Photoconductivity of Semiconducting CdS Nanowires

Undergraduate Researcher
Jonathon Milam, Northwestern University

Faculty Mentor
Lincoln Lauhon
Department of Materials Science and Engineering, Northwestern University

Graduate Student Mentor
Jonathan Allen
Department of Materials Science and Engineering, Northwestern University

Abstract

Chemical vapor deposition was used to synthesize CdS nanowires via the vapor-liquid-solid growth mechanism. After Ti/Au contacts were patterned to the nanowires using electron beam lithography, photoresponse studies were conducted. A significant response was observed when the wires were exposed to visible light; this occurred as electrons in the nanowires were excited across the CdS (2.4 eV) band gap, thereby increasing the flow of current in the semiconductor. The nanowires also showed a considerable photoresponse under varying light intensities. However, response rates due to turning the light on and off varied throughout our experiments. We believe the increased conductivity that was also observed can be attributed to the increasing light intensity. Based on these observations, this paper discusses possible applications of photosensitive nanowires.

Introduction

As the field of electronics continues to grow and expand, "limits to progress" are falling to new and exciting possibilities. Early on, microelectronics revitalized the fields of communication and technology through the bulk production of microchips and integrated circuits that contained millions of linked semiconducting devices. Foreseeably, nanoelectronic devices may replace microelectronics in communication and computer industries. The emerging field of nanoelectronics — simply defined as electronics on the nanoscale — has the potential to take electronics, as well as several other fields, further than ever imagined.[1] This is possible because reducing the size of a semiconductor to nanoscale proportions alters its electronic, magnetic, and optical properties. These enhanced properties enable multiple new applications including the integration of nanomaterials into nanodevices such as semiconducting nanowire photodetectors.

The purpose of this research project was to determine if cadmium sulphide (CdS) nanowires could be used as photodetectors. By fabricating contacts to CdS nanowires through electron beam lithography, we measured the nanowires' photoconductivity in order to test the feasibility of a CdS nanowire optical switch.

Background

Photoconductivity is defined as electrical conductivity resulting from photoinduced electron excitations in which light is absorbed. When light is shone directly onto a photodetector, energy from the light excites the electrons in the semiconductor from the valence band into the conduction band, creating additional charge carriers and thus increasing the current through the nanowire.[2,3] Our CdS nanowires are semiconducting, which means that the band gap between the two bands is small enough to permit the generation of substantial numbers of charge carriers using visible light (Figure 2).[4] Whenever a material has an increase in electrons in the conduction band due to excitations, the conductivity of that material will also increase, as seen in the linear equation for conductivity

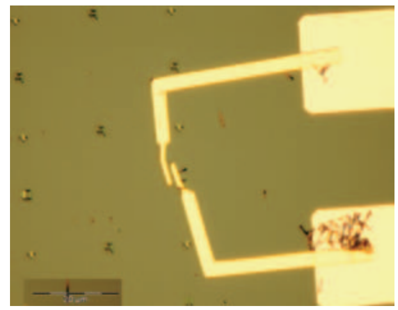

Figure 1: Gold electrode contacts made across a CdS nanowire through electron beam lithography.

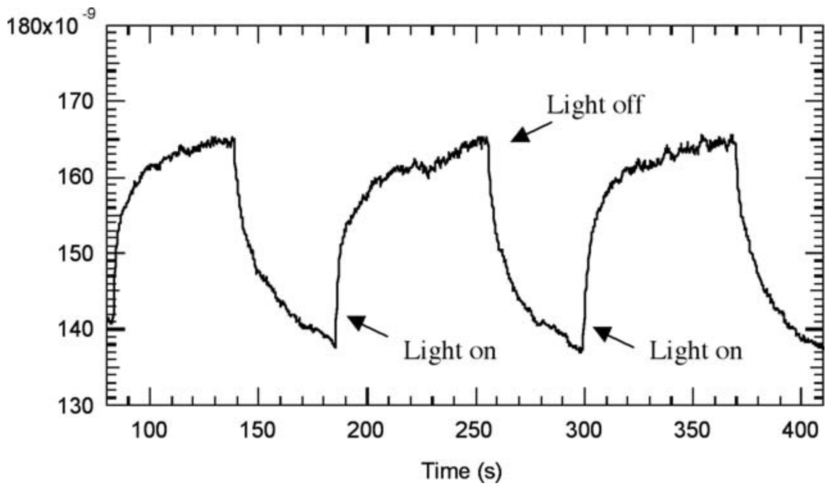

Figure 2: Current-over-time graph used to measure the photoresponse of the CdS nanowires to visible light.

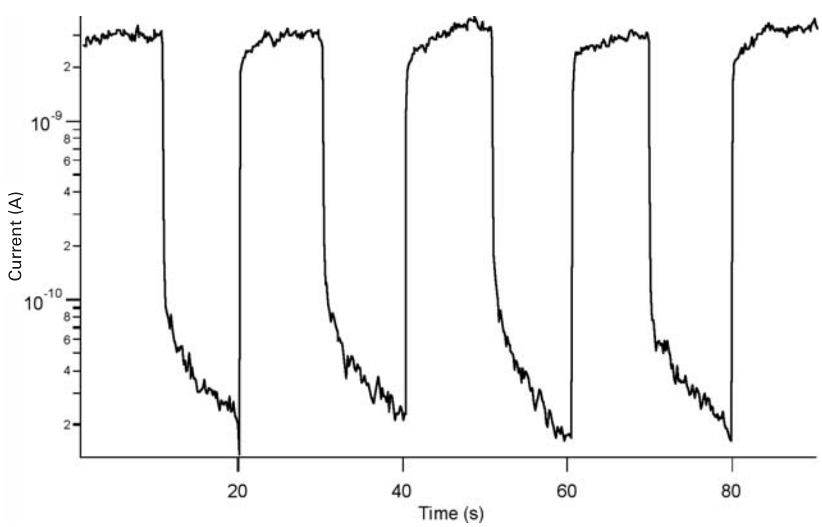

Figure 3: Photoresponse graph that shows a quicker response time.

$$\sigma = \mathbf{n}\ \mathbf{e}\ \mu_{\mathbf{e}}\ (\Omega-\mathbf{m})^{-1}$$

where **n** is the number of electrons in the conduction band, **e** is the charge of the electrons, and μ_e is the electron mobility. For these electrons to reach the conduction band, the semiconductor must have a sufficiently narrow enough band gap. CdS is a wide-band gap semiconductor (E_g = 2.4 eV), which puts the excitation wavelength at 517 nm.

Various research studies have already determined the effects of light on current in nanowires. In early 2004, research was done by Keem et al to evaluate the photocurrent in zinc oxide (ZnO) nanowires that had been grown between two Au electrodes.[6] The photocurrent and photoresponse to various wavelengths in the ZnO nanowires were measured, and from these measurements it was concluded that the light used throughout the experiments excited the electrons and produced current in the semiconducting nanowires. Hannes Kind et al also published similar findings.[7] Like Keem, Kind used light to measure the photoconductive properties of ZnO nanowires as well as their photosensitivity and reversibility. Reversibility is a condition produced by photoconductivity when light is shone directly onto a photodetector for a period of time, removed, and then shone again. The resulting data for the ZnO nanowires, which agree with data for gallium nitride (GaN) nanowires,[8] show that these nanowires have the ability to switch back and forth from high and low conductivity states (similar to the on and off states of electrical gating).[9] With this ability and their extremely short response and recovery times, these nanowires could prove to be ideal candidates for nanoscale optoelectronic switches.

It is our hypothesis that we will be able to measure the photocurrent through CdS nanowires and to characterize their electrical and optical properties.

Approach

Nanowire Synthesis
CdS nanowires were synthesized in the Lauhon laboratory in a chemical vapor deposition reactor via the vapor-liquid-solid growth mechanism. In this process, an Au particle is used to catalyze one-dimensional growth, resulting in nanowires.[10] The Cd and S atoms from the vapor precursor (Cd Diethyldithiocarbamate) form a liquid alloy with the Au particle. The alloy becomes supersaturated, and the Cd and S atoms diffuse to the deposition surface, combining to form CdS. The resulting wires typically ranged from 5 to 15 μm in length, and the distribution in wire diameters was determined by the distribution in gold particle size.

Device Fabrication
Numbered grids were written onto a silicon wafer using electron beam lithography. The synthesized CdS nanowires were suspended in isopropanol and pipetted onto each grid. An optical microscope was used to locate and image the deposited wires. With the images as a reference, contacts to the nanowires were designed using a CAD program. The Si chip was spin-coated with a polymer resist layer (MMA/PMMA) for use with electron beam lithography, which involves exposing the resist layer to high-energy electrons in a pattern defined by the CAD drawing. Through developing, the resist is removed from the exposed areas. A 15 nm layer of Ti and a subsequent layer of Au are evaporated for contacts to the measurement devices (Figure 1). After metals are deposited, the remaining polymer is removed using acetone.

Measurements
Electrical measurements were made using a probe station by applying a constant voltage across the nanowire and measuring the current while varying the light intensity. A fiber-optic illuminator was used as a light source and was switched on and off using a shutter. Current was measured while the light was switched at regular intervals. I-V curves were also acquired at various light levels. A photodiode was used to obtain light intensity data.

Results and Discussion

CdS Nanowire Photoresponse
As seen in Figure 2, the current through the CdS nanowire was observed as the intensity of light from the incandescent lamp was modified in the presence of a 3V bias across the wire. When the light was turned on, conductivity immediately increased. This observed photoresponse corresponds to a 25nA increase in current, which is approximately 18 percent of the initial (i.e., light off) value. After the light was turned off, the current returned to its original value. This process was repeated two more times.

From our data it appears to be possible to control the response of the current in a semiconducting photodetector. Because the electrons in the nanowires receive their excitation energy from the power of the light source, it is possible to "switch" these nanowires reversibly between higher and lower states of conductivity. Unfortunately, in the first example described here we did not see an optimal photoresponse. It took the current an average of 65 seconds to travel from its lowest point to its highest and nearly 50 seconds to retreat once the light was turned off. This response rate is slow, especially for an electronic device.

However, subsequent tests with other CdS nanowires from the grid showed a much quicker photoresponse/response time. As shown in Figure 3, the nanowire displayed a photoresponse speed that significantly surpassed the speed of the previous one. The response is so complete, in fact, that the amplitude of the current once the light is turned on is basically equivalent to switching the nanowire completely on and off. Also, the time it takes for the current to return to the original value is reduced from 50 seconds to nearly 10 seconds, and it takes only 1 second for the current to return to the maximum value when the light is back on. The discrepancies between the two examples lead us to believe that photoresponse varies innately from wire to wire and that more extensive research may reveal the specific characteristics of a nanowire that underlie the best possible photoresponse.

Current vs. Voltage for Various Light Intensities
Next, we conducted an experiment in order to analyze the I-V characteristics of the CdS nanowires under illumination. Here we used a sweeping voltage graph between -2 and 2 volts and measured the current for several light intensities (Figure 4). For the plot, three separate intensities were used, ranging from the minimum amount of light intensity to the maximum. As displayed on the graph, as the percentage of light intensity increased, so did the amount of current produced.

Accompanying this data is a current vs. intensity graph that allowed for simultaneous evaluation of the current's response to different light intensities (Figure 5). For the graph, the intensity was normalized between 0.0 and 1.0 in order to concentrate on the actual plot as opposed to the values presented. The first four points of

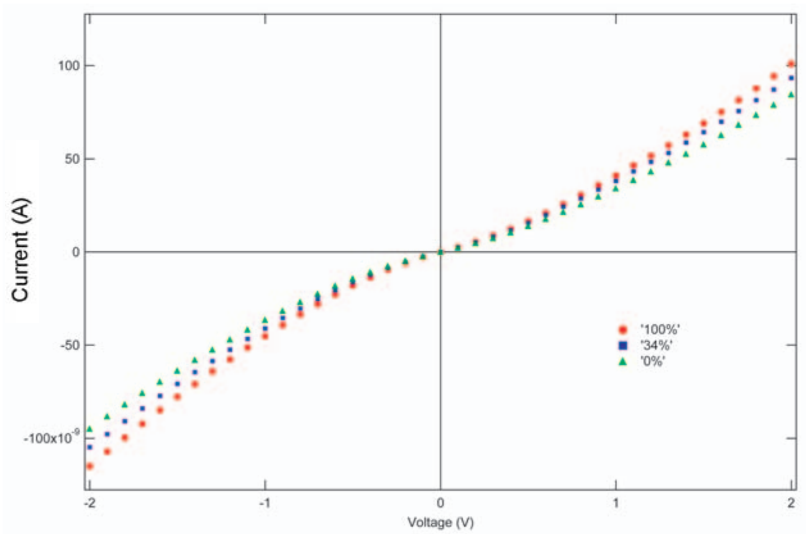

Figure 4: I-V graph that shows an increase in the current as the percentage of light intensity increases.

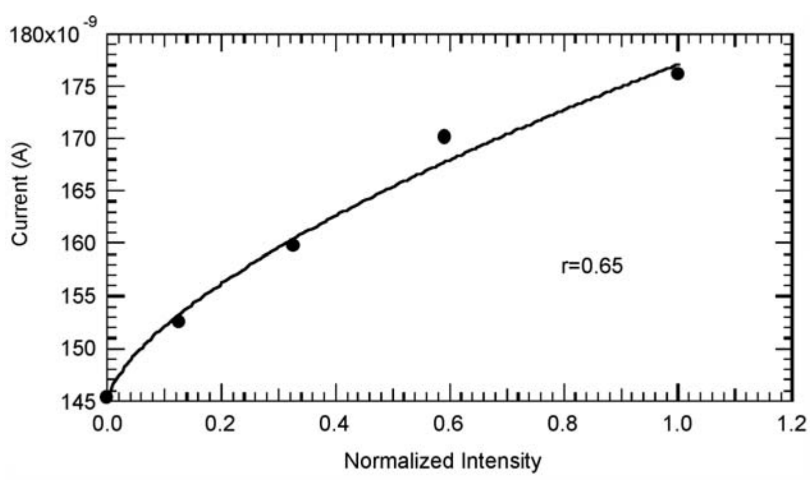

Figure 5: Current vs. intensity graph that measures the current response to varying light intensity.

data in the graph appear to be linear, as we would expect to see in an I-V graph for a semiconductor;[11,12] however, on the fifth plot of the graph the data appear to level off as the current reaches the maximum intensity. At first we took this to mean that a saturation of the charge carriers in the nanowire may have occurred when the full intensity was reached, preventing the current from increasing further. However, after taking a closer look at the graph and configuring a curve fit for the plots, we came to an entirely different conclusion. The curve fit is close to a square-root function, and with a degree dependence of .65, it seems that the graph was actually showing that our CdS nanowires represent a material between semiconductors and insulators. We knew this from the outset of our research, since CdS has a wide band gap (2.4 eV) but is nonetheless still considered a semiconductor.

Conclusions

This research brings the the development of semiconducting nanowire switches for nanoelectronic devices one step closer. From our data, CdS nanowires have been shown to have a significant photoresponse in the presence of a light source. In particular, due to their wide band gap, CdS nanowires are extremely sensitive to light in the visible range, specifically to visible light in the green spectrum. Future work with monochromatic light should be able to determine the excitation wavelength at which the conductivity of CdS nanowires is maximized, and by using a more powerful light source, it is should be possible to test their higher-intensity responses as well as their frequency response. The Lauhon group also envisions using local conductivity measurements to evaluate the current at specific points along a nanowire as opposed to along the entire wire. It is hoped that our findings, based on the information presented here and supplemented by further testing, can be incorporated into new nanoscale devices.

References

(1) Lieber, C. M. *Sci. Am.* **2001**, *285*, 58–64.

(2) Callister Jr., W. D. Optical Properties. In Anderson, W., and Malinowski, S., eds. *Materials Science and Engineering: An Introduction* (6th). John Wiley & Sons, Inc.: New Jersey, 2003; pp 707–729.

(3) Cao, L.; Chen, H. Z.; Wang, M., et al. *J. Phys. Chem*. B **2002**, *106*, 8971–8975.

(4) Callister Jr., W. D. Optical Properties. In Anderson, W., and Malinowski, S., eds. *Materials Science and Engineering: An Introduction* (6th). John Wiley & Sons, Inc.: New Jersey, 2003; pp 611–641.

(5) Neamen, D. A. The Semiconductor in Equilibrium. In Butcher, K., ed. *Semiconductor Physics and Devices: Basic Devices* (3rd). McGraw-Hill Companies, Inc.: New York, 2003; pp 103–145.

(6) Keem, K.; Kim, H.; Kim, G., et al. *Appl. Phys. Lett*. **2004**, *84*, 4376–4378.

(7) Kind, H.; Yan, H. Q.; Messer, B., et al. *Adv. Mater.* **2002**, *14*, 158–160.

(8) Han, S.; Jin, W.; Zhang, D. H., et al. *Chem. Phys. Lett.* **2004**, *89*, 176–180.

(9) Levitsky, I. A.; Euler, W. B. *Appl. Phys. Lett.* **2003**, *83*, 1857–1859.

(10) Gudiksen, M. S.; Lauhon, L. C.; Wang, J. F., et al. *Nature* **2002**, *415*, 617–620.

(11) Freitag, M.; Martin, Y.; Misewich, J., et al. *Nano Lett.* **2003**, *3*, 1067–1071.

(12) Balasubramanian , K.; Fan, Y. W.; Burghard, M. K., et al. *Appl. Phys. Lett.* **2004**, *84*, 2400–2402.