Portland State University

PDXScholar

Dissertations and Theses

Dissertations and Theses

1-1-2011

Nanostructured Extremely Thin Absorber (ETA) Hybrid Solar Cell Fabrication, Optimization, and Characterization

Darcy Erin Lambert
Portland State University

Follow this and additional works at: https://pdxscholar.library.pdx.edu/open_access_etds

Let us know how access to this document benefits you.

Recommended Citation

Lambert, Darcy Erin, "Nanostructured Extremely Thin Absorber (ETA) Hybrid Solar Cell Fabrication, Optimization, and Characterization" (2011). *Dissertations and Theses*. Paper 637.
<https://doi.org/10.15760/etd.637>

This Thesis is brought to you for free and open access. It has been accepted for inclusion in Dissertations and Theses by an authorized administrator of PDXScholar. Please contact us if we can make this document more accessible: pdxscholar@pdx.edu.

Nanostructured Extremely Thin Absorber (ETA) Hybrid Solar Cell Fabrication,
Optimization, and Characterization

by

Darcy Erin Lambert

A thesis submitted in partial fulfillment of the
Requirements for the degree of

Master of Science
in
Physics

Thesis Committee:
Rolf Könenkamp, Chair
Robert Word
Ralf Widenhorn

Portland State University
©2011

Abstract

Traditional sources of electrical energy are finite and can produce significant pollution. Solar cells produce clean energy from incident sunlight, and will be an important part of our energy future. A new nanostructured extremely thin absorber solar cell with 0.98% power conversion efficiency and maximum external quantum efficiency of 61% at 650 nm has been fabricated and characterized. This solar cell is composed of a fluorine-doped tin oxide base layer, n-type aluminum doped zinc oxide nanowires, a cadmium selenide absorber layer, poly(3-hexylthiophene) as a p-type layer, and thermally evaporated gold as a back contact. Zinc oxide nanowire electrodeposition has been investigated for different electrical environments, and the role of a zinc oxide thin film layer has been established. Cadmium selenide nanoparticles have been produced and optimized in-house and compared to commercially produced nanoparticles. Argon plasma cleaning has been investigated as a method to improve electronic behavior at cadmium selenide interfaces. The thermal anneal process for cadmium selenide nanoparticles has been studied, and a laser anneal process has been investigated. It has been found that the most efficient solar cells in this study are produced with a zinc oxide thin film, zinc oxide nanowires grown under constant -1 V bias between the substrate material and the anode, cadmium selenide nanoparticles purchased commercially and annealed for 24 hrs in the presence of cadmium chloride, and high molecular weight P3HT spin-coated in a nitrogen environment.

Acknowledgements

I am grateful to many people for their assistance throughout the course of this research. I am grateful for all of the previous members of Dr. Koenenkamp's research group who designed this solar cell and began the optimization process which I have continued. I am grateful to Dr. Koenenkamp for his generous advice and assistance throughout this research and over many revisions of this thesis. I am grateful as well to Dr. Word for his advice and assistance, and for use of his laser. I am grateful to Athavan Nadarajah for teaching me much of how to construct these cells, and for the advice, assistance, and collaboration. I am grateful to Kevin Shawver, Martha Coakley, Zach Peterson, and Brandon Giatta for listening to so many of my group presentations and for engaging in so many useful group discussions.

Table of Contents

Abstract	i
Acknowledgements	ii
List of Figures	v
Chapter 1 Introduction	1
1.1 Motivation.....	1
1.2 Background Physics	2
1.3 Extremely Thin Absorber (ETA) Solar Cell Design	9
Chapter 2 - Characterization	12
2.1 Characterization	12
2.2 Photocurrent	13
2.3 Solar Simulator Calibration for Current-Voltage (I-V) Measurement	17
2.4 Current-Voltage.....	22
Chapter 3 - Fabrication	25
3.1 Transparent Conducting Oxide	25
3.2 P-Type Polymer - Poly(3-hexylthiophene).....	26
3.3 Cadmium Selenide Nanoparticles	30
3.4 Methodology	32
3.4.1 Substrate Cleaning.....	32
3.4.2 Zinc Oxide Thin Film Deposition	32
3.4.3 Zinc Oxide Nanowire Growth.....	33
3.4.4 Oxygen Plasma Clean for Zinc Oxide Nanowires	34
3.4.5 Cadmium Selenide Dropcoat	35
3.4.6 Poly(3-hexylthiophene) Spincoat.....	36
Chapter 4 - Data & Results	37
4.1 Best Photovoltaic Response	37
4.2 Characterization of ZnO growth and morphology	39
4.2.1 Galvanostatic Deposited Seed Layer.....	41
4.2.2 Zinc Oxide Thin Film	47

4.3	Absorber Layer.....	52
4.3.1	Cadmium Selenide Nanoparticle Growth and Ligand Exchange	54
4.3.2	Argon Plasma Cleaning Treatment to Optimize Cadmium Selenide/CuSCN Contact 62	
4.3.3	Cadmium Selenide Thermal Anneal Study	65
4.3.4	Cadmium Selenide Laser Anneal Study	68
Chapter 4 - Conclusion		78
References		79

List of Figures

Figure 1: Band structure of silicon, energy vs k (Seeger)	4
Figure 2: Absorption coefficient as a function of photon energy for Si (indirect band gap) and GaAs (direct band gap) at 300 K. (Luque)	5
Figure 3: Best research-cell efficiencies (Kazmerski)	7
Figure 4: ETA solar cell design	9
Figure 5: Cadmium selenide band structure (Kobayashi)	10
Figure 6: ETA solar cell band gap alignment	11
Figure 7: Photocurrent Characterization Setup	13
Figure 8: Photodiode Responsivity Curve	14
Figure 9: ASTM Spectra of solar radiation; extraterrestrial, terrestrial direct, and direct normal + circumsolar	17
Figure 10: White Light Spectra at different power settings, mW/cm^2 , with AM 1.5 spectrum superimposed	19
Figure 11: Photodiode response vs. the number of incident photons on the photodiode area in the active wavelength range. The number of incident photons for different power levels was calculated using the spectra from Figure 10.	21
Figure 12: I-V curve with calculated power from ETA solar cell	22
Figure 13: Optical transmission and absorption of FTO on glass	26
Figure 14: Optical absorption of fluorine-doped tin oxide on glass	26
Figure 15: Poly (3-hexylthiophene) structure, individual (left) and conjugated (right) (Nicholson)	27
Figure 16: Technical Specifications of cadmium selenide from NN Labs	31
Figure 17: EQE of the best solar cell of this design	37
Figure 18: IV characteristics of the best solar cell of this design	38
Figure 19: ZnO band structure (Berger)	40
Figure 20: ZnO nanowires, standard recipe	41
Figure 21: 1 Min. galvanostatic ZnO nanowire growth	42
Figure 22: 1 Min. galvanostatic + 59 Min potentiostatic ZnO nanowire growth	43
Figure 24: 5 Min. galvanostatic ZnO nanowire growth	44
Figure 23: 5 Min. galvanostatic ZnO nanowire growth	44
Figure 25: 5 Min. galvanostatic + 55 Min potentiostatic ZnO nanowire growth	45
Figure 26: 5 Min. galvanostatic + 55 Min potentiostatic ZnO nanowire growth	46
Figure 27: SEM image of ZnO thin film on FTO substrate	47
Figure 28: EDX data of ZnO thin film on FTO substrate	48
Figure 29: EDX data of ZnO nanowires grown on ZnO thin film on FTO substrate	49
Figure 30: SEM image of ZnO nanowires grown on ZnO thin film on FTO substrate ...	50
Figure 31: EQE of solar cell made from ZnO nanowires on ZnO thin film	51
Figure 32: EQE of solar cell made from ZnO nanowires on ZnO thin film	51
Figure 33: CdSe thin film on ZnO nanowires	52
Figure 34: CdSe thin film on ZnO nanowires	53

Figure 35: Photoluminescence spectra of CdSe nanoparticles in toluene with octadecylamine ligand, supplied by NN Labs.....	55
Figure 36: Photoluminescence spectra from different batches of CdSe nanoparticles of different sizes	56
Figure 37: Large CdSe crystal on octadecene/ZnO nanowires, after 16 hour anneal	57
Figure 38: CdSe nanoparticles in octadecene, deposited on ZnO nanowires and annealed for 16 hours	58
Figure 39: Photoluminescence peak positions before and after solvent exchange, for 4 samples of different sizes.....	59
Figure 40: Homemade CdSe nanoparticles deposited in toluene as colloid, on ZnO nanowires	60
Figure 42: I-V Characterization of argon plasma cleaned (top) and not argon plasma cleaned (bottom) solar cells	62
Figure 42: I-V Characterization of argon plasma cleaned (top) and not argon plasma cleaned (bottom) solar cells	64
Figure 43: External Quantum Efficiency for different CdSe anneal times.....	65
Figure 44: Summary of External Quantum Efficiency at 650 nm	66
Figure 45: Absorption Spectra of Pyrex glass (provided by glassware supplier)	68
Figure 46: EQE of solar cell with laser annealed CdSe, 5-6 mJ for 15 minutes.....	70
Figure 48: EQE of solar cell from laser annealed CdSe, 8 mJ for 10 min	71
Figure 47: I-V curve of solar cell with laser annealed CdSe, 5-6 mJ for 15 minutes	71
Figure 49: I-V curve for solar cell from laser annealed CdSe, 8mJ for 10 min	72
Figure 50: EQE of solar cell from laser annealed CdSe, 12 mJ for 10 min	72
Figure 51: SEM of laser annealed CdSe layer, 5-6 mJ for 15 min.....	73
Figure 52: SEM image with EDX data of laser annealed CdSe, 5-6 mJ for 15 min.....	74
Figure 53: SEM image of laser annealed CdSe, 5-6 mJ for 15 min.....	75
Figure 54: SEM image of laser annealed CdSe, 5-6 mJ for 15 min.....	76

Chapter 1 Introduction

1.1 Motivation

Most sources of useable electricity are based on the combustion of limited carbon-rich fuels. Many steps of this type of power generation are hazardous, from the dangers of extracting oil (O'Rourke) and coal (Turka) to the toxic byproducts of its combustion. Combustion of hydrocarbons produces greenhouse gases such as carbon dioxide, causing global climate change that is already affecting Earth's weather patterns. In addition, global reserves of oil and coal are finite and will eventually become depleted (Deffeyes).

The Earth receives a predictable supply of solar radiation every year, and converting even a fraction of that radiation into electrical power could meet a significant portion of global energy demand, as evidenced by numerous studies (Oliver). The European Photovoltaic Industry Association recently reported that photovoltaics could provide up to 12% of the European Union's electricity demand by 2020 (Appleyard). Solar cells available today have potential, but require a large initial investment. Current industrial research focuses on reducing manufacturing costs, simplifying manufacturing procedures, using new or different raw materials, and finding designs which improve power conversion efficiency without being prohibitively expensive. The photovoltaic cell discussed here is designed to study the use of less expensive raw materials, fewer thermal processing steps, and simpler manufacturing processes.

1.2 Background Physics

Silicon is the most common material for photovoltaics due to the favorable size of its band-gap (1.11eV) (Alex), its relative abundance, and its importance in the computing technology industry, which has already developed manufacturing techniques for silicon-based semiconductor devices. Crystalline silicon solar cells had a global photovoltaic market share of 87.5% in 2008 (“Photovoltaic Technology Platform”). Silicon has some significant limitations, however, many of which are a consequence of its energy band structure.

All solar cells rely on the photovoltaic effect to generate free charge carriers from incident photons. Incident photons are absorbed by the electrons in a material, exciting them to higher energy states. As excited electrons are elevated to higher energy levels, they can be thought of as leaving holes at the initial energy level. If this occurs in a metal, where allowed energy levels are very close together so holes and electrons can have very similar energy levels, they are very likely to recombine and cannot be used to generate a current. Electrons in a semiconductor can be excited across the band gap into the conduction band, leaving holes in the valence band. This difference in energy levels between the holes and electrons makes recombination less likely, effectively increasing the recombination time for excited charge carriers. This increase in the recombination time makes it possible for excited carriers to be drawn out of the bulk absorber material via a p-n junction for example. At the interface between the p-type and n-type regions of

the p-n junction a depletion region develops where all free electrons have diffused to the p-type side and all free holes have diffused to the n-type side, leaving the interface depleted of free charge carriers. As new electrons and holes are generated they are drawn via this diffusion to opposite sides of the junction, imposing a physical separation between positive and negative charge carriers which increases recombination time.

The recombination time depends on the energy band structure of the material and on the density of defect states. Defect states provide additional allowed energy states for charge carriers to reside in, and can dramatically reduce recombination time if they exist within the band gap region. In general, a larger band gap would produce a longer recombination time if the effect of defect states is ignored, but the trade-off is that a larger band gap requires more energy to excite charge carriers across it.

The term 'energy band gap' describes the difference in energy between the populated valence band in a semiconductor and the empty, or mostly empty, conduction band. These energy bands occur as a consequence of the periodic nature of crystalline structure. For an atom, or a crystal, Schrödinger's equation can be solved to determine the possible energy levels of its constituents. In a crystalline structure the allowed energy states for individual atoms overlap in a periodic way, producing delocalized allowed energy regions for the electrons which extend across the entire crystal. A Bloch wave function satisfies this condition. The Bloch energy states, determined by a Bloch wave function, can be described using the wave vector $\mathbf{k}$ and the crystal band number n as follows (Nelson)

$$\psi_n(\mathbf{k}, \mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r})e^{i\mathbf{k} \cdot \mathbf{r}} \quad (1)$$

The eigenenergies can be found by solving the Schrödinger equation for each n , and $\mathbf{k}$.

The allowed energy levels do vary in $\mathbf{k}$, and are typically plotted for the few most important directions along the crystal lattice.

Figure 1: Band structure of silicon, energy vs $\mathbf{k}$ (Seeger)

As seen in Figure 1, the lowest energy point on the conduction band occurs at a different wavevector, $\mathbf{k}$, from the highest energy point in the valence band, meaning that silicon is an indirect band gap material. Electrons at the highest energy in the valence band which are excited to the lowest energy level of the conduction band cannot undergo a direct transition; they must interact with the lattice via phonon transfer in order to have conservation of momentum. This extra step reduces the transition probability. The effect

is a reduction in the absorption coefficient, which directly limits the efficiency of silicon photovoltaics. The absorption coefficient for a given photon energy determines the charge carrier generation rate per unit volume, G (m^{-3}), as follows (Luque)

$$G = \alpha N e^{-\alpha x} \quad (2)$$

N = photon flux into the volume (number of photons $\cdot \text{m}^{-2} \cdot \text{s}^{-1}$)

α = absorption coefficient (m^{-1})

x = distance from the surface (m)

This absorption coefficient is plotted in Figure 2 for silicon and gallium arsenide.

Figure 2: Absorption coefficient as a function of photon energy for Si (indirect band gap) and GaAs (direct band gap) at 300 K. (Luque)

Photon absorption can be maximized by increasing the mean free path of photons in the absorber material. For planar solar cells this simply means thicker wafers, but increasing wafer thickness also increases the distance which charge carriers must travel to exit the cell, which in turn increases the likelihood of recombination. This is a fundamental material limitation which is unavoidable for silicon, such that even using thick silicon wafers and assuming no reflection the low absorption coefficient limits the theoretical maximum possible power conversion efficiency to 29.8% (Tiedje). This limitation in photovoltaic efficiency could be addressed, however, by using a direct bandgap material with a higher absorption coefficient such as gallium arsenide, and by finding a way to reduce electron transport distance without reducing the mean free path of photons in the material.

Figure 3: Best research-cell efficiencies (Kazmerski)

Many different solar cell designs are currently being developed. As shown in Figure 3, the power conversion efficiencies of most solar cell design types begins quite low but increases over time with research and development. There are many good cell designs represented in this chart, but there will always be room for new innovations. Many of the designs currently being researched are polycrystalline films of cadmium telluride or $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_{2-y}$ (CIGS), many microns thick, which require large quantities of rare materials, and extremely sensitive high-temperature fabrication processes. The most efficient solar cells yet developed require concentrated light sources to achieve maximum efficiency, and most of the research cells require processes which are not feasible for industrial-scale production.

The solar cell designed at Portland State University and reported here is designed to address a number of these limitations, incorporating materials with higher absorption coefficients than silicon, which require lower temperature processes than thin-film photovoltaics, and also incorporate novel optical and electrical structures without intensive fabrication processes.

1.3 Extremely Thin Absorber (ETA) Solar Cell Design

A new photovoltaic cell has been designed at Portland State University (Nadarajah). This multi-layer, extremely thin absorber, nanostructured, hybrid organic/inorganic photovoltaic cell addresses many of the limits of traditional silicon photovoltaics in novel ways. It is composed of inexpensive materials, fabricated using entirely 'table-top' chemistry, and uses relatively low-temperature processes. The fundamental structure of this photovoltaic cell (Figure 4) is as follows: a glass base layer for mechanical support, a transparent conductive oxide front contact, a nanostructured n-type (lightly doped) conductive oxide, an extremely thin absorber layer, a p-type polymer layer, and a gold back contact. Light enters through the glass and into the cell via the transparent conductive oxide, fluorine doped tin oxide (FTO). Silver paint is applied directly onto a bare region of the transparent conductive oxide.

Figure 4: ETA solar cell design

The extremely thin absorber solar cell design relies on a highly structured substrate that increases photon path length to enhance optical absorption, while simultaneously reducing transport path length for excited charge carriers (Ernst). The highly structured substrate in this case is aluminum doped zinc oxide nanowires, which also provides the n-type side of the heterojunction. The absorber layer is cadmium selenide, a direct bandgap semiconductor selected both for optimum bandgap size and for

Figure 5: Cadmium selenide band structure (Kobayashi)

high absorption coefficient within the active photon energy region. As can be seen in Figures 5 (Kobayashi), cadmium selenide has a direct band gap structure; this gives it a higher absorption coefficient.

In addition to geometric optimization, the materials of the ETA solar cell are selected to enhance separation between dissimilar charge carriers. The band gaps of the n-type, absorber, and p-type materials are offset, as can be seen in Figure 6, such that positive and negative charge carriers excited in the absorber region are swept in opposite directions, imposing a near-immediate physical separation which reduces recombination losses within the absorber layer of the device.

Figure 6: ETA solar cell band gap alignment

Chapter 2 - Characterization

2.1 Characterization

Photocurrent and current-voltage (I-V) response measurements are used to characterize the photovoltaic properties of these solar cells. The photocurrent response of the solar cells is measured under monochromatic light and used to calculate the wavelength-specific external quantum efficiency. The I-V behavior of the solar cells are measured both in the dark and under illumination by a white light simulating natural sunlight, these measurements are used to calculate the overall power conversion efficiency of cells.

2.2 Photocurrent

Figure 7: Photocurrent Characterization Setup

Photocurrent measurements were taken using a Keithley 428 Current Amplifier, an EG&G 5208 Lock-In Amplifier, and a Sciencetech 9055 Monochromator. To measure photocurrent response, an incandescent bulb was used to shine white light through a light chopper and into the monochromator. This monochromator used a rotating diffraction grating to produce monochromatic light. This monochromatic light was then sent via fiber optic cable to the characterization platform and into the sample (Figure 7, modified from a Creative Commons image by Alison Chaiken). The characterization platform and sample was covered by a black box to block ambient light. The sample was placed on the platform and contact probes were lowered to make back contact directly above the light output and front contact through a silver paint dot on the

tin oxide layer at the edge of the cell. The incident light on the photovoltaic cell produced a current response, which was amplified by a factor of 10^5 and transformed into a voltage signal by the current amplifier. The signal was then sent through an EG&G 5208 Lock-in Analyzer to the Labview acquisition software. The lock-in analyzer amplified the input signal and used the light chopper to produce an internal reference signal with the light chopper's frequency. It then sent the product of the reference and photocurrent signals through a low pass filter to produce a DC signal proportional to the amplitude of the input signal. The amplitude of this signal is the photocurrent, as it is the difference between the total current of the cell and the dark current. The x and y modes of the lock-in amplifier output correspond to the signal amplitude times the cosine and sine (correspondingly) of the phase difference between the photocurrent signal and the reference signal. The third mode, R, is the magnitude of the signal vector so it simply represents the signal amplitude. The R mode was used for these measurements.

Figure 8: Photodiode Responsivity Curve

In order to understand a solar cell's photocurrent response for a specific wavelength, it is necessary to know the number of incident photons at that wavelength. A photodiode with known spectral responsivity ($R(\text{mA/mW})$, Figure 8) was used to calculate the number of photons per wavelength in the light source. This photodiode produced a photocurrent output ($i(\text{mA})$) when exposed to light from the monochromator, as the monochromator performed a wavelength sweep in 10nm increments from 300nm to 900nm. The intensity of light from the monochromator was calculated as follows:

$$I(\text{mW}) = i(\text{mA})/R(\text{mA/mW}) \quad (3)$$

The energy of incident photons was calculated using the following formula:

$$E_{\text{photon}} = hc/\lambda_{\text{photon}} \quad (4)$$

Where h is Planck's constant, c is the speed of light, and λ_{photon} is the wavelength of the photon. The number of photons from the monochromator at a given wavelength can then be calculated as follows:

$$\# \text{ of photons at a given wavelength/second} = I(\lambda)/E_{\text{photon}}(\lambda) \quad (5)$$

With the number of incident photons at a given wavelength, it is possible to find the external quantum efficiency of a solar cell. First, the photocurrent produced by a solar cell under illumination can be calculated from the output voltage of the lock-in amplifier (V_{out}) and the amount of applied gain (Gain) using this ratio:

$$\text{Photocurrent}_{\text{cell}}(\text{A}) = \frac{V_{\text{out}}(\text{V})}{\text{Gain}(\text{V/A})} \quad (6)$$

The number of electrons generated per second while under illumination from the monochromator for a given wavelength was found to be:

$$\text{Number of electrons per second} = \text{Photocurrent}(\text{A})/q \quad (7)$$

At this point the External Quantum Efficiency (EQE) at each wavelength, the percentage of incident photons which produce one collected electron-hole pair, can be calculated:

$$EQE (\%) = \text{electrons per second} / \text{photons per second} \quad (8)$$

The external quantum efficiency expresses the percentage of incident photons which produce collected electron-hole pairs.

2.3 Solar Simulator Calibration for Current-Voltage (I-V) Measurement

I-V characterization is used to calculate the overall power conversion efficiency and the fill factor of the solar cell. It can also provide information about the type of loss mechanisms affecting the cell. IV characteristics for a given solar cell will vary depending on the illumination spectrum, making it necessary to simulate Standard Testing Conditions as closely as possible to accurately characterize these solar cells.

Figure 9: ASTM Spectra of solar radiation; extraterrestrial, terrestrial direct, and direct normal + circumsolar

The irradiance and metrological conditions that comprise Standard Testing Conditions in the photovoltaic community (ASTM Standard Testing E1036) are cell temperature of 25°C and hemispherical air mass (AM)1.5 irradiance spectrum (Figure 9). This spectrum

is calculated using the Simple Model of the Atmospheric Radiative Transfer of Sunlight (SMARTS) program (Gueymard). The total irradiance of the AM 1.5 spectrum (direct + circumsolar) integrates to 901.3 W/m^2 between 280nm and 4000nm. The atmospheric conditions of the AM1.5 spectrum (tabulated in the American Society for Testing and Materials ASTM G173.03 table) are listed as the 1976 U.S. Standard Atmosphere, an absolute air mass of 1.5, with a receiving surface as an inclined plane at 37 degree tilt toward the equator, facing the sun (i.e., the surface normal points to the sun when it is at an elevation of 41.81 degrees above the horizon, as defined at <http://rredc.nrel.gov/solar/spectra/am1.5>). The testing conditions advocated by the Photovoltaic for Utility Scale Applications (PVUSA) Test Conditions are 20°C and 1000 W/m^2 hemispherical, 850 W/m^2 direct normal irradiance. The following process was used to replicate ASTM G173.03 conditions as closely as possible.

For this solar cell design, the important parameter for the solar simulator to match is the number of photons with energy above the band gap of cadmium selenide as the ASTM G173.03 conditions. These measurements were performed at ambient temperature of 22°C, with white light from an incandescent bulb with variable power settings directed to the samples via fiber optic cable to reduce heating effects. The white light was calibrated to simulate AM1.5 solar spectrum with irradiance of 850 W/m^2 by producing an equivalent number of photons in the 300-800nm range.

The spectrum of the solar simulator light source at different power settings is different from that of M1.5, so the calibration process required a number of steps. First, the photocurrent at zero bias (PDiode) of an OSI Optoelectronics 10DP photodiode with PIN 11-02-004, Lot # 0734-1, and with known responsivity ($R(\text{mA/mW})$, Figure 9) was measured while illuminated by the solar simulator light source at various different power settings. The light spectra of the white light source were also measured at those same power settings using a StellarNet EPP2000 spectrometer, which measures the incident

Figure 10: White Light Spectra at different power settings, mW/cm^2 , with AM 1.5 spectrum superimposed

power at a given wavelength in counts ($\text{counts}(\#/\lambda)$). The calibration scaling factor $S(\text{mW}/\text{counts})$ can be calculated as follows:

$$S(mW / counts) = \frac{PDiode(mA)}{\sum_{\lambda=300}^{1100} R(mA / mW)_{\lambda} * counts_{\lambda} = counts * mA / mW} \quad (9)$$

The intensity of the white light per surface area can now be calculated for each wavelength (figure 10):

$$I(mW/cm^2)_{\lambda} = counts_{\lambda} * S(mW/counts) / photodiode \ surface \ area \ (cm^2) \quad (10)$$

Equations (4) and (5) can now be used to calculate the number of photons per second per wavelength in the white light spectra, as well as the number of photons per second per wavelength in the ASTM 1.5 spectra. The ETA solar cell cells discussed here is not responsive to wavelengths above 800nm or below 300nm, so the number of photons in the 300-800nm range was calculated for each white light power level. This was plotted against the photodiode response which that white light power level produced (Figure 11). The number of photons in the 300-800nm range of the AM 1.5 spectra was also plotted. Their intersection indicates the photodiode response to which the white light should be tuned, as it corresponds to the power setting which produces a white light spectrum with the same number of photons as the AM 1.5 spectra in the 300-800nm range.

Figure 11: Photodiode response vs. the number of incident photons on the photodiode area in the active wavelength range. The number of incident photons for different power levels was calculated using the spectra from Figure 10.

The photodiode response which corresponds to the same number of photons in the 300-800 nm range as found in the AM1.5 solar spectra was found to be 22mA. The total irradiance of the AM1.5 solar spectra integrates to 901.3 W/m^2 , so it must be scaled down by 6 % to bring us to the standard 850 W/m^2 incident irradiance. The white light power setting must likewise be scaled down by that same percentage, to the setting which produces a 21.7mA photodiode response, to most accurately simulate 850 W/m^2 of incident power in the AM1.5 solar irradiance spectra. This white light power setting is used for all IV measurements.

2.4 Current-Voltage

Current-voltage measurements provide important information regarding the power conversion efficiency and possible loss mechanisms of the solar cell. Figure 12 shows I-V curves produced both under illumination and in the dark for this ETA solar cell design. The third line simply indicates the current and voltage which produce maximum power for this solar cell.

Figure 12: I-V curve with calculated power from ETA solar cell

The total current produced by an ideal solar cell is equal to the photocurrent (generated under illumination, I_l) minus the dark current (diode current, measured in the dark, I_D), according to the following equation (Nelson)

$$I = I_l - I_D = I_l - I_0 \left(e^{\frac{qV}{kT}} - 1 \right) \quad (11)$$

where I_0 is the saturation current of the diode, q is the elementary charge, k is the Boltzmann constant, T is the temperature of the solar cell, and V is the measured cell voltage. At zero voltage the dark current goes to zero, and the total current becomes simply the photocurrent. This is called the short circuit current, I_{sc} . For an ideal cell, the photocurrent does not change with voltage, and the change in total current as voltage changes is due to the change in dark (diode) current. It is clear from Figure 12 that the current measured under illumination is not simply the dark current offset by some amount of constant photocurrent, this is due to resistive loss mechanisms in the cell which decrease the total current for a given voltage, decreasing the ideality of the cell.

The fill factor (FF) is a means of evaluating the ideality of a solar cell, with reference to the cell's own open circuit voltage (V_{oc} , measured under illumination at zero current) and short circuit current. It is defined as the ratio between the maximum power produced by the cell, and the product of the cell's short circuit current and open circuit voltage, as follows (Nelson):

$$FF = \frac{P_{MAX}}{P_T} = \frac{I_{MP} * V_{MP}}{I_{SC} * V_{OC}} \quad (12)$$

The maximum power produced by a solar cell (P_{MAX}) is always less than P_T , due to the cell's diode behavior. If the fill factor is very small, this indicates that the cell does not have strong diode character, which can be caused by resistive losses or shunted behavior. For the I-V curve in Figure 12, for example, $V_{MP} = 0.15V$ whereas $V_{OC} = 0.24V$. The fill factor for the I-V curve pictured is 0.28, indicating the presence of significant resistive losses.

To measure IV characteristics a series of voltage steps were applied across the cell and current was measured at each step using a Keithley 236 Source Measure Unit and Labview software, first in the dark and then under illumination. The number of photons in the 300-800nm region was equivalent to a solar spectrum power of 850W/m^2 , and the area of each gold pad, equivalent to the active area of the cell, was 7.0 mm^2 . The current measured was divided by the area of the gold pad to find current per area.

Chapter 3 - Fabrication

3.1 Transparent Conducting Oxide

The substrate layer of this solar cell design is Pilkington Tec 8 glass, which is a 3.2mm thick clear soda lime glass coated on one side with a thin film of fluorine-doped tin oxide (FTO). This is the transparent conductive oxide layer with a sheet resistance of 6-9 Ohms/sq., which provides an electrical contact for the cell without blocking incident light. The soda lime glass provides mechanical support for the extremely thin active layers of the solar cell. The FTO coating provides necessary conductivity between front contacts and acts as the electrode on which zinc oxide nanowires are grown via electrochemistry. Incident light passes into the cell from this glass layer, making FTO the first electrically relevant material it reaches. Wavelength specific absorption and transmittance of this material is not provided by Pilkington, but has been characterized by an external research group (Li). Li et al tabulated the transmittance and optical absorbance of Tec 8, it is listed in Figure 13 and 14 as 'Commercial I' and 'commercial SnO₂-coated glass', respectively. Li's research indicates that the use of research grade SnO₂ coated glass rather than commercial samples increased short circuit current in thin film CdTe photovoltaic cells from 20 to 23 mA/cm². It is likely that the short circuit current of the ETA solar cell reported here could also be increased by 10% by using a research grade FTO layer rather than the commercial layer in future optimizations.

Figure 13: Optical transmission and absorption of FTO on glass

Figure 14: Optical absorption of fluorine-doped tin oxide on glass

3.2 P-Type Polymer - Poly(3-hexylthiophene)

Figure 15: Poly (3-hexylthiophene) structure, individual (left) and conjugated (right) (Nicholson)

Poly (3-hexylthiophene), P3HT, is a conductive polymer with each monomer composed of a heterocyclic ring of one sulfur and four carbon atoms, with a 6 carbon alkyl chain extending from the number three position. These monomers tend to self-organize under certain conditions by conjugating thiophene ring pi orbitals into a semi-infinite pi-orbital system spanning many monomers, as can be seen in Figure 15. The alkyl chains arrange into alternating fingers in a 2-dimensional layer. This allows the thiophene's pi orbital system to span relatively large distances, with the lowest unoccupied molecular orbital (LUMO) behaving like a semiconductor's conduction band, and the highest occupied molecular orbital (HOMO) behaving like the valence band.

Thin films of P3HT have an absorption peak around 510-530 nm (Shrotriya), corresponding to a gap between HOMO and LUMO levels of 2.39 eV (Xu), although its effective energy band gap is typically reported as 2 eV (Salzner, Bundgaard, and Hou).

As advances have been made in the synthesis and control of regioregularity of this

molecule, the HOMO and LUMO levels have been shown to shift, and the difference between HOMO and LUMO levels of the more ordered regioregular films has decreased to 1.7-1.8 eV (Roncali). These levels function somewhat like the conduction and valence energy bands of a semiconductor in terms of absorbing photons, yet they tend to produce excitons rather than free charge carriers. The excitons produced in conductive polymers have significantly lower mobilities than free charge carriers and cannot easily dissociate, which can lead to higher V_{oc} and lower J_{cs} than similar inorganic solar cells (Gregg). In addition, the P3HT/Au interface has been shown to act as a charge injection barrier, due to the small mismatch between the work function of gold and the HOMO level of P3HT (Lyon).

P3HT does exhibit some photovoltaic behavior due to this HOMO/LUMO gap, but this is not its primary role in this cell design. The P3HT layer is on the back side of the solar cell, most incident light is absorbed by the glass, FTO, zinc oxide nanowires, or cadmium selenide. For this reason, P3HT in this device primarily functions as a p-type semiconductor in the heterojunction necessary to separate charge carriers and produce a current. Commercially supplied P3HT is certified to a specific molecular weight, typically above 60,000 mol wt. for solar cell applications, which indicates the extent to which individual P3HT molecules are conjugated into a regioregular crystalline structure. The P3HT used in these solar cells was supplied by external companies, but the molecular weight differed for different batches. This had a large effect on overall cell performance, so the molecular weight of the P3HT in use will be indicated for all results.

Many of the solar cells discussed here use the 65,000 mol wt. P3HT, which is considered suitable for photovoltaics. Some of the solar cells use a lower molecular weight material, which of course had reduced electron mobility and thus reduced power conversion efficiency in the device.

3.3 Cadmium Selenide Nanoparticles

This solar cell relies on cadmium selenide (CdSe) to act as the primary absorber for incident photons. Cadmium selenide is a II/IV semiconductor with a direct band gap of 1.74 eV. Cadmium selenide has a wurtzite lattice structure at standard temperature and pressure. As a direct bandgap material, cadmium selenide has a much higher absorption coefficient than silicon, an indirect bandgap material. A similar material, cadmium telluride, is currently used to produce thin film solar cells, but cadmium is a carcinogen so the film thickness of $\sim 5\text{ }\mu\text{m}$ (Aberle) raises some environmental and health concerns among the general public. The ETA solar cell design avoids this problem by using a much thinner layer of material and increasing photon mean free path via repeated reflection rather than bulk film depth. The other cadmium selenide based solar cell designs currently being researched primarily use cadmium selenide nanoparticles to absorb photons and ‘sensitize’ the rest of the solar cell (Lee), yet the charge injection barrier between cadmium selenide nanoparticles and the substrate material remains quite high, limiting the effectiveness of the ‘sensitization’. In contrast, the solar cell design reported here relies on the small size of cadmium selenide nanoparticles suspended in solution to deliver material to the narrow gaps between nanowires, followed by annealing the nanoparticles to produce a polycrystalline thin film higher conductivity.

The cadmium selenide nanoparticles used here were 5.8nm nanoparticles in toluene as the solvent, with octadecylamine as a ligand. These were purchased from NN-Labs, and

their technical specifications can be found in Figure 16. Cadmium selenide nanoparticles were also produced in-house for use in these solar cells; these will be discussed in a later section.

CdSe Dot Nanocrystals		
Composition	CdSe stabilized by octadecyl amine (ODA) ligands	
Concentration	Order amount dependent	
Organic Impurities	<1% (not including ligands)	
Solvent*	Toluene	
Volume	Order amount dependent	
Lifetime	One year if stored properly (dark at 4-10 °C)	
PL fwhm (nm)	23-28	
UV-Vis hwhm (nm)	13-17	
UV Peak (nm)	size (nm)	Emission Peak (nm)
460 ± 10	1.9-2.1	485-510
480 ± 10	2.1-2.3	505-530
500 ± 10	2.3-2.4	525-550
520 ± 10	2.4-2.6	545-570
540 ± 10	2.6-3	565-590
560 ± 10	3-3.5	585-610
580 ± 10	3.5-4	600-615
590 ± 5	4-4.3	610-625
600 ± 5	4.3-4.7	612-617
610 ± 5	4.7-5.2	620-635
620 ± 10	5.2-6.2	615-650
640 ± 10	6.2-7.7	645-670

Figure 16: Technical Specifications of cadmium selenide from NNLabs

3.4 Methodology

3.4.1 Substrate Cleaning

Pilkington Tec 8 glass was cut into roughly 2 cm x 2 cm squares. These pieces were placed in a beaker and immersed in acetone (90% purity), which was placed in a water bath and sonicated for 30 minutes. The glass was then rinsed in de-ionized H₂O, immersed in a beaker of methanol (99% purity) and sonicated for 30 minutes. The glass substrate was then soaked in 2 Molar HNO₃ for 24 hrs, then rinsed in di-H₂O and blown dry with inert nitrogen gas.

3.4.2 Zinc Oxide Thin Film Deposition

Many of the solar cells described here employ a polycrystalline thin film of zinc oxide between the conductive tin oxide and the aluminum-doped zinc oxide nanowires. This eliminates contact between the conductive oxide and the absorber layer, thus reducing current losses due to shunting.

A zinc oxide precursor solution was produced by mixing 30mL ethanol, 1.6mL acetic acid, 0.5798 g zinc acetate (to make a 0.1 molar zinc acetate solution), 1mL H₂O, and sonicating until fully dissolved. The glass substrate was placed FTO side up on a standard hot plate and warmed slowly to 300°C. The substrate temperature was measured

using the IR thermometer of a hand-held multi-meter. The solution was airbrushed onto the substrate in 1 second layers of even sweeping spray, with 30 second pauses for solvent evaporation between layers, for 45-55 layers. Airbrushing was performed using an Iwata-Medea Eclipse series HP-BCS airbrush with 2 psi pressure using compressed clean dry air. The substrate was then annealed for 2 hours at 380°C in air, then allowed to cool slowly in the annealing oven for 2 hours.

3.4.3 Zinc Oxide Nanowire Growth

Aluminum doped zinc oxide nanowires were deposited via aqueous electrochemical deposition. Electrodeposition was performed with an EG&G Model 283 Potentiostat/Galvanostat using the PowerSTEP chronoamperometry options of the PowerSuite software. The electrodeposition solution was oxygen saturated by bubbling oxygen through the solution, which produces hydrogen peroxide. Electrons from the cathode reduce hydrogen peroxide to hydroxide ions. These hydroxide ions then react with zinc ions to produce zinc oxide and water (Leprince-Wang). The growth mechanism can be summarized as follows:

This indicates that every two electrons used produces one zinc oxide molecule, providing a direct correlation between current during nanowire growth and nanowire growth rate. The morphology of the zinc oxide deposition also depends heavily on the pH of the

solution, as a low pH solution can attack zinc oxide and a high pH solution can make thicker wires. Nanowire growth is also influenced by the cleanliness of the substrate and by the concentration of zinc ions and supporting electrolytes.

The nanowire deposition process is a standard three electrode chemical bath electrodeposition. The zinc oxide deposition solution (0.3mM ZnCl_2 , 0.1M KCl, 5 μm AlCl_3 , in H_2O) is heated uniformly to 80°C on a standard hot plate. Oxygen is bubbled through the solution while stirring to maintain uniform saturation and the solution is maintained at this state for the course of the electrodeposition. An Ag/AgCl₃ reference electrode is submerged, along with a platinum foil cathode and a platinum wire anode with substrate attached. A bias of -1.0 V was applied to the cathode to keep the cathode and anode at 1.0 V potential difference for one hour of nanowire growth. The glass substrate with its deposited zinc oxide layer was then removed from the solution, rinsed in de-ionized H_2O , blown dry with N_2 , annealed for 2 hours at 380°C in air, and then allowed to cool slowly to room temperature.

3.4.4 Oxygen Plasma Clean for Zinc Oxide Nanowires

Zinc oxide nanowires must be conformally covered with cadmium selenide nanoparticles for the ETA solar cell to function properly. Exposing zinc oxide nanowires to oxygen plasma clean has been shown to significantly improve cadmium selenide adsorption to the zinc oxide surface (Leschkies). The mechanism for this improvement is not entirely

clear, but it has been hypothesized that it could be due to the production of dangling surface bonds which activate the surface, or simply the removal of contaminants making the surface more reactive.

Immediately before depositing cadmium selenide on the zinc oxide nanowires, the nanowires were exposed to an oxygen plasma clean for 7 minutes. Oxygen plasma cleaning was performed using a Tegal corporation PLASMOD plasma cleaner, which uses an 100-Watt RF plasma generator and functions at about 500×10^{-6} ATM (0.38 Torr).

3.4.5 Cadmium Selenide Dropcoat

The absorber layer of an extremely-thin-absorber solar cell must be very thin with high conductivity, and make good contact with the zinc oxide nanowires. This is achieved by allowing cadmium selenide nanoparticles to adhere to individual nanowires, and then annealing them to release the stabilizing ligand and allow individual crystal lattices to fuse into a polycrystalline thin film. First, the substrate is warmed gently to 40°C on a hotplate. Cadmium selenide nanoparticles suspended in toluene are then drop-coated directly on the substrate, in quantities between 0.05 cc/cm² and 0.2cc/cm². The substrate is warmed to 200°C for 10 minutes to release the ligand and reduce nanoparticle migration during subsequent drop-coat layers, and then cooled back to 40°C. This process is repeated until the desired layer thickness is reached. The standard post-deposition anneal is at 380°C for 24 hours at atmospheric pressure in the presence of

CdCl_2 . Drop-coating of absorber layer was performed using solvent-resistant syringes from Beckton, Dickinson and Company and a conventional hotplate to warm the substrate.

3.4.6 Poly(3-hexylthiophene) Spincoat

P3HT is purchased from Alfa-Aesar or Sigma Aldrich, dissolved at 10g/L in chloroform, and rocked on a mechanical rocker for 24 hours. This P3HT solution is then spincoated onto the substrate using a Laurell Technologies WS-650-15 spin coater at room temperature in an inert nitrogen environment, with layers of 1000 revolutions per minute rotation speed for 40 seconds. The number of layers deposited was varied based on the molecular weight of the purchased P3HT, as determined by the supplier. The sample was then heated to 200°C for 15 minutes in vacuum, and allowed to cool to room temperature under vacuum, which takes roughly 2 hours.

Chapter 4 - Data & Results

4.1 Best Photovoltaic Response

The best photovoltaic response for this cell design was produced with 65,000 mol wt. P3HT, commercially purchased cadmium selenide nanoparticles with UV emission peak at 640nm, and a zinc oxide thin film layer between the fluorine-doped tin oxide substrate and the zinc oxide nanowires. The zinc oxide thin film was thermally annealed for one hour at 380°C; the zinc oxide nanoparticles were aluminum doped, thermally annealed for two hours at 380°C, and exposed to oxygen plasma for 7 minutes. The cadmium selenide nanoparticles were thermally annealed for 24 hours in the presence of cadmium chloride.

Figure 17: EQE of the best solar cell of this design

It is clear from the external quantum efficiency plot (Figure 17) that different pads on the cell show similar photovoltaic behavior, indicating some consistency in performance across the entire cell. This solar cell's I-V characteristics are shown in Figure 18. The cell has an overall power conversion efficiency of 0.98% and a fill factor of 28%.

Figure 18: IV characteristics of the best solar cell of this design

4.2 Characterization of ZnO growth and morphology

All versions of this photovoltaic device use zinc oxide nanowires. Zinc oxide is a transparent, conductive, nontoxic, and highly stable semiconductor which is easy to work with and has excellent optical and electrical properties for photovoltaic devices. It is inexpensive and can be easily doped n-type with a variety of donor elements (Seipel). Bulk zinc oxide has a direct band gap of 3.3 eV (Figure 19) at room temperature (Srikant) with a large exciton binding energy (60 meV, Thomas). It can be deposited as nanowires at atmospheric pressure and low temperature. These zinc oxide nanowires provides the nanoscale morphology necessary for the extremely-thin-absorber type solar cell, they also provide the n-type semiconductor necessary to produce a p-i-n heterojunction. The nanowires are grown to be 100-200 nm in diameter, roughly 1.5 micrometers tall, and aligned within 30 degrees of vertical.

Figure 19: ZnO band structure (Berger)

4.2.1 Galvanostatic Deposited Seed Layer

Figure 20: ZnO nanowires, standard recipe

It has been suggested that varying the size and shape of zinc oxide nanowires could alter this solar cell's behavior (Cheng). The electrochemical environment of the nanowire growth process is extremely influential on nanowire quality and aspect ratio. The influence of variations in the initial electrical environment during electrochemical deposition of zinc oxide nanowires was investigated. The standard zinc oxide nanowire growth recipe involves one hour of potentiostat conditions of -1.0 V and produces nanowires that are 200-250nm in diameter and 1-2 μm long (Figure 20).

Beginning deposition with one minute of galvanostatic conditions (1 mA/cm^2) produced clusters of small ($\sim 20\text{nm}$) seed crystals on some surfaces of the bare FTO substrate, accompanied by some larger ($\sim 100\text{nm}$ in diameter) rougher seed crystals with a much smaller aspect ratio than the final nanowires (Figure 21).

Figure 21: 1 Min. galvanostatic ZnO nanowire growth

An electrodeposition environment of one minute of galvanostatic conditions (1 mA/cm^2) followed by 59 minutes of potentiostatic conditions (-1.0 V) produced nanowires of various diameters ($50\text{-}200\text{nm}$), with many of them significantly narrower than the standard growth. They were all of roughly the same length, 1000nm (Figure 22). This suggests that the largest seed crystals grew significantly longer without increasing in width, or that they were above the critical nucleation size in potentiostatic conditions and

thus were redistributed into a layer of thin film or seed crystal zinc oxide. These nanowires also appear slightly rougher than those of the standard deposition, as if they are slightly unfinished or grew in a less controlled manner. It may be useful to note that this wire growth was also much less dense than the standard growth, as the FTO substrate is still visible at the base of the wires.

Figure 22: 1 Min. galvanostatic + 59 Min potentiostatic ZnO nanowire growth

A nanowire growth environment of five minutes of galvanostatic conditions ($1\text{mA}/\text{cm}^2$) produced very large ($\sim 1000\text{nm}$ diameter) disordered clumps, as well as a few rough seed crystals (Figure 23). In some regions these clumps seemed to be spreading out onto the FTO surface (Figure 24), suggesting that the largest agglomerates of zinc oxide tended to redistribute across the surface rather than producing ordered wires.

Figure 24: 5 Min. galvanostatic ZnO nanowire growth

Figure 23: 5 Min. galvanostatic ZnO nanowire growth

Following the 5 minutes of galvanostatic ($1\text{mA}/\text{cm}^2$) conditions with 55 minutes of potentiostatic conditions produced narrower nanowires (80-100nm) of more consistent size (Figure 25, 26). These wires are roughly the same length (1000nm), and their surfaces appear rougher than any of the other nanowires. Their growth distribution is also denser, as the FTO substrate is no longer visible between the wires.

Figure 25: 5 Min. galvanostatic + 55 Min potentiostatic ZnO nanowire growth

Figure 26: 5 Min. galvanostatic + 55 Min potentiostatic ZnO nanowire growth

It appears from this study that zinc oxide nanowire diameter can be controlled by modifying the electrical environment of the early growth stage. However, the highest quality nanowires were produced under purely potentiostatic conditions, so this has remained the deposition procedure for all solar cells.

SEM analysis was performed using an FEI Sirion field emission Scanning Electron Microscope, with electron energies from 5kV to 20kV. Where EDX analysis was also performed, it was performed using this FEI Sirion SEM.

4.2.2 Zinc Oxide Thin Film

The standard (FTO/nanowire zinc oxide/cadmium selenide/P3HT) solar cell discussed here involves growing zinc oxide nanowires directly on the FTO substrate. A modification which may improve cell performance has been to deposit an un-doped zinc oxide thin film via spray pyrolysis from a zinc acetate precursor solution directly on top of the FTO layer before growing zinc oxide nanowires. The thin film layer is conformal to the FTO grain structure, yet appears to be composed of individual grains of about 50nm in diameter (Figure 27). The EDX data in Figure 28 indicates that the thin film is

Figure 27: SEM image of ZnO thin film on FTO substrate

composed of zinc oxide, which is on top of fluorine-doped tin oxide, which is on top of soda-lime glass (fluorine content is too low to be detected using this EDX). The small amount of carbon present is due to the carbon tape used to affix the sample to the sample holder. The layer is deposited between FTO and the nanowires to minimize direct contact between FTO and the absorber layer (Elias). There is also some possibility that the p-type layer could contact the FTO in a region of low cadmium selenide coverage, which would greatly decrease cell efficiency by reducing shunt resistance. This zinc oxide thin film layer increases the shunt resistance of the solar cell, thus reducing current loss. It is helpful for all these cell designs, but it is most important for the solar cell with copper(I) thiocyanate (CuSCN) replacing P3HT as the p-type layer (Tena-Zaera 2006). The zinc oxide nanowires grown on a zinc oxide thin film layer are of the same composition (Figure 29) as nanowires grown directly on FTO, but they are less uniform in size and shape (Figure 30).

Figure 28: EDX data of ZnO thin film on FTO substrate

Figure 31 shows the External Quantum Efficiency of a solar cell made from the zinc oxide thin film and zinc oxide nanowires shown here.. The best pad produced relatively high external quantum efficiency, but performance was not consistent from pad to pad. This is common for cells which are not fully optimized. It was produced with 40,000 molecular weight P3HT and cadmium selenide nanoparticles from NN Labs. Figure 32 compares the external quantum efficiency of cells with and without zinc oxide thin film using 65,000 mol. wt. P3HT.

Figure 29: EDX data of ZnO nanowires grown on ZnO thin film on FTO substrate

Figure 30: SEM image of ZnO nanowires grown on ZnO thin film on FTO substrate

Figure 31: EQE of solar cell made from ZnO nanowires on ZnO thin film

Figure 32: EQE of solar cell made from ZnO nanowires on ZnO thin film

4.3 Absorber Layer

The cadmium selenide absorber layer is produced by annealing cadmium selenide nanoparticles. The absorber layer produces the majority of the photovoltaic response, so optimization of this layer is critical. Figures 33 and 34 show cadmium selenide annealed

Figure 33: CdSe thin film on ZnO nanowires

into a thin film on a sample of zinc oxide nanowires grown on fluorine doped tin oxide.

Zinc oxide is brighter than cadmium selenide in SEM images, so the bright points

indicate regions where the cadmium selenide layer is thinner. Figure 34 is zoomed in on a zinc oxide nanowire covered by a thin layer of cadmium selenide.

Figure 34: CdSe thin film on ZnO nanowires

4.3.1 Cadmium Selenide Nanoparticle Growth and Ligand Exchange

Chemical vapor deposition is the most common method for depositing cadmium selenide on a nanostructured surface. This method produces highly conformal films, but it requires high temperature and expensive equipment. Depositing cadmium selenide nanoparticles onto the highly structured surface allows the nanoparticles to fit into the small crevices between nanowires, and annealing the nanoparticles into a thin film produces good contact with the zinc oxide surfaces. This is achieved by starting with cadmium selenide nanoparticles which are passivated with a surface ligand and suspended in a stabilizing solvent, dropcoating them onto the zinc oxide nanowires, and annealing them to form a polycrystalline thin film. This is possible when the particles are small enough to fit in between nanowires, which in some places are only 10 nm apart.

This process using cadmium selenide nanoparticles to produce a conformal thin film has been achieved repeatedly in this laboratory (Konenkamp) with nanoparticles purchased from NN Labs, which certifies a very narrow (24nm) full width half max photoluminescence peak (Figure 35). The wavelength of cadmium selenide nanoparticle photoluminescence is determined by the size of the nanoparticle, so a narrow photoluminescence peak indicates a small range in particle size. It is unlikely that such a narrow size distribution is necessary for uniform polycrystalline film distribution so a study was undertaken to investigate whether cadmium selenide nanoparticles could be synthesized, processed, and deposited in-house to produce functional solar cells.

Figure 35: Photoluminescence spectra of CdSe nanoparticles in toluene with ocadecylamine ligand, supplied by NN Labs

Andrew Pearson, a summer REU student with this laboratory with a background in chemistry, and Athavan Nadarajah, a graduate student in Dr. Koenenkamp's research group, established a procedure to grow cadmium selenide nanoparticles with a relatively small size distribution in a low-temperature and relatively nontoxic procedure. Pearson and Nadarajah followed a procedure from the University of Wisconsin, Madison's

Materials Research Science and Engineering Center's Interdisciplinary Education Group webpage. This procedure is based on those of Boatman and Yu. It involved adding a selenium-containing solution to a heated cadmium-containing solution to initiate nanocrystal growth, and then removing the solution from heat to quench the growth. These nanoparticles are grown in an octadecene solvent with an oleic acid ligand. Figure 36 shows the photoluminescence spectra for batches of these homemade nanoparticles which were quenched at different times to produce nanoparticles of different sizes. A typical photoluminescence spectrum had a full width half max of 36 nm, suggesting a broader size distribution than those produced by NN Labs. In addition, the homemade nanoparticles appear to be smaller than those from NN Labs, as their photoluminescence peaks occurred at smaller wavelengths.

Figure 36: Photoluminescence spectra from different batches of CdSe nanoparticles of different sizes

Attempts to deposit these nanoparticles directly on zinc oxide nanowires and anneal them into a polycrystalline cadmium selenide thin film were unsuccessful; the material did not form a solid.

Figure 37: Large CdSe crystal on octadecene/ZnO nanowires, after 16 hour anneal

The original solvent, octadecene, has a high boiling point (320° C) (Yu) which reduced the evaporation rate. The layer would not actually harden until subjected to a long anneal. This allowed the nanoparticles time as the heated solution evaporated to grow and cluster into large cadmium selenide crystals which sit on top of the zinc oxide nanowires (Figure 37). In addition, the material that did become roughly conformal around the nanowires

appeared too disordered and irregular to be cadmium selenide. Figure 38 shows a more conformal region, with bright particles which are likely cadmium selenide particles immersed in a layer of some other, less conductive material. Solar cells produced using these films did not demonstrate any photovoltaic response

Figure 38: CdSe nanoparticles in octadecene, deposited on ZnO nanowires and annealed for 16 hours

A solvent exchange was performed in order to improve the quality of this following the procedure of the University of Wisconsin at Madison's Materials Research Science and

Engineering Center's Interdisciplinary Education group (adapted from Munroe). The solution of cadmium selenide nanoparticles in octadecene solvent was placed in a centrifuge tube, combined with ethanol, and shaken to produce an emulsion. The colloid suspension was separated in a centrifuge, and the separated clear mixture of ethanol and octadecene was removed with a pipette. This process was repeated until shaking ceased to produce an emulsion; at which point the cadmium selenide precipitated and adhered to the edges of the glass centrifuge tube rather than mixing at all with ethanol. All remaining clear liquid was removed, and toluene was added to dissolve the cadmium selenide material.

Figure 39: Photoluminescence peak positions before and after solvent exchange, for 4 samples of different sizes

Figure 39 shows the progression of the absorption peak location for four different samples as the solvent exchange to toluene was performed. The peak location moves to higher wavelengths, indicating that the average particle diameter increased. This

suggests that smaller particles are drawn off in the separated solvent rather than remaining with the rest of the nanoparticles.

The solvent exchange process was successful, but even with a volatile solvent such as toluene the ligand used for these nanoparticles made them unsuitable for dropcoating.

The ligand, oleic acid, is a monounsaturated fatty acid found in large quantities in olive oil (Matalon). Its high boiling point tends to make it burn rather than evaporate, such that

Figure 40: Homemade CdSe nanoparticles deposited in toluene as colloid, on ZnO nanowires

the ligand liquid did not evaporate from the samples, even after hours of warming on the hot-plate and annealing in the oven. Figure 40 shows the result of depositing homemade Cadmium selenide in toluene on zinc oxide nanoparticles. Solar cells made using these nanoparticles did not show a measurable photovoltaic effect.

It is possible that the ligand which stabilizes these homemade nanoparticles caused this failure to perform, so following the solvent exchange a ligand exchange was performed from octadecene to octadecylamine, the same ligand as on the NNLabs cadmium selenide nanoparticles. This was performed by exposing the homemade cadmium selenide nanoparticles to an excess of octadecylamine for 24 hours, then removing all excess material using centrifuge washes in ethanol and methanol. Toluene was added as the solvent for these nanoparticles, and they were dropcoated at elevated temperature on zinc oxide nanowires. The sample was repeatedly warmed to 200°C in air and allowed to cool to evaporate all solvent and ligand material. Each layer of cadmium selenide in solvent was initially orange, but browned with heating, and hardened upon cooling. Solar cells made using this system showed no photovoltaic response.

Homemade cadmium selenide nanoparticles produced using these methods are not suitable for this solar cell design. These might be made viable by a more successful ligand exchange process.

4.3.2 Argon Plasma Cleaning Treatment to Optimize Cadmium Selenide/CuSCN Contact

A well-documented challenge for cadmium-based thin film solar cell production is making a high quality contact between cadmium selenide (or cadmium telluride) and the metal back contact. A variety of methods have been attempted to improve this contact (Pandey). The eta solar cell discussed here does not require a metal/cadmium selenide contact, however the challenge may be just as great to make a cadmium selenide

Figure 41: I-V Characterization of argon plasma cleaned (top) and not argon plasma cleaned (bottom) solar cells

- 1: Ar plasma cleaned at 0.38 torr with PLASMOD plasma cleaner
- 2: Ar plasma cleaned at ~0.05 torr with Fischione Instruments Model 1020 plasma cleaner
- 3: Ar plasma cleaned at ~0.05 torr with Fischione Instruments Model 1020 plasma cleaner
- 4: No Ar plasma treatment

contact with the p-type layer. In traditional thin-film solar cells the cadmium telluride back contact is improved by etching the layer with an acid immediately prior to applying metal contacts (Pandey). Acid etch processes are not possible here, as the acid would attack the Zinc oxide nanowires. Plasma etch processes have been used as a replacement to etch other cadmium-based semiconductors (Srivastav). In an attempt to improve the cadmium selenide/p-type layer contact, an argon plasma etch step was introduced post cadmium selenide anneal, to clean and activate the surface prior to p-type contact. Argon plasma cleaning was performed using a Fiscione Instruments Model 1020 Plasma Cleaner, which operates at a 50×10^{-3} Torr, or a Tegal corporation PLASMOD plasma cleaner, which functions at about 0.38 Torr. The cadmium selenide contact has the largest effect when the p-type polymer is replaced by copper thiocyanate (CuSCN), an inorganic p-type semiconductor which has shown some promise in cells of this type (Tena-Zaera 2009). The effect of an argon plasma step was studied for this modified solar cell, and it was found to significantly improve the external quantum efficiency of the solar cell, as shown in Figures 41. It was also found that the lower pressure plasma clean in the Fiscione plasma cleaner produced a greater improvement in cell performance than the higher pressure Plasmod plasma cleaner. Figure 42 compares I-V curves of argon plasma cleaned (Fiscione plasma cleaner) and uncleaned samples; it indicates better rectifying behavior for the argon plasma cleaned sample. The argon plasma cleaned sample did have more pads which demonstrate short-circuit behavior, suggesting that the plasma clean may have thinned or weakened the absorber layer, causing a short circuit through

the cell. This could also indicate that contaminants and resistive ligands are removed. A thicker absorber layer may be necessary to counter this effect.

Copper thiocyanate was studied as an inorganic replacement for P3HT which would give the solar cell greater resistance to radiative damage. It was not possible at the time for our research group to improve external quantum efficiency above 10% in the 500-700nm range using our methods so study of this material was abandoned.

Figure 42: I-V Characterization of argon plasma cleaned (top) and not argon plasma cleaned (bottom) solar cells

4.3.3 Cadmium Selenide Thermal Anneal Study

Annealing is a thermal process which relaxes crystal structures so that major defects in the crystal lattice can be released. The high temperatures required for this process cause more interstitial and vacancy defects to occur, but cooling slowly allows many of these defects to migrate out of the crystal structure. The defects which remain tend to stay fairly isolated rather than producing large dislocations or extensive lattice strain.

Annealing is also often necessary to activate dopants, as it allows the dopant material to easily replace lattice atoms and become a functional part of the lattice, rather than occupying an interstitial state and adding stress to the lattice.

Figure 43: External Quantum Efficiency for different CdSe anneal times

The cadmium selenide nanoparticles in this solar cell must be heated to fuse into a polycrystalline film, but a longer anneal also reduces the trap density which can reduce the cell's ability to act like a diode. In addition to reducing defects, cadmium selenide in photovoltaics is usually lightly chlorine doped via annealing in a cadmium chloride environment. A study was undertaken to see if functional solar cells could be produced without the use of cadmium chloride, and without annealing the zinc oxide nanowires before depositing cadmium selenide.

Figure 44: Summary of External Quantum Efficiency at 650 nm

Figure 43 shows the maximum external quantum efficiencies produced for different anneal times, in atmosphere at 380°C, and Figure 44 shows a summary of those efficiencies. All cells were produced with a zinc oxide thin film, aluminum doped zinc oxide nanowires grown at -1V for 1 hr, 0.1cc/cm² of cadmium selenide nanoparticle

solution dropcoated on the nanowires, 65,000 mol. wt. P3HT spincoated on the cadmium selenide after anneal, and gold back pads thermally deposited on the P3HT layer. The zinc oxide nanowires in these cells were plasma cleaned but they were not annealed before cadmium selenide deposition. It was found that the best external quantum efficiencies could be found between 8 and 10 hours of anneal time.

4.3.4 Cadmium Selenide Laser Anneal Study

This solar cell is revolutionary in part due to its low production cost. Thermal processes increase manufacturing costs, so reducing the temperature or time of a thermal process would reduce expense further. In addition, high temperature process steps limit substrate materials to those which can withstand high temperatures, including glass and excluding most flexible substrates such as plastics. If a process step could selectively heat layers without significantly warming adjacent layers it could reduce costs while allowing for flexible substrates. Laser annealing has been shown to reduce resistivity in cadmium selenide thin films (Feenstra) and it allows for a localized energy input by tuning

Figure 45: Absorption Spectra of Pyrex glass (provided by glassware supplier)

the wavelength of the laser to the cadmium selenide absorption range. Laser annealing has been used in the semiconductor manufacturing industry (Misra) but it has not yet been applied for agglomerating and annealing semiconductor quantum dots. Laser annealing was investigated as a replacement for the zinc oxide and cadmium selenide thermal anneal steps.

A glass/FTO/zinc oxide/cadmium selenide sample with unannealed zinc oxide nanowires was mounted to a holder and sealed inside an Erlenmeyer flask made of pyrex glass. The absorption spectra of pyrex glass can be found in Figure 45. The sample was then exposed to the beam of a frequency-tripled Nd-YAG laser with a wavelength of 355 nm, which has a diameter of approximately 4mm. Multiple locations on the sample were exposed to the laser beam in order to expose the majority of the area of each sample to the laser equally.

Solar cells made from these laser annealed samples showed high photoconductivity, but did not rectify well to generate power from incident photons. Exposing a sample to 5-6 mJ laser energy at 10 Hz for 15 minutes produced such high photoconductor behavior that one pad showed a calculated external quantum efficiency of over 400%. The next best pad produced a maximum external quantum efficiency of 135%, as can be seen in Figure 46. External quantum efficiencies above 100% are not physically possible for this solar cell design, as there is no known mechanism for this cell which could produce two or more electrons from a single photon. The unusually high calculated external quantum

efficiency was due to the current produced by a small bias applied by the Keithley 428 amplifier during measurement. This bias is so small that it has no measurable effect on cells which are rectifying, nor on those which are not very conductive, but it can drive a current in a conductive cell, making it appear like that cell has a large photocurrent.

Figure 46: EQE of solar cell with laser annealed CdSe, 5-6 mJ for 15 minutes

I-V measurements confirmed that this solar cell behaves like a resistor rather than showing diode characteristics. Figure 47 shows an I-V plot for the pad with highest calculated quantum efficiency, but there is no point on the light I-V curve where power is being generated.

Figure 48: I-V curve of solar cell with laser annealed CdSe, 5-6 mJ for 15 minutes

Figure 47: EQE of solar cell from laser annealed CdSe, 8 mJ for 10 min

Figure 48 shows the external quantum efficiency of a solar cell made from annealing the cadmium selenide layer for 10 minutes in 8-10 mJ incident power. This produced a

maximum EQE of 40%. Figure 49 shows that the IV characteristics of this cell are almost entirely resistive, except for the slight curve around -0.25V.

Figure 49: I-V curve for solar cell from laser annealed CdSe, 8mJ for 10 min

Figure 50: EQE of solar cell from laser annealed CdSe, 12 mJ for 10 min

Figure 50 shows EQE after laser annealing for 10 minutes in 12mJ incident power, for a maximum EQE of 20%.

Figure 51: SEM of laser annealed CdSe layer, 5-6 mJ for 15 min

The inconsistency in behavior between different pads for all laser annealed samples may be explained by nonuniformity in laser power across the sample, the effect of which can clearly be seen in figure 51. The EDX results on figure 52 suggest that the difference in power is significant enough produce variations in the thickness of the cadmium selenide layer. Figures 53 and 54 show a texturizing effect which was observed on some regions of the layer. Cracks in the cadmium selenide layer have been observed in thermally annealed samples, but this small scale pillar-like morphology and ring pattern is new. It

Figure 52: SEM image with EDX data of laser annealed CdSe, 5-6 mJ for 15 min

appears from the EDX data that light and dark regions correspond to thicker and thinner cadmium selenide layers, respectively, but it could also be due to zinc diffusing into the cadmium selenide layer. It is likely that the variation in thickness corresponds to variation in localized laser beam power, which would produce variations in material temperature during laser anneal. This could explain variations in laser thickness and different diffusion rates in different regions. The laser beam is non-gaussian and irregular, so this small scale variation in power may be due to a beam nonuniformity from the laser itself. It is also possible that the molecules of the containment flask supplied a

diffraction grating, such that this pattern is due to constructive and destructive interference. This effect was only observed with the 15 minute, 5-6 mJ sample.

SEM images of these laser annealed layers also show a strange new film morphology produced by the laser anneal, morphology whose effect on solar cell behavior is not yet

Figure 53: SEM image of laser annealed CdSe, 5-6 mJ for 15 min

clear. These results appear to demonstrate that laser annealing can produce a polycrystalline thin film from cadmium selenide nanoparticles, one with grain boundaries too small or smooth to distinguish via SEM. These films are strongly photoconductive but do not generate power. It is possible that the rapid heating and cooling during the

laser anneal process may have fused the nanoparticles into a thin film without increasing grain size at all. This rapid heating and cooling can freeze in defects such as interstitials, voids, and crystal lattice defects, all of which can act as recombination sites to inhibit power generation.

Figure 54: SEM image of laser annealed CdSe, 5-6 mJ for 15 min

These results clearly indicate that lower laser energy produces higher external quantum efficiency than higher laser energy; this conclusion is based on the photocurrent produced by the sample. High photocurrent can indicate an efficient solar cell, but in this case the high measured current was produced by a conductor, where the current generated is due to the low resistance of the sample and the small bias applied by the measurement probes.

This is a form of measurement error which produces dramatic results when the sample is

conductive. A photoconductor behaves like a resistor rather than a diode, and cannot be used to generate power. This appears to be the case for laser annealed samples, as their I-V curves showed no open circuit voltage and no short circuit current.

Chapter 4 - Conclusion

An overall power conversion efficiency of nearly 1% has been achieved with a solar cell design using fluorine doped tin oxide, a zinc oxide thin film, aluminum doped zinc oxide nanowires deposited under potentiostatic conditions, cadmium selenide nanoparticles from NN Labs annealed into a polycrystalline thin film, high molecular weight P3HT spincoated in a nitrogen environment, and a gold pad as a back contact. The effect of a galvanostatic step during zinc oxide nanowire electrodeposition has been investigated, and it has been determined that a thin layer of polycrystalline zinc oxide between the fluorine doped tin oxide and the nanowire layers is beneficial. The cadmium selenide thin film has been shown to perform well when annealed without cadmium chloride, yet the best solar cells were produced when cadmium selenide was annealed in the presence of cadmium chloride. Laser annealing was investigated as a replacement for thermal annealing, yet it did not produce functional solar cells. An argon plasma process on the cadmium selenide layer was found to improve solar cell performance. It is quite likely that further optimization of this solar cell design will produce an even better solar cell, as this combination of band gap alignment and nanostructured morphology is theoretically quite promising.

References

- Aberle, A., *Thin Solid Films* **517** 4706 (2009)
- Alex V., Finkbeiner S., Weber J., *J. Appl. Phys.* **79** 6943 (1996)
- Appleyard D. *Renewable Energy World North America Magazine* **2** 3 (2010)
- ASTM Standard E1036, "Standard Test Methods for Electrical Performance of Nonconcentrator Terrestrial Photovoltaic Modules and Arrays Using Reference Cells," ASTM International, West Conshohocken, PA (1998)
- Boatman, Lisensky, and Nordell, *J. Chem. Educ.*, **82** 1697 (2005)
- Bundgaard E., Krebs F., *Solar Energy Materials and Solar Cells* **91** (11) 954 (2007)
- Cheng H, Chiu W, Lee C, Tsai S, and Hsieh W, *J. Phys. Chem. C*, **112** (42) 16359 (2008)
- Deffeyes, Kenneth, *Beyond oil: the view from Hubbert's Peak*; (Hill and Wang, New York, 2005)
- Elias J., Tena-Zaera R., Levy-Clement C., *Thin Solid Films* **515** (24) 8553 (2007)
- Ernst K., Belaidi A., Könenkamp R., *Semicond. Sci. Technol.* **18** 475 (2003)
- Feenstra R., Parsons R., Shepherd, F., Westwood W, Ingreys S., *J. Appl. Phys.* **50** (9) 5624 (1979)
- Gregg B., *J. Phys. Chem. B* **107** (920) 4688 (2003)
- Guyemard, C., Myers, D., *Proceedings of SPIE 49th Annual Meeting* (SPIE, Denver, CO, 2004)
- Gueymard C., Myers D., Emery K. *Solar Energy* **73** 443 (2002)
- Hofmann, Philip *Solid State Physics; An Introduction* (Wiley-VCH, Weinheim, 2008)
- Hou J., Tan Z., Yan Y., HeY., Yang C., Li Y., *J. Am. Chem. Soc.*, **128** (14) 4911 (2006)

- Kazmerski, L. "The Solar Revolution: The Tipping Point to Next Generation PV"
National Center for Photovoltaics, National Renewable Energy Laboratory, (2010)
- Kobayashi A., Sankey O., Volz S., Dow J., *Phys. Rev. Lett. B* **28** (935) 946 (1983)
- Könenkamp R., Nadarajah A., Word R. *Appl. Phys. Lett.* **95** (5) 053103 (2009)
- Lee H., Yum J., Leventis H., Zakeeruddin S., Haque S., Chen P., Seok S., Gratzel M., Nazeeruddin M., *J. Phys. Chem. C* **112** (30) 11600 (2008)
- Leprince-Wang Y., Wang G., Zhang X., Yu D., *J. Crystal Growth* **287** 89 (2006)
- Leschkies K., Divakar R., Basu J., Enache-Pommer E., Boercker J., Carter B., Kortshagen U., Norris D., Aydil E., *Nano Lett.* **7** (6) 1793 (2007)
- Li, X., Pankow, J., To, B., Gessert, T., 33rd *IEEE Photovoltaic Specialists Conference* (IEEE, San Diego, CA, 2008) pp. 1-5
- Luque, A., Hegedus, S., (eds) *Handbook of Photovoltaic Science and Engineering*, (John Wiley & Sons, Ltd, Chichester, UK, 2003)
- Lyon J., Cascio A., Beerbom, M., Schlaf R., Zhu Y., Jenekhe S., *Appl. Phys. Lett.* **88** 222109 (2006)
- Matalon S., Ji, H., *American Journal of Respiratory and Critical Care Medicine* **171** 424 (2005)
- Misra N., Xu L., Rogers M., Ko, S., Grigoropoulos, C., *Phys. Status Solidi C* **5** (10) 3264 (2008)
- Munroe A., Bardecker J., Liu M., Cheng Y., Niu Y., Plante I., Jen A., Ginger D., *Microchimica Acta* **160** (3) 345 (2007)
- Nadarajah A., Word R., VanSant K., Könenkamp R., *Phys. Status Solidi B* **245** 1834 (2008)
- Nelson, Jenny *The Physics of Solar Cells* (Imperial College Press London 2003)
- Nicholson P., Macpherson J., Unwin P., *Chem. Commun.* **8** 1052 (2005)

- Nordell K., Boatman E., Lisensky G., *J. Chem. Educ.*, **82** (11) 1697 (2005)
- Oliver M., Jackson T., *Energy Policy* **27** (7) 371 (1999)
- O'Rourke D., Connolly S. *Ann. Rev. of Environment and Resources* **28** 587 (2003)
- Pandey R., Mishra S., Tiwari S., Sahu P., Chandra B., *Solar Energy Materials & Solar Cells* **60** 59 (2000)
- Photovoltaic Technology Platform, *The Status of the Photovoltaic Industry; Photovoltaic Fact Sheets*, January 2010
- Pejova B., *Mater. Lett.* **58** 666 (2004)
- Roncali J., *Chem. Rev.* **97** (1) 173 (1997)
- Salzner U., Lagowski J., Pickup P., Poirier R., *Synthetic Metals* **96** 177 (1998)
- Seeger, K. *Semiconductor Physics: An Introduction* 9th ed. (Springer-Verlag, Berlin, 2004)
- Seipel B., Nadarajah A., Wutzke B., Könenkamp R., *Mater. Lett.* **63** 736 (2009)
- Shrotriya V., Ouyang J., Tseng R., Li G., Yang Y., *Chem. Phys. Lett.* **411** 138 (2005)
- Srivastav V., Pal R., Vyas H., *Opto-Electronics Review* **13** (3) 197 (2005)
- Srikant V., Clarke D., *J. Appl. Phys.* **83** (10) 5447 (1998)
- Tena-Zaera R., Katty A., Bastide S., Lévy-Clément C., *Chem. Mater.* **19** 1626 (2007)
- Tena-Zaera R., Ryan M., Katty A., Hodes G., Bastide S., Lévy-Clément C., *Comptes Rendus Chimie*, **9** 717 (2006)
- Thomas D., *J. Phys. Chem. Solids* **15** 86 (1960)
- Tiedje T., Yablonovitch E., Cody G., Brooks B., *IEEE Trans. Electron Devices*, **31** (5) 711 (1984)

Turka R., Gray R., “Impacts of coal mining” in Ehlen, J., Haneberg, W.C., and Larson, R.A., eds., *Humans as Geologic Agents*: (Geological Society of America Reviews in Engineering Geology, Boulder, CO, 2005)

Xu B., Holdcroft S., *Macromolecules* **26** (17) 4457 (1993)

Yuanhao G., Qian Z., Qiang G., Yupeng T., Wen Z., Lingxia Z., Shengyi Z. *Mater. Chem. Phys.* **115** 724 (2009)

Yu W., Peng X., *Angewandte Chemie International Edition* **41** (13) 2368 (2002)