated by the material availability concerns associated with CIGS. Pyrite FeS_2 nanocrystals were synthesized via an arrested precipitation reaction to produce phase-pure particles 15 nm in size. These nanocrystals were spray coated to form the active layer in several different common device architectures. These devices failed to produce any power output. The material was determined to be slightly sulfur deficient, leading to a high carrier concentration and metallic behavior in the thin films, with conductivities measured to be ~ 5 S/nm.

A nanocrystal synthesis of Cu_2ZnSnS_4 (CZTS) was also developed to produce highly dispersible crystalline particles ~11 nm in size. These nanocrystals were spray coated onto glass substrates to form the absorber layer in test PV devices, and an efficiency of 0.23% was achieved without high-temperature or chemical post-processing.

Additional studies included the synthesis of CZTS nanorods and their incorporation into functioning solar cells. The selenization of CZTS nanocrystal films was also studied as a way to improve solar cell performance. High temperature annealing in a Se atmosphere was found to produce CZTS(Se) layers, which could be used in working PV devices.

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Chapter 1: Introduction

Solar energy is an exciting alternative to fossil fuels because it is clean, abundant, and sustainable. Harvesting only a small fraction of the sun's energy that reaches earth over the course of a year is more than enough to meet annual global demands for electricity.¹ The technology to do so has existed for many years: Charles Fritts created the first photovoltaic (PV) device in 1883 by coating selenium with gold, and the first modern silicon pn junction solar cell was developed by Bell Labs in 1954.²

Unfortunately, over 50 years later, we have still yet to see widespread adoption of this technology; only 0.1% of our electricity is produced from solar energy.^{1, 3} This is due to simple economics. Solar power is still too expensive to compete with traditional sources of electricity such as coal, oil, and natural gas without government subsidies. Electricity produced from traditional sources is approximately \$0.10/kWh, while that produced from solar sources is roughly twice that, depending on location.³

Several broad routes to reduce manufacturing costs have been pursued over the last couple of decades, including increasing the efficiency of traditional Si-based photovoltaics, utilizing thin film absorbers⁴ (amorphous Si,⁵ CdTe,⁶ and CuIn_xGa_{1-x}Se₂; CIGS),⁷ and developing new low-cost platform technologies such as organic photovoltaics (OPVs)⁸ and dye-sensitized solar cells (DSSCs).⁹ More recently, there has been extensive work on a new class of PVs: nanocrystal-based solar cells. The absorber layers in these devices are fabricated from nanocrystal dispersions – "inks," or "paints," – via scalable and inexpensive methods such as roll-coating or spray-coating.^{1, 10-17}

The most extensively studied materials systems incorporated into nanocrystal based solar cells include lead chalcogenides,¹⁸⁻²⁸ cadmium chalcogenides,^{29,30} and CIGS.³¹⁻³⁸ The work presented in this dissertation focuses primarily on alternatives to

these. Alternatives, that is, to both the geometry of the nanostructures (nanowires and nanorods, instead of spherical particles) and to the materials systems used.

1.1. THE CURRENT LEADER – SILICON

Owing to parallel research and development with ubiquitous technologies such as integrated circuits, Si-based PVs currently dominate the solar cell market. Over several decades of development, advances in the electronic device industry have led to drastic improvements in material quality, device performance, and manufacturing processes. As a result, Si PVs have maintained a steady advantage over other device structures and materials for many years.

Crystalline Si solar cells have achieved the highest (single-junction) lab-scale power conversion efficiencies (PCEs) to date of around 25%.^{39,40} Larger modules, made on an industrial scale, are not too far behind: the record PCE in this category is approximately 23%.⁴¹ Due to these relatively high efficiencies, Si PVs are by far the most widely adopted solar cell technology.

On the other hand, Si is an indirect band-gap semiconductor, making it a relatively poor absorber of light when compared to other possible PV materials. In order to absorb a sufficient portion of the solar spectrum, fairly thick layers (~250 μ m for the most efficient devices)³⁹ of material must be used. Furthermore, the production of high-quality single-crystalline Si is an extremely energy intensive and expensive process. These factors lead to low throughput and high-cost manufacturing. Even with many years of development and high efficiency devices, solar energy is still not at grid parity, where electricity prices are equal to that of fossil fuels.

1.2. SECOND GENERATION PHOTOVOLTAICS

Due to the high manufacturing costs and materials usage associated with Si PVs, a "second generation" of solar cell technologies has been developed. These types of PVs are known as thin-film solar cells, and are identified by devices where the absorber or active layer is on the order of 1-2 μ m. Thin film PVs utilize direct band-gap semiconductors with much higher optical absorption coefficients than Si. Thus, less material is required, and production costs are greatly reduced.

The three leading materials systems that comprise second generation solar cells are amorphous Si (a-Si), CdTe, and CIGS.⁴² a-Si devices have achieved efficiencies of ~10%, and are relatively simple to manufacture. However, they suffer from long-term performance degradation due to the Stabler-Wronski effect.⁴³ Although a-Si PVs can be manufactured fairly inexpensively, it may prove difficult to achieve high enough PCEs with them in order to meet grid parity.

CdTe is an interesting and promising technology that has achieved lab-scale efficiencies of $17.3\%^{40}$ and module efficiencies of $15.3\%^{40}$ CdTe PV technology has been commercialized by First Solar to some degree of success: their current production cost of \$0.98 per peak watt (W_p) is low enough by some estimates to reach grid parity.⁴⁴ However, there are concerns about this technology due to cadmium toxicity, and in some countries, this material has been banned. Additionally, there are concerns of possible long-term Te availability. Together, these factors may limit the widespread adoption of CdTe solar cells.^{45,46}

Of single-junction thin film PVs, CIGS devices have demonstrated the highest PCEs to date: 20.3% on a lab-scale device,⁷ and 15.7% at the module level.⁴⁷ CIGS has also been commercialized, but this technology is still quite expensive. High efficiency CIGS devices and modules are fabricated by a multi-stage co-evaporation methodology

requiring high temperatures and vacuum.^{7, 42, 48} This fabrication technique is inherently a batch process and not amenable to high-throughput manufacturing. Furthermore, over the large areas required for industrial-scale modules, it can be somewhat difficult to control the composition of the absorber layer, which is critical to device performance.

Recent developments have led to solution-processable CIGS PVs via liquid deposition,⁴⁹⁻⁵² achieving lab-scale PCEs as high as 15.2%,⁵³ approaching that of its vacuum- deposited counterparts. This technique involves dissolving constituent elements in hydrazine to form a liquid precursor solution, which is subsequently deposited onto substrates in order to fabricate the absorber layer. This process is fully scalable to high throughput roll to roll manufacturing, which could drastically reduce production costs. However, hydrazine is extremely toxic and flammable, and utilizing this chemical in industrial solar cell production could prove to be difficult.

Due to the above issues, there is a large initiative to develop new PV fabrication technologies that are inexpensive, scalable, environmentally friendly, and can achieve high efficiencies. A possible route to this involves nanocrystal dispersions of well-established materials, like CIGS.

1.3. NANOCRYSTAL SYNTHESIS

Synthetic methods have been developed over the last couple of decades to produce nanocrystals from a wide variety of PV-ready material systems, including cadmium-, lead-, copper-, and tin-chalcogenides, Si, and CIGS.⁵⁴⁻⁵⁷ Colloidal synthesis typically involves an "arrested precipitation" reaction performed in an inert environment in which precursor solutions are combined at high temperatures to produce a nucleation

event, followed by a growth stage in which the nanocrystals grow in a controlled fashion to their desired size and shape.

Typical precursors are metal salts, organometallic compounds, or complexes formed by dissolving elemental powders in coordinating solvents. Capping ligands present during the reaction control growth and prevent coalescence and aggregation of the nanocrystals. Standard capping ligands include thiols, amines, carboxylic acids, and phosphines.

Syntheses have been developed to produce nanocrystals of many different shapes and sizes, with tightly controlled size dispersity. Ligand-capping enables the inorganic semiconductor nanocrystal core to be dispersed in organic solvents to form inks or paints. These dispersions can be deposited onto different substrates by myriad methods: spincoating, dip-coating, doctor-blading, inkjet printing, or spray coating. These films can be incorporated into a wide variety of electronic devices such as transistors, light-emitting diodes, thermoelectrics, and PVs.^{13, 58}

1.4. SOLAR CELL BASICS AND PERFORMANCE METRICS

Solar cells operate by absorbing sunlight to produce a photocurrent that is collected at a voltage bias to produce power output. Photons with energy greater than the band gap of the solar cell absorber material are absorbed, creating photogenerated electrons and holes. These charge carriers are separated at the junction in the device via a built-in electric field. The junction is generally a pn homojunction (Si devices), a pn heterojunction (CIGS devices), or a metal-semiconductor junction (Schottky barrier devices). The separated carriers then travel to their respective electrodes where they can power a load connected on the external circuit.⁵⁹

The key metrics of solar cell performance include the short-circuit current (I_{sc} ; usually reported in terms of the current density J_{sc}), the open-circuit voltage (V_{OC}), the PCE (η), and the fill factor (FF). The short-circuit current is the maximum photocurrent produced in the device operated at zero voltage bias. V_{OC} is the voltage at which no current flows in the device.

The PCE is calculated by dividing the maximum power output (P_{max} ; the point on the current-voltage curve at which the most power is generated) by P_{in} , the power of the light incident on the solar cell. P_{in} is usually taken to be 100 mW/cm², which is the incident power of an air mass (AM) 1.5 spectrum, the typical spectrum of light used to test solar cells. AM 1.5 is a standardized spectrum that is fairly representative of the average solar irradiation at mid-latitudes. The maximum theoretical efficiency of a single-junction solar cell is 33%, known as the Shockley-Queisser limit.⁶⁰

The fill factor, FF, is a metric encompassing many different device characteristics, and is calculated by the following equation:

$$FF = \frac{P_{max}}{V_{OC}J_{SC}}$$

The fill factor is essentially a measure of the "squareness" of the current-voltage curve, and is reduced by "parasitic" resistances: low shunt resistance or high series resistance. A low shunt resistance is created by alternate current pathways in the device, commonly a result of cracks or pinholes in the absorber layer. High series resistance is created by poor electronic transport in the device.

1.5. NANOCRYSTAL PHOTOVOLTAICS

A functioning nanocrystal solar cell was first reported in 1996 by Greenham et. al.⁶¹ The active layer in this device was comprised of a polymer-nanocrystal blend. In 2005, the first all-inorganic nanocrystal device was reported by Gur et. al.²⁹ This device was fabricated from CdSe and CdTe nanocrystals, and achieved a PCE of nearly 3%.

Over the last several years, nanocrystal PVs have been fabricated from a wide variety of materials, including Si,¹⁷ lead chalcogenides,²¹ Cu₂S,¹⁶ and CIGS.^{11, 35} Several different device architectures have been utilized, including simple Schottky barrier structues,¹⁹ pn homojunctions,⁶² and pn heterojunctions.⁶³ More recently, new architectures have been created such as the depleted heterojunction structure pioneered by Sargent et. al.⁶⁴⁻⁶⁷ The highest PCE attained (without any thermal annealing step) by nanocrystal PVs at this point is 7%, by utilizing PbS nanocrystals.⁶⁸ While this is a significant achievement, it is unclear at this point whether or not this materials system can achieve the necessary efficiency of 15% for grid parity.^{10, 12}

CIGS (and the related material Cu₂ZnSnS₄,^{69, 70} which is discussed later as a focal point of this dissertation), is a well-established PV material and has proven capable of achieving high PCEs. Interestingly, polycrystalline devices made from CIGS have been shown to work well, an attractive characteristic for nanocrystal-based studies, since nanocrystal films inherently have many grain boundaries.⁴² Due to these aspects, our group began PV work based on this material. The remaining portion of this introduction will briefly overview our group's work with CIGS nanocrystal PVs in order to set the stage and provide motivation for the bulk of this dissertation.

1.6. CIGS NANOCRYSTAL PVs

While many different techniques can be used to deposit nanocrystal layers, our group has focused on the spray-coating method. This method was found to produce smooth, crack-free, and pinhole-free films. It is a very flexible method: different substrates can be easily used, and the film thickness can be adjusted readily by altering the dispersion concentration or by spray-coating larger volumes. To spray coat, a standard artist's air brush is used, as shown in Figure 1.1 (courtesy of Vahid Akhavan).



Figure 1.1. Photograph of airbrush used to spray-coat thin films of nanocrystals. Typical films on glass substrates are shown in the center of the picture.

Our group has developed functioning solar cells from CIGS nanocrystals, by using a standard Au/CIGS/CdS/ZnO/indium tin oxide (ITO) device architecture. The Au back contact is deposited by thermal evaporation, the CdS layer by chemical bath deposition, and the ZnO and ITO layers by rf sputtering. So far, our group's record efficiency with this type of device is 3.1%, the current-voltage characteristics of which are shown in Figure 1.2.³²



Figure 1.2. Current-voltage characteristics of the best CIGS nanocrystal device to date.

These devices are promising, and a 3% PCE result certainly merits further work in the optimization and development of their fabrication. However, PCEs on the order of 5% are not adequate to achieve grid parity and commercialization.

Additionally, there are concerns with the scarcity of global In reserves.⁴⁶ Several reports have discussed this topic, and competition with ITO production for flat panel displays and the like may drastically increase materials costs in the future. These aspects of this material system may limit the long-term prospects of CIGS to meet our energy needs.⁴⁵

These two issues provide the motivation for this dissertation. This work involves the utilization of 1-dimensional nanostructures for the improvement of charge transport and device performance. The other main portion of this work concerns the development of alternative, earth-abundant materials in nanocrystal-based solar cells.

1.7. DISSERTATION OVERVIEW

Chapter 2 of this dissertation discusses the synthesis of $CuInSe_2$ (CIS) nanowires and their implementation in photovoltaics. Included are the details of bismuth nanocrystal seed synthesis, CIS nanowire synthetic methods, characterization of the nanowires, and fabrication details of solar cells using these nanowires as the absorber layer. The production of a CIS nanowire "fabric" is also mentioned.

Chapter 3 discusses an earth-abundant alternative material for nanocrystal PVs: Pyrite FeS_2 , commonly known as fool's gold. Nanocrystal synthesis and characterization is presented, along with attempts to use the material in several different device architectures. Compositional and electrical data and its role in device performance conclude the chapter.

 Cu_2ZnSnS_4 (CZTS) nanocrystals and nanorods are the focal point of Chapters 4-6. Chapter 4 explores the synthesis of CZTS nanocrystals and their usage in PVs. Chapter 5 describes the synthesis of CZTS nanorods, their implementation in PVs, and a brief discussion of perpendicular alignment. Selenization data is presented in Chapter 6. The thermal annealing of CZTS nanocrystal films in a Se atmosphere is explored, and the fabrication of devices from these films is discussed.

Chapter 7 is a short detour from the rest of the dissertation; this chapter discusses Si nanowire fabric, the thermal annealing of this fabric, and how annealing improves its performance as an electrode material in lithium ion batteries.

Finally, Chapter 8 wraps up the dissertation by summarizing the main points, and offering some possible areas of future work on these topics.

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Chapter 2: Solution-Liquid-Solid Synthesis of CuInSe₂ Nanowires and Their Implementation in Photovoltaic Devices*

2.1. INTRODUCTION

Copper indium diselenide (CuInSe₂; CIS) and related I-III-VI₂ compounds have been established as useful semiconductors for thin film photovoltaic devices (PVs), or solar cells, achieving high power conversion efficiencies (PCEs) and commercial use.¹ Conventional fabrication of these PVs, however, requires vapor deposition and high temperature processing, which leads to high manufacturing cost and limits the range of device architectures that can be made. Significantly lower cost could be achieved by processing the materials by inexpensive roll-to-roll printing methods with high throughput under ambient conditions. One approach to achieving this goal is to use colloidal nanocrystal inks to deposit the inorganic light-absorber layers. This approach has been demonstrated by a number of research groups,²⁻⁹ but the PCEs are still too low for commercialization.

One of the main limitations of device efficiency with absorber layers composed of nanocrystals is the large number of interfaces or grain boundaries in the film.^{7, 8} Hillhouse and Agrawal^{3, 10} have alleviated this problem by sintering their CIS-based nanocrystal films at high temperature (~500°C) under Se atmosphere to achieve PCE of greater than 10%. This approach, however, still relies on high temperature processing. In contrast to nanocrystals, nanowires do not have grain boundaries along their length.

^{*} Portions of this chapter appear in: Steinhagen, Chet; Akhavan, Vahid; Goodfellow, Brian; Panthani, Matthew G.; Harris, Justin; Holmberg, Vincent; Korgel, Brian, **Solution-Liquid-Solid (SLS) Synthesis of CuInSe2 Nanowires and their Implementation in Photovoltaic Devices.** *ACS Applied Materials & Interfaces* (2011), 3(5), 1781-1785. Vahid, Brian, and Matthew assisted with device fabrication and analysis, Justin helped with Bi nanocrystal synthesis, Vincent assisted with TEM imaging, and Dr. Korgel was the principal investigator.

Nanowires can also be dispersed in solvents and deposited on substrates under ambient conditions. Therefore, by using nanowires it might be possible to improve minority carrier diffusion lengths and device efficiency in printed inorganic PVs without sintering.¹¹⁻¹³

Recently, CIS nanowires have been synthesized by vapor-liquid-solid (VLS)¹⁴⁻¹⁷ and solution-liquid-solid (SLS)¹⁸ approaches. Since the SLS process yields large quantities of nanowires, we explored this approach to make CIS nanowires, applying a variation of the methods described by Wooten et. al.¹⁸ using bismuth (Bi) nanocrystals as growth seeds. We found that CIS nanowires can be produced in significant quantity with little particulate byproduct, but often have large concentrations of twin defects. Under some reaction conditions, the nanowires form with wurtzite crystal structure—a phase that does not appear in the bulk. The nanowires also tend to be deficient in In. As a test to determine if the nanowire are potentially viable as light-absorbing material for use in PV devices, nanowires were spray-deposited onto substrates and packaged into PV devices. The nanowires gave a measurable PV response, with a power conversion efficiency under AM 1.5 illumintation of 0.1%. Although the actual device efficiency is relatively low, these results demonstrate that the nanowires may be viable PV material.

2.2. EXPERIMENTAL METHODS

2.2.1 Chemicals

All chemicals were used as received. Tetrahydrofuran (THF, anhydrous, \geq 99.9%, inhibitor-free), Sodium bis(trimethylsilyl)amide (Na[N(SiMe_3)_2], 1.0 M in THF), bismuth chloride (BiCl₃, \geq 98%), diphenyl ether (DPE, 99%), copper (I) acetate (97%), indium (III) acetate (99.99%), indium (III) chloride (InCl₃, 99.999%), elemental selenium (Se,

99.99%), trioctylphosphine (TOP, 90%), oleic acid (OA, 99%), squalane (99%), and 1hexadecylamine (HDA, 90%) were obtained from Aldrich; methanol (MeOH), toluene, and hexane from Fisher Scientific; and polyvinylpyrrolidone-hexadecane (PVP-HDE) copolymer (Ganex V-216, MW = 7,300 g/mol, product ID 72289D) from ISP Technologies, Inc.

2.2.2. Bismuth Nanocrystal Synthesis

Tris[bis(trimethylsilyl)amino] bismuth (Bi[N(SiMe₃)₂]₃) was synthesized by previously reported methods and dissolved in THF to make a 1 M solution.¹⁹ 5 g of Ganex V216 and 15 g of diphenyl ether were combined in a 100 mL three-neck flask. The flask was attached to a Schlenk line, placed under vacuum, heated to 70°C, and allowed to degas for 1.5 hrs while stirring. In parallel, 0.5 mL of Bi[N(SiMe₃)₂]₃/THF was mixed with 2.0 mL of 1 M NaN(SiMe₃)₂ in THF and placed into a syringe. After the Ganex V216 and diphenyl ether solution was degassed, the flask was refilled with N₂ and the temperature was increased to 180°C. At 180°C, the Bi precursor solution was quickly injected into the hot solution and reacted for 30 min. After 30 min., the mixture was cooled to 60°C and 15 mL of room-temperature toluene was added.

Bi nanocrystals were isolated by centrifuging the reaction product for 3 min at 5000 RPM. The supernatant was collected and the precipitate was discarded. 30 mL of MeOH was added to the supernatant and centrifuged for 5 min at 10,000 RPM. The supernatant was discarded. The precipitate was dispersed in 10 mL of toluene. This process was repeated several times and the final precipitate was dispersed and stored in toluene at a concentration of 5 mg/mL. The Bi nanocrystals were spherical with an average diameter of 12.7 ± 0.9 nm (Figure 2.1).


Figure 2.1. Transmission electron microscopy (TEM) image of Bi nanocrystals.

2.2.3. CuInSe₂ Nanowire Synthesis

A 1 M stock solution of Se in TOP (TOP:Se) was made by dissolving 1.58 g of Se powder in 20 mL of TOP. This solution was made in a glovebox under an inert atmosphere, stirred overnight to ensure that the Se was completely dissolved, and stored in the same glovebox.

30.6 mg of copper acetate (0.25 mmol), 70.3 mg of indium acetate (0.25 mmol), 0.25 mL of OA, and 4 mL of TOP were combined in a 25 mL three-neck flask. The flask was attached to a Schlenk line and degassed while heating to 100° C. After reaching 100° C, the solution was held under vacuum for 15 minutes and stirred vigorously. The flask was then filled with N₂ and cooled to room temperature under N₂ flow.

In a separate 50 mL three-neck flask, 8.5 mL of TOP was added, attached to the Schlenk line, and degassed under vacuum at room temperature for 5 minutes. The TOP

was heated to 360° C under N₂ flow (this describes a typical reaction; other temperature, solvent, and precursor combinations were tried as described later).

The Cu and In precursor solution was then combined with 0.5 mL of the 1 M TOP:Se stock solution and placed in a syringe. To initiate the reaction, 0.25 mL of a 5 mg/mL solution of Bi nanocrystals in toluene was swiftly injected into the hot TOP, followed immediately by the Cu, In, and Se precursor solution. The reaction mixture immediately turned from a light yellow color to dark brown with some black precipitate forming. The reaction proceeded for 5 minutes followed by removal of the heating mantle, allowing the products to cool to ~50°C.

10 mL of toluene was then injected into the flask, after which this solution was removed from the Schlenk line. To separate and clean the products, this mixture was centrifuged at 4000 RPM for 5 min. The supernatant was discarded and the precipitate redispersed in 30 mL of toluene. This cleaning procedure was repeated three times and the final product was redispersed in ~10 mL of toluene. Tens of milligrams of CIS nanowires are obtained from typical reactions.

2.2.4. Nanowire Photovoltaic Device Fabrication

PV devices were fabricated on soda lime glass substrates with a layered Au/CIS NW/CdS/ZnO/indium tin oxide (ITO) structure. Gold back contacts were deposited by radio-frequency (rf) sputtering (Lesker). CIS nanowires were deposited by spray coating from a toluene dispersion. The CdS buffer layer was deposited by chemical-bath deposition. Substrates were placed on a hot plate at 90°C, and then 0.9 mL of an aqueous solution of 1.25 mL of 0.015 M CdSO₄ (Aldrich, 99.999%), 2.2 mL of 1.5 M thiourea (Fluka, 99%), and 2.8 mL of 14.28 M NH₄OH (Fisher Scientific, Certified ACS) was placed on the substrate. After 2 min, the substrates were rinsed with de-ionized water

and dried in air. ZnO/ITO top contacts were deposited by rf sputtering from ZnO (99.9%, Lesker) and ITO (99.99% 90:10 In_2O_3/SnO_2 , Lesker) targets. The active region of the device was 8 mm².

2.2.5. Fabrication of CIS Nanowire Fabric

CIS nanowire fabric was made by vacuum-filtration. A dispersion of CIS nanowires was passed through a porous alumina filter (Whatman Anodisc 13, 0.2 μ m pores). The fabric on the filter was then dried in air for ~1hr, and removed from the filter with a tweezers. The thickness of the fabric could be adjusted by adding different amounts of dispersion before drying.

2.2.6. Materials Characterization

The nanowires were characterized by TEM, SEM and XRD. TEM images were obtained on 200 mesh carbon-coated Ni grids (Electron Microscopy Sciences) using a FEI Tecnai Spirit BioTwin operated at 80 kV. High-resolution TEM images and energy-dispersive X-ray spectroscopy (EDS) data were obtained using a JEOL 2010F transmission electron microscope operated at 200 kV and equipped with an Oxford INCA EDS detector. SEM images were obtained using gold-coated soda lime glass substrates with a Zeiss Supra 40 VP scanning electron microscope operated at 1-10 keV. XRD data were acquired on a Bruker-Nonius D8 Advance powder diffractometer using Cu Ka radiation ($\lambda = 1.54$ Å) with samples on quartz substrates, scanning at 12 deg/min in 0.02° increments.

PV devices were tested on a Karl Suss probe station and an Agilent 4156C parameter analyzer. J-V data and power conversion efficiencies were obtained using a Keithley 2400 General Purpose Sourcemeter and a Xenon Lamp Solar Simulator (Newport) with an AM 1.5 filter. Incident photon conversion efficiency (IPCE) data

were collected using a lock-in amplifier (Stanford Research Systems, model SR830), a monochromator (Newport Cornerstone 260 1/4M), and Si and Ge photodiodes calibrated by the manufacturer (Hamamatsu).

2.3 RESULTS AND DISCUSSION

2.3.1. CIS Nanowire Synthesis

Figure 2.2 shows TEM and SEM images of CIS nanowires synthesized by Bi nanocrystal-seeded SLS growth. Reactions were carried out by dispersing Bi nanocrystals in toluene and adding them to a flask of hot TOP at 360 °C in an oxygen-free atmosphere, followed immediately by the injection of a reactant solution of indium acetate, copper acetate and selenium in trioctylphosphine (TOP). After 5 minutes of reaction time, the nanowires have reached several micrometers in length, with an average diameter of around 20 nm. Most nanowires had Bi particles at their tips, as in Figure 1b, and reactions carried out without Bi nanocrystals did not yield nanowires (Figure 2.3), confirming that Bi nanocrystals were indeed seeding nanowire formation.



Figure 2.2. (a-d) TEM and (e) SEM images of CuInSe₂ (CIS) Nanowires



Figure 2.3. TEM image of aggregated CIS particles produced in control reaction with no Bi nanocrystal injection.

The nanowires are crystalline, as confirmed by TEM and XRD. Figure 2.4 shows a typical XRD pattern for a nanowire sample. The XRD of this nanowire sample is consistent with tetragonal (chalcopyrite) CIS, however, elemental analysis by energydispersive X-ray spectroscopy (EDS) showed that the nanowires were deficient in In, with an average composition of $Cu_{1.0}In_{0.6}Se_{2.0}$. The CIS nanowires made by this SLS process always tended to be In-deficient. Furthermore, only slightly modified reaction conditions led to CIS nanowires with the cubic phase. The cubic phase is structurally similar to chalcopyrite, but lacks positional cation order. XRD of chalcopyrite CIS exhibits additional reflections compared to sphalerite, like the (101) and (211) planes for example. The intensity of these two peaks is characteristically low, making it difficult in practice to distinguish between the two phases; however, nanowires could clearly be made with chalcopyrite phase, as confirmed by the XRD pattern in the inset in Figure 2.4 from CIS nanowires synthesized at 400 °C in squalane (rather than TOP), but most reaction conditions led to nanowires with sphalerite structure.



Figure 2.4. XRD of CIS nanowires synthesized with InCl₃ in TOP or indium acetate in squalane (inset, plotted on a logarithmic scale to elucidate the (101) and (211) peaks) The red reference pattern corresponds to chalcopyrite CIS (JCPDS no. 97-006-8928).

2.3.2. Twinning and Wurtzite Crystal Structure

The predominant growth direction of the nanowires was always perpendicular to the chalcopyrite (112) or sphalerite (111) lattice planes. Figure 2.2c shows a high resolution TEM image of a nanowire with lattice spacing of 0.33 nm, which corresponds to either the chalcopyrite (112) or cubic (111) d-spacing. Virtually all of the CIS nanowires made by the SLS process also exhibited significant twinning. Figure 2.2d shows an example of a nanowire with lamellar twinning and its characteristic zig-zag surface structure.²⁰ In some cases, the twinning was so extensive that it led to nanowires with wurtzite structure. Figure 2.5 shows XRD patterns of nanowires that have extra diffraction peaks at 20 of ~25°, 28°, and 37°. In a previous report of CIS nanowire synthesis, a Cu₃Se₂ impurity was observed;¹⁸ however, Cu₃Se₂ does not give rise to a peak at 37°, ruling out the possibility that Cu₃Se₂ was present in the nanowires synthesized here. We found that the diffraction pattern indexes well to wurtzite $CuInSe_2$ (Figure 2.5). This phase does not occur in bulk CIS, but has been observed in nanocrystals.^{21, 22} The formation of nanowires with wurtzite structure is also well-known for III-V compounds, like GaAs, InAs, and even Si, that have cubic structure in the bulk.²³⁻²⁵



Figure 2.5. XRD patterns of CIS nanowires synthesized at 400 °C (a), 360 °C (b), 270 °C (c), and 360 °C with HDA (d). The dashed blue reference pattern corresponds to chalcopyrite CIS (JCPDS no. 97-006-8928) and the red reference pattern was simulated with CaRIne Crystallography 3.1 software using space group P6₃mc and lattice parameters a = 4.08 Å and c = 6.69 Å.

Subtle changes in the reaction conditions had a significant effect on the quality, crystal phase and morphology of the nanowire product. Figure 2.6 shows TEM images of nanowire product obtained under different reaction conditions. The amount of wurtzite

phase was generally less at lower reaction temperature, and when HDA was added (Figure 2.5). CIS nanowires made with InCl₃ instead of indium acetate had cubic structure (Figure 2.4), but the nanowires exhibited a rough, saw-tooth morphology, as the TEM in Figure 2.6c shows. Nanowires grown at 400 °C in squalane were composed of chalcopyrite CIS, but the reaction product contained a significant amount of particulate byproduct (Figure 2.6a). Figure 2.6b shows that the nanowire morphology was greatly improved when TOP was added to the solvent (for a 50/50 mixture of TOP and squalane), but a small quantity of agglomerates still remained. The highest quality nanowires were synthesized at 360 °C with HDA added to the reaction. These nanowires had smooth surfaces (Figure 2.6d), little particulate byproduct and mostly the cubic phase (Figure 2.5, pattern d).



Figure 2.6. Low resolution transmission electron microscopy (LRTEM) and high resolution transmission electron microscopy (HRTEM; c, inset) images of CIS nanowires synthesized under various reaction conditions: (a) in squalane, (b) in a 50/50 vol% mixture of squalane and TOP, (c) in TOP with InCl₃ as the In source (instead of In(acac)₃), and (d) in TOP with added HDA.

2.3.3. CIS Nanowire Fabric

One aspect of the SLS growth CIS nanowires is its compatibility with industrial scale-up and capability of producing commercially relevant quantities of material. The relatively large quantity of CIS nanowires produced by this reaction allows for the fabrication of a non-woven semiconductor "fabric." This fabric is made by a simple vacuum filtration of a CIS nanowire dispersion. Figure 2.7 shows SEM images of the CIS nanowire paper. This semiconductor nanowire fabric represents an entirely new class of materials, and opens the possibility of creating novel flexible and lightweight inorganic solar cells. Experiments are currently being conducted to assess the viability of using this nanowire fabric as the active layer in photovoltaic devices.



Figure 2.7. SEM Images of CuInSe₂ nanowire fabric.

2.3.4 CIS Nanowire PV Performance

The nanowires were tested as the light-absorbing material in a solar cell to determine if the nanowire material is viable for that application. The PV test devices were fabricated with CIS nanowires in a layered architecture of Au/CIS NWs/CdS/ZnO/indium tin oxide (ITO). The CIS nanowires were deposited by spray coating a toluene dispersion. Figure 2.8 shows the PV response of a typical test device: the open-circuit voltage (V_{OC}) is 182 mV, the short-circuit current density (J_{SC}) is 1.847 mA/cm², the fill factor (FF) is 0.297, and the PCE (η) is 0.1% under AM 1.5 illumination.



Figure 2.8. Current voltage characteristics of a CIS nanowire PV device. Inset: roomtemperature UV-vis-NIR absorbance spectrum of CIS nanowires dispersed in toluene. The optical gap of approximately 1 eV corresponds to the bulk literature value of 0.95 – 1.05 eV for CIS.²⁶

The incident photon conversion efficiency (IPCE) of the CIS nanowire devices was also measured. Figure 2.9 shows the IPCE of a typical CIS nanowire device. Although the IPCE of the device is low, there is photocurrent generation at wavelengths longer than 510 nm (the band-edge wavelength of CdS), proving that the CIS nanowires are the photo-active material in the device.



Figure 2.9. IPCE spectrum of a typical CIS nanowire PV device, measured at zero bias.

The PV response of the nanowire devices provides a proof-of-principle that these materials can perform in solar cells. The relatively poor performance of the devices is due to a variety of factors related to the device itself. The low values of V_{OC} and FF are due in part to low shunt resistance caused by voids in the nanowire film. Although the nanowire films were relatively uniform—Figure 2.2e shows an SEM image of a nanowire film—there were voids in the layer, which lead to a low shunt resistance under light. The nanowire orientation is also not optimized. Nanowires lay parallel to the electrode interface with a random orientation as a tangled mat. Charge separation would be better with nanowires spanning directly between the two electrodes. For these purposes, the

nanowires made here are probably too long. Furthermore, defects in the nanowires could be contributing to the poor device characteristics. For example, twinning in nanowires has been shown to be detrimental to carrier transport,²⁷ and vacancies related to In deficiency in the nanowires could also inhibit device performance. Ideally, phase–pure, twin-free, stoichiometric chalcopyrite CIS nanowires are desired. The phase purity of the nanowires depends rather sensitively on the reaction temperature and the presence of surfactants such as HDA, while the morphology was affected by reaction temperature, solvent and the choice of precursor and requires more optimization.

2.4. CONCLUSIONS

In summary, this is a first report of PV device fabrication incorporating solutionprocessed CIS nanowires. While the efficiency of these devices needs improvement, the absorber layer was not annealed or chemically treated in any way. Further synthetic improvements and optimization of the device fabrication should lead to PCE enhancement. There are also opportunities to combine nanowires with other materials, like nanocrystals or organics as well, to generate bulk heterojunction devices based on these nanowires. Another interesting concept is to create non-woven fabrics from semiconductor nanowires,²⁸ which in this case of CIS might be used to create lightweight and flexible PV device structures to generate power from the sun.

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Chapter 3: Pyrite Nanocrystal Solar Cells: Promising, or Fool's Gold?*

3.1. INTRODUCTION

Pyrite (FeS₂) was first explored as a photovoltaic (PV) semiconductor in the mid-1980's,¹⁻³ but there has been renewed interest in this material recently,⁴⁻¹⁰ as other thin film absorber materials like amorphous silicon, CdTe and Cu(In,Ga)Se₂ (CIGS) have gained commercial success.^{11,12} The resurgent interest in pyrite stems from its low toxicity, high abundance and low raw materials cost.⁴⁻¹⁰ Fe and S are some of the most inexpensive and earth-abundant raw materials available,^{13,14} even cheaper than other low cost alternatives such as copper sulfide and copper oxide.¹⁵.

Pyrite has properties suitable for PVs, with a band gap of 0.95 eV and very strong optical absorption, with absorption coefficients of around 10^5 cm⁻¹.³ Pyrite films can be deposited by vapor-phase methods^{1,2} or solution-based methods using colloidal nanocrystals.^{4-6,8} Some studies of vapor-deposited pyrite PVs have reported power conversion efficiency (PCE) of almost 3%, but with very low V_{oc} (~0.2 V).³ The use of colloidal pyrite nanocrystals for solution deposition under ambient conditions could enable extremely low manufacturing cost with continuous, roll-to-roll processing. There has been extensive research on nanocrystal-based solar cells during the past few years¹⁶⁻¹⁸ with power conversion efficiency (PCE) reaching up to 6% in some cases,¹⁹ and recently, robust synthetic methods for pyrite nanocrystals have been developed,⁵ yet little data has been reported for PV devices made with pyrite nanocrystals.

[†] Portions of this chapter appear in: Steinhagen, Chet; Harvey, Taylor B.; Stolle, C. Jackson; Harris, Justin; Korgel, Brian A., **Pyrite Nanocrystal Solar Cells: Promising or Fool's Gold?** *Journal of Physical Chemistry Letters* (2012), 3, 2352-2356. Taylor and Jackson assited with device fabrication, Justin helped with Raman analysis, and Dr. Korgel was the principal investigator.

Here we report the performance of PVs made with several different device structures using pyrite nanocrystals synthesized using procedures developed by Law's group.⁶ None of the device structures tested exhibited a PV response. Many of the other Fe-S compounds are metallic and composition and phase impurity can be a problem, however both X-ray diffraction (XRD) and Raman spectroscopy confirmed the pyrite phase purity of the nanocrystal films used in the devices. Based on these results it appears that pyrite nanocrystals are not well-suited for PVs.

3.2. EXPERIMENTAL METHODS

3.2.1. Chemicals

All chemicals were used as received. Iron (II) chloride (FeCl₂, 99%) tetrahydrate, octadecylamine (97%), elemental sulfur powder (99.98%), and diphenyl ether (99%) were obtained from Aldrich; chloroform, toluene, and ethanol from Fisher Scientific.

3.2.2. Pyrite Nanocrystal Synthesis

Following the procedures of Ref. 5, pyrite nanocrystals were synthesized by combining 100 mg FeCl₂ tetrahydrate and 10 g octadecylamine and heating and degassing at 120°C on a Schlenk line. In a separate flask, 96 mg sulfur powder and 5 mL diphenyl ether (Sigma-Aldrich, 99%) were mixed and degassed at 70°C. The FeCl₂ solution was then heated to 220°C under nitrogen and the sulfur reactant solution was rapidly injected. After 3 hours at 220°C, the heating mantle was removed and the reaction flask was cooled in a water bath. Once the solution reached 100°C, chloroform (10 mL) was added. The nanocrystals were finally purified by solvent/antisolvent precipitation using toluene and ethanol.

Other synthetic strategies for pyrite nanocrystals were also attempted, including the use of different Fe precursors, capping ligands, and reaction temperature. Iron pentacarbonyl, iron acetylacetonate, iron nitrate (combined with sulfur in various solvents such as oleylamine, benzyl ether, and squalane) failed to yield dispersible pyrite particles. These reactions formed very large (hundreds of nm) particles of Troilite (FeS) and Greigite (Fe₃S₄). Common capping ligands such as oleylamine, dodecanethiol, and trioctylphosphine oxide (TOPO) were also explored in conjunction with these precursors and did not yield dispersible pyrite nanocrystals, only large particles of FeS and Fe₃S₄. Even the use of the appropriate reactant mixture, but injection temperature higher than 220° C, yielded nanocrystals of FeS and Fe₃S₄ and not pyrite. As Law and coworkers have also mentioned,⁶ the combination of 220° C reaction temperature and octadecylamine capping ligand and FeCl₂ are critical to obtaining dispersible, phase purepyrite nanocrystals.

3.2.3. Materials Characterization

Transmission electron microscopy (TEM) images were obtained on 200 mesh carbon-coated Cu grids (Electron Microscopy Sciences) using a FEI Tecnai Spirit BioTwin operated at 80 kV. High-resolution TEM images were obtained using a JEOL 2010F transmission electron microscope operated at 200 kV. Scanning electron microscopy (SEM) images were obtained with a Zeiss Supra 40 VP scanning electron microscope operated at 1-10 keV. X-Ray diffraction (XRD) data were acquired on a Rigaku R-Axis Spider diffractometers with image-plate detector using Cu K α radiation (λ = 1.54 Å).

PV devices were tested on a Karl Suss probe station and an Agilent 4156C parameter analyzer. J-V data and power conversion efficiencies were obtained using a

Keithley 2400 General Purpose Sourcemeter and a Xenon Lamp Solar Simulator (Newport) with an AM 1.5 filter.

Raman spectroscopy was conducted on a Renishaw inVia Microscope with a 514.5 nm Argon laser in backscattering configuration. The instrument was calibrated to the Stokes Raman signal at 521 cm⁻¹ for a bulk single crystal of Si with the [110] direction oriented normal to the laser. The beam was focused on the sample using an optical microscope with a 50x objective lens. Samples were prepared by dropcasting the particles from chloroform dispersions onto glass slides. Spectra were obtained by single scans from 100-2000 cm⁻¹ for 300 sec at 1% (0.035 mW) laser power. Single scans from multiple areas of each sample yielded reproducible Raman spectra.

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was carried out by dissolving pyrite nanocrystals in nitric acid and using a SpectroCIROS ICP-AES instrument (Spectro Analytical Instruments, Marble Hill, TX).

3.3. RESULTS

3.3.1. Pyrite Nanocrystals

Figure 3.1 shows characterization data for the nanocrystals, including TEM and XRD. The nanocrystals are 14.8±3.6 nm in diameter with a rounded, slightly non-spherical shape and crystalline. XRD (Figure 3.1c) showed that the nanocrystals are composed only of pyrite FeS₂, accounting for all of the observed diffraction peaks. No other iron-sulfur related phases, such as pyrrhotite (Fe_{1-x}S), troilite, or greigite were observed. The optical absorption edge near 1.0 eV (Figure 1c, inset) is also characteristic of pyrite.^{6,7} Inductively coupled plasma atomic emission spectroscopy (ICP-AES) indicated that the nanocrystals were slightly sulfur deficient with average composition of

 $\text{FeS}_{1.9}$; however, Raman spectra showed only the characteristic pyrite peaks at 340, 378, and 426 cm⁻¹.^{7,8,20} Raman spectroscopy is very sensitive to phase and composition and gave no indication of other Fe-S phases in the sample.



Figure 3.1. Characterization of pyrite FeS₂ nanocrystals. (a) TEM image of a field of pyrite FeS₂ nanocrystals. (b) High-resolution TEM images of a single pyrite nanocrystal, showing crystallinity. (c) XRD of pyrite nanocrystals. The pyrite reference pattern is shown as red lines (JCPDS #03-065-1211). Crystal planes of reference pattern are in parentheses. Inset: Room temperature UV-vis-NIR absorbance spectrum of pyrite nanocrystals dispersed in chloroform. (d) Raman spectrum of pyrite nanocrystals on a glass substrate.

3.3.2. Pyrite Nanocrystal PV Performance

The pyrite nanocrystals were tested as the light-absorber layer in PV devices. Various device architectures have been explored for semiconductor nanocrystals, including Schottky junction,^{21,22} heterojunction,²³⁻²⁷ and hybrid organic/nanocrystal devices.^{5,28,29}

For all test device structures (except the hybrid device), thin films of pyrite nanocrystals were deposited from chloroform dispersions using an airbrush. The films were sprayed onto substrates to obtain opaque, black films approximately 2.5 µm thick. Figures 3.2a and 3.2b show SEM images of the films. There is a significant amount of agglomeration, which is not optimal for device fabrication, however the substrate is well-covered and there are no pin-holes or cracks that could lead to device shorting.



Figure 3.2. SEM images of spray-coated films of pyrite nanocrystals.

Devices were tested by sweeping from -1 to 1 V with a Keithley sourcemeter and measuring the current output. All devices other than the Schottky structure were tested both in the dark and under AM 1.5 conditions using a Xenon lamp solar simulator (Newport), inside a N_2 filled glovebox.

3.3.2.1. Schottky Barrier

The earliest PVs made with pyrite were Schottky diodes with Au and Ni contacts.¹ Since pyrite thin films have been reported recently to be p-type,⁷ we used a lower work function electrode of Al to make Schottky diode test structures with a nanocrystal absorber layer. The Schottky diode structure was fabricated by spray-coating pyrite nanocrystals onto gold (60 nm thick, deposited by thermal evaporation) coated glass substrates followed by deposition of Al (150 nm thick by thermal evaporation). Figure 3.2 shows SEM images of this pyrite nanocrystal film. As shown in Figure 3.3, the Schottky devices exhibited ohmic IV curves without a PV response.



Figure 3.3. Device schematic and current-voltage characteristics of a Schottky barrier device.

3.3.2.2. Heterojunction

Since the Schottky junction devices did not work, we explored the device structure illustrated in Figure 3.4. We tested a layered structure of Au/nanocrystal film/CdS/ZnO/indium tin oxide (ITO), which has been successful with other nanocrystals like CuInSe₂ and Cu₂ZnSnS₄.^{16,26} The Au/nanocrystal layers were fabricated in the same manner as for the Schottky devices, followed by deposition of a CdS buffer layer by chemical bath deposition,²⁵ and top layers of ZnO and ITO by rf sputtering. These devices also yielded no power output, as shown in Figure 3.4. These devices exhibited slightly S-shaped IV curves with some limited current rectification and photocurrent but no PV response.



Figure 3.4. Device schematic and current-voltage characteristics of typical CIS (heterojunction) device structure.

3.3.2.3. Depleted Heterojunction

Depleted heterojunction devices²⁷ were also made. A layer of TiO₂ forms a heterojunction with the nanocrystal layer and serves as a hole blocking layer to limit carrier recombination while also creating a depletion region in the nanocrystal layer. This type of structure has enabled some of the highest efficiencies of any nanocrystal solar cell to date with power conversion efficiencies of 6% using lead chalcogenide nanocrystals.¹⁹ The TiO₂ layer was deposited onto glass substrates by spin coating from a TiO₂ nanocrystal dispersion (Dyesol) diluted with terpineol using established protocols.²⁷ Pyrite nanocrystals were spray-coated onto the TiO₂ layer and 60 nm of gold was thermally evaporated through a shadow mask as the top contact. This device structure led to more current rectification than the other device structures and photocurrent was produced, but no PV response was observed (Figure 3.5).



Figure 3.5. Device schematic and current-voltage characteristics of a "Depleted Heterojunction" structure.

3.3.2.4 Hybrid

Finally, hybrid organic/pyrite nanocrystal device structures were tested with poly(3-hexylthiophene) (P3HT). This type of approach was recently reported to give a power conversion efficiency of 0.16%.⁵ A layer of poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) was spin-cast onto a glass substrate to serve as the hole transport layer and to form a smooth surface onto which the active layer was deposited. A blend of pyrite nanocrystals and P3HT was then spin-coated on top of the PEDOT:PSS and briefly annealed at 110°C on a hotplate in a N₂ filled glovebox to form this active layer. 100 nm of Al was thermally evaporated through a shadow mask to form the top contact. Figure 3.6 shows the IV data for this device. There was no PV response and less photocurrent than the other device structures in Figure 3.4 and 3.5.



Figure 3.6. Device schematic and current-voltage characteristics of an organic/nanocrystal hybrid device

3.4. DISCUSSION

All of these device structures are fairly well established for nanocrystals, and a variety of different nanocrystal materials, including lead chalcogenides,^{21,22} cadmium²⁹ and copper chalcogenides,³⁰ CIGS,²⁵ and CZTS,²⁶ have been used to make functioning PVs.³¹ We measured the electrical conductivity of the pyrite nanocrystal films and compared to typical semiconductor nanocrystal films, the pyrite nanocrystal films were found to be much more electrically conductive with conductivities in the range of 4.5 S/cm—several orders of magnitude higher than most semiconductor nanocrystal films,³² and on par with some metal nanocrystal films.³³ While it is desirable to have charge transport that is efficient enough for effective electron and hole separation, conductivities in this range indicate that the pyrite nanocrystals are either degenerately doped or metallic, which is detrimental to solar cell performance. The observation of some photocurrent indicates that the pyrite nanocrystals are most likely semiconducting, but very highly doped.

Sulfur vacancies and phase impurities (such as FeS, Fe_{1-x}S, and marcasite FeS₂) have been cited as potential problems for pyrite solar cells, as these phase impurities have small band gap that could lower V_{OC} even if present in low concentrations.⁴ The XRD and Raman spectra showed that there were no other phases present in the nanocrystal films. Some researchers suggested that sulfur vacancies pinned the Fermi level of the pyrite layer to limit V_{oc} ;^{3,4,7,34} however, pyrite is a line compound,³⁵ and bulk sulfur vacancies have been shown to be unlikely.³⁶ Furthermore, recent calculations indicated that sulfur vacancies in the bulk of the material should not even lead to Fermi level pinning.³⁶ The ICP-AES measurements of the nanocrystals did show that the material was slightly sulfur deficient and since no phase impurities were detected, this deficiency must be associated with the nanocrystal surfaces. This would make sense in terms of the

very high electrical conductivity of the pyrite nanocrystal films. Yu et al.³⁶ recently reported theoretical and experimental results indicating that pyrite surfaces decompose into sulfur deficient phases with high vacancy and carrier concentration leading to low electrical resistivity (0.1-0.7 Ω cm). The electrical measurements of the nanocrystal films (4-5 S/cm) are consistent with the very high concentration of interface sulfur vacancies predicted by Yu et al.³⁶

3.5. CONCLUSIONS

So, it appears that while pyrite has suitable optical properties for PVs and extremely low raw materials costs, its electrical properties may be difficult to control properly due to the formation of surface defects related to sulfur vacancies. This problem might be exacerbated in nanocrystal devices due to the very high concentration of interfaces. A better understanding of crystal surface and grain boundary properties is necessary to improve V_{OC} and PCE, and this work shows that it might be very difficult to ever realize reasonable efficiency in pyrite-based PVs.

3.6. REFERENCES

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Chapter 4: Synthesis of Cu₂ZnSnS₄ Nanocrystals for Use in Low-Cost Photovoltaics[‡]

4.1. INTRODUCTION

New photovoltaic (PV) materials and manufacturing approaches are needed to meet the demand for lower cost solar cells.^{1,2} Cu₂ZnSnS₄ (CZTS) is one promising new material.^{2,3} Its crystal structure and optical properties (~1.5 eV band gap energy; absorption coefficient of ~10⁴ cm⁻¹) are similar to Cu(In,Ga)Se₂ (CIGS), one of the most successful thin film PV materials with demonstrated PCEs of nearly 20% and commercial use.^{3,4} But unlike CIGS, which requires relatively rare In and Ga, CZTS is composed of abundant elements.^{2,3} CZTS PV devices have been made with power conversion efficiencies (PCE's) of up to 11.1%.⁵

The highest efficiency PV devices of CIGS and CZTS are obtained by vapor deposition, which imposes a substantial cost on the technology.¹ Alternative processing strategies with reasonable success have included electrochemical and chemical solution deposition.⁵⁻⁸ These techniques, however, still require relatively demanding processing conditions such as high temperature reactive sintering or the use of harsh chemicals like hydrazine, to reach reasonable efficiencies.⁵⁻⁸ A different approach is to pre-fabricate the PV material as a nanocrystal dispersion—a solar paint—that can be printed, sprayed or dip-coated, ideally without the need for intensive post-deposition processing.⁹⁻¹⁸ These

[‡] Portions of this chapter appear in: Steinhagen, Chet; Panthani, Matthew G.; Akhavan, Vahid; Goodfellow, Brian; Koo, Bonil; Korgel, Brian A., **Synthesis of Cu₂ZnSnS₄ Nanocrystals for Use in Low-Cost Photovoltaics.** *Journal of the American Chemical Society* (2009), 131(35), 12554-12555. Matthew assisted with nanocrystal synthesis, Vahid and Brian helped with device fabrication, Bonil assisted with nanocrystal imaging, and Dr. Korgel was the principal investigator.
paints could enable continuous roll-to-roll processing under mild conditions on nearly any type of surface.

Recently, CIGS nanocrystals have been synthesized with controlled stoichiometry and used to fabricate PV devices with reasonable efficiencies.^{11,12,15} In contrast, CZTS nanocrystal synthesis has not been reported. Here, we demonstrate CZTS nanocrystal synthesis and their implementation in functioning PV devices.

4.2. EXPERIMENTAL METHODS

4.2.1. Chemicals

All chemicals were used as received. Copper (II) Acetylacetonate ($Cu(acac)_2$, 99.99+%), zinc acetate (99.99%), Tin (II) Chloride ($SnCl_2$, 99.99+%), elemental sulfur powder (S, 99.98%), Cadmium sulfate ($CdSO_4$, 99.999%), and Oleylamine (OLA, technical grade) were obtained from Aldrich; thiourea (99%) was obtained from Fluka; and ammonium hydroxide (NH_4OH , certified ACS), chloroform, toluene, and ethanol were obtained from Fisher Scientific.

4.2.2. CZTS Nanocrystal Synthesis

The CZTS nanocrystals are made by high temperature arrested precipitation in the coordinating solvent, OLA. In a typical reaction, 0.52 g of $Cu(acac)_2$, 0.29 g of zinc acetate, 0.18 g of SnCl₂, and 0.13 g of S are added to 40 mL of OLA in a 100 mL three-neck flask on a Schlenk line. After degassing under vacuum for 2 hours and purging with N₂ for 30 min at 110 °C, the reaction mixture is heated to 280 °C for 1 hr. After cooling to room temperature, the nanocrystals are isolated by precipitation with ethanol, followed by centrifugation. Solid reaction byproducts and poorly capped nanocrystals are removed by redispersion in chloroform and centrifugation at 8,000 rpm for 2 min. The

nanocrystals are washed three more times by solvent/antisolvent precipitation with chloroform/ethanol. A typical reaction yields ~200 mg of nanocrystals.

4.2.3. Nanocrystal Photovoltaic Device Fabrication

PV devices were fabricated on soda lime glass substrates. Gold back contacts were deposited by radio frequency sputtering (Lesker). CZTS nanocrystals were deposited by spray coating from a toluene dispersion (20 mg/mL) using a standard artist's airbrush. The CdS buffer layer was deposited by chemical bath deposition: substrates were placed on a hot plate at 90 °C. 0.9 mL of an aqueous solution of 1.25 mL of 0.015 M CdSO₄; 2.2 mL of 1.5 M thiourea, and 2.8 ml of 14.28 M ammonium hydroxide was placed on the substrate. After 2 min, the substrates were rinsed with DI water and dried in air. ZnO/ITO top contacts were deposited by rf sputtering from ZnO (99.9%, Lesker) and ITO (99.99% In₂O₃:SnO₂ 90:10, Lesker) targets. The active region of the device was 8 mm².

4.2.4. Materials Characterization

The nanocrystals were characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), and X-Ray diffraction (XRD). TEM images were obtained on 200 mesh carbon-coated Ni grids (Electron Microscopy Sciences) using a FEI Tecnai Spirit BioTwin operated at 80 kV. High-resolution TEM images and energy-dispersive X-ray spectroscopy (EDS) data were obtained using a JEOL 2010F transmission electron microscope operated at 200 kV and equipped with an Oxford INCA EDS detector. SEM images were obtained using gold-coated soda lime glass substrates with a Zeiss Supra 40 VP scanning electron microscope operated at 1-10 keV. XRD data were acquired on a Bruker-Nonius D8 Advance powder diffractometer using Cu Ka radiation ($\lambda = 1.54$ Å) with samples on quartz substrates, scanning at 12 deg/min in 0.02°

increments. Scanning transmission electron microscopy (STEM) images and EDS mapping was obtained on a Tecnai G2 F20 X-Twin microscope at an accelerating voltage of 200 kV.

PV devices were tested on a Karl Suss probe station and an Agilent 4156C parameter analyzer. J-V data and power conversion efficiencies were obtained using a Keithley 2400 General Purpose Sourcemeter and a Xenon Lamp Solar Simulator (Newport) with an AM 1.5 filter.

4.3. RESULTS AND DISCUSSION

4.3.1. CZTS Nanocrystals

Figure 4.1 shows TEM and SEM images of a typical CZTS nanocrystal sample. The particles are crystalline and have an average diameter of 10.6 ± 2.9 nm, with a slightly irregular, faceted shape.



Figure 4.1. (a,b) TEM and (c) SEM images of CZTS nanocrystals. In (b), the nanocrystal is imaged down the [-1 1 0] crystallographic zone axis.

XRD (Figure 4.2) showed that the nanocrystals are composed of CZTS with kesterite structure.^{19,20} Kesterite has a tetragonal unit cell, with sulfur atoms located in a face-center cubic sublattice. The Cu, Zn and Sn atoms occupy half the tetrahedral interstitial sites within the S sublattice, with compositional order.¹⁹ Similar to

chalcopyrite CIGS, kesterite CZTS exhibits diffraction peaks in addition to those observed from the compositionally disordered sphalerite compound, such as the (101) and (211) peaks.^{19,21}



Figure 4.2. XRD of CZTS nanocrystals. The red reference pattern was simulated using CaRIne Crystallography 3.1 software using space group I4 and lattice parameters a=b=5.427 Å and c=10.848 Å for kesterite CZTS (JCPDS #26-0575).

The average composition of the nanocrystals determined by EDS analysis of 25 nanocrystals was $Cu_{2.08}Zn_{1.01}Sn_{1.20}S_{3.70}$ - the nanocrystals are slightly tin-rich and sulfur-deficient.

STEM-EDS elemental mapping of a field of nanocrystals (Figure 4.3) confirmed that Cu, Zn, Sn and S are evenly distributed among the nanocrystals and that there is no noticeable compositional distribution between the nanocrystals. The band gap energy determined from absorbance spectra of a nanocrytal dispersion (Figure 4.4, inset) is 1.3 eV, which is close to the bulk literature value of ~1.5 eV for CZTS.²²



Figure 4.3. STEM-EDS elemental map of CZTS nanocrystals.



Figure 4.4. Current-Voltage characteristics of a CZTS nanocrystal PV device. (Inset) Room temperature UV-vis-NIR absorbance spectrum of CZTS nanocrystals dispersed in toluene.

4.3.2. CZTS Nanocrystal PV Performance

PV devices were fabricated with the CZTS nanocrystals. Like CIGS, CZTS films are typically p-type,³ and test devices were fabricated with a layered structure composed of Au/CZTS/CdS/ZnO/indium tin oxide (ITO). The CZTS layer was deposited by spray coating from a toluene dispersion. The nanocrystal layer was not annealed or chemically

treated in any way. Figure 4.4 shows the PV response of a typical device, having an open circuit voltage (V_{OC}) of 321 mV, a short circuit current density (J_{SC}) of 1.95 mA/cm², fill factor (*FF*) of 0.37, and a power conversion efficiency η , was 0.23% under AM 1.5 conditions.

4.4. CONCLUSIONS

In summary, a synthetic method for producing CZTS nanocrystals has been developed. PV devices fabricated with these CZTS nanocrystals exhibited PCEs of up to 0.23%. While the efficiency of these devices is low, the absorber layers were not processed after deposition with any high-temperature or chemical means. Further optimization of the synthesis and device fabrication should lead to increases in PV efficiency.

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Chapter 5: Synthesis of Cu₂ZnSnS₄ Nanorods and Perpendicular Alignment

5.1. INTRODUCTION

As described in Chapter 4, Cu_2ZnSnS_4 (CZTS) is an interesting earth-abundant alternative material to $CuIn_x(Ga)_{1-x}Se_2$ (CIGS) for photovoltaic (PV) applications.¹⁻¹² Low-cost, solution-processable, and high-thoughput manufacturing methods are required to drive down fabrication costs, and "solar paints" of nanocrystal dispersions are a promising route to this technology.¹³⁻²⁵

However, the nanocrystal devices described in Chapter 4 suffer from poor electronic transport characteristics. The large number of surfaces and grain boundaries present in a nanocrystal film increases the likelihood of recombination. Photogenerated holes and electrons must hop from nanocrystal to nanocrystal as they move through the active layer, which limits their mobility, and limits the maximum thickness of this layer in photovoltaic devices.²⁶⁻²⁸

Unlike layers of nanocrystals, individual nanorods do not have grain boundaries along their length.^{29, 30} Additionally, nanorods can also be dispersed in various solvents to form solar paints and deposited on substrates under low-temperature and atmospheric conditions. As such, by utilizing nanorods, recombination can be reduced, carrier mobility can be increased, and device performance enhanced while still maintaining solution-processability and scalability.³¹⁻³³ In an ideal case, all nanorods making up the absorber layer in a solar cell would be perpendicularly aligned to the substrate, spanning the entire thickness of the active layer, as depicted in the cartoon in Figure 5.1.^{31, 33, 34}



Figure 5.1. Idealized cartoon of a PV device using perpendicularly aligned CZTS nanorods as the active layer in a standard device architecture.

Recently, CZTS nanorods have been synthesized using an arrested precipitation reaction scheme.³⁵ We explored this approach to produce CZTS nanorods and disperse them to form solar paints. This solar paint was used to spray coat thin films of CZTS nanorods and incorporated, for the first time, in functioning PV devices.

Small-scale perpendicular alignment of the CZTS nanorods was also achieved via dropcasting.

5.2. EXPERIMENTAL METHODS

5.2.1. Chemicals

All chemicals were used as received. Copper (II) acetylacetonate (Cu(acac)₂, 99.99+%), zinc (II) acetate (99.99%), tin (IV) acetate (no purity provided, product number 345172), 1-octadecene (ODE, 90%), *tert*-dodecylmercaptan (t-DDM, 98.5%), 1-

dodecanethiol (1-DDT, >=98%), trioctylphosphine oxide (TOPO, 99%), and cadmium sulfate (CdSO₄, 99.999%), were obtained from Aldrich; thiourea (99%) was obtained from Fluka; and ammonium hydroxide (NH₄OH, certified ACS), chloroform, toluene, and ethanol were obtained from Fisher Scientific.

5.2.2. CZTS Nanorod Synthesis

CZTS nanorods were synthesized by a high-temperature anisotropic arrested precipitation reaction carried out on a standard Schlenk line, following a similar procedure described by Ryan et. al.³⁵

To begin the synthesis, 0.261 g Cu(acac)₂, 0.91 g zinc acetate, 0.177 g tin acetate, 1.353 g TOPO, and 10 mL ODA were combined in a 50 mL flask.

This flask was connected to a standard Schlenk line, placed under vacuum, heated to 60°C, and degassed for 45 min. The heating mantle was then set to 250°C and the reaction flask was placed under N_2 flow. Once the temperature reached 155°C, a mixture of 0.25 mL 1-DDT and 1.75 mL t-DDM was quickly injected into the flask.

When the solution reached 250°C, it was held at that temperature and the reaction was allowed to proceed for 22.5 minutes. Following this, the heating mantle was removed to quench the reaction mixture.

When the products had cooled to ~100°C, 3 mL of toluene was injected into the flask, and at ~50°C, 3 mL of ethanol was added. Standard solvent (toluene) / antisolvent (ethanol) methods were used to wash the products, and centrifugation was used to isolate the nanorods. The final, washed nanorods were dispersed in toluene. This dispersion was used to dropcast samples for TEM and XRD analysis, as well as to spray coat thin films during device fabrication.

5.2.3. CZTS Nanorod Photovoltaic Device Fabrication

PV devices were fabricated on soda lime glass substrates. Gold back contacts were deposited by radio frequency sputtering (Lesker). CZTS nanorods were deposited by spray coating from a toluene dispersion (~20 mg/mL) using a standard artist's airbrush. The CdS buffer layer was deposited by chemical bath deposition: substrates were placed on a hot plate at 90 °C. 0.9 mL of an aqueous solution of 1.25 mL of 0.015 M CdSO₄; 2.2 mL of 1.5 M thiourea, and 2.8 ml of 14.28 M ammonium hydroxide was placed on the substrate. After 2 min, the substrates were rinsed with DI water and dried in air. ZnO/ITO top contacts were deposited by rf sputtering from ZnO (99.9%, Lesker) and ITO (99.99% In₂O₃:SnO₂ 90:10, Lesker) targets. The active region of the device was 8 mm².

5.2.4. CZTS Nanorod Alignment

CZTS nanorod perpendicular alignment experiments were conducted by varying the nanorods washing procedure and adjusting nanorods concentration in the final dispersion. Various concentrations were dropcast onto TEM grids in the attempt to get perpendicular alignment.

5.2.5. Materials Characterization

The nanocrystals were characterized by transmission electron microscopy (TEM), UV-Vis-NIR spectroscopy, and X-Ray diffraction (XRD), TEM images were obtained on 200 mesh carbon-coated Ni grids (Electron Microscopy Sciences) using a FEI Tecnai Spirit BioTwin operated at 80 kV. X-Ray diffraction (XRD) data were acquired on a Rigaku R-Axis Spider diffractometer with an image-plate detector using Cu K α radiation ($\lambda = 1.54$ Å). UV-vis-NIR spectroscopy data was acquired using a Varian Cary 500

UV-vis-NIR spectrophotometer. Nanorods were dispersed in toluene, and data was acquired at room temperature.

PV devices were tested on a Karl Suss probe station and an Agilent 4156C parameter analyzer. J-V data and power conversion efficiencies were obtained using a Keithley 2400 General Purpose Sourcemeter and a Xenon Lamp Solar Simulator (Newport) with an AM 1.5 filter.

5.3. RESULTS AND DISCUSSION

5.3.1. CZTS Nanorods

Figure 5.2. shows a TEM image of a typical CZTS nanorod sample. The nanorods have an average diameter of 7.8 ± 1.6 nm and an average length of 20.7 ± 4.3 nm. The nanorods disperse well in nonpolar solvents such as chloroform and toluene; they do not aggregate, as can be seen in Figure 5.2.



Figure 5.2. TEM image of CZTS nanorods.

The UV-vis-NIR absorbance spectrum of a CZTS nanorods dispersion is shown in Figure 5.3.



Figure 5.3. UV-vis-NIR absorbance spectrum of a CZTS nanocrystal dispersion in toluene. The inset shows the same data, plotted as $(\alpha hv)^2$ vs. hv (Tauc plot) in order to more clearly see the absorption onset.

The absorption onset of the nanorods is ~ 900 nm. However, there is a tail that extends out into the NIR, most likely due to the sample not being completely washed. By plotting the data as $(\alpha hv)^2$ vs. hv, the linear region can be extrapolated and it can clearly be observed that the band-gap energy is ~1.4 eV. This is in good agreement with bulk CZTS.^{35, 36}

The XRD pattern of the CZTS nanorods does not match that of stannite or kesterite crystal phases, the most common phases of this material in bulk (and nanocrystal) samples.^{15, 37} Additional peaks are present that match that of a wurtzite (hexagonal phase) crystal structure (Figure 5.4). The reference pattern shown in Figure 5.4 is a simulated XRD pattern, created using the CaRIne Crystallography 3.1 software package. The lattice parameters used for this simulation were a = 3.2 Å and c = 6.3 Å.



Figure 5.4. XRD pattern of CZTS nanorods. The blue reference pattern was simulated with CaRIne Crystallography 3.1 software.

While a wurtzite phase is not observed in bulk samples of CZTS, it has been shown for other similar materials systems (such as CIS) that hexagonal phases can be accessed in the nanoscale (i.e., in nanocrystals, nanorods, and nanowires), even though bulk material has a cubic or tetragonal structure.³⁸⁻⁴⁰

Furthermore, nanorods are typically observed to have a hexagonal crystal structure. The asymmetry allows the crystal to grow anisotropically – in this case, along the c-axis. This behavior is common in well-studied materials such as cadmium chalcogenides., and has more recently been observed in CIS nanorods.⁴¹⁻⁴⁴

In order to get anisotropic growth – to synthesize nanorods instead of nanocrystals – the combination of both 1-DDT and t-DDM was found to be critical, in agreement with Ryan et. al.³⁵ For example, reactions carried out with only t-DDM yielded only aggregated clusters of spherical nanocrystals (Figure 5.5). This suggests that these capping ligand bind preferentially to the side facets of the growing nanorod, allowing for anisotropic growth. Other capping ligands, such as oleylamine, result in nanocrystals, as described in other reports.^{15, 45}



Figure 5.5. TEM image of aggregated CZTS nanocrystals.

Additionally, other reaction conditions were found to affect the morphology of the nanorods. Figure 5.6 shows a TEM image of CZTS nanorods made with a higher concentration of precursors in the reaction flask. In this reaction, 2 mL of ODA was used as a solvent, instead of 10 mL. This reaction resulted in highly dispersible, smaller "ricelike" nanorods.



Figure 5.6. TEM image of smaller, "ricelike" CZTS nanorods.

5.3.2. CZTS Nanorod PV Performance

The nanorods were tested as the active layer in a solar cell to determine if the material is suitable for that application. The test structures were fabricated in a layered architecture consisting of Au/CZTS Nanorods/CdS/Zno/ITO. The CZTS nanorod layer was spray coated from a toluene dispersion. Contact was made to the ITO layer via silver paint. Figure 5.7 shows the current density-voltage (J-V) response of a typical device.



Figure 5.7. Current voltage characteristics of a CZTS nanorods PV device.

The open-circuit voltage (V_{OC}) is 341 mV, the short-circuit current density (J_{SC}) is 1.26 mA/cm², the fill factor (FF) is 0.42, and the power conversion efficiency (PCE, η) is 0.18%.

Figure 5.8. shows the J-V characteristics of a PV device made from the "ricelike" CZTS nanorods.



Figure 5.8. Current - voltage characteristics of a PV device made with smaller, "ricelike" CZTS nanorods.

The open-circuit voltage (V_{OC}) is 314 mV, the short-circuit current density (J_{SC}) is 0.40 mA/cm², the fill factor (FF) is 0.38, and the power conversion efficiency (PCE, η) is 0.048%.

The PV response of these nanorods devices provides proof-of-concept that this material can work in solar cells. The PCE of the first device is similar to that of test devices made with CZTS nanocrystals, because the nanorod orientation is not optimized. The layer is simply spray-coated from a nanorod dispersion, leading to a random orientation, unlike the idealized device structure depicted in the introduction of this chapter. As such, there is no PCE improvement over CZTS nanocrystal devices. The J_{SC}

suffers from the thin absorber layer, and all primary device characteristics suffer from poor electrical transport properties in the active layer.

Perpendicular alignment of the CZTS nanorods to the substrate would enable greater charge collection by channeling charge carriers to their respective electrodes. This could be accomplished via multilayers of short nanorods such as those here, or by alignment of longer nanorods / nanowires, as the absorber layer needs to be thicker in order to absorb a substantial portion of sunlight and generate more photocurrent.

5.3.3. CZTS Nanorod Perpendicular Alignment

Experiments in nanorod alignment were conducted by dropcasting various concentrations of nanorod dispersions onto TEM grids. Care was taken to not over-wash the samples. Adding too much antisolvent (ethanol), or by performing too many washing steps, the nanorods would quickly aggregate, rendering the sample unable to be aligned.

Also, dispersions that were too concentrated would lead to aggregated clumps of nanorods on the TEM grid. Dispersions that were too dilute would not lead to monolayers of aligned CZTS nanorods.

By carefully washing the sample and utilizing a concentration of ~ 0.005 mg/mL (dried sample dispersed in toluene), nanorods could be aligned in domains over 100's of nm (Figure 5.9).



Figure 5.9. TEM image of aligned CZTS nanorods.

Figure 5.9 is a TEM image of a typical domain of aligned CZTS nanorods. These are viewed down the c-axis, so they appear as a circular shape. The sample is also somewhat dirty, as can be observed in the dark contrast material surrounding the nanorods.

At this point, only 100's of nm domains can be achieved. Further optimization of the washing and post processing of the nanorods will be required to achieve alignment (and multilayer alignment) over device-scale areas.

5.4. CONCLUSIONS

In summary, CZTS nanorods were synthesized by a similar procedure reported by Ryan et. al.³⁵ Interestingly, these nanorods crystallize in a hexagonal wurtzite structure.

To the best of our knowledge, this is the first report of functioning photovoltaic devices being fabricated from CZTS nanorods. Using a device structure of Au/CZTS Nanorods/CdS/Zno/ITO, a PCE of 0.18% was achieved. Although the efficiency will need to be improved upon, the as-made nanorods comprising the active layer were not sintered or chemically treated in any way.

By optimizing the synthesis and improving the device fabrication, a PCE increase should be readily achievable. The most obvious way to do this is to synthesize longer nanorods and align them perpendicularly to the substrate surface, thereby eliminating any grain boundaries or interfaces that charge carriers would encounter on their path to collection.

Modest alignment over 100's of nm has been achieved by adjusting nanorod dispersion concentrations. By improving this to device scale areas this could enable great performance enhancement in PVs, opening up the possibility for low-cost, solution-processable PVs made from CZTS nanorods.

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Chapter 6: Selenization of Cu₂ZnSnS₄ Nanocrystal Thin Films and Their Use in Photovoltaic Devices

6.1. INTRODUCTION

Commercialization of solution-processable solar cells, fabricated via highthroughput manufacturing, requires power conversion efficiencies (PCEs) of at least 15%.¹ Both CIGS² and CZTS³ thin film-solar cells have achieved this efficiency threshold; however, they required either vacuum processing (CIGS) or processing with highly toxic chemicals such as hydrazine (CZTS).

At this point, nanocrystal based solar cells of these materials have not been able to achieve 10% PCEs (without any thermal treatment of the absorber layer). Several ideas have been explored to improve upon the device efficiencies, including using 1-dimensional nanostructures in order to improve charge carrier collection (such as in Chapters 2 and 5). Other strategies have involved novel device structures,⁴⁻⁷ or chemical processing of the nanocrystal films to improve charge transport.^{8, 9}

Hillhouse et. al. have explored the selenization of both CIGS and CZTS films as a way to increase grain size, improve charge carrier extaction, and improve device performance.^{10, 11}

Although selenization requires high temperature processing, it is useful to try and understand the sintering of nanocrystal films, in the hope that future research directions can achieve the same results via lower temperature and more ambient processing conditions.

This chapter describes some preliminary work in the area of selenization of spraycoated CZTS nanocrystal films and their utilization in PV devices.

6.2. EXPERIMENTAL METHODS

6.2.1. Chemicals

All chemicals were used as received. Copper (II) Acetylacetonate ($Cu(acac)_2$, 99.99+%), zinc acetate (99.99%), Tin (II) Chloride ($SnCl_2$, 99.99+%), elemental sulfur powder (S, 99.98%), Cadmium sulfate ($CdSO_4$, 99.999%), and Oleylamine (OLA, technical grade) were obtained from Aldrich; thiourea (99%) was obtained from Fluka; and ammonium hydroxide (NH_4OH , certified ACS), chloroform, toluene, and ethanol were obtained from Fisher Scientific.

6.2.2. CZTS Nanocrystal Synthesis

CZTS nanocrystals were synthesized following the procedure outlined in Chapter 4. The nanocrystals were cleaned and isolated as before, and dispersed in toluene (~20 mg/mL) to make the "solar paint" from which films were spray-coated during device fabrication.¹²

6.2.3. Photovoltaic Device Fabrication

6.2.3.1 Substrate Preparation

PV devices were fabricated on soda lime glass substrates. The substrates were first cleaned by sonication in acetone, isopropanol, and deionized water, and subsequently dried with nitrogen.

Molybdenum back contacts were deposited onto the substrated by radio frequency sputtering using a two-step process. 400 nm of Mo (Lesker, 99.95%) was deposited at 5 mTorr to create a highly adhesive layer to the sodalime glass, and an additional 600 nm of Mo was deposited at 1.5 mTorr for a highly conductive layer. The final sheet resistance was ~1.25 Ω/\Box

6.2.3.2. CZTS Thin Film Deposition

CZTS nanocrystals were deposited by spray coating from a toluene dispersion (~20 mg/mL) using a standard artist's airbrush. Relatively thick films were spray coated (~1-2 μ m), in contrast to films deposited in previous chapters (i.e., for device fabrication without any selenization).

6.2.3.3. Selenization

To begin the selenization step, the nanocrystal films on Mo substrates were placed into small graphite chambers. A small quartz boat containing selenium powder was placed at the bottom of the chamber to serve as the Se source. The chamber was then sealed with a fitted graphite cap (not air-tight). This setup is shown in Figure 6.1 (courtesy of Vahid Akhavan). Ar was flowed through the furnace, the temperature was increased to 500 °C and held there for 10 min, and the chambers were allowed to cool to room temperature.



Figure 6.1. (a) Side view of graphite selenization chamber. (b) Cross-sectional view of same chamber. (c) Tube furnace used for selenization step in device fabrication.

6.2.3.4. CdS Buffer Layer Deposition

The CdS buffer layer was deposited by chemical bath deposition, with a few variations from previous chapters. 160 ml of DI water was placed in a glass beaker and heated to 70°C under constant stirring. 25 ml of 15 mM CdSO4, 12.5 ml of 1.5 M thiourea, and 32 ml of ammonium hydroxide were added and the selenized films were immediately placed into the bath. The reaction was allowed to proceed for 15 minutes, after which the films were rinsed with DI water and dried.

6.2.3.5. Top Contact Deposition

50 nm of ZnO (99.9%, Lesker) was deposited by rf sputtering, followed by 600 nm of ITO (99.99% In_2O_3 :SnO₂ 90:10, Lesker) to form the top contacts of the test device. The active region of the device was 8 mm². To make electrical contact with the top contacts, silver paint was applied.

6.2.3.6. Post-Bake

Following device construction, the devices were placed in a vacuum oven at 200°C for a variable amount of time, up to 24 hrs. Variations of the post bake and their effects on device performance are discussed below.

6.2.4. Characterization

The nanocrystals and nanorods were characterized by transmission electron microscopy (TEM). TEM images were obtained on 200 mesh carbon-coated Ni grids (Electron Microscopy Sciences) using a FEI Tecnai Spirit BioTwin operated at 80 kV. The selenized films were characterized by X-Ray diffraction (XRD) and scanning electron microscopy (SEM) X-Ray diffraction (XRD) data were acquired on a Rigaku R-Axis Spider diffractometer with image-plate detector using Cu K α radiation ($\lambda = 1.54$ Å).

SEM images were obtained with a Zeiss Supra 40 VP scanning electron microscope operated at 1-10 keV.

PV devices were tested on a Karl Suss probe station and an Agilent 4156C parameter analyzer. J-V data and power conversion efficiencies were obtained using a Keithley 2400 General Purpose Sourcemeter and a Xenon Lamp Solar Simulator (Newport) with an AM 1.5 filter.

6.3. RESULTS AND **D**ISCUSSION

6.3.1. CZTS Nanocrystals and Non-Selenized Control Device

Figure 6.2 is a TEM image of a typical CZTS nanocrystal sample used for film deposition and device fabrication.



Figure 6.2. TEM image of CZTS nanocrystals used for film deposition

A non-selenized control device was fabricated to confirm that the CZTS nanocrystals performed in a similar fashion as the samples in Chapter 4, and to compare the current-voltage charcteristics to selenized devices. Figure 6.3 shows the current voltage characteristics of a typical control device, using the Au/CZTS/Cd/Zn/ITO structure described in Chapter 4. The spray-coated CZTS nanocrystal film was not annealed or chemically treated prior to device fabrication.



Figure 6.3. Current-voltage characteristics of non-selenized CZTS nanocrystal device

The four key device characteristics displayed in Figure 6.3 are comparable to the device described in Chapter 4. The power conversion efficiency of 0.2% was under AM 1.5 conditions, as before.
6.3.2. Film Characterization and PV Performance

XRD confirmed that selenization of the CZTS nanocrystal film at 500°C resulted in a near-complete conversion of the CZTS film to $Cu_2ZnSnSe_4$ (CZTSe), as shown in Figure 6.4.



Figure 6.4. XRD pattern of selenized CZTSe film. The red reference pattern corresponds to Molybdenum (JCPDS no. 01-071-3771). The blue reference pattern corresponds to CZTSe (JCPDS no. 01-070-8930).

The experimental XRD data indexed well to a reference CZTSe pattern. The experimental diffraction peaks were slightly shifted to lower angles, indicating that the selenization was not 100% complete. The unit cell of CZTS is slightly smaller than that of CZTSe, but consists of the same crystal structure. Thus, the only difference in their XRD patterns is a shifting of the diffraction peaks. The final selenized films used to fabricate PV devices were comprised of this CZTS_xSe_{1-x} (CZTSSe) material.

Figure 6.4 shows an SEM image of the selenized film.



Figure 6.5. SEM image of selenized CZTSSe film. The lower half of the image is the Mo back contact. The top half is the CZTSSe film. There are no CdS, ZnO, or ITO layers in this image.

The resultant morphology was a relatively smooth-looking film of CZTSSe. However, there appeared to be some amorphous looking carbonaceous material coating part of the surface. Additionally, it appeared as though small areas of the substrate dewetted from the surface (such as in the center of Figure 6.5, leaving bare Mo behind. Clearly, if dewetting is significant over the device area, it could lead to device shorting, a low shunt resistance, and poor device performance.

Figure 6.6 shows another SEM image from the same selenized film. Certain areas of the film exhibited hexagonal shaped platelets on their surface (seen in the background of Figure 6.6). This morphology is indicative of copper selenide phases,¹³ which is detrimental to CIS and CZTS based PV devices.¹¹ The formation of this phase is possibly due to the starting composition of the nanocrystal film. The best CZTS devices have been shown to be Cu poor,¹⁴ while the as-synthesized CZTS nanocrystals were nearly stoichiometric. The selenization conditions, such as temperature, time, or Se partial pressure could have also contributed to the formation of this phase.



Figure 6.6. SEM image of selenized CZTSSe film, showing hexagonal platelet morphology on surface.

Figure 6.7 shows the current-voltage characteristics of a typical selenized CZTSSe device.



Figure 6.7. Current-voltage characteristics of a selenized CZTSSe device.

This device had an open circuit voltage (V_{OC}) of 335 mV, a short circuit current density (J_{SC}) of 1.64 mA/cm², fill factor (*FF*) of 0.34, and a PCE (η), of 0.19% under AM 1.5 conditions.

These are quite similar characteristics to the control device. Selenization, and the resulting grain growth, should increase device performance through increased carrier collection efficiency and decreased recombination. It is possible that the carbonaceous material, dewetting of the CZTSSe film, and copper selenide formation are inhibiting the realization of device improvement.

6.3.3. Effect of Post-Bake Fabrication Step

The post-bake step following device fabrication was found to have a large impact on device performance. This step was initially developed for use in selenized CIGS nanocrystal devices, and was found to be critical to achieving high efficiencies.

Figures 6.8, 6.9, and 6.10 illustrate this effect by showing how increasing the amount of post-bake time increases the PCE. Figure 6.8 shows the current-voltage characteristics of a selenized CZTSSe device with no post-bake step. After application of Ag paint, the device was immediately tested.



Figure 6.8. Current-voltage characteristics of a selenized CZTSSe device made with no post-bake step.

The efficiency of this device was 0.046%.

Figure 6.9 shows the current-voltage characteristics of the selenized CZTSSe device with a 10 minute post-bake step.



Figure 6.9. Current-voltage characteristics of a selenized CZTSSe device made with a 10 minute post-bake step.

The efficiency of the device was 0.058%, showing a very slight improvement over the previous measurement.

Finally, Figure 6.10 shows the current-voltage characteristics of a selenized CZTSSe device with a 24 hour post-bake step.



Figure 6.10. Current-voltage characteristics of a selenized CZTSSe device made with a 24 hour post-bake step.

Although the PCE is still only 0.11%, this is a significant improvement over the shorter post-bake time. These three current-voltage curves, although they are not the best performing devices, were used to show a general trend: the longer the post-bake time, the higher the PCE. This is true up until approximately 24 hours, when this improvement levels off and increases in PCE are no longer seen. At this point, it is not entirely clear as to the mechanism of this improvement.

6.4. CONCLUSIONS

The selenization of CZTS nanocrystal films via a high temperature annealing step in a Se environment produced continous films of CZTSSe. However, the grains appeared to be covered with some amorphous carbonaceous material. Additionally, there was some dewetting of the film, along with the formation of some copper selenide material.

A device structure of Mo/CZTSSe/CdS/Zno/ITO produced a PCE of 0.19%. Although this efficiency is not an improvement over nanocrystal-only devices, it shows that this selenized material can be used in functioning solar cells.

Additionally, a post-bake step of completed devices under vacuum was found to be critical to increasing PCEs. A 24 hour post bake was found to be optimal.

It should be stressed that this is preliminary data, without any optimization of the selenization, fabrication, or post-processing steps.

Other reports of similar devices utilize a pre-annealing step in order to remove excess carbon material such as capping ligands or residual reactants in the nanocrystal dispersion. The composition of the starting material, the selenization process (time temperature, Se source), CdS deposition, and post-bake steps all require much more optimization in order to realize the full potential of this material.

Although high temperature processes such as this are not ideal for fabricating low-cost solar cells, these experiments improve the understanding of selenization of these films. With a greater understanding of these processes, other methodologies can be developed in the future to create highly efficient and cost-effective CZTS based solar cells.

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Chapter 7: Silicon Nanowire Fabric: Electrical Conductivity Enhancement and its Application[§]

7.1. INTRODUCTION

Silicon nanowires have been studied as a potential material for a variety of applications, including transistors and lithium ion battery (LIB) electrodes.¹⁻⁵ Silicon nanowires were first grown in the 1960's using the vapor-liquid-solid (VLS) mechanism to produce "forests" of nanowires grown from a substrate.⁶ While this process has been developed over the years to improve nanowire quality and extended to other semiconductor materials,⁷⁻¹⁰ the VLS method is limited in that it cannot produce large quantities of material that would be required by an industrial process.

More recently, the supercritical fluid-liquid-solid (SFLS) process has been developed and utilized to produce large quantities of silicon nanowires, enough to create free-standing "fabrics" of this material.¹¹⁻¹⁷ This fabric has potential applications in flexible electronics, including LIBs.^{5, 18-20}

In LIBs, silicon can be used as an anode material with a higher theoretical capacity than that of commercially used graphite.^{18, 21} Furthermore, nanostructured Si (such as nanowires) has the added benefit of being mechanically stable during cycling when compared to bulk Si in LIBs.^{2, 22, 23}

However, electrode materials must be sufficiently conductive in order to function properly in LIBs, and as-made Si nanowire fabric is quite resistive.¹⁸ This chapter describes the thermal annealing of Si-nanowire fabric and its increased conductivity, enabling usage in LIBs.

[§] Portions of this chapter appear in: Chockla, Aaron M.; Harris, Justin T.; Akhavan, Vahid A.; Bogart, Timothy D.; Holmberg, Vincent C.; Steinhagen, Chet; Mullins, C. Buddie; Stevenson, Keith J.; Korgel, Brian A., **Silicon Nanowire Fabric as a Lithium Ion Battery Electrode Material.** *Journal of the American Chemical Society* (2011), 133(51), 20914-20921. Chet was a co-author on this paper due to his contribution with the annealing and conductivity measurements of Si nanowire paper.

7.2. EXPERIMENTAL METHODS

7.2.1. Silicon Nanowire Synthesis

Si nanowires were synthesized via the SFLS process, described in detail elsewhere. Following synthesis, the nanowires were washed and isolated with standard solvent/antisolvent methods, using chloroform and ethanol. The final product was dispersed in chloroform at a concentration of 5 mg/mL.

7.2.2. Silicon Nanowire Fabric Formation

Si nanowire fabric was made by dropcasting the dispersion into shallow Teflon troughs. As the solvent evaporated, more of the dispersion was added to the trough, until the desired thickness was achieved. The material was then allowed to dry overnight in a fume hood to remove any residual solvent. The freestanding fabric was then carefully peeled from the trough with a tweezers.

7.2.3. Fabric Annealing

Si nanowire fabric was annealed by cutting the fabric into 1 cm x 1 cm squares, placing them in quartz boats, and loading them into a tube furnace. Annealing steps were carried at various temperatures, under forming gas flow.

7.2.4. Characterization Methods

Scanning electron microscopy (SEM) images were obtained with a Zeiss Supra 40 VP scanning electron microscope operated at 1-10 keV.

Electrical tests were performed by sandwiching the fabric between two pieces of ITO coated glass, holding the sandwich together with binder clips, and connecting the device via alligator clips to a Keithley 2400 General Purpose Sourcemeter.

7.3. RESULTS AND DISCUSSION

7.3.1. Si Nanowire Fabric

Figure 7.1 shows a picture, along with SEM and TEM images of the Si nanowire fabric (courtesy of Aaron Chockla). The fabric is mechanically robust – it can be manipulated with one's hands without tearing – and is similar in texture to a tissue paper. Depending on the quantity of nanowire dispersion used, the paper can be made in varying thicknesses, typically between 50-150 μ m. Each individual nanowire is crystalline (Figure 7.2d), but the freestanding Si nanowire fabric is flexible. Figure 7.2f shows the fabric after various annealing temperatures. Higher temperatures lead to a darker color, with 1100°C yielding a jet black material.



Figure 7.1. (a) Photograph of mechanically flexible Si nanowire fabric. (b,c) SEM images of the fabric. (d) High-resolution TEM (HRTEM) image of a Si nanowire showing its crystallinity. (e) Fast Fourier transform (FFT) pattern from the HRTEM image in (d) showing a <110> growth direction. (f) Photographs of Si nanowire fabrics annealed at the indicated temperatures under a reducing atmosphere.

7.3.2. Enhanced Electrical Conductivity of Si Nanowire Fabric via Annealing

As made Si nanowire fabric performed poorly as an anode material in LIBs. The capacity dropped to essentially zero after only a couple cycles. Conductivity tests showed that the as-made fabric was insulating, with a conductivity of ~0.2 nS/m.

Thermal annealing in a reducing atmosphere was found to greatly enhance the conductivity of the nanowire fabric, as shown in Figure 7.3. Annealing the fabric at temperatures up to 1000°C increased the conductivity several orders of magnitude to 150 nS/m, 1100°C increased it further to 1400 nS/m.



Figure 7.2. Current-potential measurements of Si nanowire fabric placed between two ITO electrodes (inset). The nanowire fabric was annealed under a reducing atmosphere at the indicated temperatures. Measurements were made with \sim 150 µm thick fabric samples with a contact area of 1cm².

Si nanowires grown by the SFLS method were found to have a polyphenylsilane shell on their surface. When the fabric is annealed in a reducing atmosphere, this shell is turned into graphitic carbon, increasing the electrical conductivity greatly.

This enhanced conductivity enabled the material to be used effectively in LIBs as an anode material. Fabric annealed at 900°C performed the best: the first cycle had a capacity of ~1,500 mA h g⁻¹, the second cycle had a capcity of ~900 mA h g⁻¹, and the capacity remained above 500 mA h g⁻¹ for over 100 cycles. In comparison, the theoretical capacity of a graphite anode is 372 mA h g⁻¹.

7.4. CONCLUSIONS

Large quantities of Si nanowires were grown using the SFLS method and used to create free-standing sheets of fabric. This material is flexible, lightweight, and mechanically stable.

Although the as-made fabric is insulating, it can be annealed under forming gas to increase its conductivity.

Initial results indicate that annealed Si nanowire fabric shows potential as an anode material in LIBs, possibly replacing the commercial standard of graphite. Capacities have been shown to be higher than that of graphite, with long-term cycle stability.

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Chapter 8: Conclusions and Future Research Directions

8.1. CONCLUSIONS

Solution-processable photovoltaics are interesting from both basic science and practical points of view. Research and development into such solar cells incorporates many different disciplines, including chemistry, materials engineering, and device physics, making for a very challenging, yet rewarding field of study. Additionally, and arguably more importantly, they offer an exciting opportunity to reach the ultimate goal of widespread and inexpensive solar energy.

Research within our group on CIGS nanocrystal PVs has enabled devices with power conversion efficiencies of 3.1%.¹ This is a substantial achievement and provides motivation for further work on these devices. However, there are two issues with this technology. Poor electronic transport in unprocessed and non-annealed nanocrystal films limits the performance of such devices, possibly rendering them unable to achieve the efficiencies necessary for commercialization. Secondly, CIGS, while an exceptional PV material, may run into materials availability problems in the future, making it unable to meet global electricity demands.²

The work presented in this dissertation had two primary goals: to develop 1dimensional nanostructures and use them to fabricate functioning solar cells, and to synthesize nanocrystals from earth-abundant alternative materials to CIGS. The first goal addresses the transport problem described above, by providing a platform technology with theoretically better electronic transport characteristics than nanocrystal-only devices. The second goal addresses the CIGS materials availability issue by developing new materials that are abundant enough to meet worldwide electricity production needs longterm.

8.1.1. CuInSe₂ Nanowires

Chapter 2 summarized the synthesis of CIS nanowires and their implementation into PV devices. They were synthesized via the solution-liquid-solid mechanism in which colloidal Bi nanocrystals were used to promote the unidirectional growth of crystalline CIS nanowires. The CIS nanowires exhibited some interesting materials properties including twinning perpendicular to the growth direction, wurtzite-sphalerite polytypism, and different morphologies dependent on the synthetic conditions.³

The CIS nanowires could be dispersed in toluene to form a solar paint, which was spray-coated, using an airbrush, to form the absorber layer in PVs. A standard CIS pn heterojunction structure was used to complete the devices. While these solar cells worked, their efficiency is still far too low for practical purposes. However, they represent proof of concept for the nanowires as a useful PV material.

While their high aspect ratio should enable more efficient charge collection, the current device geometry is not an improvement over nanocrystal devices. The nanowires are parallel to the substrate service, and would require alignment to fully realize their potential.

The synthesis was developed and scaled up in order to make fairly large quantities of material, enabling the development of a nanowire "fabric." This macroscopic material opens up the possibility of lightweight and flexible PVs without the need for a rigid substrate.

8.1.2. Pyrite Nanocrystals

Chapter 3 discussed the synthesis of pyrite FeS_2 nanocrystals. The nanocrystals were synthesized via an arrested precipitation reaction using octadecylamine as both a complexing reagent and capping ligand. A specific reaction time and temperature was found to be critical to creating phase-pure pyrite without any other iron sulfur byproducts.⁴

The nanocrystals were characterized by a variety of standard methods, and were found to be phase-pure pyrite, but with a slight sulfur deficiency. They were dispersed in toluene to form a solar paint, and could be spray coated to form smooth, crack-free thin films.

Several different device architectures incorporating the pyrite nanocrystal thin films as the absorber layer were fabricated in the attempt to create PV devices. Unfortunately, many standard structures yielded ohmic junctions or very little current rectification with no measureable photocurrent.

It was hypothesized that the sulfur vacancies led to degenerately doped or metallic behavior in the particles, as confirmed by electronic measurements. This behavior made it impossible to form junctions within the devices, limiting their performance.

8.1.3. Cu₂ZnSnS₄ Nanocrystals

Chapter 4 summarized work on CZTS nanocrystals. A synthesis was developed to produce slightly irregular spherical nanocrystals of around 10 nm with reasonable dispersity levels. Compositional characterization revealed the nanocrystals to be nearly stoichiometric, although slightly tin-rich and sulfur-deficient. STEM mapping confirmed that the composition was consistent over a large number of nanocrystals. The oleylamine-capped particles could be dispersed readily in organic solvents such as toluene and chloroform.⁵

CZTS nanocrystal dispersions were spray coated onto Au-coated glass substrates to form the absorber layer in test PVs. A CdS layers was deposited on the CZTS layer, and ZnO and ITO layers were sputtered on the CdS to form top contacts. With this device architecture, a PCE of 0.23% was achieved under AM 1.5 conditions, representing proof of concept for utilizing CZTS nanocrystals in low-cost photovoltaics.

8.1.4. CZTS Nanorods

In Chapter 5, the synthesis of CZTS nanorods was discussed. These nanorods were synthesized via anisotropic arrested precipitation by utilizing thiols as capping ligands and sulfur sources. The nanorods were 21 nm in length and 8 nm in diameter on average, and exhibited a wurtzite (hexagonal) crystal structure. Capping ligand choice and precursor concentration was found to have a pronounced effect on the nanorod morphology.

Thiol-capped CZTS nanorods were dispersed in toluene and spray-coated to form thin films. Devices consisting of an Au/CZTS/CdS/ZnO/ITO device architecture functioned as solar cells, albeit with a slightly lower efficiency than nanocrystal devices. In a similar fashion to the CIS nanowires, the aspect ratio was not utilized to its fullest extent in fabricating the devices.

Perpendicular alignment of nanorods would enable better charge collection if it could be achieved on device-scale areas. Alignment experiments were conducted, and small-scale (100's of nm) alignment observed. Further optimization of the nanorod cleanup steps, dispersion concentration, and perhaps ligand exchange could facilitate device-scale alignment.

8.1.5. Selenization of CZTS

Initial studies of the selenization of CZTS nanocrystal films were described in Chapter 6. CZTS nanocrystals were synthesized in the same manner as described in Chapter 4, and thin films were spray coated onto Mo coated glass substrates (the Mo was deposited by rf sputtering). Selenization was carried out in graphite boxes, and a tube furnace served as the heating source.

Selenization of the CZTS films resulted in the creation of a CZTSSe film. Some dewetting of the film was observed, but this layer could be used to create functioning solar cells. However, there was no improvement over CZTS nanocrystal devices.

A post-bake step, following device fabrication, was found to be critical to the devices functioning properly. This work was preliminary, and there are several steps which will require optimization in order to improve the PCE in these devices.

8.1.6. Annealing of Silicon Nanowire Fabric

Chapter 7 described how the annealing of Si nanowire fabric, carried out in a reducing atmosphere, improved its conductivity, enabling it to be utilized as an electrode material in Lithium ion batteries.

The synthesis of Si nanowires is discussed elsewhere.^{6, 7} Fabric made from these nanowires was created by a vacuum filtration setup, where a dispersion of the nanowires was dripped though a filter to a desired thickness, peeled from the filter, and allowed to dry.⁸ Initial studies of the performance of this material in Li ion batters showed that the material was too insulating. However, though annealing at high temperatures in a tube furnace under forming gas flow, the conductivity could be improved, and the fabric could be successfully integrated into Li ion batteries as an electrode material.⁹

8.2. FUTURE RESEARCH DIRECTIONS

8.2.1. CZTS Nanocrystal Photovoltaics

CZTS is a very promising earth abundant PV material, recently achieving a PCE of over 11% with a hydrazine deposition method.¹⁰ Nanocrystals offer a more 111

environmentally friendly method of fabrication, but will require better electronic performance.

A better understanding of the composition and surface defects could enable better performance. Perhaps surface modifications via ligand-exchange or post-deposition treatments could improve the electronic characteristics of the nanocrystals, and is a fairly understudied area, particularly with this material system.

Annealing and selenization studies of CZTS nanocrystal films could pave the way for a better understanding of the sintering and grain growth in this material. Although high temperature studies such as these are undesirable for low-cost manufacturing, a better understanding of these processes could lead to novel deposition and processing steps in the future that are amendable to high-throughput manufacturing.

Another nascent area of research is the development nanocrystal devices with novel device architectures, such as the depleted heterojunction devices previously described.¹¹ CZTS possibly has a home in one of these new structures.

8.2.2. Pyrite Solar Cells

Pyrite, at least at first glance, has much potential as a PV material due to its material abundance and seemingly good optoelectronic properties. Unfortunately, it has yet to realize this potential, most likely due to a poor understanding of composition and surface properties.

A better understanding of pyrite's surface chemistry and how it affects the electronic properties is essential to building efficient solar cells from this material. New studies have been emerging along these lines, but there is still much to learn.¹²

It is possible that alloying pyrite with some other elements could make it a more suitable PV material.¹³ Within the category of nanocrystal-based solar cells, surface

modifications via ligand exchange or even utilizing core-shell pyrite nanocrystals could improve the electronics properties to the point when PVs could be fabricated from them.

8.2.3. Nanowire and Nanorod Alignment

The primary issue inhibiting the efficiencies in nanocrystal photovoltaics is poor charge carrier transport. An ideal system would allow photogenerated electrons and holes to travel to their respective electrodes without encountering any grain boundaries within the absorber layer. In theory, this could be accomplished with vertical, perpendicularly aligned nanorods or nanowires.

The trick, of course, is actually aligning the materials on a device scale.¹⁴ Recently, several studies have begun to emerge on the topic.¹⁵ Functioning devices have been fabricated from aligned films of nanorods. Whether this can be achieved with good PVs materials like CIGS of CZTS will require optimization of the capping chemistry and post-synthesis processing.

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