Single-Nanowire Solar Cells

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Single-Nanowire Solar Cells

by

Sarah Faye Brittman

A dissertation submitted in partial satisfaction of the requirements for the degree of Doctor of Philosophy in Chemistry in the Graduate Division of the University of California, Berkeley

Committee in charge:

Professor Peidong Yang, Chair
Professor Stephen R. Leone
Professor Junqiao Wu

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Abstract

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The two tasks performed by a solar cell are absorption of sunlight and collection of the photo-generated charges. In a conventional planar solar cell, these two processes are coupled because charges produced by light that is absorbed deep within the semiconductor must travel a long distance to the junction near the surface before they can be separated and collected. Core-shell nanowire arrays decouple the directions of light absorption and charge separation, allowing the collection of charges from poorly absorbing materials with relatively short minority carrier diffusion lengths. Additionally, because the dimensions of nanowires are on the same length scale as the wavelength of visible light, light-trapping effects allow a film of nanowires to absorb more light than would a thin film made from the equivalent volume of material.

In the development of nanowire array solar cells, single-nanowire solar cells provide information about the optical and electronic properties of the junction in a particular material system. They are a simplified experimental platform that can be used to screen materials for their suitability for nanowire array solar cells. This work describes the opto-electronic properties of single-wire solar cells made from silicon, CdS/Cu2S, and ZnO/Cu2O. While silicon is a model system used to investigate fundamental optical effects, the oxide and sulfide heterojunctions are attractive for photovoltaics because of their low cost and elemental abundance in the earth’s crust; they are also particularly well suited for nanowire array, rather than planar, solar cells because of their sub-micrometer minority carrier diffusion lengths.

Suspended, silicon single-nanowire solar cells served as a model system with which to develop characterization techniques such as scanning photocurrent mapping (SPCM) and wavelength-dependent photocurrent measurements and to understand the optical properties of single-nanowire solar cells. These measurements and electromagnetic simulations of the wire’s absorption show that the devices exhibit enhanced photocurrent at the wavelengths corresponding to the optical resonances of the nanowire. After characterization of the devices, they were used to study the interaction between a nanoscale dielectric cavity, the silicon nanowire, and a plasmonic nanocrystal, which is summarized below.
In planar solar cells, the CdS/Cu$_2$S heterojunction is formed by a low-temperature cation-exchange reaction that creates an epitaxial interface between the two sulfides. This chemistry was adapted to single-nanowire solar cells and determined to produce high-quality junctions at the nanoscale, suitable for nanowire photovoltaics. The high carrier concentration of Cu$_2$S or one of its neighboring Cu$_{2-x}$S phases, however, often led to full depletion of the CdS nanowire core, prohibiting efficient collection of photogenerated charges. To address this difficulty, indium-doped CdS nanowires were synthesized, and single-nanowire solar cells were fabricated from them. $I-V$ curves under simulated sunlight and SPCM show that the difficulty in collecting from the CdS core was resolved, and these devices yielded single-nanowire efficiencies averaging 2.5%. These indium-doped solar cells were also used as platforms to study the interaction between a single-nanowire solar cell and plasmonic nanocrystals, discussed below. Finally, the cation-exchange chemistry was applied to hydrothermally synthesized CdS nanorod arrays to produce micro-array nanorod solar cells with efficiencies reaching 0.2%.

In recent photovoltaic research, nanomaterials have offered two new approaches for trapping light within solar cells to increase their absorption: nanostructuring the absorbing semiconductor and using metallic nanostructures to couple light into the absorbing layer. These two approaches are combined in the study of silicon and In-CdS/Cu$_{2-x}$S single-nanowire solar cells decorated with silver nanocrystals. Wavelength-dependent photocurrent measurements and finite-difference time domain (FDTD) simulations show that increases in photocurrent arise at wavelengths corresponding to the nanocrystal’s surface plasmon resonances, while decreases occur at wavelengths corresponding to optical resonances of the nanowire. SPCM experimentally confirms that changes in the device’s photocurrent come from the silver nanocrystal. These results demonstrate that understanding the interactions between nanoscale absorbers and plasmonic nanostructures is essential to optimizing the efficiency of nanostructured solar cells.

Because of the earth-abundance, non-toxicity, and low cost of copper and zinc, the ZnO/Cu$_2$O heterojunction is an attractive material system for solar energy conversion. Beginning with Cu$_2$O wires synthesized via a high-temperature, vapor-phase reaction, single-wire ZnO/Cu$_2$O and ZnO/TiO$_2$/Cu$_2$O heterostructure diodes were fabricated. Devices showed photocurrent and photovoltage under laser illumination, and a few exhibited photovoltaic performance under 1-sun illumination. The general lack of photoresponse under 1-sun conditions is attributed to full depletion of the Cu$_2$O wire’s core, greatly reducing its conductivity. For the devices that did function as solar cells under 1-sun conditions, a combination of the large size of the Cu$_2$O wires, the charge-screening ability of the TiO$_2$ buffer layer, and possible incorporation of chlorine into the wires is likely responsible for their improved performance.
To those who have believed in me when I could not.
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Chapter 1

An Introduction to Nanowire Solar Cells

Much of the content of this chapter was originally written by the author (SFB) for the following publication:

1.1 Making Large-Scale Solar Energy a Reality

Electricity and lighting, heating and cooling, computers, cars, planes—the hallmarks of modern life are synonymous with consumption of energy.\(^1,2\) Since much of the world's ever-growing population lives in societies striving to modernize, the world's need for sources of clean and renewable energy is more urgent than ever.\(^2\) Although the sun offers more than enough power to satisfy humanity's appetite for energy, technologies for solar energy conversion remain too costly to compete with fossil fuels on a worldwide scale.\(^3,4\) Research into new and improved technology is part of the solution, and photovoltaics is a mature technology with demonstrated practical potential.\(^5-7\) Photovoltaics converts sunlight into electricity: small installations can power individual homes or solar farms can light up cities. Photovoltaics has a promising future as part of the portfolio of renewable energy technologies that will be needed to wean the world from its dependence on fossil fuels.\(^7\) For this breakthrough to occur, however, it and other technologies will need to be more efficient and less costly, two challenges that, in the case of photovoltaics, nanowires can help overcome.

The potential of nanowires in solar energy applications lies in their tunable geometric effects and high surface-to-volume ratio. Since the nanowires typically employed in photovoltaic (PV) cells are too large to show quantum confinement effects, conventional semiconductor physics applies. In comparison with planar devices, however, they offer a much larger surface-to-volume ratio, with roughness factors reaching up to ~300.\(^8,9\) Because the dimensions of the nanowires are on the same scale as the wavelength of visible light and the minority carrier diffusion lengths in many solar materials, their geometry can improve light absorption and charge collection in energy conversion devices. For these reasons, the unique properties of nanowires make them promising candidates for efficient PV devices.
1.2 Principles of Photovoltaics

1.2.1 Basic Physics

Photovoltaics is the conversion of sunlight into electricity using solar cells. In conventional semiconductor solar cells, a p-n junction establishes a built-in electric field within the material\(^\text{10, 11}\) (Figure 1.1a). At the contact interface between the p-type and n-type semiconductors, excess holes and electrons recombine until the chemical potential difference is counterbalanced by an electrical potential difference. The extent of the area devoid of carriers, or depletion region, depends upon the doping levels of the two sides of the junction and the materials' dielectric constants. When a semiconductor absorbs photons, electrons are excited from its valence band to conduction band, producing an electron-hole pair. The built-in electric field at the junction, or band-bending, separates the electron and hole and accelerates them toward the solar cell's contacts to be collected as current. This current and the built-in field's voltage transform the sun's energy into electrical energy. If the photogenerated carriers originate in the semiconductor far from the p-n junction, the minority carriers must diffuse to the depletion region to be separated. Recombination during this diffusion process and recombination within the depletion region are two of the main loss mechanisms that reduce a solar cell's efficiency.

![Schematic and energy band diagram of a p-n homojunction that produces the built-in electric field used to separate photogenerated charges in a solar cell.](image)

**Figure 1.1**: Principles of solar cells. (a) Schematic and energy band diagram of a p-n homojunction that produces the built-in electric field used to separate photogenerated charges in a solar cell. (b) The AM 1.5G solar spectrum from 300-1500 nm. (c) I-V characteristic of a solar cell in the dark and light showing the metrics for quantifying its performance.

1.2.2 Metrics of Performance

Several metrics are used to evaluate and compare the performance of solar cells. The current-voltage (I-V) curve is measured under illumination from a solar simulator, which is a light source that produces 1-sun intensity (100 mW/cm\(^2\)) with an air mass 1.5 global (AM 1.5G) spectral profile\(^1\) (Figure 1.1b). It provides the open-circuit voltage (\(V_{oc}\)), the short-circuit current (\(I_{sc}\)), and the fill factor (FF), which is a measure of efficiency.

\[\eta = \frac{V_{oc} \times I_{sc} \times FF}{P_{in}}\]

---

\(^1\) The AM 1.5G spectrum is the standard reference spectrum used by the PV industry to simulate natural solar illumination and to evaluate the performance of terrestrial solar cells. Details of the spectrum's origin and a spreadsheet of it are supplied by the National Renewable Energy Laboratory (NREL) at [http://rredc.nrel.gov/solar/spectra/am1.5](http://rredc.nrel.gov/solar/spectra/am1.5).
how well photogenerated charges are extracted from the solar cell; the product of these three metrics is the maximum power produced by the solar cell (Figure 1.1c). If the material properties of the solar cell are known, the thermodynamic limits for these metrics can be calculated\textsuperscript{12, 13} to analyze the solar cell’s experimental performance and diagnose areas for improvement. Efficiency ($\eta$), which is the maximum power produced by the solar cell divided by the power of the light incident on it, is the most important metric of performance. Since the two primary processes in a solar cell are generation of electron-hole pairs and their collection, measuring both the wavelength-dependent absorption of the solar cell and its efficiency at each wavelength, referred to as the external quantum efficiency (EQE) or incident photon-to-current conversion efficiency (IPCE), allows the calculation of the wavelength-dependent internal quantum efficiency (IQE) or absorbed photon-to-current conversion efficiency (APCE). While EQE provides the net performance of the solar cell that comprises effects from both absorption and charge collection, IQE indicates how well the solar cell collects charges once they are generated.

1.2.3. Electrostatics of the Junction

Homojunction solar cells, such as those produced using $n$- and $p$-type silicon, are modeled most simply as one-dimensional abrupt junctions. The maximum built-in potential ($V_{bi}$), which sets the upper limit on a solar cell’s $V_{oc}$, is given by\textsuperscript{10}

$$V_{bi} = \frac{kT}{q} \ln \left[ \frac{N_D N_A}{n_i^2} \right]$$

and depends on only the doping concentrations of each side of the junction. Here $k$ is Boltzmann’s constant, $T$ is temperature, $q$ is the elementary charge, $N_D$ is the active donor concentration in the $n$-type material, $N_A$ is the active acceptor concentration in the $p$-type material, and $n_i$ is the semiconductor’s intrinsic carrier concentration. The junction’s total depletion width ($W$), and its depletion widths within the $n$-type ($x_n$) and $p$-type materials ($x_p$) are\textsuperscript{10}

$$W = \left[ \frac{2eV_{bi}(N_A + N_D)}{qN_D N_A} \right]^{\frac{1}{2}}$$

$$x_n = \left[ \frac{2eV_{bi}}{q} \frac{N_A}{N_D(N_A + N_D)} \right]^{\frac{1}{2}}$$

$$x_p = \left[ \frac{2eV_{bi}}{q} \frac{N_D}{N_A(N_A + N_D)} \right]^{\frac{1}{2}}$$

where $\varepsilon$ is the dielectric constant of the material. Increasing the doping level on both sides of the junction increases the $V_{bi}$ but also reduces the depletion width, which can lead to low shunt resistance and therefore low actual $V_{oc}$ if carriers tunnel across the
junction. Asymmetry in the doping levels creates a larger depletion width within the side with a lower carrier concentration, and the voltage drop falls mostly on that side of the junction. In a confined geometry such as a nanowire, the low-doped side of the junction might become fully depleted and therefore cannot support the full electric field of the junction. In this case, the maximum $V_{oc}$ would be lower than that predicted by the simple model.

The electrostatics of a heterojunction solar cell is more complicated because of the uncertainty introduced by the interface between the two semiconductors. In particular, it is difficult to predict accurately the band alignment between two different materials. The simplest, and very often incorrect, approximation is known as the electron affinity or Anderson approximation: the band alignment follows the difference in electron affinity of the two semiconductors, which is the energy required to remove an electron from the bottom of the conduction band.$^{14,15}$ This approximation neglects the role of interfacial states whose trapped charges can locally modify the electrostatics of the junction and shift the band alignment.$^{16}$ A better method for predicting band offsets is to calculate the difference between the semiconductors’ charge neutrality levels, measured relative to their valence bands.$^{17,18}$ The charge neutrality level of a surface is the energy at which the charges in its surface states are balanced, yielding no net surface dipole; however, because the charge neutrality level is determined by surface states that will certainly be modified by the local chemical bonding at the surface or interface, even the charge neutrality level can be shifted from its intrinsic level, yielding a so-called extrinsic charge neutrality level.$^{18}$ Nevertheless, this method has proven more reliable for estimating both Schottky barriers between metals and semiconductors and band offsets for semiconductor heterojunctions.$^{17}$

Once an approximation has been made for the band offset, the built-in potential and depletion widths within the heterojunction are given by equations analogous to those for a homojunction but modified for the dielectric constant of each semiconductor.$^{14}$

1.3 Nanowires for Photovoltaics

1.3.1 Nanowire Array Solar Cells vs. Single-Nanowire Solar Cells

Research into nanowire photovoltaics falls into two categories: nanowire array solar cells and single-nanowire devices. Although other designs have been proposed,$^{19,20}$ conventional nanowire array cells consist of vertical nanowires electrically contacted in parallel so that they generate currents comparable to thin-film PV cells. These devices are the most relevant for calculating efficiencies and comparing metrics with planar solar cells, and they take advantage of the improved charge collection, transport, and light trapping that occurs in nanowire films. In contrast, single-nanowire solar cells offer fundamental information about the optical and electronic properties of the solar cell’s materials and the quality of its charge-separating junction. They provide insight into improving the performance of array solar cells.
1.3.2 Collection and Transport of Charges

One of the key advantages of nanowires for the conversion of solar energy is their potential for more efficient separation and collection of photogenerated charges. Radial junctions decouple the directions of light absorption and charge separation: absorption occurs along the long axis of the wire or is scattered from neighboring wires, while the photogenerated minority carriers travel only the radial distance to be separated and collected (Figure 1.2). Once separated, the now majority carriers have a direct path to their electrode through the continuous and conductive core of the nanowire. Materials whose optical absorption length is much longer than their minority carrier diffusion length benefit most from this geometry, but it is still useful for materials with excellent absorption and transport such as GaAs. Because the core-shell...
geometry relaxes the requirements on minority carrier diffusion length, nanowires can allow solar cells to be made from materials that are unsuitable in a planar geometry. Candidates include sulfides, oxides, and low-purity or heavily doped silicon, which have the advantages of being inexpensive and abundant in the earth’s crust. Dye-sensitized solar cells and semiconductor-organic hybrid solar cells also employ this geometry in order to improve charge collection from the dye or low-mobility organic phase.

Equivalent circuit models are used to describe the transport of electrons within a PV cell and to analyze how to improve its performance (Figure 1.3). In a solar cell, the p-n junction is a rectifying diode because the built-in electric field allows current to flow appreciably in only one direction. The forward bias current increases exponentially as the applied bias counteracts the built-in potential of the junction, lowering the barrier for carriers to diffuse across it (diffusion current). The reverse saturation current arises from thermally generated carriers that drift to their respective contacts via the built-in field (drift current). Additional diodes, which can also be conceptualized as voltage-dependent variable resistors, can be added in parallel with the drift-diffusion diode to represent recombination processes, such as the recombination within the depletion region, or at grain boundaries. Shining light on the solar cell generates a constant flow of electrons and holes, modeled as a current source that opposes the diode’s diffusion current and shifts the I-V curve on the current axis. Resistance that impedes transport through the quasi-neutral regions of the solar cell or its contacts is labeled series resistance and reduces the current output and fill factor of the solar cell. Stray current paths that bypass the potential of the junction lower the solar cell’s shunt resistance and reduce its open-circuit voltage and fill factor. The ideal diode model of a solar cell exhibits no series resistance and infinite shunt resistance; for best performance from a practical standpoint, the series resistance should be much smaller and the shunt resistance much larger than the characteristic resistance of the solar cell $R_{ch}$, which is given by $V_{oc}/I_{sc}$.

Radial junctions offer many opportunities for improved PV cells, but careful design and control over material properties are necessary to realize their benefits. To avoid degrading the device’s efficiency with low built-in voltage or high series resistance, fully depleting the carriers on either side of the junction must be avoided. Because of their small size, the core or shell of a nanowire with low carrier concentration can be easily depleted if the junction’s other side is more heavily doped. For this reason, the core and shell thicknesses and doping levels must be carefully controlled to ensure optimized performance.

Additionally, interface and surface states play a much larger role in nanowire devices than in their planar counterparts. Nanowire PV cells are particularly sensitive to depletion-region recombination because of their large junction area. Experimental work on silicon and CdS/Cu$_2$S single-nanowire solar cells indicates that the quality of the junction is crucial to their efficiency. By controlling the crystallinity of the shell and the abrupt doping structure of the homojunction, the $V_{oc}$ of p-i-n silicon single-nanowire solar cells has improved from 260 mV to up to 500 mV and the FF from 55% to 73%. These figures still trail those of planar crystalline silicon, whose record values are 706 mV and 83%, and such a difference is typical for single-nanowire solar cells produced from other materials such as GaAs and the GaN/In$_x$Ga$_{1-x}$N system.
CdS-Cu$_2$S single-nanowire solar cells, however, exhibit $V_{oc}$ and FF values that slightly exceed those of their planar counterparts, which is attributed to their high-quality heteroepitaxial junction.$^{23}$

One challenge inherent to charge collection within a nanowire array is its dilution of photogenerated carriers across a larger interface, resulting in lower $V_{oc}$ or photovoltage as compared to planar PV cells.$^{37}$ Assuming that the dominant recombination mechanisms in the planar and nanowire solar cells are the same, which is an assumption that depends on the specific material system,$^{42}$ this effect is analogous to a planar cell with the equivalent junction area operating in lower light conditions. Fortunately, the nanowire geometry itself can create such concentration effects because of its unique optical properties.

1.3.3 Light Trapping in Nanowire Arrays

Nanowires in ordered or random arrays exhibit light-trapping effects because of their microscopic arrangement and sub-wavelength diameters. These effects allow a film of nanowires to absorb more light than would a thin film made from the equivalent volume of material. A portion of this increase arises from the nanowires’ acting as an anti-reflection coating, which can be understood as grading the refractive index difference between air and the material of the nanowire;$^{43, 44}$ however, the specific geometry of the interfaces within the nanowire film dictates the film’s optical modes, which also lead to increased absorption.$^{45}$ The record nanowire array solar cell, made from InP nanowires with axial $p$-$i$-$n$ junctions, relies on light trapping: its nanowires cover only 12% of the area of the cell but produce 83% of the short-circuit current of the best InP planar cells.$^{46}$ Although even random arrays exhibit light trapping, carefully engineered arrays in theory can exceed the light trapping of a randomly textured surface$^{47}$ and produce a nanowire solar cell whose efficiency exceeds that of its planar counterpart.$^{48, 49}$ Much experimental work has demonstrated increased absorption within nanowire and microwire films.$^{46, 50-52}$

1.3.4 Approaches for Reducing Costs

The commercial relevance of a solar technology depends both on its efficiency and its cost of implementation.$^3$ Even the most efficient technologies, such as multijunction concentrator solar cells, are not in widespread use because they are still prohibitively expensive.$^{53}$ Lower production costs, as compared to crystalline silicon modules, have driven the expansion of the thin-film PV industry.$^{54, 55}$ and nanowires can be viewed as the natural heir in this succession of inexpensive, yet efficient technologies. The extensive literature on low-temperature, solution-based, and scalable syntheses of nanowires indicates that nanowire PV cells will ultimately be less expensive to produce than their thin-film counterparts. In addition, the unique optical and transport properties of nanowires will allow less actual material to be used in a PV cell to achieve similar efficiencies.$^{46, 48}$ Finally, like organic solar cells and some thin-film PV, nanowire array cells can be produced using lightweight, flexible substrates that will make them less expensive to implement and suitable for mobile applications.$^{56}$
1.4 Single-Nanowire Photovoltaics

1.4.1 Motivation for Their Study

Single-nanowire devices are useful platforms with which to study the electrical and some of the optical properties of nanowire PV cells. The typical device geometry in which the nanowire lies flat on an insulating substrate does not capture the benefits of orthogonal light absorption and charge separation, but it does provide a way to investigate the quality of the charge-separating junction, the charge transport through the nanowire, and the wavelength-dependent photocurrent of the nanowire solar cell. Since the fabrication of array solar cells can be plagued with difficulties in reducing series resistance and maximizing shunt resistance, single-nanowire solar cells allow some fundamentals of the material system to be investigated before extensive effort is put into developing an array solar cell.

1.4.2 Transport within Single-Nanowire Solar Cells

Current-voltage (I-V) curves of single-nanowire solar cells determine if the chosen material junction rectifies and separates photogenerated carriers. Reducing parallel and series resistances in single-nanowire solar cells is simpler than in an array device. While low shunt resistance often obscures rectifying behavior in array solar cells, the shunt resistance of single-nanowire solar cells arises from the quality of the material junction since much spatial separation exists between the top and bottom contacts. Series resistances are also less important than in array solar cells because single-nanowire devices source only pico- or nanoamperes of current; consequently, their junction’s characteristic resistance is many orders of magnitude larger than that of an array solar cell, allowing the $I_{sc}$ and FF to remain relatively unaffected by kilo- or even mega-ohm series resistances. Additionally, ohmic behavior and quantitative contact resistance at the metal/semiconductor interfaces can be evaluated by four-point resistance measurements on the devices. Although absorption of light in single-nanowire solar cells can be a challenge because of the small path length and potentially small active area for axial junctions, power and temperature dependencies of the solar cell's parameters under concentrated light sources can still offer insight into the junction quality. Because the excitation geometry of typical single-nanowire solar cells does not match that of an array device, efficiency estimates based on single-nanowire solar cells are less relevant. Also, since single-nanowire solar cells are typically smaller in diameter than the wavelength of light in the visible spectrum, their absorption cross-section can exceed their geometrical cross-sectional area, which increases their apparent efficiency.\(^{37}\)

1.4.3 Optical Properties of Single Nanowires

Because of their subwavelength dimensions, single nanowires exhibit optical resonances in the visible portion of the spectrum that increase their absorption of light. These resonances are modeled as the electromagnetic modes of a dielectric cylinder.
and can be either bound modes or leaky modes, depending on whether their propagation constant is real or complex, respectively. Bound modes confine and guide incident light along the axis of the cylinder, while leaky modes allow energy to radiate from the system as the light propagates along the wire. At the wavelengths of these resonances, the nanowire's absorption cross-section is much larger than its geometrical cross-section, essentially concentrating light within the wire. The positions and intensities of these modes depend sensitively on the nanowire's refractive index and diameter, but similar trends are seen for nanowires with various cross-sectional geometries. Two- and three-dimensional numerical electromagnetic simulations, which solve Maxwell's equations for the light-wire system, can be used to predict enhancements in absorption that agree well with experimental results. These resonances increase the estimated efficiency of a single-nanowire solar cell because they allow the wire to collect light from beyond its geometrical cross-section, meaning that the external quantum efficiency of the wire can exceed unity at resonance wavelengths even when the internal quantum efficiency is lower and limited to unity. This increase in single-wire efficiency, however, does not necessarily translate into more efficient array solar cells. Using these modes to improve the efficiency in array devices implies sparse coverage of a substrate with nanowires, since dense arrays would make the concentrating effect unnecessary. In this case, since nanowire solar cells operate more efficiently under concentrated light, an array device might perform better by concentrating light into a few nanowires rather than harvesting dilute light over a dense array of many nanowires. Achieving such an optimal architecture requires predicting the diameter and pitch of the nanowire array necessary to create sufficient concentration of light within the nanowires, as well as experimental realization of such a design. Numerical electromagnetic simulations will therefore continue to play a key role in the design of nanowire PV, although they must be complemented with synthetic techniques that can achieve spatial control over the growth of regular nanowires. The next step will be to integrate electromagnetic simulations with models of the device physics to understand where charges are generated within the wires so that they can be collected most effectively.

1.5 Conclusions and Future Outlook

The field of nanowire photovoltaics has made much progress in understanding how the nanowire geometry can be leveraged for improved performance. Applying this knowledge to develop large-area solar cells, however, will take a combined effort. Chemists and material scientists continue to develop new nanowire syntheses, yet they must work closely with device physicists to ensure that the properties of their nanowires are suitable for PV applications, particularly for solution-synthesized nanowires. Currently, their conductivity and optical quality often lag behind those of nanowires grown at high temperature in vapor-phase syntheses. Also, creating high-quality junctions and interfaces for charge separation and collection is essential, and much fundamental science in this area still remains to be explored. By combining synthetic control of nanowires' material, size, doping, and junctions with electromagnetic and device simulations, it will be possible to optimize large-scale array solar cells to yield...
efficiencies comparable to those of current thin-film technology. As materials and designs become more mature, the final step will be integrating these solar cells into inexpensive, flexible substrates to realize the full potential of nanowire PV.

Clearly nanowires hold much promise for improving the performance and lowering the cost of thin film solar cells. Realization of this potential, however, demands a thorough investigation of the electrical and optical properties of nanowire solar cells, beginning with model systems such as silicon, and later applying this knowledge to the study of systems more reliant on the advantages of nanowires to create inexpensive nanostructured solar cells, such sulfides and oxides.

1.6 References

Chapter 2

A Model System: Suspended, Single-Nanowire Silicon Solar Cells

Much of the content of this chapter was originally written by the author (SFB) for the following publication: Brittman, S.,* Gao, H.,* Garnett, E.C., and Yang, P. Absorption of Light in a Single-Nanowire Silicon Solar Cell Decorated with an Octahedral Silver Nanocrystal. *Nano Letters* 11, 5189-5195 (2011). Reprinted and adapted from the above publication with permission. Copyright 2011, American Chemical Society.

2.1 Silicon Nanowire Solar Cells: A Model System

The materials science and optical and electronic properties of crystalline silicon have been studied for over 50 years, making it an excellent model system with which to begin investigations of single-nanowire solar cells. By suspending the nanowires above the substrate, their optical properties could be investigated without interference from the underlying substrate.

2.2 Fabrication of the Solar Cells

Silicon single-nanowire solar cells suspended above the substrate were fabricated using chemical vapor deposition (CVD) and standard high-temperature doping processes (Figure 2.1a). Briefly, trenches were etched to the buried oxide layer in heavily doped \( p \)-type silicon-on-insulator (SOI). Using gold colloids as catalysts for one-dimensional growth, silicon nanowires were grown to bridge the trenches above the substrate.\(^1\) The wires were then doped \( p \)-type with boron in a gas-phase reaction and subsequently masked with silicon dioxide deposited using plasma-enhanced chemical vapor deposition (PECVD). Photolithography and wet etching removed the mask from one end of the nanowires and one of their contacts, and the rectifying junction was formed by \( n \)-type vapor-phase doping with phosphorous. The PECVD-deposited oxide mask was permeable to the phosphorous dopant, but the difference in the thickness of the mask on each wire and its unexposed contact resulted in a core-shell \( p-n \) junction in only the wire, as confirmed by scanning photocurrent mapping, discussed below. After removal of the mask, the devices were coated with 4 nm of aluminum oxide deposited by atomic layer deposition to serve as a surface passivation layer.\(^1\) A false-color

\(^1\) Additional details of the fabrication process can be found in Appendix A.
scanning electron microscopy (SEM) image of a typical finished device denotes the p-type contact, the core-shell region of the nanowire, the fully n-type region of nanowire, and the n-type contact (inset, Figure 2.1b).

2.3 Experimental Characterization and Numerical Simulations

Current-voltage (I-V) measurements and scanning photocurrent mapping confirmed that individual nanowires functioned as solar cells. Measured under simulated 1-sun, AM 1.5G illumination, the I-V curve for a typical device (Figure 2.1b) shows a short-circuit current of 108 pA, an open-circuit voltage of 0.32 V, and a fill factor of 0.59. Scanning photocurrent mapping (SPCM) was used to visualize the active region of individual devices. By comparing the scanning photocurrent map (Figure 2.1c) and the optical image obtained simultaneously (Figure 2.1d), it is clear that only the core-shell region of the nanowire is active, not the n-type region or either of the contacts. The inactivity of the n-type side of the nanowire results from a very short minority carrier.

Figure 2.1: Fabrication and characterization of the suspended, single-nanowire silicon solar cells. Fabrication scheme (a) and typical I-V curve under simulated solar illumination (b) of a suspended silicon single-nanowire solar cell. The inset in (b) is a side view SEM image of a completed device with false coloring to denote the p (green) and n (blue) contacts and the core-shell region of the device (brown). SPCM of a single-nanowire solar cell (c) and its corresponding scanning optical image collected simultaneously (d). Lighter regions in the optical image correspond to regions of reduced reflection. The scans were taken at \(\lambda=442\) nm, \(P\sim7\) W/cm².

**Details about the experimental and numerical methods can be found in Appendix A.**
diffusion length in that region, which is consistent with the high doping level expected from the phosphorous doping reaction. The uniform photocurrent along the length of the wire that shows no decay indicates that the junction is core-shell. While such uniform photocurrent would also appear if the minority carrier diffusion length were much longer than the nanowire’s physical length, scanning photocurrent mapping of axial junctions produced by shortening the phosphorous diffusion time indicates that the minority carrier diffusion length within the nanowire is less than 1 µm (Figure 2.2).

Experimental measurements and numerical simulations\(^\text{iii}\) show that the nanowire solar cell exhibits peaks in its photocurrent at wavelengths corresponding to the wire’s optical resonances. The spectrally resolved short-circuit current, normalized to the incident photon flux, is shown for a nanowire with a diameter of 288 nm (Figure 2.3a). Because silicon absorbs weakly in the red and near-infrared wavelengths,\(^2\) the experimental setup was modified slightly (Appendix A) to measure these wavelengths; therefore, the short (Figure 2.3a) and long wavelength (Figure 2.3b) data appear separately. Error bars reflect the precision of the experimental setup and were calculated from one standard deviation of six replicated photocurrent

\[\text{Figure 2.2: SPCM of an axial junction. Scanning optical image (a), corresponding scanning photocurrent map (b), and top view SEM image (c) of a single-nanowire solar cell with an axial instead of a core-shell junction. The current decays rapidly from the junction on both sides, indicating short minority carrier diffusion lengths (< 1 µm) in both the p- and n-type regions of the wire.}\]

\[\text{Figure 2.3: Measured photocurrent spectra and simulated absorption of a single-nanowire solar cell (288 nm diameter) in the 400-650 nm (a) and 650-1000 nm (b) regions. 3D FDTD simulations of the absorption within the wire are overlayed. Error bars on the experimental data reflect the precision of the experimental setup.}\]

\(^{\text{iii}}\) Dr. Hanwei Gao performed the numerical simulations.
measurements taken at every wavelength on the same device. While the absorption coefficient of silicon decreases monotonically throughout this wavelength region, the silicon nanowire solar cell exhibits many small peaks in its photocurrent spectrum (Figures 2.3a,b). A three-dimensional finite-difference time domain (FDTD) simulation of the hexagonally faceted nanowire under illumination was used to calculate the nanowire’s absorption. The results are superimposed on the experimental photocurrent data (Figures 2.3a,b). Clear peaks appear in the nanowire’s simulated absorption spectrum and correspond to optical modes within the nanowire that are determined by its geometry, an effect that has been characterized well in germanium and silicon nanowires. The peaks in the experimental spectrum are less well defined than those in the simulation, likely because the nanowire in the experiment was tapered. Two-dimensional FDTD simulations predict that the wavelengths of the optical modes in a silicon nanowire are highly sensitive to its diameter (Figure 2.4). Although the nanowire’s diameter changes by only 20 nm over 9.5 µm, this tapering broadens the wire’s optical resonances, which causes closely spaced peaks, such as those in the blue region of the spectrum, to merge (Figure 2.4). Since the nanowire solar cell has a core-shell

Figure 2.4: 2D numerical simulations of tapered nanostructures. Tapering of a silicon nanostructure broadens the peaks in its absorption spectrum that correspond to its optical resonances. In (a), hexagonal wires of diameters 285 nm, 290 nm, and 295 nm show that the optical resonances red shift with increasing diameter. In (b), a plane of silicon whose thickness tapers from 295 to 285 nm over 4 µm (red curve) shows broadened resonance peaks whose maxima lie between the resonances predicted by the dimensions of either end, 285 nm (green curve) and 295 nm (blue curve). A nanowire tapering from 285 to 295 nm would therefore be expected to exhibit a broadened peak as in (b) but centered at the blue peak positions in (a). It should be noted that (a) is a two-dimensional simulation, so its peaks do not quite match those of the simulation in the main text, which shows a three-dimensional simulation.

Figure 2.5: Dependence of the short-circuit current (I_sc) on light intensity for a silicon single-nanowire solar cell. The device responds linearly to increasing illumination.
junction, the device’s internal quantum efficiency should be nearly constant for all wavelengths$^6,7$ so that the photocurrent spectrum reflects differences in the nanowire’s absorption at each wavelength. The nanowire devices responded linearly to changes in light intensity (Figure 2.5), indicating that any changes in photocurrent were directly proportional to their absorption of light.

2.4 Summary and Conclusions

Suspended single-nanowire solar cells were fabricated, and their electrical and optical properties were investigated experimentally and using numerical electromagnetic simulations. SPCM shows that the nanowires are core-shell structures with short (<1 μm) minority carrier diffusion lengths. Wavelength-dependent photocurrent measurements and simulations indicate that the devices exhibit enhanced photocurrent at the wavelengths corresponding to the optical resonances of the wire. After characterization of the single-nanowire silicon solar cells, they were used as a platform with which to study the interaction between a nanoscale dielectric cavity, the silicon nanowire, and a plasmonic nanocrystal, which is discussed in detail in Chapter 4.

2.5 References

Chapter 3

A High-Quality Interface: CdS/Cu$_2$S Nanowire Solar Cells

3.1 Motivation for Sulfide Nanowire Solar Cells

Although silicon currently remains the behemoth to beat in the commercial solar energy market because of the familiarity and scalability of its manufacturing processes, as well as its proven durability, thin-film solar cells made from chalcogenides such as CdTe and CuIn$_x$Ga$_{1-x}$(S,Se)$_2$ (CIGS) have made inroads into the market because of their much less expensive processing techniques.$^{1,2}$ In this sense, nanowire solar cells are positioned to become the next phase of this march toward efficient, yet inexpensive solar cells. Like thin-film solar cells, however, they must be produced from materials that can take full advantage of their benefits while also mitigating their challenges.

The high surface-to-volume ratio of nanowires means that core-shell nanowire solar cells will have a larger junction area relative to their volume than a similar planar solar cell; consequently, the quality of the junction, namely minimizing recombination, becomes critical to achieving efficient nanowire solar cells. Additionally, since one of the key advantages of nanowire solar cells is their potential to be produced via inexpensive, low-temperature processes, the high-temperature diffusion reactions required to produce charge-separating junctions in homojunction solar cells are undesirable. To address this challenge, cation-exchange chemistry is a low-temperature, solution-based process that has the demonstrated ability to produce a high-quality, epitaxial junction in the CdS/Cu$_2$S material system. This heterojunction creates a type-two band alignment (Figure 3.1),$^3$ which has been demonstrated in planar solar cells to separate charges and function as an efficient photovoltaic cell.$^{4-6}$

3.2 Sulfide Solar Cells Produced by Cation-Exchange Chemistry

3.2.1 Cation-Exchange Chemistry and the Phases of Cu$_{2-x}$S$^i$

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$^i$ The author thanks former SHARP mentee Kevin Chen for writing the Matlab program plotjunctions, which was used to draw the CdS/Cu$_2$S band diagram.

$^i$ The author is grateful to graduate students Andrew Wong and Dandan Zhang for many discussions regarding the chemistry and phases of Cu$_{2-x}$S and their extensive work on controlling the phase produced by cation-exchange reactions.
Cation-exchange chemistry offers a simple way to create a semiconductor heterojunction interface by replacing the cation in one compound with another that diffuses into the material from solution. The hallmark of this exchange process is that the anionic sublattice remains intact during this conversion, templating the final product onto the morphology and crystal structure of the original material.\(^7,8\) When single-crystalline nanostructures are used as the starting material, interfaces produced by cation exchange are of particularly high quality,\(^9,10\) perhaps because of the nanostructure’s ability to relax interfacial strain via its high surface-to-volume ratio.\(^11,12\) Because of their relatively small lattice mismatch and similar hexagonal sulfur sublattices,\(^13,14\) Cu\(_2\)S and CdS form an epitaxial interface when CdS is exposed to a solution of Cu\(^+\) cations and undergoes the exchange reaction.\(^15\)

Although cation-exchange chemistry is intended to produce a CdS/Cu\(_2\)S heterojunction, stoichiometric Cu\(_2\)S is only one of three hexagonal phases that appears on the Cu-S phase diagram near the 2:1 ratio.\(^16-19\) Cu\(_2\)S is a p-type semiconductor whose high intrinsic carrier concentration, typically \(\sim 10^{19} \text{ cm}^{-3}\),\(^20\) arises from Cu vacancies in the crystal. As Cu leaves the lattice, the structure continuously tunes its arrangement of Cu atoms with only minor changes to the sulfur sublattice. Beginning with stoichiometric chalcocite, djurleite exists for stoichiometries \(x=1.94-1.97\), and roxbyite for stoichiometries \(x=1.75-1.86\); compositions between these ranges are usually treated as mixtures of phases. Cubic phases of Cu\(_{2-x}\)S do exist as well, namely digenite \((x=1.8)\) and anilite \((x=1.75)\), but the barrier for phase transformations between these phases and the hexagonal phases is expected to be much higher than for interconversion between phases with similar sulfur sublattices. Experimental observations suggest that djurleite is actually more thermodynamically stable than chalcocite, especially as the crystal’s Cu deficiency increases.\(^21\)

Controlling and accurately determining the phase of Cu\(_{2-x}\)S has been a problem in the literature, with careful examination of the system’s complex x-ray diffraction (XRD) pattern being the most reliable method. Control of the phase is of critical importance for solar cells, however, because it has been established experimentally that stoichiometric chalcocite produces the most efficient photovoltaics.\(^22\) The exact physical explanation for this phenomenon has yet to be resolved, and previous investigation focused on comparing chalcocite with djurleite or chalcocite-djurleite mixed phases. The three types of proposed explanations include reduction of the absorption coefficient, reduction of the minority carrier diffusion length and therefore charge collection, and changes in the junction quality or band alignment that reduce collection efficiency.\(^23,24\) Literature reports suggest that the absorption coefficient of non-stoichiometric phases is lower.
than that of chalcocite, although whether this change arises from a Burstein-Moss shift\textsuperscript{25, 26} resulting from filling of the valence band by the increased carrier concentration or a change in the band structure of the crystal has not been resolved.\textsuperscript{24, 27, 28}

### 3.2.2 Solar Cells from Cation-Exchange Chemistry

In the 1970’s and 1980’s, the cation-exchange reaction between CdS and Cu\textsubscript{2}S was extensively investigated as a method to produce solar cells, achieving an efficiency at nearly 1-sun conditions of 9.15\%.\textsuperscript{5} In these devices Cu\textsubscript{2}S functioned as the primary absorbing layer, while CdS served as a means to separate and collect photogenerated charges. With a band gap of approximately 1.2 eV, however, the theoretical efficiency of a solar cell using Cu\textsubscript{2}S as the absorber can be estimated at 19.2\%, assuming a \( V_{oc} \) of only 0.6 V because of the offset in conduction bands between Cu\textsubscript{2}S and CdS and standard thermodynamic considerations, a corresponding maximum fill factor of 0.8, and a \( J_{sc} \) of 40 mA/cm\(^2\) in accordance with the band gap of Cu\textsubscript{2}S. While the record cell, which was measured under 87.9 mW/cm\(^2\) sunlight, approached the ideal \( V_{oc} \) and FF with values of 0.516 V and 0.714, its photocurrent density was only 21.8 mA/cm\(^2\), which is 24.8 mA/cm\(^2\) corrected linearly to full 1-sun, 100 mW/cm\(^2\), intensity.\textsuperscript{5} Clearly most of the loss in efficiency comes from reduced photocurrent, suggesting either inadequate absorption of light within the solar cell or inadequate collection of the photogenerated carriers. Because of the relatively short minority carrier diffusion length in Cu\textsubscript{2}S, a tradeoff exists between obtaining more absorption with a thicker layer but reducing collection efficiency.\textsuperscript{4}

This dilemma—a mismatch between the length scales of light absorption and charge collection—is exactly the challenge that the nanowire array geometry has been designed to address;\textsuperscript{iii} consequently, the CdS/Cu\textsubscript{2}S pair is an excellent system in which the benefits of the nanowire geometry might be realized to surpass the performance of planar solar cells. Investigation of this material system began at the single-nanowire level, first using vapor-phase-grown CdS nanowires to evaluate the performance of the heterojunction. Early work established the promise of CdS/Cu\textsubscript{2}S nanowire solar cells\textsuperscript{10} but faced challenges in reproducibility, as discussed in detail below. Since the ultimate goal was to realize a nanowire array solar cell whose efficiency could be compared directly to that of previous planar work, efforts shifted to applying the cation-exchange chemistry to hydrothermally grown CdS nanorod arrays.

\textsuperscript{iii} In addition to the challenge of achieving high-efficiency solar cells, researchers’ interest in the CdS/Cu\textsubscript{2}S system waned as difficulties arose in stabilizing the phase and the Cu ion mobility of Cu\textsubscript{2}S, which led to the development of CuInS\(_2\) and ultimately CIGS.\textsuperscript{42} Also, most of the solar cells produced in the 1970’s and 1980’s were made from polycrystalline CdS films, which showed a tendency for Cu\textsuperscript{+} to infiltrate between the grain boundaries of the film and might eventually have caused the cells to fail.\textsuperscript{43} Additionally, although stoichiometric chalcocite was determined to be the desired phase for photovoltaics, it was difficult to maintain its stability because Cu\textsubscript{2}S is easily oxidized at its surface to produce djurleite or mixed phases.\textsuperscript{20, 44}
3.3. Growth of CdS Nanowires by Physical Vapor Transport

CdS nanowires were grown by physical vapor transport (PVT) in a standard tube furnace setup (Figure 3.2). In this approach, an alumina boat filled with CdS powder was heated to induce sublimation; the vapor was transported to a cooler part of the quartz reaction tube via the flow of argon, an inert carrier gas; and the vapor recrystallized onto a substrate that had been seeded with gold nanoparticles to facilitate growth of nanowires, presumably by the vapor-liquid-solid (VLS) mechanism.

The synthesis of nanowires by vapor-phase methods is a crystal growth reaction whose products are determined by the interplay of thermodynamics and kinetics. In a simplified conception of nucleation and growth, the supersaturation of the precursor reaches a point at which its chemical potential exceeds that of the chemical potential of the crystalline solid, inducing nucleation of the solid. With a steady stream of precursor, the crystal continues to grow, but its morphology is determined both by how stable particular crystal facets are in the growth environment (thermodynamics) and by how rapidly particular crystal facets nucleate and grow (kinetics). Both of these energetic concerns can be tuned by many experimental parameters, including, but not limited to, the substrate used for growth, the presence of a catalytic metal particle and its composition, the temperature of the reaction, and the supply of the precursor. Metal nanoparticles are often used to induce and control growth by the VLS mechanism, in which the precursor dissolves in the liquid metal, reaches supersaturation,
and then precipitates out of the solution to form the crystal. The triple-phase-boundary between the vapor-phase precursor, the metal-precursor solution, and the growing crystal lowers the free energy of the crystal’s formation, causing nucleation and growth to occur there preferentially and thus catalyzing the growth of the crystal. Often the size of the nanowires can be controlled by the size of the initial metal particle, and the crystallographic growth direction results from minimizing the energy at the interface between the metal and the growing crystal.

Although wurtzite CdS grows readily as nanowires or nanoribbons, control over this reaction similar to that achieved in silicon or ZnO nanowires has yet to be reported in the literature. Unlike some crystals whose growth can be easily templated by using a lattice-matched substrate for epitaxy, similar to the approach taken in the growth of epitaxial thin films, wurtzite CdS exhibits poor lattice matching with common substrates that are stable under the reaction conditions. The (111) face of zincblende InP exhibits excellent lattice matching with CdS, but it is unstable at the growth temperatures necessary for the reaction. Silicon’s (111) face, with an 8% mismatch, is the best of all the common substrates, yet at growth temperatures of ~680°C or greater, Cd₄SiS₆ alloy nanowires can be formed instead of pure CdS wires (Figure 3.3). Increasing the vapor pressure of CdS, and therefore perhaps outcompeting incorporation of silicon vs. cadmium into the crystal, mitigated this effect and returned the XRD pattern to CdS; however, the uncertainty of possible trace contamination of the wires by silicon remained. The greatest success was achieved by coating mica substrates with a CdS thin film deposited by chemical bath deposition (CBD), which is known to be c-axis oriented. Growth on these substrates yielded predominantly c-axis nanowires mixed with nanoribbons.

*Figure 3.4:* Changes in the morphology of CdS nanostructures. SEM images go from lowest (a) to highest (f) temperature of the growth substrate, which also corresponds to lowest to highest vapor pressure of the CdS precursor. All scale bars are 1 µm.
In general, the morphology of the product was a mixture of nanowires and nanoribbons and was highly sensitive to the temperature of the substrate as well as the vapor pressure of CdS during the reaction. Reactions used a 20-nm gold film to form the catalyst particles. The hottest part of the substrate, which also would receive the most CdS vapor, was predominantly wide ribbons. Further downstream, the morphology transitioned to mixtures of wires and ribbons. Cooler regions of the substrate exhibited kinked growth (Figure 3.4).

Without gold catalyst particles, however, growth of wires and ribbons did still occur just with lower density. This observation suggests that both the VLS and vapor-solid (VS) growth mechanisms compete during the reaction, and the balance between the two mechanisms determines the resulting products. Because the triple-phase boundary in VLS growth lowers the free energy of nucleation, the VLS mechanism is typically favored at lower concentrations of reactant. Efforts were made to lower the vapor pressure of the CdS by lowering the temperature of the reaction and finding a regime when growth would occur by only the VLS mechanism. In this case, a sapphire substrate was covered with clumps of wires whose tips were capped with gold particles (Figure 3.5), indicating that nucleation on the sapphire substrate was not energetically favorable. Similar reactions on gold-coated silicon substrates failed to produce any wires, suggesting the difficulty of nucleating on crystalline silicon possibly because silicon alloys into the molten gold catalyst droplet. Amorphous substrates such thermally oxidized silicon and quartz displayed much denser nucleation and growth for a given set of reaction conditions.

Overall, reproducible control of the PVT growth reaction of CdS nanowires was not achieved, although individual substrates with nanowires suitable for devices could be obtained. In general, it is likely that the concentration of CdS vapor from the PVT reaction was too poorly controlled, and possibly also the temperature of the reaction substrate. Because of the possibility of contamination from silicon substrates and the lack of stable, lattice-matched substrates, growth on CBD films of CdS or on amorphous substrates such as quartz would likely be the most promising future directions. Since the substrate could not be used to template the growth, investigation of other catalyst metals to replace gold and therefore control the metal-CdS interface during growth could also be pursued.

3.4 CdS/Cu$_2$S Single-Nanowire Solar Cells

3.4.1 Fabrication of the Devices
CdS nanowires grown by PVT were used as the starting material to produce core-shell CdS/Cu$_2$S single-nanowire solar cells according to previous work. Briefly, the nanowires were dry transferred to SiO$_2$/Si substrates; KI/I$_3^-$ solution was applied to remove the gold catalyst particles; and the wires were coated with 10 nm of alumina by ALD to serve as a mask for the later cation-exchange reaction. Lithography and e-beam evaporation were used to define the In/Au contacts to the CdS nanowire, with a brief etch in dilute BHF to remove the alumina. A second step of lithography defined the window for the core-shell region, and the photoresist and alumina were used as a mask during the cation-exchange reaction. Finally, a third lithographic step and Pt/W/Pt metallization were used to contact the shell.

### 3.4.2 Performance of the Solar Cells

The performance of the nanowire solar cells was measured under simulated, 1-sun illumination. Devices were produced using cation-exchange conditions similar to those optimized in previous work, yet the results only rarely achieved the past level of performance (Figure 3.6, Tables 3.1-2). It should be noted that the substrates were too sparse to obtain reliable XRD data to assign the Cu$_2$S phase as chalcocite; therefore, these newer devices will be denoted as CdS/Cu$_{2-x}$S, although x could be 0. These devices were designed with a 30-μm window for the cation-exchange reaction, yet their extremely low photocurrent suggested that either the original CdS nanowires or the cation-exchange chemistry had not been robustly reproduced. To investigate the dependence on the CdS starting material, devices made from wires grown from various

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iv Additional details of the fabrication process can be found in Appendix B.

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### Table 3.1: Electrical properties of single-nanowire CdS/Cu$_{2-x}$S solar cells under 1-sun illumination.

Devices were made from samples grown on different substrates. Old Si <100> refers to wires that were grown around the same time that the best devices were made (Figure 3.6). (a)-(c) were made with 30-µm windows, while (d) were made with windows of only a few micrometers and some were electrically connected in parallel (Figure 3.7). $R_{sh}$ was estimated with a linear fit to the $I-V$ curve near 0 V, while $R_s$ was estimated with a linear fit to the high-voltage region of the curve. Because of the poor performance, the active area could not be reliably measured; therefore, the devices’ efficiencies could not be estimated. The best performing devices are highlighted in orange and yellow.

#### (a) CBD CdS on Mica

<table>
<thead>
<tr>
<th>Reaction Time</th>
<th>$V_{oc}$ (V)</th>
<th>$I_{sc}$ (pA)</th>
<th>$P_{max}$ (pW)</th>
<th>FF</th>
<th>$R_{sh}$ (GΩ)</th>
<th>Est. $R_{in}$ (GΩ)</th>
<th>Est. $R_s$ (MΩ)</th>
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<th>Est. $R_{in}$ (GΩ)</th>
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<td>10.4</td>
<td>4.6</td>
<td>0.77</td>
<td>54.8</td>
<td>1656</td>
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<tr>
<td>5s B</td>
<td>0.55</td>
<td>2.5</td>
<td>0.9</td>
<td>0.66</td>
<td>220.0</td>
<td>960</td>
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</tr>
<tr>
<td>8s A</td>
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<td>0.5</td>
<td>0.65</td>
<td>340.0</td>
<td>2800</td>
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<td>8s B</td>
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<td>1.7</td>
<td>0.6</td>
<td>0.71</td>
<td>294.1</td>
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<td>830</td>
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<tr>
<td>10s A</td>
<td>0.54</td>
<td>29.3</td>
<td>12.7</td>
<td>0.80</td>
<td>18.4</td>
<td>690</td>
<td>29.8</td>
</tr>
<tr>
<td>10s B</td>
<td>0.57</td>
<td>128.0</td>
<td>56.5</td>
<td>0.78</td>
<td>4.5</td>
<td>2424</td>
<td>17.2</td>
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<tr>
<td>10s C</td>
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<td>38.4</td>
<td>14.5</td>
<td>0.78</td>
<td>13.0</td>
<td>397</td>
<td>4.0</td>
</tr>
<tr>
<td>12s A</td>
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<td>4.0</td>
<td>1.6</td>
<td>0.69</td>
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<td>1047</td>
<td>375</td>
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<tr>
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<td>4.3</td>
<td>1.9</td>
<td>0.80</td>
<td>130.2</td>
<td>3081</td>
<td>1.18</td>
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<tr>
<td>15s B</td>
<td>0.56</td>
<td>8.3</td>
<td>3.5</td>
<td>0.70</td>
<td>67.5</td>
<td>1194</td>
<td>84.7</td>
</tr>
</tbody>
</table>

#### (d) Si/SiO$_2$ (1 µm thermal oxide), reaction time 5-10 s

<table>
<thead>
<tr>
<th>Device ID</th>
<th>$V_{oc}$ (V)</th>
<th>$I_{sc}$ (pA)</th>
<th>$P_{max}$ (pW)</th>
<th>FF</th>
<th>$R_{sh}$ (GΩ)</th>
<th>Est. $R_{in}$ (GΩ)</th>
<th>Est. $R_s$ (MΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A2n1p2</td>
<td>0.65</td>
<td>9.0</td>
<td>4.0</td>
<td>0.68</td>
<td>72.2</td>
<td>511</td>
<td>8400</td>
</tr>
<tr>
<td>A3n3p1</td>
<td>0.63</td>
<td>12.3</td>
<td>5.0</td>
<td>0.65</td>
<td>51.2</td>
<td>355</td>
<td>10800</td>
</tr>
<tr>
<td>B2n2p1</td>
<td>0.65</td>
<td>6.2</td>
<td>2.8</td>
<td>0.68</td>
<td>106.5</td>
<td>640</td>
<td>214</td>
</tr>
<tr>
<td>B3n1p3</td>
<td>0.65</td>
<td>14.8</td>
<td>6.8</td>
<td>0.71</td>
<td>43.9</td>
<td>379</td>
<td>247</td>
</tr>
<tr>
<td>D1n1p2</td>
<td>0.65</td>
<td>9.1</td>
<td>4.3</td>
<td>0.72</td>
<td>71.4</td>
<td>651</td>
<td>637</td>
</tr>
<tr>
<td>D2n2p1</td>
<td>0.65</td>
<td>5.1</td>
<td>2.2</td>
<td>0.66</td>
<td>127.5</td>
<td>957</td>
<td>3040</td>
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<tr>
<td>D4n1p3</td>
<td>0.64</td>
<td>8.9</td>
<td>4.0</td>
<td>0.71</td>
<td>71.9</td>
<td>906</td>
<td>12100</td>
</tr>
<tr>
<td>F5n3p1</td>
<td>0.65</td>
<td>13.9</td>
<td>6.3</td>
<td>0.70</td>
<td>46.8</td>
<td>522</td>
<td>1320</td>
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<tr>
<td>F7n3p1</td>
<td>0.65</td>
<td>5.6</td>
<td>2.5</td>
<td>0.68</td>
<td>116.1</td>
<td>902</td>
<td>6160</td>
</tr>
</tbody>
</table>
substrates were measured, but nearly all showed high $V_{oc}$'s accompanied by lower FF's and very low $I_{sc}$'s as compared to previous results. These features suggest that conductivity through the CdS core might be the source of the problem, since a highly resistive core would limit the active area of the solar cell; if an electron-hole pair were generated within the core far from the pristine CdS and its collection contact, then the electron would have to travel through the resistive core to be collected. If the resistance were too high, the electron would recombine before being collected, so essentially that portion of the core-shell region would not provide photocurrent and would appear inactive in a photocurrent map. Even for the active portion of the core-shell region, the core’s high series resistance could degrade the solar cell’s fill factor, but the $V_{oc}$ would remain relatively unchanged. To test this hypothesis, three-terminal devices were fabricated, in which an active core-shell region was placed in the middle of two separately contacted CdS regions (Figure

Table 3.2: Summary statistics of the CdS/Cu$_{2-x}$S solar cells. The attributes of devices fabricated from different wire samples were similar except for the $V_{oc}$ of the old CdS wires. As an inconsistency in the cation-exchange reaction could also cause such a deviation, it would be premature to conclude that there is a difference between these wires and the others.

<table>
<thead>
<tr>
<th>CdS Growth Substrate</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>Sample Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>CBD Mica</td>
<td>0.62 ± 0.01</td>
<td>0.65 ± 0.07</td>
<td>8</td>
</tr>
<tr>
<td>Si &lt;100&gt;</td>
<td>0.61 ± 0.01</td>
<td>0.72 ± 0.04</td>
<td>8</td>
</tr>
<tr>
<td>Old Si &lt;100&gt;</td>
<td>0.55 ± 0.03</td>
<td>0.74 ± 0.05</td>
<td>10</td>
</tr>
<tr>
<td>Si/SiO$_2$</td>
<td>0.65 ± 0.01</td>
<td>0.69 ± 0.02</td>
<td>9</td>
</tr>
</tbody>
</table>

Figure 3.7: Optical image of small CdS/Cu$_{2-x}$S nanowire devices. One (top left) is wired individually while the other two are wired in parallel.

Figure 3.8: Three-terminal CdS/Cu$_{2-x}$S solar cells. (a) Schematic of the three-terminal devices that allowed collection through the CdS core to be tested. (b) Solar cells made from undoped CdS wires showed different photocurrents depending on if the right or left CdS electrode was contacted. When both electrodes were contacted in parallel, the currents summed, showing that photocurrent was not collected from the CdS core. In contrast, solar cells made from In-doped CdS produced their full photocurrent when either CdS electrode was contacted, indicating excellent conductivity through the core.
The current collected in parallel from the two separate CdS contacts was the sum of the current collected from each side individually, which established that the transport through the depleted core was not sufficient to allow collection of photogenerated carriers along the full length of the core-shell region. In contrast, devices made from In-doped CdS wires (discussed below) produced the full current when contacted at either terminal.

Lastly, one device fabricated from nanowires grown on a substrate that showed a mixed XRD pattern of CdS and Cd₄SiS₆ exhibited performance similar to the that reported previously (Figure 3.9). This result suggests the hypothesis that trace incorporation of silicon in the CdS, which is thought to be an $n$-type dopant, might be responsible for the exceptional performance of certain devices in the previous work.

### 3.4.3 Solar Cells from In-doped CdS Nanowires

The results of using extrinsically doped CdS nanowires to fabricate solar cells further confirmed the diagnosis of poor transport in the CdS core and ruled out the possibility of a non-uniform cation-exchange reaction along the length of the wire. CdS nanowires were grown with In$_2$S$_3$ powder upstream of the CdS to yield In-doped CdS nanowires. Measurements on single-nanowire field-effect transistors (FETs) fabricated from these wires confirmed that they were $n$-type and had carrier concentrations of approximately $10^{17}$ cm$^{-3}$ and electron mobilities ranging from 16 to 80 cm$^2$/Vs. Devices fabricated from In-doped CdS nanowires exhibited much higher photocurrents than any previously fabricated devices (Table 3.3). Additionally, scanning photocurrent mapping (SPCM) shows that the entire wire could be active under both blue and red illumination (Figures 3.10a,b), although a few devices still displayed collection difficulties under red illumination. Investigation of three-terminal devices and spectrally resolved photocurrent measurements under white-light bias then confirmed that under uniform illumination of any color, collection through the core CdS nanowire was no longer a problem (Figure 3.10c). Single-nanowire efficiencies of large (30 µm) and small (3-9 µm) devices were estimated and yielded an average of 2.3±0.2% and 2.5±0.3%, respectively, which was

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$^v$ Details of the FET measurements are included in Appendix C.
(a) Large (30 µm) In-doped devices

<table>
<thead>
<tr>
<th>Reaction</th>
<th>V_{oc} (V)</th>
<th>I_{sc} (pA)</th>
<th>J_{sc} (mA/cm²)</th>
<th>FF</th>
<th>R_{sh} (MΩ)</th>
<th>R_{mp} (GΩ)</th>
<th>R_{sc} (Ω)</th>
<th>Diameter (nm)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10s D</td>
<td>0.48</td>
<td>357</td>
<td>5.98</td>
<td>0.70</td>
<td>9.5</td>
<td>15.2</td>
<td>1.3</td>
<td>199</td>
<td>2.0</td>
</tr>
<tr>
<td>10s E</td>
<td>0.53</td>
<td>474</td>
<td>6.90</td>
<td>0.67</td>
<td>5.1</td>
<td>7.6</td>
<td>1.1</td>
<td>229</td>
<td>2.4</td>
</tr>
<tr>
<td>15s A</td>
<td>0.53</td>
<td>318</td>
<td>5.89</td>
<td>0.70</td>
<td>6.0</td>
<td>22.8</td>
<td>1.7</td>
<td>180</td>
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</tr>
<tr>
<td>15s B</td>
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<td>421</td>
<td>6.34</td>
<td>0.64</td>
<td>1.4</td>
<td>7.6</td>
<td>1.2</td>
<td>220</td>
<td>2.1</td>
</tr>
<tr>
<td>21s M</td>
<td>0.47</td>
<td>266</td>
<td>6.72</td>
<td>0.69</td>
<td>4.9</td>
<td>17.2</td>
<td>1.8</td>
<td>132</td>
<td>2.2</td>
</tr>
<tr>
<td>21s N</td>
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<td>7.1</td>
<td>9.0</td>
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<tr>
<td>21s O</td>
<td>0.53</td>
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<td>10.3</td>
<td>10.9</td>
<td>1.5</td>
<td>162</td>
<td>2.6</td>
</tr>
<tr>
<td>21s P</td>
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<td>609</td>
<td>6.46</td>
<td>0.61</td>
<td>1.9</td>
<td>6.2</td>
<td>0.9</td>
<td>314</td>
<td>2.0</td>
</tr>
<tr>
<td>21s Q</td>
<td>0.52</td>
<td>370</td>
<td>6.53</td>
<td>0.70</td>
<td>5.7</td>
<td>11.5</td>
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<td>2.4</td>
</tr>
<tr>
<td>Average</td>
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<td>0.67</td>
<td>5.8</td>
<td>12.0</td>
<td>1.4</td>
<td>201</td>
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</tr>
<tr>
<td>Std. Dev.</td>
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<td>99</td>
<td>0.49</td>
<td>0.03</td>
<td>3.0</td>
<td>5.4</td>
<td>0.3</td>
<td>51</td>
<td>0.2</td>
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</table>

Table 3.3: Metrics of the In-doped CdS/Cu_{2-x}S solar cells. (a) Devices with 30-µm windows exhibited large photocurrents because their full window was active for solar energy conversion, as demonstrated by SPCM (Figure 3.10). (b) Smaller In-doped devices exhibited similar properties to their larger cousins. Efficiencies were estimated based on the devices’ geometrical cross-sections as measured in SEM.

(b) Smaller In-doped devices, 15 s cation-exchange reaction

<table>
<thead>
<tr>
<th>Device</th>
<th>V_{oc} (V)</th>
<th>I_{sc} (pA)</th>
<th>J_{sc} (mA/cm²)</th>
<th>FF</th>
<th>R_{sh} (GΩ)</th>
<th>R_{mp} (GΩ)</th>
<th>R_{sc} (Ω)</th>
<th>Length (µm)</th>
<th>Diameter (nm)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDD</td>
<td>0.53</td>
<td>134</td>
<td>5.4</td>
<td>0.68</td>
<td>4.0</td>
<td>98.0</td>
<td>1.0</td>
<td>6.11</td>
<td>406</td>
<td>1.9</td>
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<td>HDAp2n2</td>
<td>0.53</td>
<td>68</td>
<td>6.3</td>
<td>0.69</td>
<td>6.0</td>
<td>57.2</td>
<td>1.2</td>
<td>6.87</td>
<td>202</td>
<td>2.3</td>
</tr>
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<td>HDAp1n3</td>
<td>0.52</td>
<td>49</td>
<td>6.3</td>
<td>0.69</td>
<td>10.6</td>
<td>108.6</td>
<td>7.6</td>
<td>3.78</td>
<td>206</td>
<td>2.5</td>
</tr>
<tr>
<td>LDAp2n2</td>
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<td>44</td>
<td>6.5</td>
<td>0.69</td>
<td>12.5</td>
<td>129.7</td>
<td>6.7</td>
<td>4.46</td>
<td>151</td>
<td>2.4</td>
</tr>
<tr>
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<td>0.66</td>
<td>3.6</td>
<td>50.3</td>
<td>3.2</td>
<td>9.12</td>
<td>204</td>
<td>2.7</td>
</tr>
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<td>LDAp3n2</td>
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<td>77</td>
<td>7.3</td>
<td>0.67</td>
<td>7.4</td>
<td>57.2</td>
<td>2.5</td>
<td>4.02</td>
<td>203</td>
<td>2.8</td>
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<tr>
<td>HDAp1n3</td>
<td>0.53</td>
<td>61</td>
<td>7.7</td>
<td>0.67</td>
<td>8.7</td>
<td>67.2</td>
<td>2.2</td>
<td>3.20</td>
<td>247</td>
<td>2.7</td>
</tr>
<tr>
<td>HDAp1n2</td>
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<td>7.9</td>
<td>0.70</td>
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<td>166.1</td>
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<td>2.98</td>
<td>157</td>
<td>3.0</td>
</tr>
<tr>
<td>Average</td>
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<td>79</td>
<td>6.9</td>
<td>0.68</td>
<td>8.4</td>
<td>80.3</td>
<td>3.2</td>
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<td>2.5</td>
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<td>Std. Dev.</td>
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<td>0.9</td>
<td>0.04</td>
<td>4.0</td>
<td>49.2</td>
<td>2.5</td>
<td>2.13</td>
<td>81</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Figure 3.10: Opto-electronic properties of the In-doped solar cells. (a) SPCM at λ=442 nm (a) and λ=658 nm (b) showing the entire window as fully active. EQE spectrum (photocurrent normalized to the photons incident on the device’s geometrical cross-section) of an In-doped solar cell using several experimental setups. pA biases indicate that white light sufficient to produce the given photocurrent was focused on the sample during the wavelength-dependent measurement (using a chopped monochromatic source and lock-in amplifier) in order to test the charge extraction’s dependence on illumination. No changes in the charge extraction efficiency were observed.
significantly less than the 5.4% previously reported for the undoped devices. Only 27% of the difference could be attributed to reductions in the $V_{oc}$ and FF, indicating that less photocurrent density was still being collected from the doped devices. The cation-exchange conditions were not optimized on the doped devices, however, so it is possible that the increased photocurrent in the undoped devices arose from a thicker shell of Cu$_2$S. Such an explanation is consistent with the larger relative photocurrent beyond the 510-nm band gap of CdS displayed by those devices (Figure 3.6b) in comparison to the photocurrent spectrum of the doped devices (Figure 3.10c).

While the electrical properties of the doped CdS/Cu$_2$S nanowire devices were well characterized, the structural properties of the interface and resulting copper sulfide layer after cation exchange were not investigated. Low signal yield because of the sparse coverage of the wires on the growth substrates made XRD of the copper sulfide’s phase inconclusive. Additionally, the fate of the indium during the cation-exchange reaction is unknown; it might collect near the interface of the two materials or perhaps become incorporated into the copper sulfide, which could explain the lower $V_{oc}$’s of the doped devices. High-resolution TEM of the interface and copper sulfide layer or EDS elemental mapping might serve to answer these questions in the future.

3.5 CdS/Cu$_{2-x}$S Nanorod Micro-Array Solar Cells

3.5.1 Fabrication of the Devices

The high quality of the epitaxial junction produced by cation exchange and its solution-based, low-temperature processing make cation-exchange chemistry an attractive method with which to produce nanowire array solar cells. Because of the difficulty in controlling the vapor-phase growth of CdS nanowires, nanorod arrays were grown on transparent and conductive substrates using a hydrothermal method. Although SEM images suggested that the buffer layer of CdS beneath the nanorods was continuous (Figure 3.11), all efforts to fabricate large-area solar cells simply by protecting the substrate’s edges and dipping the array into the cation-exchange solution failed; electrical shorting occurred between the Cu$_{2-x}$S shell and the underlying conductive substrate beneath the CdS, even for brief (5 s) reaction times or low (50°C) temperatures, which should allow the exchange reaction to progress less than 10 nm. These initial results suggested that the buffer layer must exhibit pinholes at which the Cu$_{2-x}$S layer comes directly into contact with the underlying transparent conducting oxide.

\[\text{vi} \] Growth and optimization of the CdS hydrothermal nanowire arrays were performed by graduate student Andrew Wong, who adapted the method of reference 40.
To address this challenge, a scheme to protect the underlying buffer layer while exposing the nanorods’ tips was designed, and micro-array solar cells were fabricated in order to increase the probability that a device would avoid a shunt defect in case the protection layers failed locally as well (Figure 3.12a). Briefly, the hydrothermal array was coated with 25 nm of aluminum oxide by ALD. Then the array was filled in with poly(methyl methacrylate) (PMMA) and coated with photoresist. The micro-arrays were patterned using standard photolithography, and an O$_2$ plasma etched the PMMA to expose a few hundred nanometers of the ends of the nanorods (Figure 3.12b). BHF etching of the alumina layer exposed the clean surface of the nanorods and a post-annealling treatment allowed the PMMA to reflow into the crevices around the nanorods created by removing the alumina (Figure 3.12c). These substrates were dipped into the cation-exchange solution to form the junction, and then photolithography and sputtering were used to form individual Pt top contacts for each device. Because the Pt was opaque, measurements were performed in a setup designed for backside illumination through the FTO-coated glass substrate.$^\text{vii}$

**3.5.2 Performance of the Micro-Array Solar Cells**

In the first and currently only test of this device fabrication, two different types of substrates (ITO and FTO on glass) were used with two different temperatures (70°C and 75°C) for the cation-exchange reaction. Both reactions were run for only 5 s to minimize the potential for shorting the devices to the underlying ITO or FTO. XRD on previous macroscopic samples converted under these conditions indicates that the

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$^\text{vii}$ Additional details of the device processing can be found in Appendix D.
70°C samples were roxbyite, while the 75°C samples were djurleite. Devices of three different sizes, approximately 7×7 (small), 17×17 (medium), and 52×52 μm (large), were fabricated on all of the substrates to determine the approximate length scale of the suspected pinholes that led to shunting in the macroscopic devices.

Functioning solar cells were produced from three of the four substrates. On the ITO substrate converted at 70°C, only a few of the smallest devices survived and were located near the edge of the substrate where it is expected that the polymer protection layer might be thicker than in the center. These devices supported reasonable $V_{oc}$’s and FF’s, but their photocurrent levels were low, yielding current densities of only 37 ± 29 µA/cm² (Figure 3.13).

No functioning devices survived on the 75°C ITO substrate. The two substrates grown on FTO, however, at first appeared to yield junctions of much poorer quality than those produced on the ITO substrate as seen by their poor $V_{oc}$, FF, and low breakdown voltage in reverse bias.

![Figure 3.13](image-url)  
*Figure 3.13: I-V curve and metrics of array solar cells made from ITO substrates converted at 70°C for 5 s. 12 7×7 μm devices were measured.*

![Figure 3.14](image-url)  
*Figure 3.14: The effect of annealing on CdS nanorod array solar cells. (a) Solar I-V curve of an as-made 7×7 μm solar cell. (b) The same solar cell after annealing in air at 200°C for 5 mins, showing significantly increased $V_{oc}$ and FF.*

<table>
<thead>
<tr>
<th>(a) As-made FTO devices converted at 70°C for 5 s</th>
<th>(b) After annealing in air at 200°C for 5 mins</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Small</strong></td>
<td><strong>Medium</strong></td>
</tr>
<tr>
<td>$I_{sc}$ (nA)</td>
<td>0.46 ± 0.22</td>
</tr>
<tr>
<td>$J_{sc}$ (mA/cm²)</td>
<td>0.93 ± 0.45</td>
</tr>
<tr>
<td>$V_{oc}$ (V)</td>
<td>0.13 ± 0.02</td>
</tr>
<tr>
<td>FF</td>
<td>0.39 ± 0.03</td>
</tr>
<tr>
<td>η (%)</td>
<td>0.05 ± 0.03</td>
</tr>
</tbody>
</table>

*Table 3.4: Summarized metrics for the nanorod array solar cells fabricated on an FTO substrate and converted at 70°C for 5 s. (a) Performance of the as-made devices. 3 large, 6 medium, and 9 small devices were measured. (b) Improved performance of the devices after annealing in air at 200°C for 5 mins. 7 medium and 13 small devices were measured. The large devices were shorted after the anneal.*

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viii Tables with full metrics for all the measured devices can be found in Appendix D.
The devices produced at 75°C (Table 3.5), however, did exhibit larger photocurrent than those produced at 70°C, which is expected as the Cu$_2$S phase becomes less Cu deficient at higher conversion temperatures.\textsuperscript{22} On these substrates, several small and medium devices survived and even a few of the largest devices; since a thicker buffer layer of CdS forms when the nanorods are grown on FTO in comparison to ITO, it is possible that this buffer layer acts as a final barrier to shorting if the exchange reaction does penetrate the PMMA protection layer.

Upon annealing the 70°C FTO substrate in air for 5 mins on a 200°C hot plate, the junction quality and energy conversion efficiency of the devices improved dramatically (Figure 3.14, Table 3.4). A less drastic increase was seen for a shorter anneal of the 75°C substrate, but increasing the annealing time further led to the shorting of the devices on this substrate. Such an improvement in junction quality with annealing has been reported in the literature of planar CdS/Cu$_2$S solar cells, yet the physical explanation was never determined conclusively. Some studies even report its reversibility when the annealing occurs in an oxidizing or reducing environment.\textsuperscript{6, 41} Various explanations have been proposed, such as the infiltration of oxygen at the junction\textsuperscript{41} or reversible changes in the phase of the Cu$_2$S that alter the series resistance and light absorption of the cell.\textsuperscript{6} While it is reasonable that oxidation of the Cu$_2$S would affect the solar cell’s performance, series resistance is not a limiting factor for these micro-solar cells, so increased conductivity in the Cu$_{2-x}$S does not explain the increase in $V_{oc}$ and FF, as was suggested in planar solar cells. One possibility arises from the fact that the band alignment of semiconductor heterojunctions is highly sensitive to the interfacial dipole at the junction and can shift if the charge distribution is altered. If annealing alters this interfacial dipole, for instance by the energetic redistribution of interfacial trap states, then the band alignment between the two sides of the heterojunction would shift. It has already been demonstrated mathematically that such a shift in band alignment would lead to the dramatic changes in $I_{sc}$, $V_{oc}$, and FF that have been observed in this system after heat treatments.\textsuperscript{41} While some might propose that diffusion of Cu$^+$ ions at the interface would cause such an effect, such diffusion is not expected to be reversible and is therefore inconsistent with experiment.

### 3.5.3 Hypotheses and Future Directions

Although certain conclusions cannot yet be drawn, these initial experiments suggest several hypotheses for improving the performance of these low-temperature, solution-processed nanorod array solar cells. The first step would be to reproduce this fabrication scheme to determine how much of the observed variation arises from changes in the PMMA protection layer and etching rather than the growth substrate of

<table>
<thead>
<tr>
<th></th>
<th>Small</th>
<th>Medium</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_{sc}$ (nA)</td>
<td>0.76 ± 0.37</td>
<td>3.9 ± 0.50</td>
</tr>
<tr>
<td>$J_{sc}$ (mA/cm$^2$)</td>
<td>1.55 ± 0.77</td>
<td>1.4 ± 0.20</td>
</tr>
<tr>
<td>$V_{oc}$ (V)</td>
<td>0.16 ± 0.02</td>
<td>0.12 ± 0.01</td>
</tr>
<tr>
<td>FF</td>
<td>0.43 ± 0.03</td>
<td>0.40 ± 0.04</td>
</tr>
<tr>
<td>$\eta$ (%)</td>
<td>0.10 ± 0.05</td>
<td>0.07 ± 0.01</td>
</tr>
</tbody>
</table>

*Table 3.5: Summarized metrics for nanorod array solar cells fabricated on an FTO substrate and converted at 75°C for 5 s. The higher photocurrent is consistent with the phase of Cu$_{2-x}$S transitioning from roxbitye to less Cu-deficient djurleite.*
the CdS nanorods or the cation-exchange conditions. Consistent with the failure of all attempted macroscopic devices, these devices suggest that the length scale of the shunt paths that form during cation exchange are on the order of tens of microns. It is possible, however, that this result might arise from differences in how the PMMA coats the nanorods grown on ITO and FTO substrates that could be resolved with an improved technique for filling the nanorod array with polymer. Additionally, it should be investigated whether the extremely low photocurrent levels result from simply poor absorption in the thin layer of non-stoichiometric Cu$_{2-x}$S, which could be confirmed by a simple UV-visible absorption measurement, or if the difficulty arises more from the collection of the photogenerated carriers.

3.6 Conclusions and Future Outlook

The CdS/Cu$_2$S heterojunction is a promising material system for nanowire solar cells. The demonstrated quality of its interface produced by cation-exchange chemistry is an essential component to achieving efficient nanowire solar cells in particular because of their high surface-to-volume ratio. Additionally, the sulfides are easily processed in solution at low temperatures, making them a suitable test system for integrating all of the key benefits of nanowire solar cells into a single device.

In addition to this promise, however, critical challenges in the materials science of this sulfide system still remain. Lacking the benefit of the decades of research dedicated to understanding and controlling the opto-electronic properties of silicon, researchers of CdS/Cu$_2$S must contend with uncertainties in the electrical conductivity and luminescence efficiency of the starting CdS, in the phase and stability of the Cu$_2$S, and in the band alignment and stability of the heterojunction itself. In particular, the phase and stability of Cu$_2$S is of key concern because it was precisely this challenge that led researchers to abandon Cu$_2$S and move to ternary and quaternary alloys. While it is possible that nanostructured Cu$_2$S might be engineered or encapsulated for greater stability, this question should be resolved as soon as possible to ensure that research efforts are not wasted on a material with little practical future. If indeed the stability of Cu$_2$S remains a challenge, then an abundance of synthetic techniques can be used to convert it to more stable alloys. As the quality and conductivity of the CdS are also of critical importance for adequate collection of charges in a core-shell nanowire solar cell, additional work is also required to characterize the optical and electronic performance of solution-synthesized CdS nanorods and nanowires. Of particular importance is measuring and controlling the carrier concentration and mobility of these materials. Only once the properties of the starting materials are well understood can the details of the junction’s formation and stability be tackled.

In a broader sense, the CdS/Cu$_2$S heterojunction can be viewed as an example of how cation-exchange chemistry can produce high-quality heterojunctions. Translating this chemistry to more suitable solar materials, e.g. nontoxic and more stable sulfides or potentially even oxides, would be a tremendous achievement in both the fundamental science of cation exchange and the materials chemistry of solar cells.
3.7 References


Chapter 4

Interactions Between Plasmonic Nanocrystals and Single-Nanowire Solar Cells

Sections 4.1 and 4.2 were originally written by the author (SFB) for the following publication:

4.1 Increasing Light Absorption in Solar Cells with Nanostructured Metals and Dielectrics

In recent photovoltaic research, nanomaterials have offered two new approaches for trapping light within solar cells to increase their absorption: nanostructuring the absorbing semiconductor and using metallic nanostructures to couple light into the absorbing layer. As discussed in Chapter 1, arrays of vertically aligned micro- and nanowires absorb more light than their planar counterparts,\(^1\)-\(^3\) while individual nanowires support optical resonances that can increase their absorption at various wavelengths.\(^4\)-\(^6\) Additionally, a core-shell wire geometry allows absorption of light over the full length of the wire while maintaining the wire’s much smaller radius as the relevant distance for charge collection.\(^7\) As all of these effects arise from the geometry of nanowires, such nanostructuring offers a way to improve a material’s absorption without modifying its composition.

Metal nanostructures also offer intriguing possibilities for increasing absorption of light in poorly absorbing materials. Near a metal’s surface, collective oscillations of the free electrons produce excitations known as surface plasmons. The resonance frequencies of these plasmons depend sensitively on the metal’s free electron density and band structure, the nanostructure’s size and geometry, and the local dielectric environment.\(^8\)-\(^\text{12}\) Excitation of surface plasmons by incident light leads to intense evanescent electric fields at the nanostructure’s surface, particularly at sharp edges and points,\(^13\),\(^14\) as well as to enhanced scattering and absorption cross sections.\(^15\) Both evanescent and scattered fields can yield increased absorption of light within the surrounding dielectric media,\(^16\)-\(^19\) which then leads to higher energy conversion efficiencies in solar cells.\(^20\)-\(^25\) Since the plasmonic properties of metal nanostructures...
are tunable throughout the visible and near infrared regions of the spectrum,\textsuperscript{8, 26} they offer another way to modify the absorption of a solar material without changing its composition.

In either approach used to improve absorption–nanostructuring the dielectric solar material or coupling it to metal nanostructures–light interacts with subwavelength features. To combine these two approaches, single-nanowire solar cells decorated with silver nanocrystals were studied. The nanocrystals modified the nanowire’s photocurrent in a highly wavelength-dependent manner. Three-dimensional finite-difference time domain (FDTD) simulations show that increases in the photocurrent result from the surface plasmon resonances of the nanocrystal while decreases occur at the wavelengths of the nanowire’s optical resonances. Such insight into how the nanowire’s absorption of light arises from the metal nanocrystal-nanowire interaction is essential to the design of efficient nanostructured solar cells.

4.2 A Suspended, Single-Nanowire Silicon Solar Cell Decorated with an Octahedral Silver Nanocrystal

4.2.1 Wavelength-Dependent Photocurrent

Immediately following characterization of the suspended, single-nanowire silicon solar cells (Chapter 2), octahedral silver nanocrystals were deposited onto the devices. Note that the devices had previously been coated in 4 nm of alumina as a passivation layer, which now acted as a dielectric spacer between the wire and the nanocrystal. The nanocrystals, whose edges measured about 270 nm, were synthesized\textsuperscript{i} by the polyol method using poly(vinyl pyrrolidone) (PVP) as the shape-controlling agent.\textsuperscript{27} Capped in PVP, the nanocrystals were suspended in ethanol and drop cast onto the devices. After allowing the ethanol to dry, the devices were rinsed in isopropanol and blown dry with nitrogen. Because of the solution’s low concentration, typically only a single nanocrystal was deposited onto an individual nanowire. Most often, the nanocrystal adhered to the facet on the wire’s underside (Figure 4.1c). Following the addition of the silver nanocrystal, the short-circuit current was re-measured, and FDTD simulations using the geometry shown in the inset of Figure 4.1a were used to calculate the wavelength-dependent absorption of the nanowire decorated with the nanocrystal (Figures 4.1a,b).

Plotting the relative change in photocurrent at each wavelength reveals the highly wavelength-dependent effect of the silver nanocrystal (Figure 4.1d). The experimental changes in photocurrent are in excellent agreement with those predicted by the FDTD simulation, demonstrating that the simulation does capture the relevant interactions between light and the nanocrystal-nanowire structure. Notable features include the two broad peaks in enhancement centered at 981 nm and 750 nm, as well as the several dips in absorption that occur at wavelengths corresponding to the nanowire’s optical resonances. Although the experimental photocurrent spectra were measured using unpolarized light, the origin of these features can be better understood by studying the simulated polarization-dependent electric field distributions at the relevant wavelengths.

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\textsuperscript{i} Dr. Xing-Yi Ling synthesized the silver octahedral nanocrystals.
4.2.2 Interpretation Using Numerical Simulations of the Electric Field

By considering the electric field distribution of the system when illuminated by light polarized along the wire’s axis, the two broad peaks in enhancement centered at 981 nm and 750 nm can be attributed to the nanocrystal’s predominantly dipolar and quadrupolar surface plasmon resonances, respectively. The geometry of the simulation is shown in Figure 4.2a, in which the cross-sectional plane slices the edge of the octahedron. When the particle and wire are excited by light propagating in the negative z-direction and polarized in the x-direction, the phase of the x-component of the electric

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ii Dr. Hanwei Gao performed the FDTD simulations for the silicon nanowire solar cells. Interpretation and analysis of the simulations was a collaborative effort between Dr. Gao and the author (SFB).
field \((E_x)\) at the edge of the octahedron does not change in the direction of propagation, while the phase of the \(z\)-component \((E_z)\) does change sign (Figures 4.2a,b). This field orientation at the edge of the nanocrystal is consistent with the expected electric field of a dipole surface plasmon resonance (Figure 4.2c). At 750 nm, the phase of \(E_x\) changes once and the phase of the \(E_z\) changes twice, which is consistent with the particle’s quadrupolar resonance (Figures 4.2c-e). Since the light is polarized parallel to the long axis of the nanowire, the silver octahedron’s charge oscillations are perturbed uniformly along their path by the nearby dielectric; consequently, the optical response reflects the free-space resonances of the nanocrystal but shifted to longer wavelengths by the polarizability of the local dielectric (Figure 4.3). This excitation and its result are

Figure 4.2: Simulated response of the nanowire-nanocrystal system to \(x\)-polarized light. Geometry of the plane of the simulated field plots, in which the cross-sectional plane slices the edge of the octahedron (a). In the following plots, dashed lines outline the octahedron’s rectangular edge and the nanowire’s hexagonal cross section. The nanowire and octahedron were simulated as being illuminated by an \(x\)-polarized plane wave propagating in the negative \(z\)-direction. Simulated \(E_x\) (b) and \(E_z\) (c) in the \(y-z\) plane at the octahedron’s edge at \(\lambda=981\) nm. The unchanged phase of \(E_x\) and the changing phase of \(E_z\) in the \(z\)-direction indicate that the octahedron exhibits a dipolar resonance along the \(x\)-direction (d, top left). Black arrows in (d) indicate the electric field lines with the phases of \(E_x\) (purple) and \(E_z\) (green) labeled. Because the simulation plane is cut at the edge of the octahedron, only the field components in the dashed boxes are visible. Simulated \(E_x\) (e) and \(E_z\) (f) in the \(y-z\) plane at the octahedron’s edge at \(\lambda=750\) nm. The changing phase of \(E_x\) and the changing phase of \(E_z\) in the \(z\)-direction indicate that the octahedron exhibits a quadrupolar resonance in the \(x-z\) plane (d, bottom right). Magnitudes of the field components are in arbitrary units.
analogous to the common experimental geometry in which a metal nanocrystal sitting on a dielectric substrate is excited with light that is incident normal to the substrate.\textsuperscript{11, 28, 29}

In contrast, when the light is polarized along the $y$-direction, the dielectric of the wire perturbs the charge oscillations asymmetrically along their path. The geometry of this simulation is shown in Figure 4.4a, in which the cross-sectional plane slices through the center of the octahedron. At 981 nm, the several lobes surrounding the nanocrystal in both $E_y$ and $E_z$ suggest that the strong interaction between the particle and the wire causes the charge oscillations to de-phase, and the resonance takes

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4_3.png}
\caption{Extinction spectrum of the silver octahedra suspended in ethanol. The predominantly dipolar (\textasciidetilde 780 nm) and quadrupolar (\textasciidetilde 510 nm) peaks are visible.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4_4.png}
\caption{Simulated response of the nanowire-nanocrystal system to $y$-polarized light. Geometry of the plane of the simulated field plots, in which the cross-sectional plane slices through the center of the octahedron (a). In the following plots, dashed lines outline the cross sections of the octahedron and the nanowire. The nanowire and octahedron were simulated as being illuminated by a $y$-polarized plane wave propagating in the negative $z$-direction. Simulated $E_y$ (b) and $E_z$ (c) in the $y$-$z$ plane at the octahedron’s center at $\lambda=981$ nm. The node in $E_y$ at the nanocrystal’s surface suggests that the resonance has partial quadrupole character. (d) Simulated change in the nanowire’s absorption for unpolarized (green), $y$-polarized (blue), and $x$-polarized (red) illumination showing the dependence of the peak positions on polarization. Simulated $E_y$ (e) and $E_z$ (f) in the $y$-$z$ plane at the octahedron’s center at $\lambda=750$ nm. The similar symmetry also suggests quadrupole character. Magnitudes of the field components are in arbitrary units.}
\end{figure}
on some quadrupole character (Figures 4.4b,c). The absorption peak of the nanocrystal-nanowire system for this polarization is blue-shifted from the same peak for x-polarized illumination, as expected for the mixing of the dipole and quadrupole resonances (Figure 4.4d). At 750 nm, similar nodal symmetry appears in the $E_y$ and $E_z$ field components (Figures 4.4e,f), although the lobes are more pronounced. This enhancement peak has red-shifted from its position for x-polarized illumination (Figure 4.4d), suggesting that it too now reflects a mixture of the particle’s dipole and quadrupole resonances. From both the $y$-polarized and x-polarized field plots, it is clear that the solar cell’s increased photocurrent arises because the silver octahedron’s surface plasmon resonances couple light into the wire.

A third notable feature in the photocurrent spectrum is the sharp decrease in photocurrent near 660 nm. For x-polarized light, the wire exhibits a whispering gallery resonance at 661 nm at distances far from the nano-octahedron (Figure 4.5a). Closer to the nanocrystal (Figures 4.5b,c), this resonance becomes distorted and the field within the nanowire decreases, indicating that the absorption in the wire is reduced locally because of the nanocrystal. Under y-polarized illumination, a Fabry-Pérot resonance exists in the wire at 657 nm, which is also locally perturbed by the octahedron (Figures 4.5d-f).

![Figure 4.5: Disruption of optical resonances in the nanowire. $E_x$ in the y-z plane under x-polarized illumination of $\lambda=661$ nm at positions along the wire of 700 nm (a), 140 nm (b), and 0 nm (c) from the center of the octahedral nanocrystal (NC) showing the local perturbation of the nanowire’s whispering gallery mode. $E_y$ (d, e, f) under y-polarized illumination of $\lambda=657$ nm at positions along the wire of 700 nm (d), 140 nm (e), and 0 nm (f) from the octahedron’s center showing the local perturbation of the nanowire’s Fabry-Pérot mode. Magnitudes of the field components are in arbitrary units.](image)
4.5d-f), causing a reduction in absorption. This decreased absorption at an optical mode of the solar cell has been predicted theoretically\textsuperscript{30, 31} and observed experimentally\textsuperscript{23} in nanoscale thin-film solar cells that support propagating modes. Such decreases are not expected, however, when the design of the solar cell isolates the absorbing material from the plasmonic metal structures with a relatively thick (\~{}10 nm) dielectric layer\textsuperscript{32, 33}. Since the octahedral nanocrystal does not exhibit a resonance near 660 nm, the local disruption of the nanowire's modes arises from its geometric perturbation of the wire and is expected to occur for any other such perturbation, such as a dielectric particle or notch in the nanowire.

### 4.2.3 Scanning Photocurrent Mapping

Scanning photocurrent mapping (SPCM) experimentally confirms that changes in the device's photocurrent do arise from the position of the nanocrystal. Before the addition of the nanocrystal, the nanowire displays uniform photocurrent throughout its active area (Figure 2.1c). With the addition of the nanocrystal to the underside of the wire, the photocurrent map shows a localized increase in photocurrent at the position of the particle (Figure 4.6a) and a point of reduced reflection appears in the scanning optical image (Figure 4.6b). The small photocurrent enhancement at 442 nm is consistent with the FDTD-simulated increase in absorption for a nanowire of this size,

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure46.png}
\caption{Scanning photocurrent map (a) of the single-nanowire solar cell (320 nm diameter) shown in Figures 2.1a,b after the addition of a silver octahedron. Corresponding scanning optical image collected simultaneously showing the scattering at the position of the octahedron (b). Each scan is approximately 12.6 \textmu{}m by 6.3 \textmu{}m. The scans were taken with \lambda{}=442 nm, P\~{}7 W/cm\textsuperscript{2}. The enhancement in photocurrent is localized to the position of the silver octahedron and is consistent with the enhancement in absorption predicted by an FDTD simulation for a nanowire of this size (c). Top view SEM of the same device (d), and the inset is a side view SEM of the octahedron attached to the wire.}
\end{figure}
320 nm in diameter (Figure 4.6c). The top and side view SEM images show the octahedron on the underside of the wire (Figure 4.6d and inset). The octahedron is clearly the source of the change in photocurrent, in agreement with similar measurements performed on silicon nanowire photodetectors; however, this measurement cannot distinguish between local field enhancement and far-field scattering effects since collection of the photocurrent is not localized. While numerical simulations show that some of the enhancement arises from near-field effects (Figure 4.7), scanning photocurrent mapping suggests that some of the enhancement also arises from far-field scattering because nanocrystals situated on the non-active portion of the nanowire appear in the photocurrent maps (Figure 4.8).

Because all of the reported results arise from a single nanocrystal on the solar cell’s active region that measures about 6.6 µm in length, each additional isolated nanocrystal on the wire’s underside is expected to create a comparable change in the device’s photocurrent. If the nanocrystals were close enough to couple to each other, however, the surface plasmon resonances would change, and interactions between the wire and these new resonances would have to be considered. As demonstrated in the case of a single nanocrystal, new resonances at wavelengths far from the nanowire’s modes would enhance the photocurrent, but the case in which the resonances of the nanowire and plasmonic particles occur at the same wavelength requires further study. Additionally, since the wavelengths of the nanowire's resonances can be tuned by changing the wire's diameter and the nanocrystal's resonances are

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**Figure 4.7:** Numerical simulations of the magnitude of the electric field before (a-d) and after (e-h) the addition of the silver octahedron on the wire with a 288 nm diameter. The plots are cross-sections through the center of the nanocrystal, and the wavelengths correspond to the nanocrystal's quadrupolar (750 nm) and dipolar (981 nm) resonances. Both x-polarized and y-polarized excitations are shown. The particle clearly enhances the field within the wire in all cases except (f). In this case, the field enhancement occurs near the edge of the nanocrystal rather than at its center (plot not shown).
sensitive to the particle’s size and shape, much latitude exists for tailoring the interaction between the wire and nanocrystal to optimize enhancement of the photocurrent.

4.2.4 Summary and Conclusions

The wavelength-dependent effect of an octahedral silver nanocrystal on the absorption of a silicon nanowire solar cell has been quantified experimentally and interpreted using FDTD simulations. Increases in the nanowire’s absorption and photocurrent arise from the coupling of the nanocrystal’s dipolar and quadrupolar resonances to the wire. Decreases occur at wavelengths for which the particle perturbs the resonances of the nanowire itself; consequently, when seeking to enhance the performance of nanostructured solar cells using plasmonic nanocrystals, care must be taken to ensure that the enhancements in photocurrent outweigh the losses.

For isolated nanocrystals, simulations and scanning photocurrent mapping indicate that the observed increases in photocurrent do arise from the nanocrystal and result from both near-field interactions and far-field scattering. Clearly, when engineering light trapping using nanoscale absorbers and plasmonic nanostructures, understanding all the interactions between these structures is key to making efficient nanostructured solar cells.

Figure 4.8: SPCM of a single-nanowire solar cell (289 nm diameter) before (a) and after (b) the addition of silver octahedra. The larger increase in peak photocurrent (1.3 nA) occurs at the position of the silver octahedron on the active portion of the wire (large circle, top inset in (c)), while a smaller increase (0.8 nA) arises from the far-field scattering of the dimer of octahedra on the inactive portion of the wire (small circle, lower inset in (c)). Both scans show the same device and were taken using a laser with λ=650 nm, P~28 W/cm². Top view scanning electron microscopy (SEM) image of the same device (c), and insets are side view SEM images of the octahedra attached to the wire.
4.3 Silver Nanocubes and Single-Nanowire CdS/Cu$_{2-x}$S Solar Cells

After this initial exploration of the effect of a single octahedral nanocrystal on a silicon nanowire solar cell, the effect of smaller silver nanocubes was also studied. Since the enhancement of the octahedral nanocrystal appeared mostly in the red and near-infrared wavelengths, the smaller nanocrystals were expected to provide enhancements in the longer-wavelength visible region of the spectrum. Indium-doped CdS/Cu$_{2-x}$S solar cells were used as the platform for these studies with the intent to improve their photocurrent at these longer wavelengths. The devices were first coated by a 4-nm layer of alumina, using ALD at 50°C, and then the concentration of the nanocubes was controlled by their dilution in ethanol before they were drop cast onto the substrate. SPCM, wavelength-dependent photocurrent measurements, and numerical electromagnetic simulations were used to understand the interaction between the nanocubes and the sulfide nanowire solar cells.

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ii Dr. Joel Henzie synthesized the silver nanocubes.
Although both simulation and experiment demonstrated the expected increases in the longer-wavelength response of the devices, this additional photocurrent was counterbalanced by losses in the shorter-wavelength region (Figure 4.9). In the work on suspended silicon nanowires, the nanocrystals tended to adhere to the underside of the wires, reducing losses from direct absorption of the particles. Additionally, larger nanocrystals such as the octahedra exhibit a much greater scattering-to-absorption ratio than small nanocrystals such as the nanocubes.\(^{12}\) According to numerical simulations, for the CdS/Cu\(_{2}\)S solar cells lying on a planar substrate, a nanocube on top of the wire produces a direct shadowing effect that drastically reduces the photocurrent in the blue

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**Figure 4.10:** SPCM of 70-nm silver nanocubes on CdS/Cu\(_{2}\)S nanowire solar cells. Top view (a) and side view (b) SEM images of the silver nanocubes on the devices. Scale bars are 100 nm. (c) Scanning optical reflection image superimposed on the SEM image of the device whose photocurrent maps (λ=532 nm) with silver (d) and without silver (e) are shown below. Using the optical image, the maps have been vertically aligned to correspond to the SEM, allowing the photocurrent hotspots (white circles) or losses (yellow circle) generated by the silver nanocubes to be identified. (f)-(h) A similar measurement (λ=658 nm) for another device showing the isolated enhancement from selected silver nanocubes when they are scanned in red light. (g) and (h) were normalized to slightly different peak photocurrents because the laser intensity at the sample drifted during the hours that separated the measurements.
region. Such shadowing is much less for a nanocube sitting next to the wire, although a minor reduction does still appear. Because the wire’s diameter is smaller than the wavelength of the incident light, it can collect light from a larger spatial region than its geometrical volume. The placement of silver, which absorbs short wavelengths well, within this region of collection still has a slight shadowing effect, though it is much reduced from the case of direct shadowing. While the exact peaks in the simulated and experimental spectra vary, the general behavior of loses in the shorter wavelengths and increases in the red wavelengths is consistent. Because the actual devices were coated with many cubes of varying orientations to the wire as well as some aggregate cubes (Figures 4.9, 4.10a,b), exact agreement between experiment and simulation is not to be expected.

SPCM also provided a spatial map of the effect of the nanocubes on the solar cells. While the photocurrent of the nanowire before adding silver nanocrystals is uniform, addition of the particles creates variations in the collected photocurrent (Figure 4.10). For samples with only a few nanocubes, the increases in the photocurrent could often be matched with the positions of the nanocrystals as identified in SEM (Figures 4.10f-g). Not all relatively isolated nanocubes yielded an enhancement; however, since the enhancement is expected to be highly sensitive to the position of the nanocrystal relative to the wire and the illumination beam, it is possible that only certain geometries give rise to enhancements large enough to detect with SPCM. An extensive screening of isolated single nanocrystals studied by SPCM and then imaged in SEM from multiple angles to determine the 3D geometry would be necessary to confirm this hypothesis. Additionally, SPCM shows that aggregates of nanocrystals lead to reductions in photocurrent, likely because light scattered by the nanocrystals is absorbed in neighboring nanocrystals rather than in the wire.

4.4 Conclusions and Future Outlook

The work on both silicon and sulfide single-nanowire solar cells shows that the interactions between plasmonic nanocrystals and dielectric nanowires are highly wavelength-dependent and sensitive to the precise geometry of the structure: sizes determine the resonances of the individual nanostructures, while separation distances and orientations determine the extent of their optical coupling. Electromagnetic simulations can accurately predict such interactions as well as provide physical insight into the interactions that occur between the nanostructures. Because of this confirmed predictive ability and the challenges of controlling assembly of nanostructures on the single-nanometer level, future work on such complex structures should be confirmed using simulations before it is undertaken experimentally.

These results also suggest that the greatest enhancement in absorption in single-nanowire solar cells arises when the nanocrystals do not interfere with the wires’ natural optical modes and do not block light from coupling into them. Because of the extensive tunability of plasmonic resonances in metallic nanocrystals, it might be possible to design a structure specifically to avoid such reductions and therefore allow the enhancements to dominate. Additionally, further work is required to determine if hybrid modes between the nanowire and nanocrystals might be designed, for example...
by coupling a wire and nanocrystal that each exhibit individual modes at the same wavelength and would therefore be expected to interact strongly. Perhaps such modes might lead to greater enhancements in absorption within the wire or other interesting optical effects.

4.5 References

Chapter 5

All-Oxide, Single-Wire Solar Cells

Much of the content of this chapter has been written by the author (SFB) for the following future publication: Brittman, S.,* Yoo, Y.,* Dasgupta, N., and Yang, P. Synthesis of Cu$_2$O Nanowires and Single-Wire All-Oxide Solar Cells. In preparation.

5.1 The ZnO/Cu$_2$O Heterojunction

5.1.1 Cu$_2$O as a Solar Absorber

Efficient yet inexpensive and non-toxic solar cells are the ultimate goal of current photovoltaic research. While silicon remains the lead contender in this area, all-oxide solar cells are potentially attractive alternatives because their materials would be much cheaper to produce than high-quality silicon, and they are more chemically stable than the chalcogenides that currently dominate the thin-film PV industry. Cuprous oxide (Cu$_2$O) possesses a band gap suitable for conversion of solar energy, 2.1 eV, giving it a maximum theoretical efficiency of 20%.\(^1\)\(^2\)

Cu$_2$O is intrinsically \(p\)-type because of copper vacancies.\(^3\)\(^4\) Except for scattered, unreliable reports, doping it \(n\)-type has so far not been possible,\(^1\) precluding the formation of a homojunction solar cell.\(^4\)\(^6\) Because of Cu$_2$O’s extremely low carrier concentration,\(^2\)\(^4\) typically between \(10^{13}\) cm$^{-3}$ and \(10^{14}\) cm$^{-3}$,\(^2\)\(^4\)\(^7\) the idea of forming a built-in electric field by inversion is promising, but initial attempts have yet to produce a reasonable device.\(^8\) Instead, Cu$_2$O is paired with other \(n\)-type oxides to form a heterojunction for separation and collection of photogenerated charges (Figure 5.1\(^iii\)). As heterojunction theory indicates that the efficiency of such solar cells is highly sensitive to the materials’ interface, this design is complicated by two significant challenges: no simple \(n\)-type oxide exhibits a sufficiently good lattice match with Cu$_2$O to produce a

\[\text{---}\]

\(^i\) Reports of \(n\)-type Cu$_2$O typically determine the carrier type using electrochemical measurements. It is well established that an inversion layer from surface states can cause a \(p\)-type material to appear \(n\)-type in such measurements.

\(^\text{ii}\) Cu$_2$O films deposited by sputtering instead of high-temperature processes exhibit higher conductivities and have been doped to relatively high levels;\(^14\) however, the solar cells produced from such films have not yet yielded competitive efficiencies.

\(^\text{iii}\) The author thanks former SHARP mentee Kevin Chen for writing the Matlab program plotjunctions, which was used to draw the band diagram.
high-quality interface with low recombination, and \( \text{Cu}_2\text{O} \) can be both oxidized to \( \text{CuO} \) and reduced to \( \text{Cu} \) metal at the interface. It is widely reported that only metals more noble that copper, such as Pt and Au, form ohmic contacts to \( \text{Cu}_2\text{O} \) because other metals become oxidized at the interface while reducing the \( \text{Cu}_2\text{O} \) surface to \( \text{Cu} \), which results in a \( \text{Cu}-\text{Cu}_2\text{O} \) Schottky contact.\(^9,10\)

### 5.1.2 ZnO/\( \text{Cu}_2\text{O} \) Solar Cells

Because of its high conductivity, transparency to visible light, and range of deposition methods, ZnO is the most popular \( n \)-type collector paired with \( \text{Cu}_2\text{O} \) in solar cells. Minami and co-workers at the Kanazawa Institute of Technology in Japan hold the record 4.12%-efficient planar solar cell.\(^2\) In their device, \( \text{Cu}_2\text{O} \) is grown at high temperature by thermally oxidizing \( \text{Cu} \) metal, which yields a polycrystalline film with low carrier concentration, \( \sim 10^{13} \text{ cm}^{-3} \), and relatively high mobility of \( \sim 100 \text{ cm}^2/\text{Vs} \). ZnO is deposited using pulsed laser deposition (PLD) rather than a more damaging technique such as sputtering. Their detailed studies have concluded that the efficiency of the solar cell is highly sensitive to the conditions used to prepare the heterojunction, in particular the partial pressure of \( \text{O}_2 \) used when depositing the ZnO, the temperature of the substrate during deposition, and any interfacial species actively introduced. Such behavior is typical of heterojunction solar cells because the barrier height at the interface, and therefore the recombination rate and built-in potential of the junction, is determined by the exact surface interaction between the two materials. Because of its potential to be either oxidized to \( \text{CuO} \) or reduced to \( \text{Cu} \) metal, the \( \text{Cu}_2\text{O}/\text{ZnO} \) interface can be altered by the state of oxidation or reduction of the \( \text{Cu}_2\text{O} \) surface. Based on their results that a specific \( \text{O}_2 \) pressure and low PLD deposition temperatures are required for the highest efficiency solar cells, Minami and co-workers hypothesize that deposition conditions that preserve the \( \text{Cu}_2\text{O} \) surface are advantageous. They further find that if they insulate the \( \text{Cu}_2\text{O} \) surface with a layer of nearly intrinsic ZnO deposited at low temperature, then the performance of solar cells with subsequent aluminum-doped ZnO films deposited at higher temperatures is less sensitive to the increasing deposition temperature. The fact that it does remain sensitive to the subsequent deposition temperatures, however, suggests that diffusion or oxidation-reduction reactions at the \( \text{Cu}_2\text{O}/\text{ZnO} \) interface can still occur even after its initial creation. This sensitivity to heating will play a role in later discussions of the performance of the single-wire solar cells.

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Figure 5.1: Band diagram of the ZnO/\( \text{Cu}_2\text{O} \) junction. It is assumed that the band offset is determined by electron affinities, and carrier concentrations are \( 5 \times 10^{13} \text{ cm}^{-3} \) for \( \text{Cu}_2\text{O} \) and \( 2 \times 10^{18} \text{ cm}^{-3} \) for ZnO. The depletion region falls entirely within the \( \text{Cu}_2\text{O} \).
5.2 Motivation for Single-Wire Solar Cells

With a record 4.15% efficiency when the Shockley-Queisser limit for Cu$_2$O is 20%, it is clear that further improvement of the heterojunction solar cell is necessary. Much of the loss arises from the conduction band offset between Cu$_2$O and ZnO, which is estimated to be approximately 1 eV, and therefore reduces the theoretical maximum efficiency to about 10%, considering the loss in open-circuit voltage (Figure 5.1). Remedying this situation will require extensive materials development such as alloying ZnO to raise its conduction band or replacing ZnO altogether. Working within the Cu$_2$O/ZnO system, however, additional loss arises from the quality of the interface between the two oxides, which results in a less-than-ideal $V_{oc}$ of 0.72 V and a particularly low FF of $\sim$0.59. Series resistance through the thick Cu$_2$O layer likely contributes to the low FF, and perhaps reduced shunt resistance as well. The obtained short-circuit current density of $\sim$10 mA/cm$^2$ is 79% of the 12.7 mA/cm$^2$ maximum for Cu$_2$O, leaving some room for improvement; consequently, interfacial engineering requires attention as well as methods for increasing light absorption within a thinner Cu$_2$O layer in order to reduce its series resistance or doping of the Cu$_2$O layer. For this latter reason, Cu$_2$O is an attractive candidate for nanostructured solar cells if the required junction quality for efficient charge collection can be obtained first.

Solar cells fabricated from single-crystalline Cu$_2$O nano- or microwires can offer some insight into the contributions from interface quality, series resistance, and shunt resistance. Because of their flat rather than layered design, the performance of single-wire solar cells suffers no degradation from reduced shunt resistance related to the deposition of the metal contacts. All shunting arises from the junction itself. Additionally, series resistance impacts the photocurrent and FF of a solar cell only when it becomes near the same order of magnitude as the characteristic resistance of the solar cell’s junction. Because of the extremely small junction area of a single-wire solar cell, the junction resistance can reach mega- or even giga-ohms, meaning that series resistances in the kilo-ohm range can be easily tolerated without adverse effects on the device performance; consequently, single-wire solar cells offer an opportunity to isolate the effect of the junction quality on the performance of the solar cell. Finally, as Cu$_2$O does exhibit a mismatch between the several micrometers required for its full absorption of light and its minority carrier diffusion length that is estimated to be several hundred nanometers, it is an attractive candidate for nanowire array solar cells. The first step

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vi It should be noted, however, that a better design for a nanowire array solar cell is using a ZnO nanowire array coated with a relatively thin film (in the hundreds of nanometers) of appropriately p-type doped Cu$_2$O. ZnO nanowires would provide a conductive scaffold for the collection of carriers, while Cu$_2$O would provide light absorption increased by light trapping within the nanowire array. While such a design has been realized using electrochemical deposition of Cu$_2$O onto ZnO nanowire arrays, the film thickness is not optimized and more significantly, the carrier concentration of the Cu$_2$O is too low to realize the full built-in potential of the junction, leading to low $V_{oc}$. Also, surface treatments to optimize the interfacial quality of the heterojunction were not applied or investigated. Another potential architecture not yet investigated is a highly conductive p-type Cu$_{2}$S nanowire array thermally oxidized at the surface to produce Cu$_2$O to function as the absorber and coated with ALD ZnO as a transparent conductive top contact. Thermally oxidizing Cu$_2$S directly to Cu$_2$O without other products such as CuO or CuSO$_4$, however, is difficult, although some progress toward this goal has been reported in the literature.
toward such a goal, however, is a better understanding of the heterojunction interface.

5.3 Synthesis of the Wires and Fabrication of the Devices

5.3.1 Vapor-Phase Synthesis

To realize the Cu$_2$O/ZnO single-wire solar cells, first single-crystalline Cu$_2$O wires were grown using chemical vapor deposition. A copper slug in an alumina boat was placed in the center of a quartz tube heated in a tube furnace to 1140°C. A lattice-matched MgO <110> substrate was placed downstream of the copper slug at a temperature of approximately 860°C. The source and substrate were sealed within the tube, evacuated to rough vacuum of several hundred milliTorr, and brought to a pressure of ~15 Torr by flowing a mixture of Ar and trace O$_2$ gases. After a reaction time of one hour, the substrates were removed and found to be covered with wires with triangular cross-sections that grow along the <110> surface of the MgO substrate (Figure 5.2). XRD confirmed their composition as Cu$_2$O, and based on the geometry of the Cu$_2$O lattice, it is concluded that the basal plane is <110>, while the side facets are the more stable <111> planes (Figure 5.2c). Dimensions of the wires' bases ranged from a few hundred nanometers to two or three micrometers, while heights were typically under one micrometer. The wires ranged in length from a few micrometers up to ten micrometers.

![Figure 5.2: SEM images of the Cu$_2$O wires. Broad view (a), single wire (b) and cross-sectional images.](image)

5.3.2 Electrical Properties of the Cu$_2$O Wires

The electrical conductivity of the nanowires was measured using a four-point contacting geometry to remove the effects of series resistance at the contacts. Photolithography and sputtering of ~60 nm of Pt metal was used to fabricate the devices directly on the insulating MgO substrate (Figure 5.3a). No surface pre-treatment or post-annealing was necessary to achieve ohmic contact to the Cu$_2$O. Conductivities ranged from 0.19 to 0.57 mS (Table 5.1). Assuming a hole mobility of 100 cm$^2$/Vs, based on the literature value of high-quality bulk Cu$_2$O films,$^4,7$ the carrier concentration was

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$^v$ The synthesis of the Cu$_2$O nano- and microwires was developed and executed by Dr. Youngdong Yoo.
estimated to be $\sim 2 \times 10^{-13}$ cm$^{-3}$.\textsuperscript{vi} As these wires are quite large, it is not expected that their surface would significantly reduce their carrier mobility. The conductivity and estimated carrier concentration are consistent with those found in high-quality Cu$_2$O thin films used in the record planar solar cells.\textsuperscript{2, 7} The wires also exhibited photoconductivity under simulated solar illumination (Figure 5.3b).

\textsuperscript{vi} Preliminary efforts to fabricate field-effect transistors (FETs) to measure the wires’ mobility and carrier concentration directly were complicated by the epitaxial adhesion of the wires to the MgO substrate. The wires could not be removed from the insulating substrate, precluding the fabrication of back-gate FETs. The possibility of top-gate FETs was investigated, but depositing suitable gate dielectrics such as aluminum oxide by ALD and e-beam evaporation or SiO$_2$ by PECVD damaged the Cu$_2$O wires, as determined by changes in their morphology or conductivity after the thin-film depositions.
5.3.3 Fabrication of the Devices

Fabrication of the heterojunction solar cells was a multistep process applied to the MgO substrate. After growth of the wires, one end was contacted with Pt to collect from the Cu$_2$O. Next, the substrate was spin-coated with a bilayer of poly(methyl methacrylate) (PMMA) and photoresist. Photolithography was used to pattern the regions that would become the heterojunction, and O$_2$ plasma etching removed the PMMA using the patterned photoresist as a mask. After selectively removing the photoresist in isopropanol and baking the PMMA in vacuum to remove any residual solvent, the substrates underwent pseudo-atomic layer deposition of either ZnO (~30 nm) or ~10-20 nm of amorphous TiO$_2$ and then ZnO. Such depositions had to be performed well below the glass temperature of PMMA (~120°C) to avoid damaging the lithographic patterning or excessively annealing the oxide interface. ZnO deposition was performed using diethylzinc and water as precursors at 85°C. For some devices, a spacer layer of TiO$_2$ was deposited at 100°C using tetrakis(dimethlyamido)titanium(IV) and water. It was found that depositing TiO$_2$ using a TiCl$_4$ precursor severely damaged the wires (Figure 5.4), likely because of etching from the HCl produced in the reaction. After deposition of the films, the PMMA was lifted off, yielding the patterned device. Ti/Au contacts to the ZnO film were patterned lithographically and deposited using e-beam evaporation after a brief O$_2$ plasma etch to clean the ZnO’s surface. No post-annealing treatments were required to achieve ohmic contact to the ZnO film.

For true monolayer-by-monolayer ALD processing, ZnO is typically deposited above 100°C. Depositing at lower temperatures, however, allowed tuning of the film’s conductivity, carrier concentration, and to some extent mobility as determined by Hall-effect measurements (Table 5.2). Films deposited at higher temperatures are also of higher crystalline quality, as determined by XRD. Deposition at 85°C was selected as a compromise between sufficient electrical

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Thickness (nm)</th>
<th>Growth Rate (A/cycle)</th>
<th>Carrier Concentration (cm$^3$)</th>
<th>Mobility (cm$^2$/Vs)</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>32.3</td>
<td>1.30</td>
<td>1.0E+15</td>
<td>0.1</td>
<td>1.78</td>
</tr>
<tr>
<td>65</td>
<td>39.4</td>
<td>1.58</td>
<td>1.0E+17</td>
<td>2.7</td>
<td>1.85</td>
</tr>
<tr>
<td>85</td>
<td>45.1</td>
<td>1.80</td>
<td>2.0E+18</td>
<td>3.3</td>
<td>1.89</td>
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<td>150</td>
<td>41.5</td>
<td>1.66</td>
<td>1.0E+20</td>
<td>8.1</td>
<td>1.89</td>
</tr>
</tbody>
</table>

*Table 5.2: Temperature-dependent electrical properties and index of refraction (n) of ZnO deposited by pseudo-ALD. 150°C is a typical temperature used to achieve true surface-limited ALD.

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vi Additional details of the process can be found in Appendix E.
conductivity and crystallinity and the low-temperature processing that has been found to be beneficial in planar Cu$_2$O/ZnO solar cells.

5.4 Performance of the Devices

The heterojunction devices typically functioned as diodes, especially when the TiO$_2$ interlayer was included to protect the surface of the Cu$_2$O during deposition of the ZnO. Most devices did not exhibit photocurrent or photovoltage under 1-sun illumination, and their $I$-$V$ scans show significant hysteresis, which might have arisen from the charging and discharging of trap states at the interface (Figure 5.5). Under more intense illumination, provided by a HeCd laser at $\lambda=442$ nm, the devices did produce photocurrent and a photovoltage as expected; however, the current increased only 3-5 times with each order of magnitude of light intensity rather than exhibiting the typical linear relationship (Figure 5.6a).

The predicted electrostatics of the junction and scanning photocurrent mapping (SPCM) suggest a possible explanation for these observations. The doping of the heterojunction is highly asymmetric, with ZnO exhibiting a carrier concentration of

![Figure 5.5: All-oxide single-wire devices. (a) SEM image showing the ZnO/TiO$_2$/Cu$_2$O device's structure, whose cross-section is diagrammed in the inset to (c). (b) Detailed SEM image of the Cu$_2$O wire and the thin-film blanket that forms its shell. (c) A typical $I$-$V$ curve of a device in the dark and under solar illumination. While the devices did show evidence of photoconductivity, they did not exhibit a photovoltage or photocurrent without more intense illumination. Devices also showed hysteresis, with more current produced during the backward scan (down from higher to low voltage) than during the forward scan.](image-url)
2 × 10^{18} \text{ cm}^{-3}, \text{ while } \text{Cu}_2\text{O} \text{ is } \sim 10^{13} \text{ cm}^{-3}. \text{ This asymmetry produces a large depletion width within the Cu}_2\text{O wire that leads to full depletion of the wire in contact with the ZnO shell. The core of depleted Cu}_2\text{O would therefore contribute a high series resistance that increases with the distance holes must travel to reach the undepleted Cu}_2\text{O near the Pt contact, preventing most of the core-shell region of the wire from contributing to the photocurrent of the device; consequently, only a small region of the Cu}_2\text{O near the edge of the ZnO shell could contribute to the photocurrent. SPCM supports this conclusion, showing that the photocurrent is localized to the edge of the ZnO shell and decays rapidly from this interface moving into the core-shell region (Figure 5.6b). The decay length into the pristine Cu}_2\text{O is limited by the minority carrier diffusion length within the wire. For bulk samples, this length is estimated to be a few hundred nanometers,}^{12} \text{ which is on the order of the resolution of SPCM and therefore not able to be quantified by this technique.}

The simplest remedy for this full depletion of the wire is to increase the carrier concentration of the Cu}_2\text{O core.}^{viii} \text{ Extrinsic dopants such as silicon and chlorine were introduced into reactions via the co-evaporation of silicon powder or in-situ decomposition of MgCl}_2. \text{ In all samples, XRD measurements confirmed that the wires were Cu}_2\text{O, and four-point resistivity measurements were conducted to determine if the}

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\[ ^{viii} \text{ Increasing the size of the wire would also be an option except that the junction’s doping is so asymmetric that the wire would need to become several microns larger in order to support the full depletion region; however, it is possible that some combination of the two approaches might help.} \]
wires displayed increased conductivity (Table 5.3). While marginal increases were measured, avoiding full depletion within the core Cu$_2$O wire would require carrier concentrations in the $10^{15}$-$10^{16}$ cm$^{-3}$ range, according to a one-dimensional model of the junction, which could not be achieved with these doping methods. It is possible that the dopants increased the carrier concentration but correspondingly also reduced the mobility of the carriers, yielding similar conductivity; however, it is unlikely that the mobility was reduced by the several orders of magnitude that would be necessary to offset the desired increase in carrier concentration.

In spite of the disappointing conductivity of the doped wires, large (bases > 1.3 µm) Cu$_2$O wires grown with chlorine were coated with TiO$_2$ and ZnO to make devices in an attempt to screen the ZnO’s high charge density from the Cu$_2$O core. This approach is similar to the incorporation of an intrinsic ZnO layer between Cu$_2$O and aluminum-doped ZnO taken in the design of planar solar cells.$^2, 7$ Surprisingly, several devices fabricated on two separate MgO substrates exhibited photocurrent and photovoltage under simulated, 1-sun illumination (Figures 5.7a,b). SPCM of these devices also displayed a larger active area, suggesting that the Cu$_2$O core was not fully depleted (Figure 5.7c). Subsequent experiments have focused on reproducing these devices as well as determining which of the components are critical for such 1-sun operation: the size of the wire, the level of chlorine incorporation, the TiO$_2$ interlayer, or some combination of these variables. Small wires that were not exposed to chlorine during growth but were coated with TiO$_2$ displayed rectifying behavior but did not exhibit a photoresponse, nor did all chlorine-grown wires coated with TiO$_2$. These results suggest

<table>
<thead>
<tr>
<th>Dopant and Device</th>
<th>4-pt Resistance (MΩ)</th>
<th>Base’s Width (nm)</th>
<th>Length (µm)</th>
<th>Conductivity (mS)</th>
<th>Est. Carrier Conc. (cm$^{-3}$) (μ=100 cm$^2$/Vs)</th>
</tr>
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<tbody>
<tr>
<td>Si A</td>
<td>46.0</td>
<td>1120</td>
<td>0.75</td>
<td>0.74</td>
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<td>Si C</td>
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<td>Cl A812</td>
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<td>Cl A821</td>
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<td>889</td>
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<td>0.85</td>
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<td>Cl B821</td>
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<td>Cl C821</td>
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<td>1282</td>
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<td>Cl 808A12</td>
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<td>959</td>
<td>0.70</td>
<td>0.71</td>
<td>4.4E+13</td>
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<td>Cl 806A12</td>
<td>11.4*</td>
<td>702</td>
<td>0.74</td>
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<td>4.7E+14</td>
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<tr>
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<td>86.8*</td>
<td>735</td>
<td>0.73</td>
<td>0.89</td>
<td>5.5E+13</td>
</tr>
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</table>

Table 5.3: Conductivities and estimated carrier concentrations of the Cu$_2$O wires grown in the presence of silicon or chlorine, assuming a hole mobility of 100 cm$^2$/Vs based on the literature value for undoped Cu$_2$O thin films. Length refers to the distance between the Pt electrodes. Because of the triangular shape of the wires, their height is about 35% of the width of their base. The asterisk (*) indicates a two-point instead of four-point conductivity measurement, indicating that the conductivity and carrier concentration could actually be higher than the measured value because contact resistance has not been subtracted.
that the screening of charge by the TiO$_2$ is not enough to prevent full depletion of the wires. The fact that some large wires grown with chlorine did not exhibit photocurrent under 1-sun conditions suggests that varying levels of chlorine incorporation are responsible for the 1-sun performance. This hypothesis could be confirmed by measuring the conductivity of the individual wires used to make solar cells and correlating these values to their photovoltaic performance on the single-wire level.

For the devices that exhibited a clear photoresponse under 1-sun conditions, their performance was evaluated quantitatively. Efficiencies were calculated based on the cross-sectional area of the devices as measured by SEM (Table 5.4). SPCM showed, however, that not all of the core-shell region was necessarily active, which accounts in part for the low efficiency. FF’s below the theoretical limit of 0.25 arose from the inverse curvature of some of the $I$-$V$ curves in the fourth quadrant, suggesting a voltage-dependent series resistance or recombination mechanism. Wavelength-dependent photocurrent measurements showed absorption within the devices out to approximately 600 nm, which corresponds to the band gap absorption of Cu$_2$O (589

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**Figure 5.7:** (a, b) Two examples of the ZnO/TiO$_2$/Cl-Cu$_2$O solar cells under 1-sun illumination. Hysteresis has been removed for clarity. (c) SPCM ($\lambda=532$ nm) of a similar device displaying a much larger active area than seen for devices made from undoped wires. The far end of the core-shell region is the most active portion, which is likely an optical artifact of particularly good coupling of the laser into the device at the end facet. The line of blue noise on the right side of the image is an artifact of the measurement geometry. (d) The optical reflection image obtained simultaneously with the above SPCM. Maps are approximately 16x8 $\mu$m but were not calibrated with SEM. (e) Wavelength-dependent photocurrent of the solar cells, which is consistent with the absorption of Cu$_2$O.
nm) given that the full-width, half-maximum of the monochromatic excitation was approximately 15 nm (Figure 5.7e). The low $V_{oc}$’s and FF’s are reminiscent of Cu/Cu$_2$O Schottky junctions, perhaps produced by the occurrence of oxidation-reduction chemistry at the wire’s surface. Alternatively, since a reduced shunt resistance from the metal contacts is unlikely based on the geometry of the device, either there is a light-activated shunt resistance across the interface itself, or the photocurrent collection within the Cu$_2$O is assisted by the electric field rather than mediated by diffusion to the junction. This second explanation is consistent with the expectation that the Cu$_2$O core of the wires is nearly fully depleted, so assuming the carriers have a relatively low drift mobility-lifetime product ($\mu\tau$), the efficiency of charge collection could depend upon the strength of electric field within the Cu$_2$O, which is reduced as forward bias is applied.

### 5.5 Summary and Conclusions

Starting with Cu$_2$O wires that were synthesized using a high-temperature, vapor-phase reaction, single-wire ZnO/Cu$_2$O and ZnO/TiO$_2$/Cu$_2$O heterostructure diodes were fabricated with high reproducibility and stability. Most devices showed photocurrent and photovoltage under laser illumination, and some exhibited photovoltaic performance under 1-sun illumination conditions, yielding efficiencies up to 0.39%. Initial investigations suggest that the general lack of photoresponse under 1-sun conditions arises from the full depletion of the Cu$_2$O wire’s core, greatly reducing its conductivity. For the devices that did function as solar cells under 1-sun conditions, a combination of the large size of the Cu$_2$O wires, the charge-screening ability of the TiO$_2$ spacer layer, and chlorine incorporation into the wires is responsible for their performance. Additionally, I-V curves suggest that the depletion in the core yields field-dependent charge collection within the devices, which reduces their $V_{oc}$ and FF.

<table>
<thead>
<tr>
<th></th>
<th>$V_{oc}$ (V)</th>
<th>$I_{sc}$ (pA)</th>
<th>FF</th>
<th>$P_{max}$ (pW)</th>
<th>Area (cm$^2$)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.24</td>
<td>197.7</td>
<td>0.37</td>
<td>18</td>
<td>4.6E-08</td>
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</tr>
<tr>
<td>B</td>
<td>0.33</td>
<td>61.6</td>
<td>0.42</td>
<td>8.5</td>
<td>8.2E-08</td>
<td>0.10</td>
</tr>
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<td>25.6</td>
<td>0.26</td>
<td>0.2</td>
<td>2.2E-07</td>
<td>0.0009</td>
</tr>
<tr>
<td>E</td>
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<td>25.0</td>
<td>0.27</td>
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<td>4.4E-08</td>
<td>0.055</td>
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<td>0.22</td>
<td>12.5</td>
<td>5.8E-08</td>
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</tr>
<tr>
<td>H</td>
<td>0.30</td>
<td>20.8</td>
<td>0.27</td>
<td>1.7</td>
<td>6.0E-08</td>
<td>0.028</td>
</tr>
<tr>
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<td>214.9</td>
<td>0.22</td>
<td>16.4</td>
<td>7.9E-08</td>
<td>0.21</td>
</tr>
</tbody>
</table>

*Table 5.4: Photovoltaic metrics of seven ZnO/TiO$_2$/Cl-Cu$_2$O solar cells under 1-sun illumination. Areas were measured from SEM images, based on the entire core-shell region of the wire.*
5.6 References

Chapter 6

Future Directions in Nanowire Photovoltaics

6.1 Non-Traditional Solar Materials

To uncover fundamental physical principles of light trapping and charge separation, the field of nanowire photovoltaics rightly has focused on well-characterized materials such as silicon, germanium, and GaAs. Now that many of the guiding physical principles have been elucidated, however, it is time to use this knowledge to take advantage of the unique properties of new materials. For widespread application, these materials will need to be made from relatively abundant elements and processed inexpensively at large scale. Solution-processed nanowires offer a solution, but currently many of the best-performing solar devices rely on high-temperature vapor-phase techniques. Little work has been done to compare the electrical and optical properties of solution-grown nanostructures with their vapor-phase counterparts. Additionally, the surface treatment of solution-synthesized nanostructures often plays a significant role in their optical and electronic properties; understanding and controlling such interactions will be crucial if these materials are to be integrated to create efficient solar cells.

Synthetic techniques have been discovered to produce semiconductor nanowires from materials throughout the periodic table, from elemental semiconductors to transition-metal and main-group nitrides, oxides, and sulfides and even to alloys of such materials. The readiness with which these single-crystals can be produced, coupled with the relaxed constraints on material quality offered by the core-shell geometry of a nanowire solar cell, opens a world of new materials whose potential for solar energy conversion has yet to be investigated. After demonstration of a reproducible synthesis, the next step in screening such materials must be detailed electrical and optical characterization coupled with development of the chemistry for doping, surface passivation, and production of high-quality interfaces.

6.2 High-Quality Interfaces

Creating, understanding, and stabilizing high-quality interfaces at the nanoscale are also crucial tasks for improving PV cells. Much experimental and theoretical work has centered on growing abrupt interfaces via vapor-phase techniques such as chemical vapor deposition or molecular beam epitaxy, but solution-synthesized
nanostructures are more often processed similar to organic bulk heterojunction solar cells. As demonstrated in the CdS/Cu$_{2}$S system, cation-exchange chemistry offers the ability to create high-quality heterojunctions templated by the anion sublattice. Using this chemistry in CdS/Cu$_{2}$S solar cells or extending it to other more suitable material systems could be the much-needed breakthrough to efficient nanowire array solar cells.

6.3 Advanced Characterization

Truly understanding nanowire solar cells or any other opto-electronic device requires that dynamic processes such as generation, separation, recombination, and transport of charges be understood with nanoscale spatial resolution. Experimental techniques that probe these processes such as photoluminescence, radiative lifetime measurements, photocurrent mapping, transient absorption or transmission spectroscopy, scanning Kelvin probe force microscopy, and near-field scanning optical microscopy have lately been adapted to ensemble and single-nanostructure samples to begin to understand the dynamics of charges in nanostructures. Correlation between these processes and structural or geometric characteristics is also paramount to unravel the structure-function relationships that will help optimize nanowire devices.

6.4 Numerical Simulations and Modeling

As demonstrated by the extensive insight that electromagnetic simulations have provided into the study of plasmonics and nanowire resonators, numerical simulations and modeling must continue to play a large role in the investigation of nanowire solar cells. Key processes such as photogeneration and transport of charges, as well as the kinetics and thermodynamics of the nucleation and growth of nanowires, can be modeled and simulated to provide insight into which variables define the process. Additionally, this synthetic control must be combined with integrated device physics and optical simulations to optimize performance.

6.5 Nanowire Photovoltaics Beyond the Laboratory

Further into the future, commercial considerations such as device stability and lifetimes, availability of materials, and production costs will need to be evaluated for particularly promising nanowire systems. It will take the combined, collaborative efforts of chemists, physicists, and engineers, both experimentalists and theorists, to achieve the next level of understanding in these systems and to realize the full potential of nanowires for solar energy conversion.
Appendix A:

Fabrication and Measurement of the Suspended, Single-Nanowire Silicon Solar Cells

A.1 Fabrication

Trench substrates were fabricated from heavily doped ($\rho < 0.01 \ \Omega \text{cm}$), $p$-type (boron) silicon-on-insulator with a 5 $\mu$m device layer oriented $<110>$ and 500-nm buried oxide layer (Ultrasil Corp.). The device layer was etched to $\sim 2.2 \ \mu$m using anisotropic plasma etching with SF6 (Surface Technology Systems). Then 8-$\mu$m-wide trenches were patterned with photolithography and anisotropically etched into the device layer to the buried oxide. Photoresist was removed in PRS-3000 heated to 85°C and piranha solution heated to 120°C.

Silicon nanowires were grown bridging the trenches via the vapor-liquid-solid (VLS) mechanism using 250-nm gold catalyst particles. Prior to growth, the trench substrates were etched in 10:1 buffered hydrofluoric acid (BHF) for 10 seconds. 10% aminopropyl-trimethoxysilane or 10% aminopropyl-triethoxysilane in ethanol was used as a linking molecule for the 250-nm gold colloids (Ted Pella, Inc.) drop cast onto the substrates. Silicon nanowires were grown at 850°C using SiCl$_4$ as a precursor and 10% hydrogen in argon in a home-built, chemical vapor deposition (CVD) system consisting of a quartz tube in a tube furnace. Reactions to grow wires bridging the trenches lasted from 15 to 45 mins.

After growth the nanowires were $p$-doped with boron. Prior to doping, the nanowires were etched for $\sim$30 seconds in 10:1 BHF and soaked in I$_3$/KI gold etchant (Transene) for at least 20 minutes. The nanowires were then $p$-doped in a tube furnace using 1% BCl$_3$ in argon and 10% hydrogen in argon at 800°C. For the first hour, 1 sccm of dilute BCl$_3$ with 100 sccm of hydrogen/argon was used, followed by a two-hour anneal in 50 sccm of hydrogen/argon and no BCl$_3$. Assuming uniform radial doping, the doping concentration was estimated to be $\sim 10^{17} \ \text{cm}^{-3}$ based on the resistivity approximated from two-point electrical measurements and geometric estimates from the scanning electron microscopy (SEM) images.

After $p$-doping, the nanowires underwent an additional gold etch and were then coated in $\sim$400 nm of silicon dioxide deposited using plasma enhanced chemical vapor deposition (PECVD) using silane and nitrous oxide precursors at 350°C (Oxford Corp.). Oxide-coated trench substrates were then exposed to hexamethyldisilazane (HMDS) vapor before coating in photoresist and lithographically exposing the bridging nanowire’s left contact and a portion of the nanowire. The exposed oxide was etched in
5:1 BHF for 2 to 2.5 minutes, and the photoresist was removed by soaking for over an hour in PRS-3000 (Baker) heated to 85°C.

The nanowires were then annealed at 800°C under rough vacuum for 1.5 hours about 1 mm beneath a silicon substrate coated with P509 phosphorus spin-on dopant (Filmtronics Corp.). After annealing, the oxide mask was removed with 5:1 BHF. The nanowire substrate was then coated with 4 nm aluminum oxide in a home-built atomic layer deposition system using water and trimethylaluminum as precursors at 200°C. Electrical contact was made to the single-nanowire devices by wirebonding aluminum wires from the sides of the trenches to the bonding pads of a dual-inline-pin package.

A.2 Optical and Electrical Measurements

A 150 W xenon arc lamp (Newport Corp.) with an AM 1.5G filter was used to measure the nanowire’s photovoltaic response. The light intensity was calibrated using a 1.1 mm x 1.1 mm silicon photodiode referenced to a calibrated silicon photodiode (Newport Corp.). I-V characterization was performed with a Keithley 236 source-measure unit (SMU).

A home-built confocal microscope with piezoelectric scanning stage was used for simultaneous reflection imaging and scanning photocurrent mapping (SPCM). A helium-cadmium laser ($\lambda=442$ nm) was focused to a diffraction-limited spot through the microscope's objective lens (NA = 0.95), with power density ~7 W/cm$^2$. At each point in the reflection image, the photocurrent was recorded by a Keithley 236 SMU. Photocurrent maps were plotted using MATLAB®, and the reflection images were processed using Image SXM. The spatial resolution of SPCM is largely determined by the size of the laser’s spot and its interaction with the sample. Since the nanowire sample is three-dimensional and photogenerated carriers can diffuse away from their point of origin, the minimum distance that can be resolved in the photocurrent map is typically larger than the laser’s diffraction-limited spot.

The dependence of the photocurrent on wavelength (photocurrent spectrum) was obtained by measuring the current generated in the device at 10-nm increments, normalized by the photon flux of the source. A 300 W xenon arc lamp (Newport Corp.) was coupled to a monochromator (Newport Corp.) to obtain monochromatic illumination. The output of the source was measured using a 1.1 x 1.1 mm silicon photodiode (Hamamatsu Corp.) referenced to a calibrated silicon photodiode (Newport Corp.). For wavelengths below 650 nm, a diffuser made of ground quartz was positioned between the source and device to make the spot more spatially uniform. This provided greater positioning tolerance. The diffuser was removed for wavelengths longer than 650 nm to obtain more light since silicon absorbs poorly at longer wavelengths. To achieve the greatest precision between measurements, devices were positioned using a micrometer driven translation stage (Thorlabs).

References

Appendix B:

Fabrication of the CdS/Cu$_2$S Single-Nanowire Solar Cells

After growth, the nanowires were dry transferred to piranha-cleaned SiO$_2$/Si substrates, rinsed in water, and dried with pressurized N$_2$. KI/I$_3^-$ solution was applied for 30 s to remove the Au catalyst particles, followed by a rinse in DI water and drying again with pressurized N$_2$.

The wires were then coated approximately 10 nm of alumina by ALD, deposited at 50°C to serve as a mask for the later cation-exchange reaction. The growth rate was faster at this low temperature, so usually 50 cycles were applied.

Photolithography using i-line photoresist defined the contacts. Before metallization, an O$_2$ plasma descum for 30 s at 50W (180 mTorr O$_2$) was performed, followed by 30 s etching in 10:1 BHF to remove the alumina immediately before loading the sample into the e-beam evaporator. In/Au (3 nm/110 nm) contacts to the CdS nanowire were evaporated, and liftoff was performed in warm acetone.

A second step of photolithography using i-line resist defined the window for the core-shell region. After a 30-s descum (conditions same as above), the alumina was etched for 30 s in 10:1 BHF before dipping the sample into the cation-exchange solution.

The cation-exchange reaction was performed in aqueous CuCl solution. First, 75 mL of water was mixed with 12 mL of concentrated HCl. 0.5 g CuCl was dissolved in the solution while stirring. 7 mL of hydrazine monohydrate was added dropwise, making sure to dissolve any precipitates. The final pH of the solution was adjusted to 3 with drops of 1 M HCl, at which point the solution was transparent. Then 20 mL of this solution was heated to 80°C and then cooled to 50°C, at which temperature the cation-exchange reaction was performed. The remainder of the solution was stored in an air-tight container for future use. Since the fabrication of these devices, later work has suggested that the phase of the Cu$_2$S produced is highly sensitive to these reaction conditions; consequently, the phase of Cu$_{2-x}$S in the later single-nanowire devices and In-doped devices is uncertain.

After cation exchange, the devices were immediately coated with i-line photoresist and contacts to the Cu$_2$S shell were defined lithographically. After a 30-s etch in 10:1 BHF, the devices were loaded into the sputterer, pumped down for 3 hours to improve the adhesion of the platinum contacts, and Pt/W/Pt (5 nm/80 nm/5 nm) was deposited. Liftoff in warm acetone followed. No O$_2$ plasma was used after lithography to avoid oxidizing the Cu$_2$S.
Appendix C:

In-doped CdS Nanowire Field Effect Transistors

In-doped CdS nanowire field effect transistors (FETs) were fabricated by transferring the nanowires to degenerately doped silicon substrates covered with 300 nm of thermal oxide. Wires were coated with 10 nm of alumina deposited by ALD for protection during the fabrication process, and lithography was used to define four electrodes on each wire. After a 30-s O₂ plasma clean to remove residual photoresist, the alumina was etched for 30 s in 10:1 BHF and then the exposed wires were subjected to an argon plasma for 30-60 s to locally dope the surface n-type by making it Cd rich. Ti/Au (10 nm/110 nm) contacts were then deposited by e-beam evaporation. No annealing was necessary to achieve ohmic contact.

Four-point resistivity measurements and transconductance measurements were used to characterize the electrical properties of the devices. Based on the crudest model for the capacitance of the system that assumes the nanowire is a metal cylinder uniformly surrounded by the gate dielectric, the measured threshold voltage was used to calculate the wire’s carrier concentration. From the slope of the transconductance plot at 0V, the electron mobility was calculated. The carrier concentration was then calculated based on this mobility and the four-point resistivity measurements and was found to be in reasonable agreement with the value calculated based on the transistor’s threshold voltage.

<table>
<thead>
<tr>
<th>Device</th>
<th>4-pt Resistance (kΩ)</th>
<th>Diameter (μm)</th>
<th>Length (μm)</th>
<th>Conductivity (S)</th>
<th>Transconductance Slope at 0V, 500 mV Bias (A/V)</th>
<th>Capacitance/µm</th>
<th>Mobility (cm²/Vs)</th>
<th>Carrier Conc. (cm⁻³)</th>
<th>FET Vθ (V)</th>
<th>Carrier Conc. (cm⁻³) from FET Vθ</th>
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Table C.1: FET calculations to determine the carrier concentration of the In-doped CdS nanowires.

Figure C.1: A representative transconductance plot from an In-doped CdS nanowire FET.
Appendix D:

Fabrication and Metrics of the CdS/Cu$_{2-x}$S Micro-Array Nanorod Solar Cells

D1. Fabrication of the Micro-Array Solar Cells

20-30 nm of alumina was deposited by ALD at 200°C onto the hydrothermally grown CdS arrays. Trimethylaluminum and water were used as precursors. After being primed with HMDS vapor, the arrays were coated in PMMA 950 C4 and then i-line photoresist. The viscosity of the PMMA dictated its thickness on the arrays and therefore the etching time required to expose the nanorods' tips using the O$_2$ plasma later on. Photolithography using about 1.5 µm of i-line was used to define the micro-arrays, followed by O$_2$ etching (~2 mins, 50W, 180 mTorr) to expose the tips of the nanorods. The etch depth was confirmed using a sacrificial sample sputtered with gold and imaged in SEM.

10:1 BHF was used to remove the alumina layer from the rods, yielding a clean surface after the etching of the PMMA. The chip was then annealed at 170°C for 30 mins in argon to reflow the PMMA and fill in crevices left by the removal of the alumina. Then the chip was dipped in the cation-exchange solution.

Immediately after cation exchange, the arrays were primed with HMDS vapor and coated with new i-line to define the top platinum contacts. Immediately after development, the samples were loaded into the sputterer, pumped down for 3 hours to ensure a clean deposition, and coated with ~100 nm of platinum. Liftoff was performed in isopropanol (IPA) instead of acetone to maintain the integrity of the PMMA filling the arrays. Liftoff conditions were soaking for 2 hours in IPA, interrupted by 3 s of ultrasonication after 1 hour, and concluded by 3-5 s of ultrasonication. Ultrasonication was minimized because there is a literature report that it can alter the phase of Cu$_2$S.

Contact to the underlying FTO or ITO was made by scraping the polymers off of a corner of the array, pressing a piece of indium to the exposed corner, and melting the indium into contact using a soldering iron.
## D2. Metrics of the Micro-Array Solar Cells

**ITO substrate, 70°C conversion for 5 s (roxbyite):**

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<th>Device ID</th>
<th>$I_{sc}$ (pA)</th>
<th>Approx. $J_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>Power (pW)</th>
<th>Approx. Efficiency (%)</th>
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**FTO substrate, 70°C conversion for 5 s (roxbyite), as-made:**

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<th>Device ID</th>
<th>$I_{sc}$ (nA)</th>
<th>Approx. $J_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
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FTO substrate, 70°C conversion for 5 s (roxbyite), after 5 min in air at 200°C:

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<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>Power (nW)</th>
<th>Approx. Efficiency (%)</th>
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FTO substrate, 75°C conversion for 5 s (djurleite), as-made:

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<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>Power (nW)</th>
<th>Approx. Efficiency (%)</th>
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<tbody>
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<td>0.44</td>
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Appendix E:

Fabrication of the Single-Wire Oxide Solar Cells

After growth of the wires, photolithography directly on the MgO substrates using i-line resist was used to pattern a contact on one end of the wire. Within 36 hours of developing the resist, the samples were loaded into the sputterer to deposit ~60 nm of platinum after pumping down for 3 hours to ensure a clean surface (200W, RF, 10 mins). Liftoff was performed in warm acetone. Samples held for several days before metallization exhibited non-ohmic contacts. No cleaning or etching steps were performed on the wires before metallization.

Next, the substrate was spin-coated with a bilayer of poly(methyl methacrylate) (PMMA) and i-line photoresist. The PMMA was estimated to be 300-500 nm thick. Photolithography was used to pattern the windows that would become the heterojunction, and O₂ plasma etching (3 mins, 50W, 180 mTorr) removed the PMMA using the patterned photoresist as a mask. After selectively removing the photoresist by soaking the chip in isopropanol for 20 mins, the PMMA was baked in rough vacuum (400 mTorr) at 90°C for 30 mins to remove any residual solvent. A final 30 s O₂ descum (same conditions as above) was used to clean the surface before deposition of the n-type layer; however, SEM images show that residual particles from the PMMA still remained.

Substrates then underwent pseudo-ALD of either ZnO (~30 nm) or ~10-20 nm of amorphous TiO₂ and then ZnO. Such depositions had to be performed well below the glass temperature of PMMA (~120°C) to avoid damaging the lithographic patterning and to reduce heating of the oxide interface. ZnO deposition was performed using diethylzinc and water as precursors at 85°C. While its thickness varied between depositions, its carrier concentration and mobility were found to be quite consistent. TiO₂ films were deposited at 100°C using tetrakis(dimethlyamido)titanium(IV) as the titanium precursor at the Stanford Nanoprototyping Laboratory. Films deposited using the same precursor in the Stanford Nanofabrication Laboratory did not produce working devices.

After deposition of the films, the PMMA was lifted off by soaking the substrates in acetone at room temperature for 24 hours and then ultrasonicating for 30-180 s. A third lithographic step was then used to pattern Ti/Au (10 nm/100-150 nm) contacts on the ZnO film. A 30-s O₂ plasma descum was used to prepare the ZnO before metallization, and liftoff was performed in warm acetone. No post-annealing treatments were required to achieve ohmic contact to the ZnO film.
Appendix F:
Publications

*Indicates equal authorial contributions.


