

Electrochemical Synthesis of Multi-Material Nanowires as Building Blocks for Functional Nanostructures

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ABSTRACT

Nanostructures are electrochemically deposited into alumina or polycarbonate templates resulting in monodisperse, anisotropic particles with a range of tunable sizes. These particles have been synthesized with diameters of 20–250 nm and with lengths of 1–10 μm . Currently, structures have been made with stripes of Au, Ag, CdSe, Co, Cu, Ni, Pd, and Pt. These materials offer a variety of different properties. In particular, many of the metals in this group are excellent conductors, meaning these particles can actually be used as nanowires. Co and Ni are ferromagnetic and may be used for separation or assembly. CdSe is a semiconductor, possibly allowing for the synthesis of electronic devices such as transistors. Furthermore, many of these materials have different surface chemistries, making the orthogonal functionalization and assembly of these nanowires more accessible. This research focuses on increasing the number of materials available, especially semiconductors, incorporating these potentially useful materials into multilayered nanowires and evaluating their electrical properties, either individually or in small bundles. In addition, the surface chemistry of the various materials in the nanowires is being compared to aid in orthogonal self-assembly of functional nanostructures such as memory devices. The work presented will demonstrate the effects of rod composition on electrical properties. In particular, the effects of changing the work function of the materials on either side of a semiconductor to form Schottky junctions or ohmic contacts will be shown.

INTRODUCTION

Over the past few decades there has been tremendous growth in the computer and communications industries. In part, this growth has been spurred by the continual miniaturization of electronic components. As predicted by Moore in 1965, the density of transistors on a Si chip has doubled every 18 months.^[1] However, in order to maintain this growth, a great deal of capital has been invested in lithographic methods.^[2] Even though at present lithography enjoys a complete domination of the electronics industry, other methods of component assembly must be investigated in order to keep this growth on track. Some possible methods of computation that have been proposed include quantum computing and DNA computing.^[3-14] One approach that is showing a lot of promise is molecular electronics, a method that uses molecules to act as wires, diodes, and resistors.^[15-20] Rather than the “top-down” approach of lithography, molecular electronics allows devices to be designed and built on the atomic scale, from the “bottom-up.” Although there have been several successes with this method, there is still a lack in the middle scale, 10-200 nm. Something is needed that can

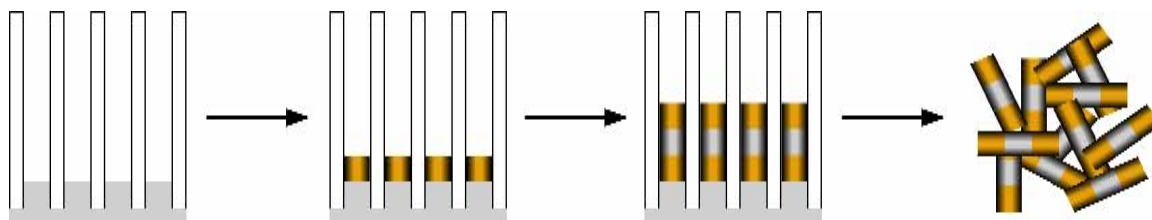
connect molecular scale devices to the macroscale world. We propose that nanowires can be used in that role.

Nanowires grown in a template have been investigated by a variety of groups [21-29]. Also, it has been shown that it is possible to orthogonally assemble molecules on the segment of an Au-Pt-Au nanowire[28]. This ability, in combination with a variety of different types of wires will allow an even greater number of combinations. The work presented herein will detail the characterization and electrical properties of one type of nanowire with a semiconductor section along the axis that may offer the ability to assemble a nanodiode.

EXPERIMENTAL DETAILS

Alumina templates were Anodisc 25 filtration membranes purchased from Whatman. The diameter of the pores used for these experiments were nominally 200 nm. The thickness of the membranes was $> 60 \mu\text{m}$, so these templates are more than long enough to accommodate the growth of the $< 10 \mu\text{m}$ long nanowires. Au plating solution at 1 troy oz./ gal., Ag plating solution at 6 troy oz./gal., and Ni (S) sulfamate plating solutions were obtained from Technic. CdSe and CdTe plating solutions were made in-house with 0.3 M CdSO_4 , 0.25 M H_2SO_4 , and 0.7mM SeO_2 or TeO_2 as described by Klein et al[29].

Scheme 1 depicts the synthesis of multi-component nanowires. The nanowires were synthesized using a modification to a method previously described [21,22]. A thin film of $\sim 5000 \text{ \AA}$ of Ag was vapor deposited on one side of an alumina template using a BOC Edwards Auto 306 evaporation system. The membrane was then placed in an electrochemical cell and electrodeposition of Ag was performed on the coated side at 2 mA/cm^2 for 10 minutes to fully cover all the pores with Ag. The membrane was then repositioned to allow for the penetration of the plating solution, and more Ag was plated through the open side of the membrane down into the pores at 0.5 mA/cm^2 for 20 min. In a typical experiment, Au and/or Ni were electrodeposited at 0.5 mA/cm^2 for a period of time long enough to make a segment of $3 \mu\text{m}$ long, approximately 1 hr for Au and 2 hr for Ni. In order to include a segment of a different metal, the plating solution was removed, the cell rinsed, and the new solution introduced while holding the current at 0.03 mA/cm^2 . The solutions were then changed and CdSe or CdTe was deposited using a cyclic voltammetry technique, similar to that described by Martin and coworkers [29]. The potential range used was from -350 mV to -800 mV with a scan rate of 750 mV/sec . This produced a segment of material that deposits with a rate of approximately 2 \AA/scan ; a typical run of 5000 scans produces a segment of $\sim 1 \mu\text{m}$. A second layer of metal was then plated on the layer of semiconductor as described above. Nanowires were synthesized with compositions of: Au-CdSe-Ni-Au, Au-Ni-CdSe-Ni-Au, Au-CdTe-Au and Au-CdTe-Ag-Au.



Scheme 1. The growth of multi-material nanowires in an alumina template, followed by dissolution of the Ag in HNO_3 and of the template, leaves the individual nanowires suspended in solution.

The nanowires were removed from the alumina template in a two step process. The Ag backing was dissolved by dissolution in 4 M HNO₃. The template containing the nanowires was then dissolved in 3 M NaOH for 30 minutes. Following several centrifugation and rinsing steps, the nanowires from each membrane were finally suspended in a 1-ml aliquot of CH₃CH₂OH. An aliquot of the nanowires was then dried on a glass microscope slide and the wires were examined by optical microscopy. SEM samples were prepared by lift-off of the nanowires from the glass slide with carbon tape affixed to an aluminum stud.

The ethanolic nanowire solution was diluted 10:1 with isopropanol and aligned in an electric field across lithographically defined Au pads [26]. The substrate was then masked and Au contact pads were evaporated on the ends of the nanowires. Electrical measurements were obtained by contacting the Au pads with Ti microprobes of a probe station.

DISCUSSION

Microscopy images of the nanowires are shown in Figure 1. A layer of CdSe was deposited along the axis of the nanowire between two Au sections. Due to its lower conductivity, the CdSe shows up darker than the Au in both images. In the optical microscopy image, 7 μm long nanowires are shown with a semiconductor segment of 1 μm. The SEM image shows 6 μm long nanowires with a 2 μm CdSe segment. The length of the Au segments is well controlled, showing a perfectly linear relationship with the amount of charge passed. The segments are routinely synthesized with a polydispersity of <10%. The length of the CdSe segments can be varied proportionately to the number of scans and shows <25% dispersity. Currently work is being undertaken to improve monodispersity.

Energy dispersive x-ray spectroscopy (EDAX) was used to determine elemental composition of the deposited material. A 1 μm thick CdSe or CdTe film was deposited on an Au

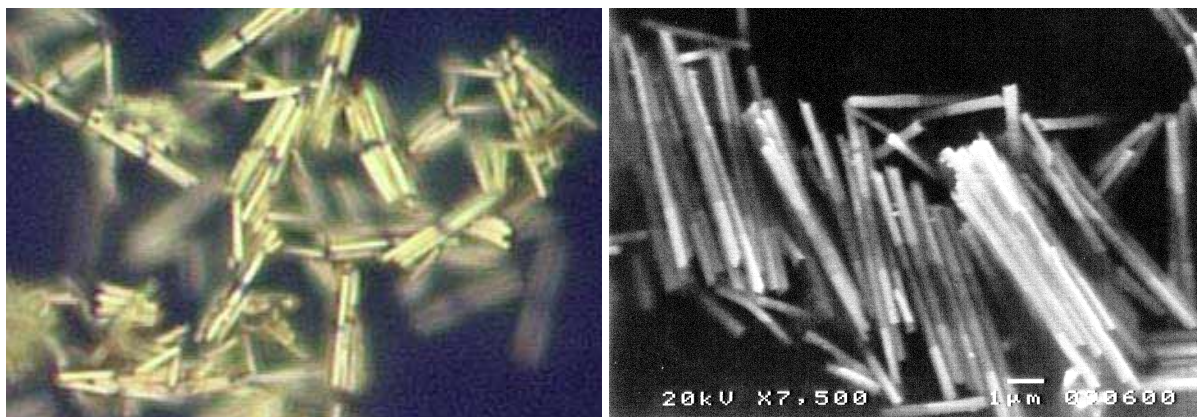


Figure 1. Optical microscope image (left) and scanning electron microscope image (right) of 200 nm diameter nanowires.

film that was prepared by thermal evaporation on a glass microscope slide. The concentration of the SeO₂ and TeO₂ were varied from 0.4 mM to 1.4 mM while keeping the CdSO₄ at a constant concentration of 0.3 M. Figure 2 shows a typical EDAX scan taken from a CdSe sample that was prepared with 0.7 mM SeO₂ solution. Four prominent peaks are observed: Se K at 1.41 keV, Si K at 1.74 keV, Au L at 2.12 keV, and Cd L at 3.14 keV. Due to the high energy of the incident electrons, penetration through the CdSe film and the Au film to the glass substrate

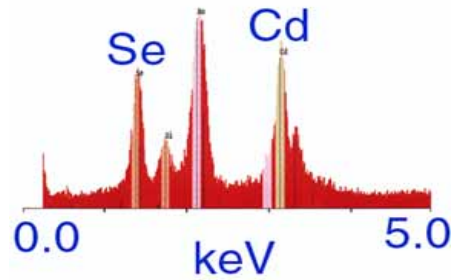


Figure 2. EDAX spectrum of a CdSe film deposited on an evaporated Au film.

occurs, giving rise to a Si peak. From the relative heights of the peaks of Cd and Se, a ratio of 1:0.909 Cd:Se is obtained. Values for all samples ranged from 1:0.874 for the 0.4-mM sample to 1:1.03 for the 1.4-mM ratio. Since it is generally known that the electrical properties of the semiconductor are highly dependent on the stoichiometry of the elements, this gives us a rational method of control over the material.[30]

The semiconductor nanowires show interesting electrical characteristics. As can be seen in Figure 3, rather than the linear behavior typical of a conductor, these nanowires exhibit symmetric rectifying behavior. The flow of current is restricted until a threshold voltage is reached, allowing the flow of current in either direction. The symmetry of this behavior would seem to indicate that the semiconductor segment of the nanowire is acting as an insulator, similar to a semiconductor with an applied reversed bias. In addition, these nanowires show the symmetric behavior irrespective of the identity of the metal in the metal-semiconductor junctions. Our data can be understood as two Schottky junctions back-to-back. Briefly, the forward bias for one junction is the reverse bias for the second. Because of this, only the break down voltages of the junctions would be seen, giving rise to the observed behavior. The high value of ~ 3 V as the turn on voltage, compared to <1 V typical for bulk samples, and the not

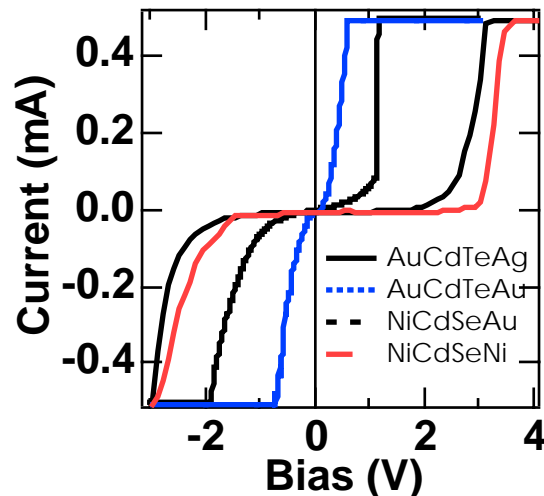


Figure 3. Plots showing the symmetry of the electrical characteristics of nanowires with a CdSe or CdTe inclusion.

completely symmetric behavior that can be seen for the CdSe nanowires supports this interpretation.

CONCLUSIONS

It has been possible to include segments of a II-IV semiconductor along the axis of a nanowire. The length and stoichiometric composition of these semiconductors can be well controlled and adjusted for optimum performance. By incorporating these segments into the nanowire, we are able to change the electrical characteristics of the nanowire. However, for a rectifying diode, one of the metal-semiconductor junctions along the axis must be changed in order to create an ohmic contact. Research is ongoing to accomplish this by changing the metal and/or the doping of the semiconductor. Furthermore, we are looking into the effects of the length of the semiconductor section and the diameter of the nanowires on the electrical characteristics.

ACKNOWLEDGMENTS

Funding for this research was provided by ONR/DARPA under grant # N00014-98-1-0846.

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