Teacher's Preparatory Guide

Exploring Factors Effecting Deposition, Morphology, and Thickness of Thin Metallic Layer of Copper

Purpose: Students will create thin layers of copper and nickel in an electrochemical reaction to understand how an electric current passed through an ionic solution will result in a chemical reaction which will separate materials. In addition students will also explore the various parameters effecting deposition, morphology, and thickness of the film to be deposited.

Time Required:
Two 90 minute class periods

Level: High School (preferably successfully completed Algebra)

Teacher Background:

Nanotechnology is an interdisciplinary field where science and engineering intersect. It is a rapidly growing field in which scientists and engineers work with atoms and molecules to create new devices and materials. At the nanoscale, many materials behave differently which allows for the development of these new devices and materials. Nanotechnology has continued to produce many astounding technological innovations. It holds a near limitless potential for applications in all branches of science and everyday life.

Depositing of thin film layers is a particular facet of nanotechnology that holds provocative applications in several disciplines of science that could benefit mankind. Thin films consist of a layer of material ranging from a few nanometers to several micrometers in depth. Because it is both possible to deposit organic and inorganic thin film compounds biological sciences stand to benefit from thin film technologies as well. In particular, thin film technologies hold possible breakthroughs in solar cells, fuel cells, and even DNA identification technologies.

This laboratory will focus on identifying the factors that affect the surface morphology and thickness of a thin film layer of copper. Different surface structures on thin film layers could imbue the film with positive or negative attributes depending on their shape.

Electroplating will be the method of deposition in this laboratory experiment. This process is analogous to the method by which car rims and jewelry are made. "Electroplating is the process of using electric potential to transfer electrons (at the nanoscale) and deposit a layer of material onto a desired substrate. Acidity of the solution and duration and strength of voltage will be investigated to demonstrate changes in substrate deposition.

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Materials Per Group

- Balance
- Metal Shears
- Drying Oven or heat lamp
- AA Battery
- Ruler
- Acetone
- Copper wire (3 lengths)
- Alligator Clips
- (2) 500mL beakers
- 1 glass stirring rod
- Magnetic Sir Bar & Stirrer
- 100 mL graduated cylinder
- Forceps
- Toothpicks
- Copper II Sulfate (Anhydrous)
- 10% Nitric Acid
- Hammer
- Cu foil (2) 3x5cm
- Nail Polish (Red)
- Connecting Electrical wires
- 1 large watch glass
- 16 oz soft drink bottles
- Microscope
- Spatula
- Voltmeter
- Voltmeter
- dH20 Squirt bottle
- Nickel Foil
- Sulfuric Acid

Advance Preparation: All preparation methods are calculated for a class of 30 students separated into groups of three.

Nitric Acid Preparation (Cleaning Solution)

1. Nitric acid will serve as the cleaning solution for the copper to be plated as well as the electrodes. It should also be explained to students that because nitric acid is a strong oxidizing agent, it is useful in cleaning metals.
2. In a fume hood, prepare 300 mL of 10% HNO_3 by placing 30 mL of concentrated nitric acid in 270 mL of distilled H_2O.
3. Place in a container and label 10% HNO_3.

H_2SO_4 Preparation

1. The sulfuric acid will be incorporated into the copper (II) sulfate solution to facilitate ion transfer.
2. In a fume hood, prepare 300mL of 10% H_2SO_4 by placing 30mL of concentrated nitric acid in 270 mL of distilled H_20.
3. Place in a container and label H_2SO_4.

$CuSO_4$ Preparation

1. Prepare 1.5 L of .1M solution of $CuSO_4$ (anhydrous)
2. In a 500mL beaker place 23.94 grams of $CuSO_4$, then fill with 300mL of distilled H_20.

3. If a magnetic stirrer is available leave the mixture to stir until it is fully homogenous. The solution can also be carefully stirred with a stirring rod if a magnetic stirrer is not available.
4. To this solution, add 20mL of concentrated sulfuric acid to facilitate electron transfer.
5. Place in container and label $CuSO_4$ (anhydrous).

Copper & Nickel Foil

1. Using metal shears, cut 20 strips of copper foil approximately 5 cm in length and 3 cm in width.
2. Smooth out the copper foil by firmly rubbing the head of a hammer along the surface of the copper foil until it becomes smooth. See Figure 1.
3. Be mindful that the force of the hammer is distributed evenly along the entire surface area of the copper foil, to insure a uniform thickness of the foil.
4. Set strips aside.
5. Next, cut 10 strips of nickel foil, 3.5cm X 4 cm and repeat steps 2-4.
6. Cut the nickel strips so that they are now .7cm X 4cm. 5 strips of nickel foil should be derived from the original cut.

Figure 1: Copper Foil

Copper Wire

1. Cut a total of 30 pieces of medium gauge copper wire, each 8 cm in length. The wire should be the thickness of a pencil lead.
2. Set strips aside for cleaning and use in experiment.

Electrochemical Cell

1) Take a 16 oz soft drink bottle and mark off 6 cm from the bottom with a marker around the circumference of the bottle.
2. Make an incision into the bottle with a razor blade or box cutter along a section of the line large enough to insert the tip of a pair of scissors.
3. Cut with scissors along the line made in step number one trying to maintain as smooth a cut as possible.
4. See figure 2 for an example of the cut soda bottle.
5. After the bottle has been cut, it is now time to create holes throw which the electrode wires must rest. This can be done by using a nail a little larger in diameter than the copper electrode post.
6. Two holes need to be made through the center line at opposite ends of the bottle, just below the top line. Another set of opposite holes need to be made approximately three centimeters to the left and to the right of the center line. A total of 6 holes should be punched in all.
7. With a permanent marker, write W.E. (working electrode) below the center pole post, and CE1 and CE2 (counter electrode 1 and 2) on the outer holes.

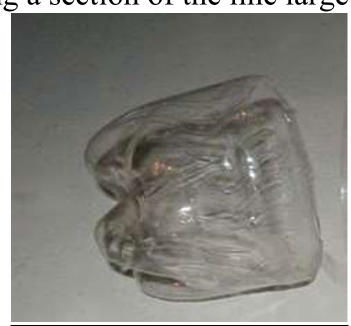

Figure 2: Electrochemical Cell

Safety Information: Have the proper Materials Safety Data Sheets (MSDS) for each chemical and follow your school's laboratory safety procedures for working with chemicals and electrical devices. MSDS sheets can be accessed at:

http://fscimage.fishersci.com/msds/16550.htm
http://www.jtbaker.com/msds/englishhtml/C5918.htm

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Directions for the Activity

1. In preparation for the activity, have students separate into groups of three. The concept of electrolysis should have already been discussed in a previous class session. If electrolysis is not covered in your text, information can be found at:
   http://en.wikipedia.org/wiki/Electrolysis
   http://science.howstuffworks.com/electrolysis-info.htm
   Discuss with students what is nanotechnology and the importance of thin films to this emergent field.

2. Have students discuss electrolysis process and instruct them to write down as a group two items of information they understand and one item they did not understand concerning electrolysis and electroplating.
   a. Be sure the following are discussed:
      i. What are similarities and differences of electrolysis and electroplating?
      Electrolysis is merely a chemical reaction such as the decomposition of water induced by electric current
      Electroplating is the deposition of a material onto a substrate through the use of electric current

      ii. How is nanotechnology related to electrodeposition?
      Nanotechnology often involves depositing thin layers of material to carry out certain processes.

      iii. Faraday's Law related to electrolysis?
      The mass of substance deposited at an electrode is proportional to the quantity of the electricity transported to the electrode

      iv. What factors affect the deposition morphology during electroplating?
      Current, surface area, acidity

      v. What are some of the new technologies that may come about as a result of thin film electroplating?
      Fuel cell, solar power, biosensors

      vi. List the names and function of equipment used in the electroplating process.
      Working electrode- site where deposit occurs
      Counter electrode- site which provides ions for deposition
      Electrolysis cell- apparatus which provides chamber for electrodeposition to occur
      Potentiostat- a device which **keeps potential constant across working electrode**

   b. As an alternative these questions could be prewritten and randomly assigned to individual groups by having them choose the prewritten questions out of a box. Subsequent discussion of group responses can take place. Student led discussion is preferred. However, the instructor will be responsible for smooth facilitation.

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3. Instruct each group to choose one spokesperson for the group who will also serve as the group leader for the laboratory experiment and whose role will be to bring group questions to the instructor.
4. Assign each group a particular parameter to test. Intermittent exposure to voltage source, acidity, time will be examined. One group must serve as the reference group.
5. Have each group go through the list of questions compiled from the pre-lab collaboration with the teacher facilitating class discussion.
6. Once the discussion is complete, the instructor will issue the student activity sheets and instruct the class to read the procedure silently to themselves, following which a group discussion of the material will take place.
7. At this time the instructor may want to give a safety briefing for the laboratory, ensuring students know what to do in the event of any contamination during the experiment. Also, appropriate waste disposal methods should also be discussed.
8. After group discussion of the experiment has taken place, instruct students that they are to secure the materials they need for the experiment, after which they may begin the experiment.
9. The instructor's role at this point is that of astute observer, taking note of group collective thought, interaction, and execution. Questions should only be taken from the representative group leaders from each group.
10. Any student caught not wearing gloves or goggles should not be allowed to participate in the laboratory session, as there are strong acids involved in this laboratory. In addition, any student not in proper laboratory attire should also not be allowed to participate in the laboratory exercise.
11. Once the initial layer of copper sulfate is deposited, instruct the group to dry the plated sample, and dispose of excess copper sulfate solution in the designated container.
12. Next, have the groups calculate the approximate thickness of the layer deposited according to their procedure section. Have them report their answers in nanometers, micrometers, and meters.
13. Once step I is completed the group may work on subsequent calculations after which, the group can begin planning for part II of the experiment.

Procedure (from Student Activity Guide)

Cu Foil and Electrode Preparation (wear protective gloves and safety glasses)

1. Obtain two pieces of copper foil and 1 piece of nickel foil from the designated area. Measure the length and width of the copper foil in centimeters and record in the table provided.
2. Determine the density of copper using your desired research method and record in the designated table.
3. Smooth out the foils with a hammer as demonstrated by the instructor.
4. Using forceps, you will clean the copper foil using a solution of nitric acid. Set solution aside for later use.
5. Pipette the nitric acid solution into a large watch glass 1 inch from the outer boundary.
6. Holding the foil firmly with the forceps, submerge the foil into the nitric acid and gently agitate the foil in the solution until it appears to be lustrous.
7. Clean each of the foil pieces in this manner.
8. Using a distilled water squirt bottle, hold the foil over your water rinse beaker and liberally rinse the foil completely.
9. Set aside the foil on clean paper towel, and blot dry. The foil must not be touched with bare hands once cleaning is completed

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10. Using toothpick and nail polish, label one copper foil piece "CE1"(counter electrode 1) and the other, "CE2" (counter electrode 2) respectively.
11. Record the mass of each of the foil pieces and label in the appropriate table.
12. Obtain 3 lengths of copper wire that will serve as electrode posts and clean with the nitric acid in the watch glass.
13. Hang the copper foil on the copper wire post by carefully bending the outer long edge boundary of the foil along the electrode post. Try to expose as much of the foil surface as possible.
14. Check to be sure that the foil is firmly contacted to the electrode post to ensure proper connection. Ask instructor if unsure of connection between the copper foil and post.
15. Next, take the remaining nickel foil and bend the short edge around the remaining electrode post so that as much of foil is exposed as possible.

Electrolysis Cell

Figure 3: Electrodeposition Chamber

1. Obtain the electrode chamber and rinse thoroughly with distilled water. Dry thoroughly with a paper towel.
2. Place the ends of the foil electrode posts through the appropriate holes in the electrode chamber in a way that the foil surface area exposed is maximized.
3. Check to be certain the setup is stable. See Figure 3.
4. Next, transfer approximately 130mL of copper (II) sulfate solution and carefully pour into the electrode chamber. Fill to just below the holes punched.
5. It is imperative that the electrode post remain dry.

Battery, Connections, Exploration

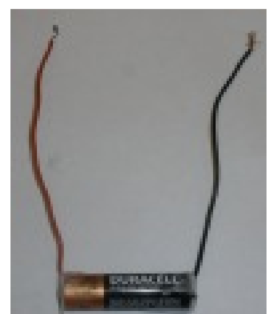

Figure 4. Battery

1. Obtain a AA battery and two insulated wires. With electrical tape, secure one wire to the positive terminal, and the other wire to the negative terminal. Set aside for later use. See Figure 4.
2. Using a wire with alligator clips secure it to one end of the working electrode post (center post) and connect the other end to the negative terminal wire on the battery.
3. Decide what parameters the group as a whole will test and perform the necessary steps to implement the test. All groups should have five strips on nickel foil in which either voltage, acidity, or time will be tested. One strip will serve as the control.
4. Label the strips with nail polish according to the parameter tested.
5. Due to the limited availability of nickel strips and time constraints, students should only conduct five test with the five nickel strips which they have.

Voltage Parameter

1. In this test, the experimenter will cyclically alter the voltage exposure duration of the nickel substrate to examine the affects of the copper deposition.
2. As an example, the experimenter might choose to start with a five second voltage exposure with a one second pause, or the experimenter might start with a one second voltage exposure or a five second pause.

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3. It is up to the individual group to decide in what way the parameter will be tested. The only stipulation is that the voltage must be tested in such a way that leads to a clear relationship between cyclic duration and copper film deposit thickness.

Acid Concentration

1. In this test, the experimenter will alter the concentration of sulfuric acid in the $CuSO_4$ solution.
2. Again, it is up to the individual group to decide the manner in which the acid concentration will be altered to gain a clear picture of its effect on the deposition of copper.

Time Parameter

1. In this test, the experimenter will alter the time the electro-deposition is allowed to take place.
2. Again, it is up to the group to decide the appropriate times to test.

The Reaction

1. Once the parameters to be tested are known, secure a split wire and connect the split wires to both electrode posts on opposite sides of the foil post. Connect it to the positive end of the battery.
2. Record the time that the reaction began, and allow to run for 2 minutes (except those groups testing time)

Copper Foil Processing

1. After the reaction has run for 2 minutes, disconnect the battery terminal wires to stop the reaction.
2. Carefully remove the nickel foil from the electrode chamber.
3. Remove the foil from the electrode post by sliding the copper wire away from the foil.
4. Rinse the nickel foil gently with distilled water.
5. Place the nickel foil in a clean beaker and dry for 10 minutes under a heat lamp or in a drying oven.
6. Once the foil is completely, dry obtain the mass of the foil sample and record in the appropriate table.
7. Repeat this process with the four remaining strips.

Microscopic observations

1. Describe the overall appearance of the deposited film, and make detailed notes of your observations.
2. Compare and contrast the surface of the plated copper to the other parameters tested.
3. Save a picture of your deposited layer using the computer connection to the microscope (if available).
4. How might a scanning electron microscope (SEM) allow one to study the sample in more detail.

   The SEM is a more powerful tool which has greater magnification possibilities. It would allow for a higher resolution and to see much smaller details of the deposition than that possible with an optical microscope.

Cleanup:

1. Any discarded nitric acid should be placed in the designated acid disposal container.
2. Acetone rinse should not be placed in the sink but in a bottle designated for organic waste disposal.
3. Excess copper sulfate solution should be placed into a container designated for inorganic waste disposal.
4. Copper wire electrodes not used up in the reaction should be cleaned in nitric acid, rinsed with distilled water, and placed in a beaker to dry. These may be used for future experiments.

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Data

I. Nickel Foil

Length(cm)	**Width**(cm)	**Height**cm (before)	**Height**cm(after)	**Volume**(cm^3)	**Mass** before	**Mass**after	**Density**(g/cm3)

	Mass C1	**Mass C2**
Cu Foil massbefore		
Cu Foil massafter		

II. Voltage Parameter

Voltage Cycle	**Height of Deposit** (μm)

III. Voltage Interval

Application Time	**Height of Deposit** (μm)

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IV. Exposure Time

Time of Exposure	Height of Deposit (μm)

V. Acidity of Solution

Acid Concentration	Thickness of Deposit (μm)

IV. Determining Thin Film Thickness

1. The height of the film will be equal to the difference in thickness (height)of the copper foil before and after the reaction.
2. The volume and density equations will be used in tandem to determine the thickness (height) of the foil post reaction.

Calculations

Height Before Reaction __.0046cm_ **mass nickel before = __.62g____**

V_{foil}= l * w * h **D=m/v**

l= 5 cm w = 3 cm

V_{foil}= mass/$Denisty_{copper}$

h= V_{foil}/l*w **mass=.62g $Density_{copper}$= 8.956 g/cm^3**

h= .06292cm3/5cm*3cm **V_{foil} = .62g/8.956 g/cm^3 = .0692 cm3**

h= .0046cm

Height After Reaction .0067cm **mass nickel after= ___.9g____**

V_{foil}= l * w * h **D=m/v**

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l= 5 cm w = 3 cm

V_{foil}= mass/Denisty$_{nickel}$

h= V_{foil}/l*w

mass=.9g   Density$_{nickel}$= 8.956 g/cm^3

h= .1005cm3/5cm*3cm

V_{foil} = .9g/8.956 g/cm^3 = .1005 cm3

h= .0067cm

Height of Thin Film= Height After Rxn – Height Before Rxn

= .0067 cm - .0046 cm

= .0021 cm, 21micrometers

Analyze the Results:

1. Did you observe what you predicted? If not, how did your observation differ from your prediction?

   Answers will vary by group

2. What technologies do thin films stand to revolutionize?

   DNA identification, solar power, fuel cell technology

2. Which electrode served as the cathode in the electrolysis chamber?

   Copper foil post

3. Which electrode served as the anode in the electrolysis chamber?

   Nickel foil

4. Why might intermittent voltage affect deposition thickness and morphology?

   A constant current may cause the copper to be deposited very quickly where as an intermittent voltage exposure may allow more time for deposition to take place

5. Why might solution acidity affect deposition thickness and morphology?

   An acidic solution has more electrons readily available to facilitate the reaction taking place within the chamber

6. How might the use of a scanning electron microscope (SEM) improve the analysis of the deposited copper film?

   SEM have a very high resolution within a few nanometers, this allows researchers to focus on clusters of atom to better analyze surface morphologies.

Assessment

The calculations derived will serve as the primary assessment tool. Students will be required to write a lab report summarizing their work, hypotheses, and results. The reports will be evaluated based upon a lab rubric.

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Resources:
To learn more about nanotechnology, here are some web sites with educational resources:

American Elements
http://www.americanelements.com/nanotech.htm
National Institute of Health
http://www.becon.nih.gov/nano.htm
Nanowerk (Collection of Nanotechnology Articles)
http://www.nanowerk.com/phpscripts/n_spotlight.php
National Nanotechnology Infrastructure Network
http://www.nnin.org/

National Science Education Standards

High School Content Standards

- Standard A
  - Identify questions and concepts that guide scientific investigations
  - Understanding about scientific inquiry
- Standard B
  - Structure of atoms
  - Structure and properties of matter
  - Interactions of energy and matter
  - Chemical reactions
- Standard E
  - Abilities about technological design
  - Understanding about science and technology
- Standard G
  - Nature of scientific knowledge

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