



Teacher's Guide

Nanofabrication Tools: Etching and thin films

Grade Level: High School & Undergraduate

Subject area(s): Chemistry

Time required: (6) 55 minute classes

Learning objectives:
Understand and used the chemical reactions of micro/nano-fabrication.

Summary: This is a four-part lesson designed to help students understand the terminology, procedures, and equipment used to manufacture micro and nanoscale products. It helps them explore the processes used in nanofabrication including electroplating, PCB etching and etch time. In this lesson, students will learn basic ways of transferring pattern to build these devices and design a membrane with specific requirements. The lesson ends with a design challenge using information gained in the first three activities. A pre-lab is recommended as either a homework assignment or as an in-class activity. Students will either view a video or read about the fabrication process used in semiconductor manufacturing.

Lesson Background: The quest for ever-more-powerful computers and communications devices has ignited interest in nanotechnology. Nanotechnology holds the key to future devices not only in computer industry but also in the medical field using robotic surgical tools and serum analyzers. The designing and manufacturing of device with dimensions measured in nanometers, is called nano-fabrication. One nanometer is 10^{-9} meter, or a millionth of a millimeter. In early computers, the calculations were performed by large vacuum tubes and that resulted in computers the size of a room. These days the same processes can be performed by microprocessors the size of a penny.

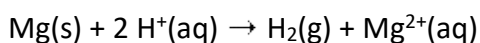
Nanofabrication manufacturing involves making devices at the smallest dimensions. While it was first used in the semiconductor industry, the technologies are now used for a wide variety of applications. These include miniature sensor arrays for biology and medicine, miniature valves, turbines for fluidics, flat panel displays for computers, and integrated circuits. Creating a microprocessor, or any other kind of integrated circuit, requires photolithography, which is process of creating patterns on a piece of semi-conducting material, such as silicon, using light. Photolithography is a multi-step process, each step being partially controlled by computers, because the scale of the etching is too small for human to properly work with. Multiple layers of semi conducting materials are laid on top of each other, and the shapes etched into them. The actual patterns themselves are able to function as transistors and internal data pathways.¹



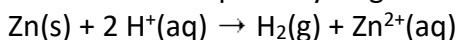
Nanofabrication involves two types of methods to transfer patterns onto the semiconducting material. First is the “Bottom up” approach, where smaller components of atomic or molecular dimensions self-assemble together, according to a natural physical principle or an externally applied driving force, to give rise to larger and more organized systems. The second is “Top-down” approach, a process that starts from a large piece and subsequently uses finer and finer tools for creating correspondingly smaller structures.

When etching a pattern into the substrate, a mask must be put over the parts that need to be saved from either etching or deposition. The masks can be a positive mask leaving everything that is masked and etching other parts away, or a negative mask where the mask stays but other parts are electrodeposited. A positive mask generally describes when there is a 1 to 1 transfer of the pattern from the mask to the substrate. The areas that are dark in the original masking pattern are made dark on the substrate. The clear regions on the masking material are made clear on the substrate. Negative masks are the opposite. Dark regions on the original mask are made clear on the substrate and clear regions are made dark on the substrate. The negative mask areas are built up from a deposition technique, where electroplating is how it will be accomplished in this lesson.

In this lab, the students will learn about a positive mask using a copper clad printed circuit board (PCB) and negative masking by electroplating the non-masked areas of quarters. Both the processes involve oxidation reduction reactions with one metal replaced by another based on their position in an activity series, a list of substances ranked in order of relative reactivity. For example, magnesium metal can replace hydrogen ions out of solution, so it is considered more reactive than elemental hydrogen:

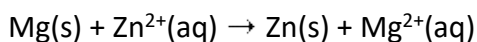


Zinc can also displace hydrogen ions from solution:



so zinc is also more active than hydrogen.

But, magnesium metal can remove zinc ions from solution:



Magnesium is more active than zinc, and the activity series including these elements would be $\text{Mg} > \text{Zn} > \text{H}$. Each metal can reduce the cation of metals below it to their elemental forms.



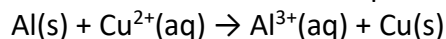
Most active (most strongly reducing) metals appear on top, and least active metals appear on the bottom.

displace H ₂ from water, steam, or acids	Li	$2 \text{Li(s)} + 2 \text{H}_2\text{O(l)} \rightarrow 2 \text{LiOH(aq)} + \text{H}_2\text{(g)}$
	K	$2 \text{K(s)} + 2 \text{H}_2\text{O(l)} \rightarrow 2 \text{KOH(aq)} + \text{H}_2\text{(g)}$
	Ca	$\text{Ca(s)} + 2 \text{H}_2\text{O(l)} \rightarrow \text{Ca(OH)}_2\text{(s)} + \text{H}_2\text{(g)}$
	Na	$2 \text{Na(s)} + 2 \text{H}_2\text{O(l)} \rightarrow 2 \text{NaOH(aq)} + \text{H}_2\text{(g)}$
displace H ₂ from steam or acids	Mg	$\text{Mg(s)} + 2 \text{H}_2\text{O(g)} \rightarrow \text{Mg(OH)}_2\text{(s)} + \text{H}_2\text{(g)}$
	Al	$2 \text{Al(s)} + 6 \text{H}_2\text{O(g)} \rightarrow 2 \text{Al(OH)}_3\text{(s)} + 3 \text{H}_2\text{(g)}$
	Mn	$\text{Mn(s)} + 2 \text{H}_2\text{O(g)} \rightarrow \text{Mn(OH)}_2\text{(s)} + \text{H}_2\text{(g)}$
	Zn	$\text{Zn(s)} + 2 \text{H}_2\text{O(g)} \rightarrow \text{Zn(OH)}_2\text{(s)} + \text{H}_2\text{(g)}$
	Fe	$\text{Fe(s)} + 2 \text{H}_2\text{O(g)} \rightarrow \text{Fe(OH)}_2\text{(s)} + \text{H}_2\text{(g)}$
displace H ₂ from acids only	Ni	$\text{Ni(s)} + 2 \text{H}^+\text{(aq)} \rightarrow \text{Ni}^{2+}\text{(aq)} + \text{H}_2\text{(g)}$
	Sn	$\text{Sn(s)} + 2 \text{H}^+\text{(aq)} \rightarrow \text{Sn}^{2+}\text{(aq)} + \text{H}_2\text{(g)}$
	Pb	$\text{Pb(s)} + 2 \text{H}^+\text{(aq)} \rightarrow \text{Pb}^{2+}\text{(aq)} + \text{H}_2\text{(g)}$
H₂		
can't displace H ₂	Cu	
	Ag	
	Pt	
	Au	

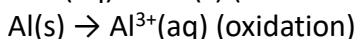
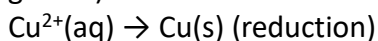
The activity series helps to predict the products of metal displacement reactions. For example, placing a strip of zinc metal in a copper(II) sulfate solution will produce metallic copper and zinc sulfate, since zinc is above copper on the series. A strip of copper placed into a zinc sulfate solution will **not** produce an appreciable reaction, because copper is below zinc on the series and can't displace zinc ions from solution. The predictions are accurate for aqueous solutions at room temperature.²

Aluminum and Copper chloride reaction:

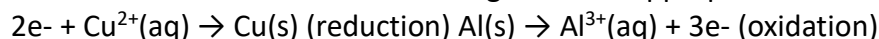
The unbalanced net ionic equation for the reaction is given below:



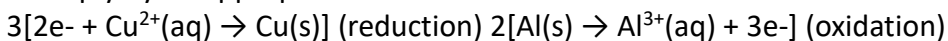
1. Aluminum is oxidized. The oxidation state increases from zero to plus three (3 electrons lost). The copper is reduced. The oxidation state decreases from 2+ to zero (2 electrons gained). The two half-reactions are as follows:



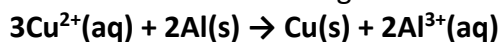
2. To balance the half reactions for charge add the appropriate number for electrons:



3. Multiply by an appropriate factor:



4. Add the half reactions to get the net ionic equation:

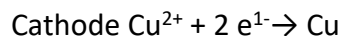
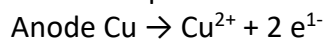


This reaction is exothermic and the temperature rise of the solution can be measured using a thermometer.



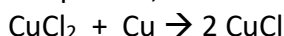
Electroplating:

In this activity, copper is plated onto the surface of a Copper nickel alloy object. Copper from the anode is oxidized to Cu^{2+} which is reduced at the cathode (coin) to form the solid copper plating. The copper sulfate solution serves as an electrolyte solution as well as the source of the Cu^{2+} to be plated on the cathode. H_2SO_4 is added as an additional electrolyte.



Printed Circuit Board (PCB) Etch:

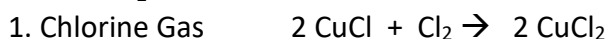
CuCl_2 is a rather messy, yellow-brown, hygroscopic solid, usually sold as the green crystalline dihydrate salt, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. It is commonly used acidic and comprises the copper salt, water and hydrochloric acid (HCl). The etching of copper with CuCl_2 can be expressed by the following chemical equation;



The copper surface gets attacked by CuCl_2 while cuprous chloride (CuCl) is formed. One copper atom with one cupric ion produces two cuprous ions. Copper etching with CuCl_2 solution is controlled strongly during the etching process.³

Regeneration of waste etchant

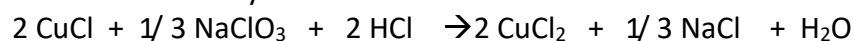
The waste CuCl_2 can completely be regenerated. There are various regeneration processes available for CuCl_2 .



2. Hydrogen Peroxide and Hydrochloric Acid



3. Sodium Chlorate and Hydrochloric Acid



Sources:

1. Kozierok, C.M., (2001) Photolithography: Making the Chips. The PC Guide.
<http://pcguide.com/ref/cpu/char/mfgPhoto-c.html>
2. Fred Senese (2010) <http://antoine.frostburg.edu/chem/senese/101/redox/faq/activity-series.shtml>
3. Cakir, O. (2006) Copper etching with cupric chloride and regeneration of waste etchant http://www.journalamme.org/papers_amme03/1229.pdf

Pre-requisite Knowledge: Understanding of chemical reactions and how to balance equations.

Materials: Per lab group of 3 students

Activity 1: Electroplating

- Acidified CuSO_4 Solution 0.5 M (pH 2.0 using HCl or H_2SO_4) 50 mL
- (1) quarter coin
- Steel wool
- Sharpie marker
- (4) Alligator clips



- 3V battery pack
- Forceps/tweezers
- Copper strip or penny
- 100 mL beaker
- Rubbing alcohol
- Paper towels
- Disposable gloves

Activity 2: Printed Circuit Board (PCB) etching

- Copper clad PCB 1 inch x 1 inch
- CuCl_2 6M in 6M HCl (10 mL)
- Sharpie
- Rubbing alcohol
- Forceps/tweezers
- Paper towels
- Petri dish (100x15)
- Steel wool

Activity 3: Aluminum etch time

- Aluminum tape 2 inch wide
- 1 inch hole punch (crafting punch or a hollow punch)
- 3 glass slides
- 2 stain jars
- CuCl_2 0.5 M 50 mL
- Dino-Lite Microscope or other microscope
- Paper towel
- Q tips

Activity 4: Project

- Aluminum tape 2 inch wide
- 1 inch hole punch (crafting punch or a hollow punch)
- Glass slide
- 2 stain jars
- CuCl_2 0.5 M 50 mL
- Dino-Lite Microscope or other microscope
- Paper towels
- Q tips

Safety Information: Students must wear safety glasses at all times. Caution them not to get any chemical in their eyes or mouth. It is recommended to wear disposable gloves and a safety apron. If gloves are not used, hands must be washed when finished.



Vocabulary and Definitions:

Photolithography: the process of transferring geometric patterns on a mask to the surface of a substrate, typically a silicon wafer.

Mask: Something that hides parts e.g., a mask will cover part of your face. In photolithography, it is an transparent plate that has an opaque pattern on it that can be transferred to a substrate by shining light through it.

Positive mask: contains an exact copy of the pattern which is to remain on the wafer. The dark regions of the mask will remain on the substrate, while the clear regions will be removed.

Negative mask: Masks used for negative photoresists that contain the inverse (or photographic "negative") of the pattern to be transferred. The dark regions on the mask will be removed, while the clear regions on the mask will be protected and remain.

Photoresist/Resist: Photoresist, also known as resist, protects regions on a substrate from the fabrication process its is undergoing. For example, in etching applications, the area under the resist will not be removed, while areas that are not under the resist will be. In electroplating applications, material will only be deposited in the areas not covered by the resist. Photoresist is patterned using light illuminated through a mask. (Students may guess that this is light that resists something or a substance that resists light. It is important to identify this misconception early.)

Electrolyte: a chemical compound that conducts electricity by ionizing when melted or dissolved into a solution. A common one is a solution of a salt. Electrolytes conduct electricity via movement of ions, not electrons.

Etching: Removing material from a substrate that leaves behind a desired pattern on the material.

Semiconductor: An element or compound whose ability to conducts electricity lies between that of a metal (strong conductor of electricity) and that of an insulator (very poor conductor of electricity).

Nanoscale: measured in nanometers; typically referring to materials between 1 and 100 nm but others use up to several hundred nanometers.

Nanometer: 1×10^{-9} or one billionth of a meter.

Nanotechnology: Nanotechnology is science, engineering, and technology conducted at the nanoscale, which is about 1 to 100 nanometers. It is the study and application of extremely small things and can be used across all the other science fields, such as chemistry, biology, physics, materials science, and engineering.

Advanced Preparation:

1. Purchase materials. A list of possible sources is below:

Material	Source/Website
Copper clad PCB	Amazon https://www.amazon.com/Single-Sided-Copper-Laminate-Circuit/dp/B01LX99SO8 Also at mouser.com
Aluminum foil tape	Findtape.com: High heat aluminum foil tape @ https://www.findtape.com/shop/results.aspx? keywords=high%20heat%20aluminum%20foil%20tape Also at Digikey.com
Stain Jar; chemicals	At science suppliers



Dino-lite USB microscope, USB microscope; classroom microscope	Amazon for Dino-lite or other USB microscopes
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2. Prepare solutions:

- Acidified CuSO_4 Solution 0.5 M (pH 2.0 using HCl or H_2SO_4)
- CuCl_2 6M in 6M HCl
- CuCl_2 0.5 M

3. Cut pieces of copper clad PCB -1"x1"

Suggested Teaching Strategies: This lab will fit in the Redox unit of chemistry. The most efficient way will be to work in groups of 2-3.

For the **pre-lab**, have students either watch a video on the fabrication process or read about it for homework. Have them discuss these questions before viewing or reading:

- Microchips are some of the most intricately patterned manmade objects in the world with some having over a billion components, each smaller than a red blood cell.
 - What is the smallest thing you have made?
 - How did you make it?
 - How do you think such tiny things are made?
 - How would you do it?
- Microchips are some of the most intricately patterned manmade objects in the world. How might photoresists and etching help in the manufacture of microchips? Answer: *By removing material in very specific spots, complex patterns of material can be built up.*

In class, discuss the steps in making computer chips.

Possible videos and resources for pre-lab:

- VLSI Fabrication Process: <https://www.youtube.com/watch?v=fwNkg1fsgBY>
- Making Silicon Chips by Intel: <https://www.intel.com/content/www/us/en/history/museum-making-silicon.html> and <https://www.intel.com/content/www/us/en/support/articles/000015079/programs.html>
- Semiconductor Manufacturing by Hitachi: <https://www.hitachi-hightech.com/global/products/device/semiconductor/process.html>
- How Chips are Made by How Stuff Works: <https://computer.howstuffworks.com/euvl1.htm>
- Making Microchips by Computer World: <https://www.computerworld.com/article/2576786/making-microchips.html>

Before beginning the lab, review the answers to the vocabulary. Vocabulary may be assigned as homework or done in class. Review the terms in class to avoid any misconceptions.

Directions for the Activity: These are below in the Student Guide with answer.



Assessment:

Students will be able to:

- Formulate a focused problem/research question and identify the relevant variables, design a method for the effective control of the variables, and develop a method that allows for the collection of sufficient relevant data.
- Record appropriate quantitative and associated qualitative raw data including units, process the raw data correctly, present processed data appropriately and, where relevant, include errors and uncertainties.
- State a conclusion with justification based on a reasonable interpretation of the data, evaluate weaknesses and limitations, and suggest realistic improvements in respect of identified weaknesses and limitations.

Additional Resources:

- Electroplating. Chemistry LibreTexts: [https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Supplemental_Modules_\(Analytical_Chemistry\)/Electrochemistry/Electrolytic_Cells/Electroplating](https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Supplemental_Modules_(Analytical_Chemistry)/Electrochemistry/Electrolytic_Cells/Electroplating)
- How Does Electroplating Work? Fuse School: https://www.youtube.com/watch?v=OxhCU_jBiOA
- Chemical Milling. Wikipedia: https://en.wikipedia.org/wiki/Chemical_milling#Etching
- Chemical Etching: A Tour Through The Process (3D Animation). Veco Precision: <https://www.youtube.com/watch?v=2O1TyJGXuWY>
- Photolithography. Wikipedia: <https://en.wikipedia.org/wiki/Photolithography>
- Photolithography. University of Massachusetts at Amherst: <https://www.youtube.com/watch?v=oBKhN4n-EGI>
- What is Nanofabrication? NanoWerk: <https://www.nanowerk.com/nanofabrication.php>

Next Generation Science Standards:

HS-PS1-1. Use the periodic table as a model to predict the relative properties of elements based on the patterns of electrons in the outermost energy level of atoms.

HS-PS1-2. Construct and revise an explanation for the outcome of a simple chemical reaction based on the outermost electron states of atoms, trends in the periodic table, and knowledge of the patterns of chemical properties.

HS-PS1-3. Plan and conduct an investigation to gather evidence to compare the structure of substances at the bulk scale to infer the strength of electrical forces between particles.

HS-PS1-4 & HS-PS1-8. Develop a model based on evidence to illustrate the relationships between systems or between components of a system.

HS-ETS1.A. Defining and delimiting engineering problems.

HS-ETS1.B. Developing possible solutions.

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Student Worksheet
(with Answers in Red)

Nanofabrication Tools Etching and Thin Films

Safety

You must wear safety glasses at all times. Be careful not to get any chemical in your eyes or mouth. Wear safety gloves and apron if available.
Wash hands immediately after using chemicals

Introduction:

Nanotechnology is the science of the very small – atoms and molecules. Scientists and engineers are creating new materials and devices by using unique properties of nanoscale materials. The quest for ever-more-powerful computers and communications devices has ignited interest in nanotechnology. Nanotechnology holds the key to future devices not only in computer industry but also in the medical field using robotic surgical tools and serum analyzers.

Nanofabrication manufacturing involves making devices at the smallest dimensions. While it was first used in the semiconductor industry, the technologies are now used for a wide variety of applications. Creating a microprocessor, or any other kind of integrated circuit, requires photolithography, which is process of creating patterns on a piece of semi-conducting material, such as silicon, using light. Photolithography is a multi-step process and a complex integrated circuit on a silicon wafer can take up to a month to create.

The following activities will allow you to experience some of the processes used in nanofabrication including thin film layer deposition (electroplating) and etching. You will be experimenting with variables that may or may not affect the deposition of thin films.

Pre-Lab: You teacher may ask you to watch a video or read about the fabrication processes used in semiconductor manufacturing.

Directions for the Activities:

Day1 Electroplating

1. Prep a quarter using fine steel wool to remove any oxides or dirt. Use gloves to avoid any more finger prints.
 1. Using a sharpie, mask off some area/pattern that you don't want to be electroplated. Make sure to completely cover the areas of interest with sharpie ink.
 2. Put 50 mL of CuSO_4 solution in the beaker.
 3. Attach the penny or the copper piece to one of the alligator clip.
 4. Attach the quarter to another alligator clip



5. Attach the penny to +ve end of 3V battery pack. This is the anode.
6. Connect the quarter to the cathode (-ve end of the battery)
7. Immerse penny and quarter in solution for 1 minute.
8. Remove quarter and change clip position for even plating.
9. Immerse coin again and repeating for total of 3 minutes.
10. Remove quarter and rinse well with water.
11. Remove sharpie/mask using rubbing alcohol.
12. Bring to shine by light rubbing with fine steel wool.

Day 2 PCB Pattern:

1. Prep the PCB Board using fine steel wool bring to a shine.
2. Draw a pattern on the shiny copper side using a sharpie, making sure to completely cover the area.
3. Pour 10 mL of the etch solution CuSO_4 in a petri-dish.
4. Place the PCB in the etch solution with pattern side completely covered with the etch solution. Place it face down for complete coverage.
5. Check on the board frequently by picking it up out of solution using forceps.
6. Once completely etched away, completely rinse the board with water.
7. Remove sharpie marks using rubbing alcohol.
8. Bring to shine by light rubbing with fine steel wool.

Day 3 Etch Time:

1. Label clean slides on one end depending on the experimental design.
2. Punch 3 holes in aluminum foil tape and place the three discs on each slide.
3. Place all the slides in the staining jar and pour CuCl_2 solution.
4. Start timer and remove the slides at appropriate times.
5. Place these slides in another staining jar containing water.
6. Shake the slides slightly to remove any copper buildup.
7. Using forceps, pull the slides out and place on a clean paper towel.
8. Clean the foil discs using q-tips while applying very light pressure.
9. Using the Dino-lite microscope to measure the size and number of pits in three areas of each foil disc. Find the average.
10. Plot a graph using pore size as a function of time.
11. Find the regression for the line. You would need this for the next activity.

Day 4 Design Challenge:

1. Using the information from last three activities design a process to get three areas of different pore sizes on a 1 inch round foil disc.
2. Get your design checked by the teacher.
3. Make measurements and take pictures of your foil disc showing three areas of different pore sizes.
4. Include pictures in your lab report.

Record your Observations:

Day 1: Take a picture of your electroplated quarter and include with the lab report.



Day 2: Take a picture of your etched PCB board and include with the lab report.

Day 3:

Table: Etch time and pore size relationship

Time (minutes)	Pore size (μm)			
	Replicate 1	Replicate 2	Replicate 3	Average
1.0	30 28 68 79 45 29 90			
2.0	56 98 67 89 64 100 56 99			
3.0	99 101 90 89 110 117			
4.0	109 119 128 130 99 119			



5.0	179			
	120			
	134			
	143			
	150			

Day 4: Prepare the membranes with three distinct areas and include the pictures.

Analyze the Results:

Day 3: Plot a scatterplot with pore size as a function of time and find a best fit regression line for your data. You will use this graph for next part of your lab.

Draw Conclusions:

1. Did your quarter electroplating activity result in what your expected?
Answers will vary but should discuss the areas plated versus those that were not.
2. Did the etching in activity 2 result in a pattern that you expected?
Answers will vary but they should discuss results in relation to their technique.
3. For activity 3, discuss how your etched pores and shapes either differed or were similar on the three discs. How did etch time effect the pores and shapes? *Answers may vary like the pores were not even size or shapes*
4. What technologies do thin films stand to revolutionize?
Computer based technologies like cell phones and also medical equipment.
5. Which electrode served as the cathode in the electrolysis chamber?
The penny or copper strip
6. Which electrode served as the anode in the electrolysis chamber?
The quarter.

