Hiding Behind the Mask

Purpose: This lab is designed to help students understand one aspect of semiconductor manufacture: selective layering.

Level: High school chemistry or physics

Time required: Three 50-minute class periods

Teacher Background: Semiconductor microchips are in almost every device in our lives, from toasters to CD players, from computers to car engine management systems, from iPods to kitchen stoves, from drills to door bells. The bedrock of the microchip industry is ultra-pure silicon, often purified so as to have only one impurity atom in a billion (10^9) atoms. However, silicon this pure is merely the starting point, as it is relatively boring.

When you introduce other atoms into the silicon in a controlled pattern, the conduction of the silicon will differ from place to place in the silicon pattern. Build up some layers of this patterned material and very interesting things start to happen, like using voltage in one conducting part to control electron flow in a neighboring part—the basis of transistor switches. A few transistors linked together can make logic gates like AND, NOT and XOR, which can be used to add numbers together and make a calculator. Put two billion transistors on one silicon chip (like Intel did in April 2008) and you have a computer capable of simulating almost anything you can describe.

The question is how to make the patterns that you need, given that these patterns are smaller than a red blood cell. In creating a transistor, lenses are used to reduce the image size and create very complex patterns. How does someone make the larger pattern before it shrinks? These patterns are made by shining ultraviolet (UV) light through a stencil (called a mask) onto silicon or a metal covered in a paint-like chemical, called photoresist. Photoresist can be used to pattern the silicon by only allowing etching in one place and resisting the etching in other places. The photoresist used in this experiment is a “negative” resist, the polymer of which is strengthened by UV light as it forms cross-links. The unstrengthened polymer is washed away with developer, leaving gaps where the stencil lines (or, mask) were. The etching only occurs where the gaps allow the electricity to flow through the electrolyte to the metal surface. There are such things as positive resists that UV light weakens and behave in the opposite way.

Electrochemical etching of the metal occurs when sufficient voltage is applied to two electrodes immersed in an electrolyte. Because the electrolyte can only conduct electricity by moving ions and not by just moving electrons through it, atoms of metal are oxidized by the voltage and dissolve into solution at the positive anode, etching away the anode. Then the positively charged metal ions move through the electrolytic solution attracted by the negatively charged cathode and are reduced back to a metallic form, plating the negative cathode with metal. The metal loses an electron at the positive anode to become oxidized and gains an electron
at the negative cathode to become reduced. Etching with direct current (DC) causes simple
removal of the etched pattern. Etching with alternating current (AC) causes an oxide layer to be
built up in the etched pattern. The Etch-O-Matic normally etches with AC, but comes with a
diode deep etching adaptor clip for DC etching.

Materials per class
- Martronics Etch-o-Matic Mark 440 photo-stencil kit (~$170), http://www.etch-o-matic.com
  This kit includes:
  - Etch-O-Matic etching unit
  - UV exposure unit with special 365 nanometer UV bulb (120 W)
  - aluminum exposure tray with compression foam and glass top
  - 16 oz. bottle stencil developer, plus developing tray with lid
  - 4 white developer sponges
  - digital timer
  - 10 dura-film unexposed stencils (5” x 6”)
  - 5 sheets transparency films
- blank laser or inkjet printer transparencies (1/student)
- packet steel wool for shining steel, if necessary
- roll of aluminum foil
- pre-printed transparencies with simple shapes
- laser or inkjet printer
- metric rulers (1/student)
- magnifying glasses (1/student)
- digital camera (optional, for independent inquiry lab only)

Materials per student
- 1¼” (32 mm) steel discs (e.g., dog tags from Pet House; must have conductive surface, i.e.
  unpainted)
- timer or clock with a second hand
- unexposed photoresist sheet
- printed design on transparency
- UV exposing unit
- developing tray
- developing solution
- rinsing water
- paper towel
- metric ruler (mm)
- magnifying glass

Safety Information Wear safety glasses, protective gloves, and lab coats during these activities.
The developer and dissolved resist may cause mild skin and eye irritation. Spills should be wiped
up with plenty of water.

Advance Preparation
1. PREPARE PHOTORESIST SHEETS
Cut 2 in. × 2 in. pieces of unexposed photoresist sheet. Wrap each photoresist sheet in foil to prevent light exposure.

2. PURCHASE STEEL OR ALUMINUM DISCS
Purchase steel or aluminum discs at a pet supply shop (round dog tags work great). If you purchase these online, call ahead to ensure that these have no varnish/coating on them. The metal must be conductive for the etching to work; you can use a continuity testing multimeter or simple conductance tester (battery and light) to check this.

3. PREPRINT SIMPLE DESIGNS
Preprint simple designs on transparencies—geometric shapes with 1–2 mm line width work well—to provide to students. All prints should be black and white only; any grey lines will not be etched.

4. PREPARE LIGHTING IN ROOM
Prepare room with dim lighting for exposing and developing photoresist; red lighting works best, but dim lighting will work if students minimize working time.

5. PREPARE STATIONS
In the dim room, there should be a UV exposure station with timer and a developing tray station with sponge and rinse tray. If multiple rounds of exposure are required to complete the whole class, no exposing can be done before the previous round of developing is complete. For part 2 of this lab, set up an etching station, with all materials in the Etch-O-Matic kit.

Here is a series of photos on the etching process. The first four steps are done in a dim room, until the dura-film is developed.

(1) Put photoresist film under the pattern and glass.          (2) Put tray under UV lamp.
(3) Turn lamp on for 60 seconds.

(4) Peel off front and back protective films, then rub blue photoresist with developer for 2 minutes.

(5) Notice the pattern and the developed photoresist.

(6) Etch-o-Matic grounding plate, electrolyte, and dog tag to be etched.

(7) Put electrolyte on photoresist and felt pad; put etcher over dog tag for 10 seconds.

(8) Remove photoresist, rinse and dry.
(9) Etched dog tag with oxide pattern and photoresist film.

**Resources** You may wish to use these resources either as background or as a resource for students to use:

<table>
<thead>
<tr>
<th>For connecting photoresist and etching to the fabrication of semiconductor chips, use the transistor applet at <a href="http://www.micro.magnet.fsu.edu/electromag/java/transistor/index.html">http://www.micro.magnet.fsu.edu/electromag/java/transistor/index.html</a> and identify the photoresist steps to the class at the end.</th>
</tr>
</thead>
<tbody>
<tr>
<td>For background, there are many general semiconductor applets at <a href="http://jas.eng.buffalo.edu/">http://jas.eng.buffalo.edu/</a>. Some are more high school level than others.</td>
</tr>
<tr>
<td>Do an internet search of “applets semiconductor” for additional web resources.</td>
</tr>
</tbody>
</table>

**Directions for the Activity: Three parts to the activity**

**Teaching Strategies:** Guide the patterning and etching in small groups (2–4 students). Designing etching patterns should be done individually, so that the student can feel ownership.

**Guided Dialog:** Before beginning the lab, ask students questions to provoke thought and review what they may already know. For example:

1. 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?
2. What is the meaning of the following terms:

- **Mask** Something that hides parts (e.g., of your face).
- **Resist** To act against some event—in this case, the photoresist resists the etching process; in other cases, it can be used to resist plating or implantation processes. For example, masking tape resists the application of paint to a wall or canvas.
- **Photoresist** A light-activated compound that forms a “resist;” in other words, a resist that is made using light to pattern it. (Students may guess that this is light that resists something or a substance that resists light. It is important to identify this misconception early.)
- **UV** Ultraviolet light (high frequency, high energy, short wavelength (300 nm)).
- **Electrolyte** A solution of a salt. (Electrolytes conduct electricity via movement of ions, not electrons.)
- **Etching** Removing material and leaving a depression behind.
- **Semiconductor** A metalloid element or compound that conducts electricity less than a metal and more than an insulator.

3. Microchips are some of the most intricately patterned manmade objects in the world. How might photoresists and etching help in the manufacture of microchips? By removing material in very specific spots, complex patterns of material can be built up.
Part 1: Lights, Developer, Pattern!

Name: _______________________________ Date: ______________ Class: __________________

Student Worksheet
(with answers)
Part 1: Lights, Developer, Pattern!

Resist-ance is Useful

Safety
Wear safety glasses, protective gloves, and lab coats. Developer and dissolved resist may cause mild skin and eye irritation. Spills should be wiped up with plenty of water.

Introduction
Just as a painter will mask off areas that they do not want to be painted, microchip makers mask off areas of the silicon wafer that they do not want to alter. They do this using a photoresist, which is a compound that can be patterned using a mask and ultraviolet (UV) light. It will then resist etching only in certain parts of the pattern. These lab activities explore photoresist masking and etching, essential parts of semiconductor manufacture. A semiconductor is a material (often silicon) that has electrical resistance between that of an insulator and a conductor. Semiconductors are the center of the electronics industry and are found in microprocessors and transistors. They are the basis for making your I-Pod, cell phone, microwave, digital camera, etc.

In this short, guided activity you will make a simple photoresist mask and etch this design onto a piece of metal. Afterwards, you will design your own patterns to etch into metal.

Materials
• unexposed photoresist sheet
• printed design on transparency
• metric ruler (mm)
• magnifying glass
• timer
• UV exposing unit
• developing tray
• developing solution
• rinsing water
• paper towels

Question
Do you think your pattern will look like the stencil you create or the reverse?

Example answer: I think the area in black will be washed away by the developer, so it will look the opposite of my stencil.
Procedure

(Important: Keep your unexposed photoresist film in the protective pouch until you are in the darkened room.)

1. Make observations of your simple pattern on the transparency in the space provided below.

2. Working quickly in the darkened room, remove the photoresist sheet from the protective envelope and put it on the black foam pad. Place your transparency with your design on top of the sheet and weigh everything down with the glass plate.

3. Once all the groups have their sheets in place, place the exposing tray under the UV lamp. Expose the sheets with UV light for 60 seconds.

4. Remove the photoresist sheet and peel off the front and back protective films. Notice how the blue sheet looks now. Place the blue sheet in the developing tray and cover with a thin layer of developing solution.

5. With a sponge, use moderate pressure to rub the sheet on the front and back for 2 minutes until the blue material has been thoroughly removed from the patterned parts of the mesh.

6. Rinse the sheet thoroughly with water. Pat dry with a paper towel.

7. Once the sheets are developed, they can be used in well-lit areas. Make observations of the developed photoresist sheet using a magnifying glass and ruler.

Record Your Observations

1. Observations of original pattern (include a drawing, measurements and description):

   Example observation: Star shape with 6 points, about 20 mm across; star is made by thick black outline about 2 mm thick.

2. Observations of developed photoresist (include a drawing, measurements and description):

   Example observation: Blue film with white star pattern on it.

   Magnifying glass shows white part is a mesh and blue part is
where solid still covers the mesh.

**Analyze the Results**

1. What part of the film will resist the etching?
   
   *Example answer: The blue part where the solid film material still is found.*

2. Some photoresist polymers are weakened by UV when the high energy light releases acid within the polymer. Other photoresist polymers form cross-links between their molecules when hit by UV light, making them stronger. Use your observations to justify: which of these two processes is happening to your blue film?
   
   *Example answer: The part that was exposed didn’t develop away, so it got stronger. The cross-linking process is probably happening.*

**Draw Conclusions**

Use your prediction, observations, and analysis of the results to sum up this activity.

*Example answer: The prediction that the black part of the pattern would be washed away by the developer was correct. The UV light strengthened the photoresist polymer so the area under the black ink was still weak and could be developed away. This is due to the photoresist polymer forming cross-links when exposed to UV light.*

**Cleanup** Waste etching electrolyte can be flushed down the drain with excess water.
Part 2: To AC or not to AC?

You probably know that electricity can be in two forms: direct current (DC) or alternating current (AC). You are going to try electrochemical etching with both and observe the difference.

Question
What do you think your final pattern will look like on the metal disc?

Answer example: I think the white pattern of the photoresist will be etched into the metal.

Procedure
1. Clean your metal disc with water and a paper towel. If necessary, use steel wool to shine the metal disc.
2. Arrange your pattern (mask) on top of your clean metal piece and place both on top of the metal grounding plate.
3. Get a petri dish and fill half full with water. This will be used for rinsing.
4. Attach the white clip (AC) to the metal plate and put a few drops of electrolyte on top of the white parts of your pattern.
5. Put 5 drops of electrolyte on the center of the white felt pad of the etcher.
6. Make sure the etcher is plugged in. Firmly press the etcher down onto your pattern for 10 seconds (etching for longer than 10 seconds will overheat the disc).
7. Remove the etcher and use tweezers to pickup your film and metal disc. Rinse them with water and dry them with a paper towel.
8. Turn the metal piece over and place the metal piece down so that the pattern faces down on the grounding plate. Put your pattern (mask) on top of the metal disc.
9. Attach the white clip to the metal ring on the red DC adaptor clip and attach the red clip to the metal plate.
10. Put a few drops of electrolyte on your pattern and five drops on the pad of the etcher.
11. Make sure the etcher is plugged in. Firmly press the etcher onto your pattern for 10 seconds.
12. Remove the etcher. Rinse your pattern and metal with water and dry them with a paper towel.
13. Examine and compare the etch patterns for AC and DC. You may want to use a magnifier.

**Record your Observations:**

1. Observations of etch with white clip:
   
   *Example observation: Pattern came out dark brown where the white part of the photoresist was.*

2. Observations of etch with red clip:
   
   *Example observation: Pattern was etched down into the metal where the white part of the photoresist was. Etch was not dark brown.*

**Analyze the Results**

1. The red adapter clip changes the etcher output from alternating current (AC) to direct current (DC). How did it change the result?
   
   *Example answer: The DC did a deep etch that was not colored. The AC gave a dark brown finish with not so deep an etch.*
2. The brown oxide pattern is formed according to the reactions:

\[
\begin{align*}
\text{Fe} & \rightarrow \text{Fe}^{3+} + 3e^- \\
\text{O}_2 + 4e^- & \rightarrow 2\text{O}^{2-}
\end{align*}
\]

The overall reaction is:

\[4\text{Fe} + 3\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3\]

Why does the alternating current allow this to happen when the direct current doesn’t?

The alternating current switches between oxidation and reduction at the same electrode so the iron can oxidize in close proximity to the dissolved oxygen being reduced and form iron oxide. The DC mode keeps these processes separate.

Draw Conclusions

Use your prediction, observations and analysis of the results to sum up this activity.

Example answer: The prediction that the white part of the pattern would be etched into the metal was correct. The AC current makes a brown colored pattern that is iron oxide. The DC current only removes material because it doesn’t reduce oxygen at the iron’s surface and makes an etch mark that is not colored.
Part 3: Etch-Your-Sketch

Student Worksheet
(with answers)

Resist-ance is Useful

Safety
Wear safety glasses, protective gloves, and lab coats. Developer and dissolved resist may cause mild skin and eye irritation. Spills should be wiped up with plenty of water. Etching for longer than 10 seconds will overheat discs. Use tweezers to pick up heated discs.

Introduction

Part 3: Etch-Your-Sketch

Challenge #1
Make your own coin or pendant with a unique design!
Tips:
- Make two black-and-white designs either on the computer or paper (maximum 30 mm in diameter).
- Print out the designs or photocopy onto transparency (you may need to adjust your design to get deep blacks first).
- Etch your designs into both sides of a blank metal disc using your choice of either AC or DC etch, using the instructions in Part 2.
- Take photos of your finished disc for display.

Challenge #2
Design a coin that uses more than one layer of photoresist paper in the process.
Rules:
- At least 2 lines must overlap well or one design must be centered within the other.

Challenge #3
Can you make the reverse image using the same stencil? Take what you have learned about AC and DC etching and apply this knowledge.

Materials
- unexposed photoresist sheet
- printable transparency
- timer
- UV exposing unit
- developing tray
- developing solution
- Etch-O-Matic etching unit
- 30 mm metal disc
- electrolyte solution
- DC etching adapter
- grounding plate
- rinsing water
- paper towels
- digital camera
Etch one image using the AC oxide finish. For the other image put an AC oxide finish on the whole surface, then DC etch through that layer to reveal the metallic surface underneath.

**Enhancing understanding:** Cover this section after the activity.

- Photoresist allows you to put complicated patterns onto a surface.
- The photoresist resists the etching.
- Masks can also be used to pattern plating as well as etching.
- Both AC and DC electricity can be used to etch, with different results.

Revisit transistor applet, which builds up the many layers needed to form a transistor [http://www.micro.magnet.fsu.edu/electromag/java/transistor/index.html](http://www.micro.magnet.fsu.edu/electromag/java/transistor/index.html), and identify the photoresist processes (steps 2–4, 7–9, 15–17, 21–23) and etching processes (steps 5, 11, 18, 24). Ask the students what other processes they see in the applet. *building up material (depositing) and doping silicon with impurities*

**Going Further** Students who have a good grasp of the content of the lab can be further challenged with these questions:

1. How might microchip companies use similar techniques to build microchips with tiny complex patterns on them? *Use lenses to make the patterns smaller on the photo resist. Overlay patterns to make complex features. Etch different depths in different places.*
2. What other processes might be used in making microchips? *Implanting ions; coating on material (depositing)*

**Assessment**

Each student should turn in completed lab scripts with observations and a completed simple etched piece, answer the questions with correct responses, and photo document (if used) their finished piece. Students who completed challenges #2 or #3 can be awarded special credit.

**National Science Education Standards (Grades 9–12)**

Content Standard A: Science as Inquiry
- Abilities necessary to do scientific inquiry

Content Standard B: Physical Science
- Structure and properties of matter
- Chemical reactions

**California Science Education Standards (Grades 9–12)**

Physics, Content Standard 5: Electric and Magnetic Phenomena
- Students know the properties of transistors and the role of transistors in electric circuits.

Chemistry,

Content Standard 3: Conservation of Matter and Stoichiometry
- Students know how to identify reactions that involve oxidation and reduction and how to balance oxidation-reduction reactions.