Fabrication of Single Nanowire Devices by Lithographic Electrochemical Step Edge Decoration

Background

Materials with dimensions below 100 nm, commonly called nanomaterials, are currently a hotbed of research throughout fields in science and engineering. One-dimensional nanomaterials, called nanowires, are simply wires of material with widths or radii below 100 nm. Nanowires are of interest for a broad range of applications including chemical sensors,[1] photodetectors[2], and thermoelectric generators.[3] Although the future applications are promising, it has proven extremely difficult to synthesize small nanowires and even more difficult to pattern them. Many in the physics and physical chemistry community are also interested in single nanowire measurements as opposed to measurements of nanowire arrays, since it simplifies the explanation of the behavior of the device and because theoretical predictions can be more easily realized. Single nanowire measurements are difficult since you have to first be able to place the nanowire on an insulating or semiconducting surface in a well-known location and then pattern a measurement device on top of it. The Penner group, in the last year, has developed a method to create nanowires from a potentially diverse range of materials and control the height, width, and patterning of the wires directly onto insulator surfaces for device applications. Although other methods have been developed to pattern nanowires[4-5], they often lack the ability to create single nanowire devices made from a variety of materials.

The new method builds on top of the previous method of growing nanowires in the Penner Lab called Electrochemical Step Edge Decoration (ESED). This method uses the natural crystal defects found on highly oriented pyrolytic graphite (HOPG) to electrochemically deposit nanowires of over twenty different materials. The long (up to 1 mm) arrays of nanowires have been used in a variety of applications, including chemical sensors and thermoelectric devices. The new method, dubbed Lithographic Electrochemical Step Edge Decoration (LESED), creates artificial, patterned step edges that metal nanowires can be electrodeposited on. The method has been painstakingly developed mostly through trial and error, and the bulk of this proposal is to further develop the method and attempt to create nanowires of two more materials, Cd metal and Ag metal. If this method becomes fully developed and a wide range of single nanowire devices can be created, it could have a tremendous effect on the current study of

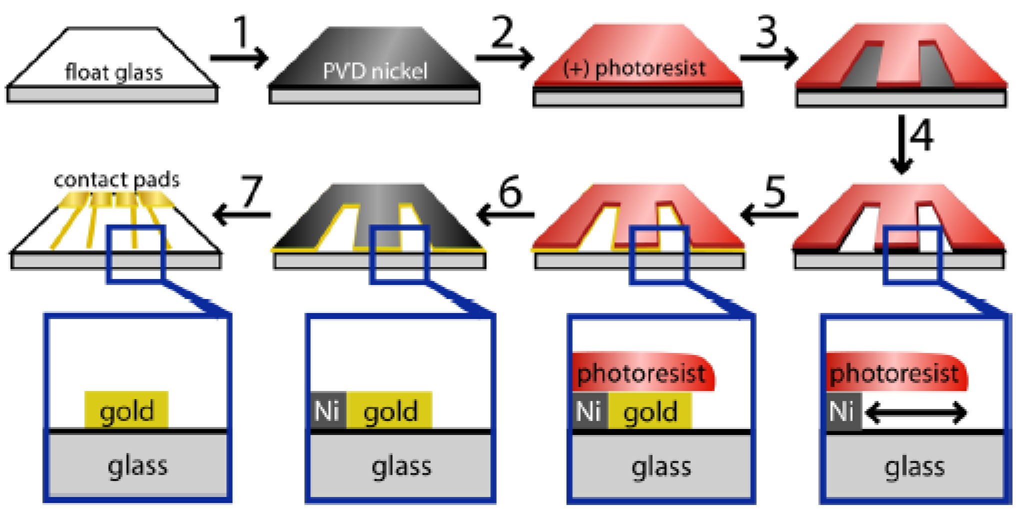

Figure 1: Schematic outlining the LESED process for creating patterned nanowires on an insulating surface.

nanowires.

The entire LESED method is outlined in figure 1. In LESED the step edges are prepared by lithographic patterning of nickel on a glass surface. First, a nickel surface that is 10-100 nm thick is evaporated onto a rigorously clean glass slide using physical vapor deposition. Next standard lithographic procedures are used to pattern a photoresist layer on top of the nickel. The entire assembly is then placed into an acidic solution containing supporting electrolyte, and the nickel that is not covered by photoresist and exposed to the solution is dissolved electrochemically. This etching process leaves behind a thin nickel edge covered with a photoresist overhang. The next step, also the simplest step, is the electrodeposition of the desired nanowire material onto the nickel step edge. After that, the nickel supporting the wire is removed with a dilute nitric acid solution. The key factor in this process is that the deposited wire is confined to the nickel step that was created. The height of the nickel step edge can be accurately controlled by the evaporation of the nickel onto the glass. The overhang of the photoresist, referred to as the "undercutting", is controlled precisely by the nickel etching time. The longer the etching time, the wider the undercut will be. In figure 2 there are some examples of palladium nanowires grown by this method. The undercutting section of the wire width can be seen in long growth times next to the "blooming" section of the wire that occurs when the wire grows past the undercutting of the photoresist. These wires can be as narrow as 40 nanometers and can easily be as long as 1 cm. Atomic force microscopy measurements have confirmed the vertical confinement of the wires underneath the photoresist undercutting. The method has also been successful with MoO_2, Pt and Au wires as well.

Objectives:

The goal of this summer's research is to grow a variety of nanowire materials using the LESED method. Two very important materials that will be the target of this summer's research will be silver and cadmium. Silver nanowires can be made into single nanowire ammonia sensors, while cadmium wires could be converted into photoluminescent cadmium sulfide nanowires for single nanowire optical devices. Cadmium sulfide is a II-VI semiconductor with a band gap that also makes it useful for solar cells in addition to sensors and light emitting diodes. Both materials, especially cadmium sulfide, are currently the focus of considerable research in the field and single nanowire devices are often difficult or near impossible to realize with other

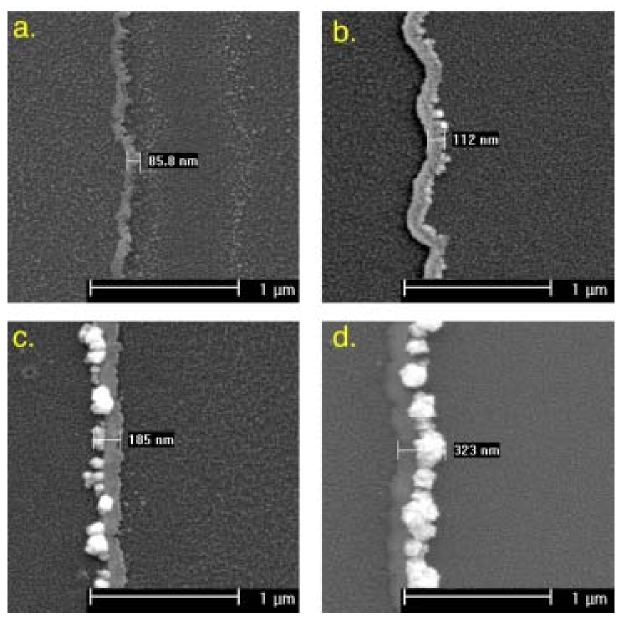

Figure 2: Scanning electron micrographs of palladium nanowires grown on glass. Wires were electrodeposited on the Ni step for a) 25 s b) 50 s c) 100 s and d) 200 s. Note that the wire is flat on one side where the growth is occurring underneath the photoresist overhang, while at longer times the wire appears to "bloom" on one side where it is no longer confined by the resist layer.

methods. Silver will be attempted first since it is closer chemically to the other materials that have been grown using LESED, and then cadmium, which presents some unique challenges as discussed in the research plan, will be grown next. Ten weeks should be enough time to characterize the growth of silver, the evaluation of ammonia sensing by the wires, and the growth and characterization of cadmium nanowires, but this research project could easily be extended into the next year. In addition to making nanowires of these two materials, the proposed research plan will further develop this method, which has the potential to produce single nanowires of many more materials.

Research Plan:

First the noble metal family of nanowires that have already been grown will be extended by growing silver nanowires. I have already completely characterized the growth of platinum nanowires using the LESED method and thus I can start growing silver right away since I am already familiar with the method. Silver nanowires are interesting since they can be used as single wire ammonia sensors[6-7]. Much of the research in the Penner group is devoted to nanowire chemical sensors. There was a hypothesis proposed that attributed the chemical sensing ability of the silver nanowires to interparticle oxide defects called chemically reactive interparticle boundaries (CRIBs). Before the advent of LESED, the sensors were made from arrays of hundreds of wires, which make it difficult to spot single CRIBs. Single nanowires of silver would be perfect subjects to test the theory since it easy to look at and test a single wire for these oxide defects. First, a suitable deposition potential for the deposition of silver wires will be found. This should take about a week. Next the wires will be grown for a variety of deposition times and their widths will be characterized by scanning electron microscopy. A growth time dependence of the widths of the wires will be found. After SEM characterization, nanowires of different heights will be grown by varying the thickness of the nickel step edge and these heights will be measured by atomic force microscopy. Once the nanowires are characterized, they will be placed in the gas sensing apparatus built by graduate students in the Penner lab, and the resistance modulation in response to ammonia gas exposure will be probed. This is a routine procedure in the Penner lab. If CRIBs are present in the wire, then there should be a massive, reversible resistance change (>50%) due to the chemisorption of ammonia on the oxide boundaries. It is possible that the resistance change of a single CRIBs containing silver nanowire could have an even larger, faster resistance change than an array of hundreds of silver nanowires, some with CRIBs and some without.

After silver is grown, cadmium will be the next target material since it can be readily converted into cadmium sulfide by annealing with H_2S in a tube furnace and the resultant wires can be used as single nanowire optical switches and photodetectors[8-10]. Cadmium will be grown and characterized in exactly the same manner as listed above for silver. The Penner lab is setup to quickly assess the photoluminescent properties of the nanowires and the spectroscopy will be considerably easier than the growth of the nanowires. After the nanowires are characterized the nanowire size dependence on the photoluminescence will be explored. Since the height, width, and length of a single nanowire can be controlled with LESED, the effect of all of these parameters can be seen. Some of the problems anticipated in growing the cadmium sulfide nanowires include the deformation of the glass surface during annealing and difficulty in stripping nickel without stripping cadmium. If these problems arise then alternative insulators, such as mica, can be used instead of glass. Also, a different metal other than nickel could be used as the step edge material. A goal is to use a metal with a similar reduction potential to the metal being deposited. This summer the research should only go as far as characterization of the growth of cadmium wires, but CdS could be synthesized and characterized in the fall.

Since this method is so new, it is impossible to accurately predict progress. Hopefully, the progress with cadmium will be made at the same rate as the other materials that have been deposited with this method. This method is fantastically time-consuming. To make suitable progress, at least 50 hours per week must be spent preparing nanowires, not even including characterization. It takes 10 hours just to make a few samples. Perhaps one of the goals of the summer should be to reduce the amount of preparation time in making these wires! With the help of a SURP fellowship, I am confident that great strides can be made not only for research in the Penner group, but also for the nanoscience community as a whole.

Timeline

Weeks	Task
1-3	Growth and SEM characterization of silver nanowires
4	AFM characterization of silver nanowire heights
5-7	Make and test single silver nanowire ammonia sensors
8-10	Growth and SEM characterization of cadmium nanowires
Fall Quarter	Creation of cadmium sulfide single nanowire devices.

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