Remote Access Laboratory Guide

Electrodeposition of Nickel Nanowires

In this exercise, you will:

- Understand the process of electroplating and its use at the nanoscale.
- Describe the function of a template as it applies to electrodeposition.
- Construct an apparatus for electrodepositing metal into a nanoscale template.

Background

Electrodeposition is a bottom-up manufacturing technique in which positively charged metal ions in solution are reduced (electrons added) at a surface. Electrodeposition occurs onto an electrode, which is a conductive surface that can pass electrons into the solution. The metal atoms form a metal film that grows in thickness as more ions from solution reach the electrode and are reduced. If a template, such as a pre-formed porous pattern, covers the electrode, then the growing metal film will fill in the template structure and take on its shape. The growth of nano-wires in column-like pores is illustrated schematically below in Figure 1.

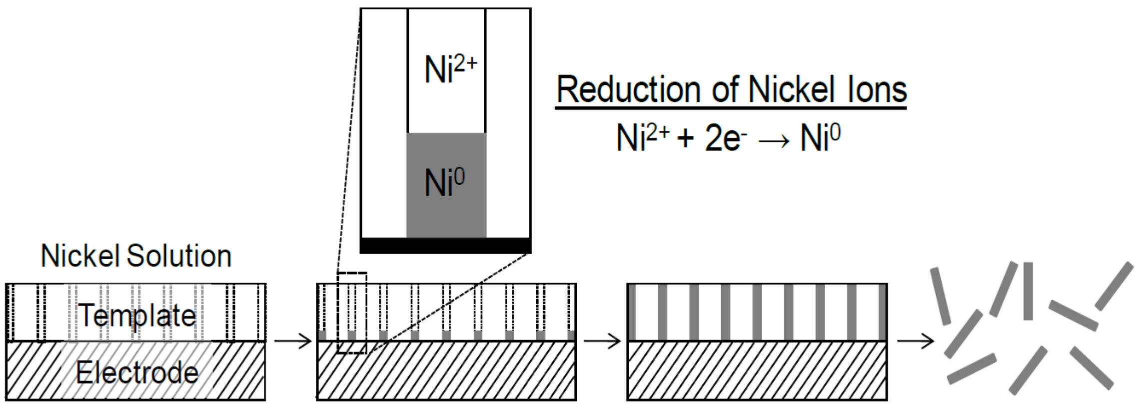

Figure 1: The growth of nickel nanowires, via a template.

Background

In this lab an alumina membrane filter, commonly used in chemistry for separation, will serve as your growth template. Figure 2 below are a few images of an alumina template taken with the FESEM in which you can see the growth path of the metal deposition that form the nanowires will have, see arrow in middle image. Another key point to note is the small pore openings at the back (bottom) of the templates. It will be critically important for the experiment to identify the back of template which has the smaller openings. You will grow nickel nanowires and examine them under Field Emission Scanning Electron Microscope or FE-SEM. A group of scientists who work in this field will help you determine the width and length of the nanowires via an internet connection.

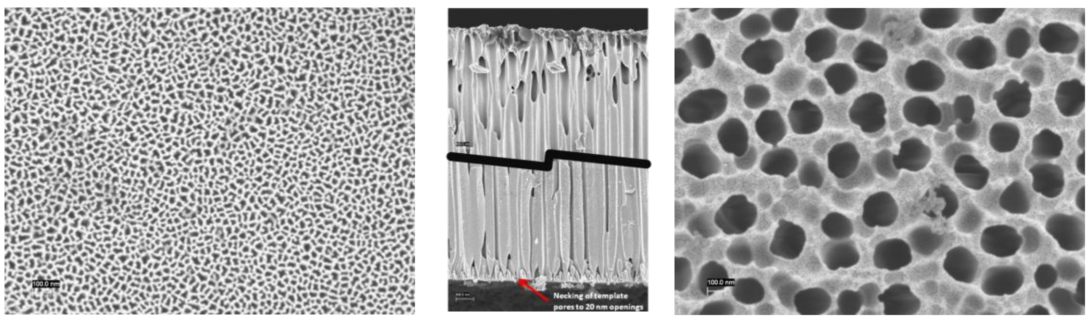

Figure 2: FESEM images of the alumina template from three different views: far left is of the back side at 50k mag., far right is of the top side also at 50k mag., and middle is a split cross-section of the template. The cross-sectional view shows the small, ~20 nm, pores at the bottom and the ~150 nm pore openings at the top. Also, ignoring the break-line, the pores channels can be seen running vertically through the template.

Background

For this lab exercise, you will need the following:

- Whatman Anodisc alumina filters 25mm with polypropylene support rings and 0.02 micrometer pores (#09-926-34 can be obtained from here or #28138-067 can be obtained from here).
- GaIn Eutectic (49542-5 can be obtained from here) .
- Ni wire (#AA41361-G6 can be obtained from here. Nickel is an irritant and carcinogen, try to avoid contact)
- Watts Nickel plating solution: $NiSO_4.6H_2O$, 45 g/L H_3BO_3 and 45 g/L $NiCl_2.6H_2O$
- Tweezers, cotton swabs, water wash bottle, beaker
- Nitric acid concentration & 6 M Sodium Hydroxide (NaOH) solution & Isopropanol
- Thick satin finish copper sheet (#9801K11 can be obatined from here).
- O-ring (#9452K32 can be obtained from here. Note: Should have the same diameter with the used 1" syringe!)
- 30 mL plastic syringes (66064-760 can be obtained from here). Use a saw to cut the syringe at the 15 mL mark and cut the plunger at the support closest to the end.
- AA Battery holder (can be obatined from here).
- Strong magnet & 1-1/4" binder clips & AA battery & Wooden support blocks
- Wires with alligator clips (can be obtained from here).
- Shipping Supplies

Procedure

Throughout the procedure MRSEC's video will be followed. The video can be reached at: https://www.youtube.com/watch?v=B_Ui21P3kw8#t=434. Please watch the video very carefully to build the circuit for electroplating . Steps shown in the video will be synchronized with the steps shown below.

I. Obtain the Anodisc filter. Remove the disc from the packaging using a tweezer, remembering which side was up in the box.

II. Coat one side of a nano-porous template with a conductive material, which will serve as the electrode. This can be done either by painting GaIn alloy onto one side of the template.

III. Note: Step 3 is given as an additional step in the video. However, it should not be misleading. Alternative to GaIn alloy painting, coating can also be handled by sputtering a silver film onto one side of the template. Be sure to coat the proper side of the template. Both of these methods (steps 2 and 3) will cap the 20 nm pore openings and leave the rest of the channel open to receive nickel in the electrodeposition step.

IV. Assemble a water-tight container that holds the templated electrode in contact with a nickel sulfate solution. One possible way is shown in the video by a) placing a cupper electrode on a stand b) putting the template on the cupper electrode c) placing an o-ring on the disc and d) standing the cut-off syringe barrel on the o-ring. Make sure the metal coated side (step#1) of the template is in contact with the copper plates to complete the negative portion of the electrical circuit.

Procedure

V. Firmly hold the barrel in place while securing opposite sides of the barrel with binder clamps. Look down the barrel of the syringe to make sure it is centered over the o-ring. This should prevent liquid leakage (nickel sulfate solution) from the container.

VI. Use a battery to apply a voltage between the templated electrode and the solid Ni counter electrode, which is suspended inside the nickel solution. Note that the nickel atoms in solution are partially oxidized. They exist as Ni^{2+} ions that are soluble in water. This causes ions near the electrode surface to be reduced from Ni^{+2} to Ni^{0}. To accomplish this, electrons must be transferred from the electrode to the Ni^{2+}. Two electrons are required for each atom of nickel that deposits into the template.

VII. After 20-30 minutes of electroplating, the nickel film will have mostly filled the nanopores in the template. Plating is stopped by removing the voltage. Pour the nickel solution back to its container and rinse the barrel with water.

VIII. Remove the disc from the circuitry, put the disc on a glass slide with metallic side (shiny side) facing up.

IX. Wash the template with nitric acid solution for 5 mins using the cotton applicator to remove the shiny GaIn or Ag coating. Make sure that you do not start dissolving Ni.

X. Have a DI water bath standing by to stop the reaction.

XI. Thoroughly rinse the template with DI water and then use 5 mL 6 M sodium hydroxide (NaOH) solution for 10 mins. The NaOH dissolves the alumina template, but not the nickel wires.

Procedure

XII. Nickel is a magnetic material, so the behavior of the nano-wire suspension can be observed in the presence of a magnetic field. After rinsing, the nano-wires are dispersible in water. A magnet can be used to gather the nanowires onto the bottom of a beaker. Then, they can be rinsed without losing them in solution. Thoroughly rinse the resulting cluster of nanowires with DI water, and then decant the water away. Repeat this DI water rinse three times total. Suspend the Ni nanowires in isopropanol and transfer to a small container. The isopropanol is a volatile compound that will evaporate quickly when the Ni nanowires are transferred to a substrate for characterization. Use a minimal amount (~5 mL) of solvent in this step. There is no need to send us samples for this experiment. We already have samples pre-made and ready to go. However, if you have additional samples or special requirements, we are willing to assist you in obtaining whatever images and data you require.

Video ends here, next steps involve measurements and observations that can be carried out either at your classroom or remotely using FE-SEM with the help of our scientists.

Procedure

XIII. Perform Characterization in your classroom

- Nickel is a magnetic element. The magnetic properties of the nanowires can be visualized in your classroom. For example, observe the reaction of the nanowires when a magnet is brought close to a vial containing the nickel nanowires dispersed in a solvent. Alternatively, a drop of the nanowire-solvent mixture can be placed on a microscope slide and covered by a cover slip. Place the sample under an optical microscope and observe what happens in the presence of a magnet (e.g., spin the magnet alongside the microscope stage).

XIV. Perform Remote FE-SEM Analysis

- The FE-SEM is used to visualize and measure nano-scale objects. The nanowires produced by the procedure outlined above are typically 200 nm in diameter and microns long. The visible objects dispersed in solution are generally aggregates that are made up of bundles of many individual nanowires. Samples for FE-SEM can be prepared by drop-casting onto a suitable substrate. Evaporation of the solvent leaves behind nano-wires which can be physically and chemically characterized with the FE-SEM. An example is shown in Figure 3 at the top of the next page.

Procedure

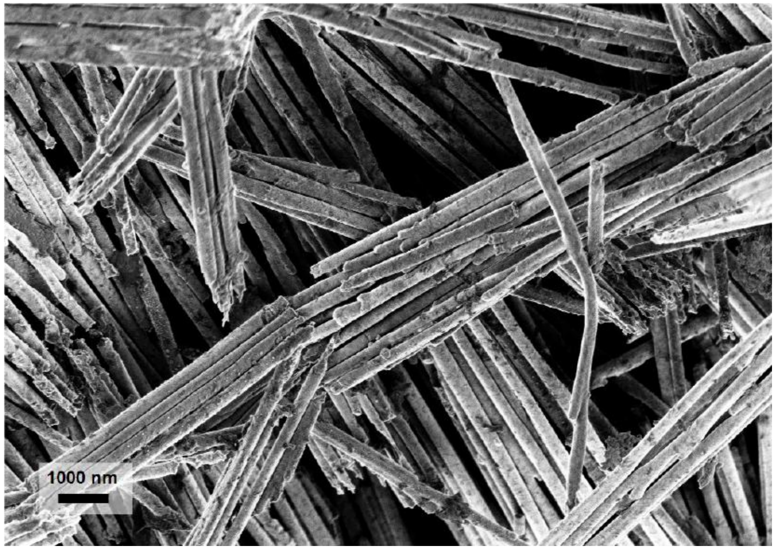

Figure 3: An FE-SEM image of nickel nanowires.

Additional Activity (optional)

- You can prepare samples that were electrodeposited for various times (e.g., 15, 20, 25, 30, 35, 40 minutes). In such a case send samples to Remote Access centers for measurement in the FE-SEM. Then, construct a graph of nano-wire length versus time. Determine the rate of electrodeposition from the slope of the graph. Once you ship the samples to Remote Access centers, we will prepare the samples for characterization. The mailing address and contact info can be found in our web site: http://nano4me.org/

Remote Access Connection Instructions

What makes these labs different and unique from other classroom experiments is that we have incorporated a section in each activity to remotely characterize your nanoscale samples from your classroom. Remote access to a variety of characterization tools can enhance the visualization of nano-related concepts by allowing students to see the effects of their work first hand. You can choose to mail your samples to our facility to be analyzed at a later date or you can use our samples that have been processed using the same procedure. Please use the following steps to successfully complete a remote session.

I. Request a remote lab session specifying pertinent information such as: the day, the time, and the instrument you are interested in using by visiting our web site http://nano4me.org/ Go to the *Educator's* tab and select the *Remote Access* tab in that section. You will see the list of partners with the instruments provided to chose from.

II. You will be contacted by a Remote Access staff member to set up a test run to ensure you are set up properly and have the required infrastructure.

III. Send samples or verify the in-house sample you would like us to prepare and load for characterization. Send your samples to the Remote Access center that you chose on your request.

IV. There are two communications soft-ware packages, that will allow us to communicate instructions and answer questions during the session.

    I. Zoom: You can obtain a free download at: https://www.zoom.us/

    II. TeamViewer: You can obtain a free download at: https://www.teamviewer.com/en/index.aspx

Remote Access Connection Instructions

V. You will need:

a) Computer with administrator access to install plug-ins and software

b) An internet connection

c) Speakers

d) Microphone

e) Projector connected to the same computer

f) Web browser (Firefox preferred)

VI. During the test run you can refer to this guide to perform the following steps, but it's very important that you only proceed with these steps during your scheduled times. You may interfere with other remote sessions and potentially damage equipment if you log in at other times.

a) Open and logon to your Zoom/Team-viewer account. You will be given the access code to enter at the time of your test and then again during the remote session.

- If you are using the Zoom software, Remote Access staff will give you the access code.
- If you are using the Team-viewer software, Remote Access staff will give you the ID & password.

b) You should soon see the Remote Access desktop and at this point you can interact with the icons on the screen as if it were your desktop.

c) Switch to full screen mode by selecting the maximize screen option in the top right corner of the screen.

d) Upon completion of the session, move your mouse to the top right corner of the screen, and click on the X to disconnect the remote session. It will ask if you want to end the remote session. Click Yes.

References and Supplemental Material

- For this lab, you will replicate the procedure which is posted on the University of Wisconsin's MRSEC website: http://education.mrsec.wisc.edu/288.htm. Please visit the website and review the procedure. The website also contains video clips which demonstrate each step.

The Nanotechnology Applications and Career Knowledge (NACK) Center was established at the Penn State College of Engineering in September 2008 through the National Science Foundation (NSF) Advanced Technological Education program.

Please contact a NACK representative today to assist you in increasing the awareness of nanotechnology and education related opportunities across the nation. Visit our website for an expanded contact list.

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National Center

Building College-University Partnerships for Nanotechnology Workforce Development

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