

Author



Electrodeposition and Kinetically-Controlled Electrooxidation of Antimony Nanowires

Michael Thompson

Chemistry

Research has given Michael Thompson an understanding of the life of a research chemist, and helped him decide to work toward becoming one. He first became involved in research, under the guidance of Professor Penner, during winter 2004. Michael has been working on developing a unique method for synthesizing nanowires out of antimony. He had the opportunity to present his research to several European collaborators in Corfu, Greece. Michael's advice to new researchers is to "work hard and get results," adding that there is no better feeling than seeing so much hard work leading to exciting and important results.

Abstract

There is increasing interest in materials with dimensions smaller than 100 nm across disciplines ranging from electrical engineering to molecular biology. Materials in this size regime display interesting size-dependent properties that have already found applications in electronics and chemical and optical sensors. There are several different classes of these nanomaterials. Nanowires are a special type of nanomaterial that have an almost one-dimensional structure. A nanowire can be defined as a wire, made of any material, with a diameter below 100 nm. This paper introduces a new method for the synthesis of antimony nanowires that involves electrodeposition of antimony onto the step edges of highly oriented pyrolytic graphite and the subsequent "stripping" using kinetically-controlled electrooxidation to create longer and thinner antimony nanowires. This technique is important because it creates antimony nanowires with widths as small as 33 ± 7 nm and lengths of over 100 μm , which allows for easy integration into devices. Also, the kinetically controlled electrooxidation technique is the only method, to our knowledge, that can shrink the size of any nanostructure without roughening the surface.

Faculty Mentor



Antimony is one of three metals of special interest to physicists (arsenic and bismuth are the other two). In these metals, conduction electrons travel long distances without scattering, and this has practical applications for the use of these metals in devices like magnetic sensors. Michael has developed methods for preparing nanowires of antimony and for reducing the diameter of these nanowires into the 50 nm regime. We are working with physicists in Finland to study electron transport in these diminutive conductors.

Michael's nanowire etching method is especially exciting because it is applicable to nanowires of many different metals, prepared by a wide variety of technologies.

Key Terms

- ♦ Antimony
- ♦ Electrodeposition
- ♦ Electrooxidation
- ♦ Nanowires

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Introduction

Nanotechnology has already had a profound impact on everyday life. For example, the microprocessor in a state-of-the-art personal computer uses technology within these dimensions. Nanomaterials, materials with dimensions below 100 nm, are so small they cannot be viewed using standard light microscopy. One special case of a nanomaterial is a nanowire, a wire of any composition with a diameter in the range of 1–100 nm. Nanowires are a topic of intense research in many fields because they could improve a range of technologies including electronics (Friedman et al., 2005; Goldberger et al., 2006; Melosh et al., 2003), thermoelectric generators (Heremans et al., 2000; Menke et al., 2004; Prieto et al., 2001), and chemical sensors (Cui et al., 2001; Favier et al., 2001; Kolmakov et al., 2003). Because of the small size and quasi-one-dimensional nature of nanowires, quantum mechanics begins to take a large role in the behavior of nanowires. Also, the basic physics and chemistry of these wires offers insight into the transition between single atom and bulk behavior.

There are many methods of synthesizing nanowires, most of which can be divided into two categories. A more developed, but less promising technique is called “top-down” wire synthesis, through which macroscopic precursors are sized down into microscopic ones by lithography or scanning-probe techniques. The methods that hold the most promise are so-called “bottom-up” approaches, which use atomic or molecular precursors as catalysts or forms for the creation of the wire. The bottom-up approaches are more promising because they can provide more control over the crystallinity of the nanowire and they are not limited by the diffraction limit of either UV light or an electron beam.

In this paper we explore the bottom-up synthesis of antimony nanowires using electrodeposition onto graphite. Nanowires composed of the base metal antimony are interesting because, at a certain critical diameter (~ 9 nm), the electronic behavior of these nanowires switches from metallic to semiconducting. The reason for this phenomenon is the increased separation between the valence and conduction bands as the wires are made more one-dimensional (Heremans et al., 2001). Currently, no applications have been found for antimony nanowires but, if the predicted physics are experimentally verified, the wires could find use in a variety of electronic applications. Antimony nanowires also have increased magnetoresistance compared to the bulk because of the long electron mean free path in antimony. A long electron mean free path means that the

electrons travel farther on average before scattering. This property could be used in magnetic memory components.

The most common method for the synthesis of antimony nanowires involves either electrodeposition or pressure injection into an ordered alumina membrane template (Zhang et al., 2002). This method creates uniform nanowires with diameters ranging from 10 to 100 nm and lengths of up to 10 μm . It is time-consuming and the nanowires are very short, which makes it difficult to use them in devices or measure their properties.

This paper discusses the synthesis of antimony nanowires by electrochemical step edge decoration (ESED), a method developed in the Penner Lab at the University of California, Irvine. This method involves depositing nanowires onto the step edges of highly oriented pyrolytic graphite (HOPG), and it has been used to deposit wires of many different materials, including noble metals and semiconductors such as CdS and CdSe (Li and Penner, 2005; Walter et al., 2002; Zach et al., 2000). The wires created using ESED can be up to 1 mm in length and can be transferred into an insulating cyanoacrylate (superglue) film. Two gold contacts can then be evaporated on top of the nanowires embedded in the film to create a simple two terminal device.

Here we present a new method for the synthesis of long (>100 μm) antimony nanowires with diameters down to 33 nm. This synthesis involves two steps. The first is the direct electrodeposition of antimony wires with diameters of ~ 120 nm on the step edges of highly oriented pyrolytic graphite. The wires are then immediately oxidized in the same solution by applying a slightly positive overpotential that causes slow, kinetically-controlled electrooxidation of the nanowires, thus decreasing their diameter linearly with growth time. The deposition and electrooxidation steps in this process are fully characterized in this paper.

Experimental Details

Nanowire Deposition

All nanowires were deposited out of a 50 mL, glass and Teflon, one-compartment, three-electrode cell, and all potentials are referenced to a saturated calomel electrode (SCE). The glass and Teflon equipment were rigorously cleaned using a NoChromix[®] solution (Godax laboratories, Cabin John, Maryland). All solutions were aqueous and made with Nanopure water ($\rho > 18$ M Ω). Solutions were purged with $\text{N}_2(\text{g})$ prior to each deposition. Nanowires were deposited on the basal plane surface of ZYB-grade highly oriented pyrolytic graphite (HOPG) supplied by Advanced

Ceramics Inc. (Cleveland, OH). The graphite was placed in a Teflon holder that exposed a circular area of 0.2 cm² of the HOPG basal plane to the solution. The depositions were carried out using an EG&G model 273 potentiostat/galvanostat. Antimony nanowires were deposited from a plating solution of 5 mM SbCl₃ (Aldrich, 99.99+%), 0.1 M HNO₃, and 0.1 M tartaric acid (Aldrich, 98%). The deposition was carried out using a four-pulse potential program, which is discussed in the Results and Discussion section.

Microscopy

Scanning electron microscopy (SEM) was carried out using a Philips FEG 30-XL microscope equipped with an EDAX elemental analyzer.

Results and Discussion

Figure 1 outlines the basic principles of this synthesis strategy. There are four constant potential steps applied to the graphite electrode. The first is oxidation at 0.8 V vs. SCE for 5 s. At this potential the step edges on the HOPG surface are oxidized to produce oxygen-containing organic functional groups that are attractive to metal ions. Next, a short pulse is administered at a very negative potential, 40 ms at -1.0 V vs. SCE. This pulse creates small metal aggregates evenly distributed along the step edge. The third step is a slightly negative overpotential (10–100 mV) applied for a longer amount of time. This potential is positive of the nucleation barrier on the graphite, meaning that no new nuclei will be formed during this process. This period causes the particles on the step edge created during nucleation to grow slowly in size until they coalesce into a continuous nanowire. The fourth and final step is to apply a very low positive overpotential (<50 mV) to the working electrode causing a constant, kinetically-controlled oxidation current density on the surface of the nanowire. This constant current density is proportional to a constant oxidation reaction rate on the surface, which results in a linear reduction of the diameter of the wire with time.

The growth potential was chosen by adjusting the applied potential until a quasi-constant current resulted. This method also creates nanoparticles on the basal plane, alongside the nanowires on the surface of the HOPG. These particles form on the terrace during the nucleation step. They are typically not important because, when these nanowires are transferred from the graphite surface to an insulating polymer, the particles are not in electrical contact with the wires and do not affect electrical measurements. The wire growth is characterized by a constant, convection-controlled current, i_{growth} . This allows us to derive the following expression

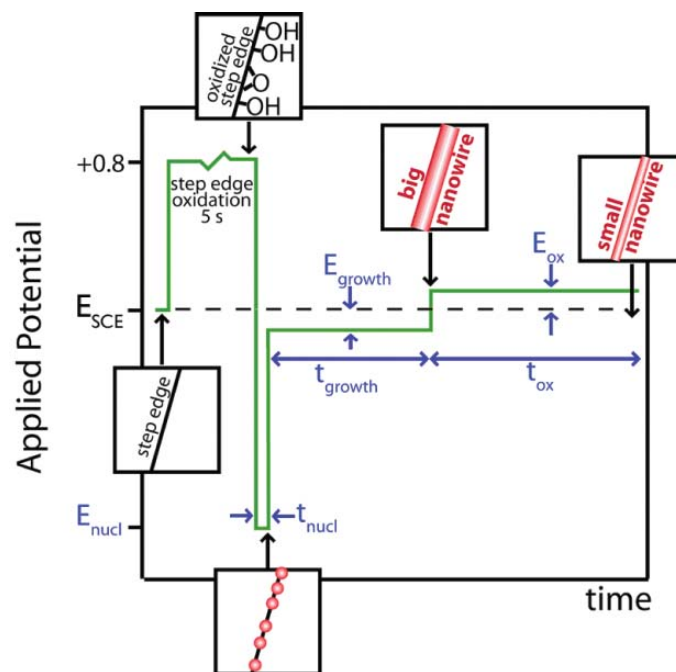


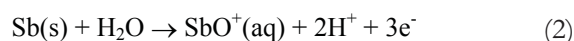
Figure 1

Schematic illustrating the four potential pulses applied to the graphite electrode and the purpose of each step during the deposition of antimony nanowires. (Source: Thompson et al., 2006)

for the radius of the nanowire as a function of time during this step.

$$r(t) = \sqrt{\frac{2i_{growth} t_{growth} V_m}{\pi n F l}} \quad (1)$$

Where t_{growth} is the deposition time, V_m is the molar volume, l is the total length of wires on the surface, n is moles of electrons per mole of reduced metal, and F is the Faraday constant. These wires are excellent examples of the ESED method of instantaneous nucleation and slow growth without further nucleation. The particles are hemispherical and have the same size even when the particles are very close to each other. This suggests that there is no inter-diffusional coupling during the growth step (Penner, 2002). The wires are also exceptionally smooth for metal wires prepared using ESED. Because the radius is proportional to the square root of the deposition time, the standard deviation of the wire diameter decreases. Thus, a long growth step can turn a rough nanowire into a smooth nanowire, which is important for the fourth step in the synthesis. A smoother nanowire can be oxidized to a smaller diameter than a rough nanowire. The reaction associated with this step is given by Equation 2:



Because the applied overpotential is low (< 50 mV), the reaction should be kinetically controlled. To run an electrochemical reaction under condition of kinetic control indicates a constant reaction rate on the surface of the substrate. The constant current rate is represented by a constant current density on the surface of the nanowires and nanoparticles, j_{ox} . The change in volume of each nanowire is proportional to the current density multiplied by the area of the nanowire:

$$\frac{nF}{V_m} \frac{dV}{dt} = -j_{ox} A \quad (3)$$

From Equation 3, and using the formulas for the volume and surface area of a hemicylinder, the following expression for the radius of the nanowires as a function of time can be derived (t_{ox} is the oxidation time):

$$r(t) = r(0) - \frac{j_{ox} t_{ox} V_m}{nF} \quad (4)$$

This equation also implies that the roughness of the wire, σ_{dia} , will remain constant during the oxidation step. The result is significant since, to our knowledge, no other method has been developed to shrink nanowires while still retaining the smoothness of the original wire. The nanoparticles on the basal plane of the graphite surface will also be oxidized during this process. A similar derivation can show that the radius of the hemispheres as a function of time will be the same as Equation 3.

Figure 2 shows a cyclic voltammogram of the graphite electrode in the antimony solution. The cyclic voltammogram shows two waves, one to the left representing the reduction of antimony ions in solution onto the graphite surface, and the wave on the right representing the oxidation reaction (Goldberger et al., 2006). The electrooxidation potential of -0.060 V (vs. SCE) is also highlighted. This oxidation potential is ideal for thinning the nanowires without inducing roughening. Note the very low current associated with this potential as compared with the peak current.

Figure 3 illustrates the effect of potential on the oxidation and the roughness of the resultant antimony nanowires. As a more positive potential is used, the wire begins to break. The breaks can be explained because a more positive overpotential would cause a faster reaction rate and also cause a loss of kinetic control. The loss of kinetic control results in an uneven oxidation current density along the surface of the wire and, hence, surface roughening. The choice of

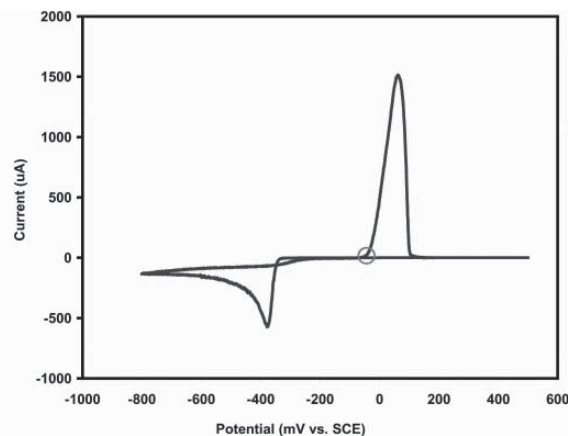


Figure 2

Cyclic voltammogram taken at a scan rate of 20 mV s^{-1} for a graphite electrode into antimony plating solution that consists of 5 mM SbCl_3 , 0.1 M tartaric acid, and 0.1 M HNO_3 . The circle indicates the low oxidation potential applied in the fourth step.

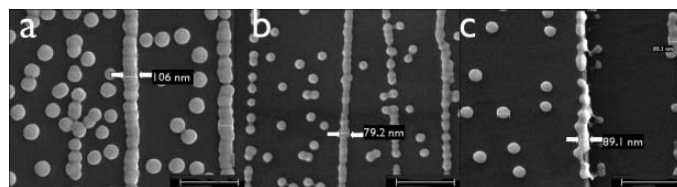


Figure 3

Representative SEM micrographs of antimony nanowires oxidized at: a) -0.060 V vs. SCE, b) -0.040 V vs. SCE, and c) -0.025 V vs. SCE. Scale bar is 500 nm . These images illustrate the loss of kinetic control with a more positive oxidation potential.

-0.060 V (vs. SCE) was made because it is the most positive potential that still allows for kinetic control.

Figure 4 shows two low magnification SEM images of antimony nanowires (a) as deposited and (b) after electrooxidation for 500 s . Figure 5 shows a plot of nanowire diameter versus electrooxidation time and images of nanowires etched for (a) 0 , (b) 250 and (c) 500 s . The diameters were measured using SEM, and each data point is the mean of a histogram containing measurements from 50 different nanowires. As can be seen from the plot, the standard deviation does not significantly increase during the oxidation step—all of the above being evidence that supports Equation 4. From the slope of the trendline we can solve for the oxidation current density using Equation 2, and it is $137 \mu\text{A cm}^{-2}$. The final wire diameter can be reduced to an extremely thin diameter of 36 nm without sacrificing the original smoothness of the wire. The 36 nm wires were also still continuous for $100 \mu\text{m}$. Oxidation for times longer than 500 s resulted in wires that were electrically continuous for less than $100 \mu\text{m}$.

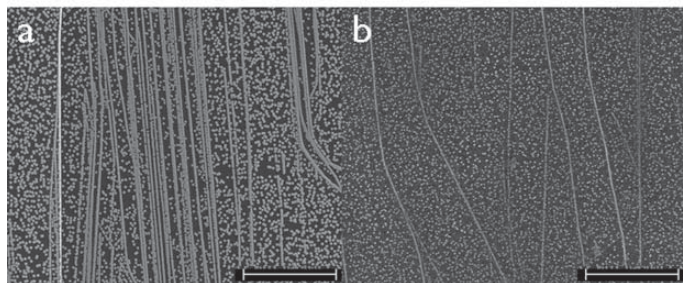


Figure 4

Representative low magnification SEM images of different samples of antimony nanowires (a) as deposited and (b) after oxidation at -0.060 V vs. SCE for 500 s. Scale bar is $5\ \mu\text{m}$. The mean diameter of the wires in (a) is $122\ \text{nm}$ and the average diameter of the wires in (b) is $36\ \text{nm}$. The average length of the wires in both images is over $100\ \mu\text{m}$.

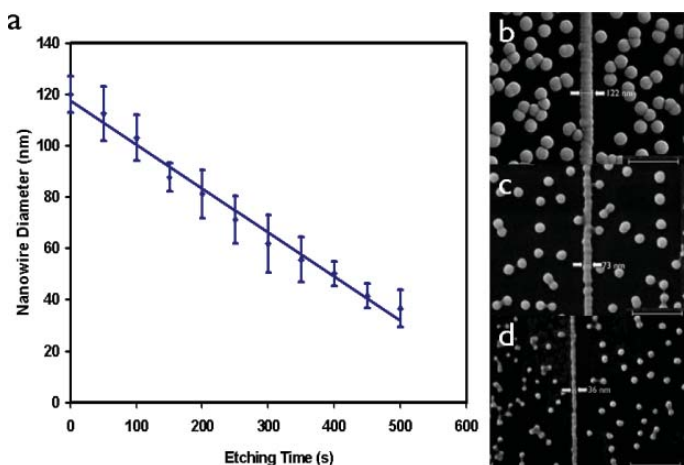


Figure 5

(a) Plot of antimony nanowire diameter versus oxidation time. Each data point is the mean of a collection of 50 diameter measurements. The trendline is a least squares fit of the data in accordance with Equation 3. The error bars represent the standard deviation of each associated histogram. (b-d) Representative SEM images of nanowires oxidized for: (b) 0 s (c) 250 s, and (d) 500 s. The average diameter of the nanowires in each sample was 122 , 73 , and $36\ \text{nm}$, respectively.

The major limitation of this method is that the $30\ \text{nm}$ wires are too fragile to transfer to cyanoacrylate. This means that the properties of the nanowires cannot be measured unless a new method is found to remove the wires from the graphite surface, which could take substantial research. Also, the nanowires could be made smaller by further refinement of the technique, especially during the growth stage, but this is a much smaller challenge than the transfer of the wires from the HOPG.

Conclusions

Antimony nanowires with diameters ranging from 36 to $122\ \text{nm}$ and lengths over $100\ \mu\text{m}$ have been synthesized using electrochemical step edge decoration. The wires were grown by a four-step process using both slow growth and kinetically controlled electrooxidation. The kinetically controlled electrooxidation step was shown to be successful in reducing the diameter of the wires while still retaining their original smoothness. This technique is important because it creates very thin antimony nanowires with widths as small as $33 \pm 7\ \text{nm}$ and lengths above $100\ \mu\text{m}$, for relatively easy integration into devices. More importantly, the kinetically controlled electrooxidation technique is the only method, to our knowledge, that can shrink the dimensions of any nanostructure without roughening the surface, which could have important applications in the field. With more improvements, these wires can be transferred and their electrical properties measured.

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Works Cited:

- Cui, Y., C.M. Lieber, H.K. Park and Q.Q. Wei. "Nanowire Nanosensors for Highly Sensitive and Selective Detection of Biological and Chemical Species." *Science* 293 (2001): 1289.
- Favier, F., T. Benter, R.M. Penner, E.C. Walter and M.P. Zach. "Molybdenum Nanowires by Electrodeposition." *Science* 293 (2001): 2227.
- Friedman, R.S., D. Ham, C.M. Lieber, M.C. McAlpine and D.S. Ricketts. "High-speed integrated nanowire circuits." *Nature* 434 (2005): 1085.
- Goldberger, J., R. Fan, A. Hochbaum and P. Yang. "Vertical silicon nanowire field effect transistors" *Nano Letters* 6 (2006): 973.
- Heremans, J., S. Cronin, M.S. Dresselhaus, Y.M. Lin, J.F. Mansfield, C.M. Thrush and Z. Zhang. "Transport properties of antimony nanowires" *Physical Review B* 61 (2000): 2921.

- Heremans, J., S.B. Cronin, M.S. Dresselhaus, Y.M. Lin and C.M. Thrush. "Transport Properties of Antimony Nanowires" Physical Review B 63 (2001).
- Kolmakov, A., M. Moskovits and Y.X. Zhang. "Topotactic Thermal Oxidation of Sn Nanowires: Intermediate Suboxides and Core-Shell Metastable Structures" Nano Letters 3 (2003): 1125.
- Li, Q.G. and R.M. Penner. "Photoconductive Cadmium Sulfide Hemicylindrical Shell Nanowire Ensembles" Nano Letters 5 (2005): 1720.
- Melosh, N., A. Badolato, A. Boukai, F. Diana, B. Gerardot, J.R. Heath and P. Petroff. "Ultra-high density Nanowire Lattices and Circuits." Science 300 (2003): 112.
- Menke, E.J., Q. Li and R.M. Penner. "Bismuth Telluride (Bi_2Te_3) Nanowires Synthesized by Cyclic Electrodeposition/Stripping Coupled with Step Edge Decoration" Nano Letters 4 (2004): 2009.
- Penner, R.M. "Mesoscopic Particles and Wires by Electrodeposition" Journal of Physical Chemistry B 102 (2002): 3339.
- Prieto, A.L., R. Gronsky, M.S. Martin-Gonzalez, M.S. Sander, T. Sands and A.M. Stacy. "Electrodeposition of Ordered Bi_2Te_3 Nanowire Arrays." Journal of the American Chemical Society 123 (2001): 7160.
- Thompson, M.A., C.C. Martens, E.J. Menke, and R.M. Penner. "Shrinking Nanowires By Kinetically-Controlled Electrooxidation" Journal of Physical Chemistry B 110 (2006): 36.
- Walter, E.C., F. Favier, M. Grunze, G. Kaltenpoth, B.J. Murray and R.M. Penner. "Noble and Coinage Metal Nanowires By Electrochemical Step Edge Decoration" Journal of Physical Chemistry B 106 (2002): 11407.
- Zach, M.P., K.H. Ng and R.M. Penner. "Molybdenum Nanowires by Electrodeposition" Science 290 (2000): 2120.
- Zhang, Yong, G. Li, W. Song, Y. Wu, B. Zhang and L. Zhang. "Antimony Nanowire Arrays Fabricated by Pulsed Electrodeposition in Anodic Alumina Membranes" Advanced Materials 14 (2002) 14: 1227.