Teacher's Preparatory Guide

Wet Etching Process used in Nanofabrication

Overview: This lab explains how scientists sculpt tiny electrical components used in everyday electronic devices such as an iPod.

Purpose: This lab will help students understand how chemical reactions are used to create the specific shapes on surfaces of crystalline materials, which make up functional components within electronics. The fabrication of electronic devices is now reaching into the nanoscale with the capability of more transistors on a single chip.

Time Required: Three 55-minute periods

Level: High school chemistry; Middle school physical science

Big Idea:

Teacher Background: Many nanoscale electronic components are sculpted using a variety of processes. This lab focuses on one aspect of a selective layering nanofabrication process called *wet etching*, which simply involves putting a material in a liquid solution (often an acid) which dissolves that material.

To sculpt a material, or *substrate,* we need to mark off, or *mask,* certain areas from the acid so the acid only etches the exposed areas. One must find a mask that will not dissolve or at least etches much slower than the material to be sculpted. The figures below are examples of two different types of etched (sculpted) substrates[1]. The red shows the masking layer. The gold shows the substrate being etched.

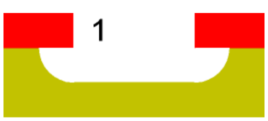

Figure 1: An *isotropic etch* is a shape which *undercuts* the substrate below the mask at the same rate as it penetrates into the substrate making a wider channel than may be expected.

Figure 2: An *anisotropic etch* forms a square shaped hole. Some single-crystal materials, such as silicon, exhibit *anisotropic etching* in certain chemicals. *Anisotropic etching*—in contrast to isotropic etching—means different etch rates in different directions in the material. (Image from Wikipedia)

Although this laboratory is simple, the chemistry involved at the surface/liquid interface of the substrate and etching solution is more complex and can be used to introduce and distinguish two very important and useful chemical reactions:

- The *double replacement* is the exchange of ions between the substances being mixed, producing two distinctly different substances.
- In a *decomposition reaction,* a large particle substance is broken down into smaller particle substances.

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This lab exposes these substrates: *antacid* tablets ($CaCO_3$), *Alka-Seltzer®* ($NaHCO_3$) and *art plaster* ($CaSO_4$); they will be exposed to these etchant solutions: *vinegar* $H(C_2H_3O_2)$, *lemon juice* (citric acid $C_6H_8O_7$), and *phosphoric acid* (H_3PO_4). The following chemical reactions are examples of some of these reactions:

Vinegar etchant:

Vinegar (acetic acid, CH_3COOH or $H(C_2H_3O_2)$) + *antacid* substrate (calcium carbonate, $CaCO_3$):

1. Double Replacement reaction $2H(C_2H_3O_2)_{aq} + CaCO_{3\,aq} \rightarrow H_2CO_{3\,aq} + Ca(C_2H_3O_2)_{2\,aq}$
2. Decomposition reaction $H_2CO_{3\,aq} \rightarrow H_2O_{\,l} + CO_{2\,g}$

Vinegar (acetic acid, CH_3COOH or $H(C_2H_3O_2)$) + *Alka-Seltzer®* substrate (sodium bicarbonate, $NaHCO_3$):

1. Double replacement reaction $NaHCO_{3\,s} + H(C_2H_3O_2)_{aq} \rightarrow Na(C_2H_3O_2)_{aq} + H_2CO_{3\,aq}$
2. Decomposition reaction $H_2CO_{3\,aq} \rightarrow H_2O_{\,l} + CO_{2\,g}$

Since *vinegar* is a very weak acid, its reaction with *art plaster* ($CaSO_4$) is negligible or very slow, providing very little activity, so no reaction takes place:

$CaSO_{4\,s} + 2H(C_2H_3O_2)_{aq} \rightarrow$ No reaction takes place

Lemon juice etchant:

Lemon juice (citric acid, $C_6H_8O_7$), + *antacid* substrate (calcium carbonate, $CaCO_3$):

1. Double replacement reaction: $2(C_6H_8O_7) + 3CaCO_3 \rightarrow Ca_3(C_6H_5O_7)_2 + 3H_2CO_3$
2. Decomposition reaction: $3H_2CO_{3\,aq} \rightarrow 3H_2O_{\,l} + 3CO_{2\,g}$

Lemon juice (citric acid, $C_6H_8O_7$), + *Alka-Seltzer®* substrate (sodium bicarbonate, ($NaHCO_3$):

1. Double replacement reaction: $C_6H_8O_7 + 3NaHCO_{3\,s} \rightarrow Na_3(C_6H_5O_7) + 3H_2CO_3$
2. Decomposition reaction: $3H_2CO_{3\,aq} \rightarrow 3H_2O_{\,l} + 3CO_{2\,g}$

Coca-Cola etchant:

Coca-cola contains a very dilute *phosphoric acid* (H_3PO_4) and carbonic acid (H_2CO_3) formed with the dissolved carbon dioxide (CO_2) in the solution. The reaction between the acids and the substrate is very slow because the concentration of the phosphoric acid is very dilute and the decomposition of the carbonic acid is what is releasing the gas bubbles observed on the surface of the substrate *antacid* tablet.

1. Double replacement reaction $2H_3PO_{4\,aq} + 3CaCO_{3\,s} \rightarrow Ca_3(PO_4)_{2\,s} + 3H_2CO_{3\,aq}$
2. Decomposition reaction $3H_2CO_{3\,aq} \rightarrow 3H_2O_{\,l} + 3CO_{2\,g}$

Sources:

1. Image credit: Wikipedia. "Etching (microfabrication)." (accessed August, 2011) http://en.wikipedia.org/wiki/Etching_(microfabrication)

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Materials per group of 3 students:

- 3 safety glasses (one per student)
- 25 in. black electrical tape
- 50 in. clear tape
- 25 in. masking tape
- 9 Alka-Seltzer® tablets
- 11 antacid tablets
- 9 art plaster molds
- pair of scissors
- metric ruler
- 9 index cards
- pen
- 10 Petri dishes, having 3 compartments each, catalog number 08-758-3 from www.fishersci.com
- 3 beakers, 100 ml each
- 100 ml vinegar
- 50 ml lemon juice
- 50 ml Coca-Cola® or cola containing phosphoric acid
- 4 disposable pipettes, about 3.4 ml per squeeze, 5.8 ml capacity (does not have to be exact); this lab used catalog number 13-711-9AM from www.fishersci.com
- pair of tweezers, catalog number 10300 from www.fishersci.com
- tripod 10× magnifying lens, catalog number S19006 from www.fishersci.com
- 4 white board markers, different colors
- white board or poster
- *Optional:* a timer or stopwatch

Materials per class:

- 2 rolls of black electrical tape
- 2 rolls of clear tape
- 2 rolls of masking tape
- box of art plaster mold
- water (about 1–2 cups)
- bottle of vinegar
- bottle of lemon juice
- bottle of Coca-Cola®
- 24 cavity bite-size brownie squares silicone mold (this lab used Wilton brand purchased at Michaels, also found online: http://www.wilton.com/store/site/product.cfm?id=AF414343-1E0B-C910-EAF4100780D53DC6)
- bowl to mix the plaster, 2 quart capacity
- spoon or stirring stick
- roll of paper towels
- classroom clock, if groups do not use a timer or stopwatch

Suggestions for the lesson: Show your students an old mother board or other electronic circuit board from a cell phone etc. Ask them if they know what they are looking at. Explain that they are looking at an integrated circuit (IC) which consists of several electronic circuits on a chip. The chip is made of a semiconductor material – typically silicon. Explain that these integrated circuits make up nearly all of the electronic devise that they use every day. You might want to ask them how many transistors might be in an IC. Thanks to micro and nano-electronics ICs are made to contain large numbers of transistors resulting in faster processing and smaller devices. The first Intel 4004 IC had 2,300 transistors while the new core i7 quad has 731,000,000. You may want to show them a chip making video from Intel's You Tube channel listed in the resource section.

Advance Preparation: The ruler, clear tape, masking tape, scissors, poster paper, and white board markers can be purchased at an office supply store, the electrical tape at a hardware store,

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the art plaster (plaster of Paris) and the brownie square silicone mold at Michaels or a craft store, the vinegar, lemon juice, and Coca-Cola® at a supermarket, and the Alka-Selzer® and antacid tablets at a drugstore. Purchase the remaining items online from an educational supply house.

1. ***Prepare the plaster substrates.***
   The art plaster mold substrates should be made the day before the lab. Mix plaster and water until it resembles pancake batter. Pour the slurry into the molds (to a thickness of an antacid tablet) and wait for them to harden.
2. ***Dispense fluids into beakers.***
   The vinegar, lemon juice, and Coca-Cola® can be dispensed directly from their own container or the liquid can be transferred to the beakers in advance.

Safety Information: Students should wear safety glasses while using the vinegar, lemon juice, and Coca-Cola®, for they all contain dilute amounts of acid and may burn if splashed into their eyes. Scissors can be a cutting hazard, so tell students to use caution when handling them.

Instructional Procedure:

Time	Activity
Day 1	**Materials characterization: What is the best mask, substrate, and etchant?**
15 min	Review the terms in the *Guided Dialog* section. Review the content of the etching solutions: vinegar (acetic acid), lemon juice (citric acid), and Coca-Cola (phosphoric acid + carbonic acid). Students make their predictions on the lab*, Part 1: Wet Etching.*
25 min	Demonstrate the procedure. Students investigate the reaction of the etching solutions on the substrates (antacid tablet, Alka-Seltzer®, and art plaster tablet) using different masks (tape).
10 min	Students analyze the results and draw conclusions on *Part 1: Wet Etching.*
5 min	Clean up.
Day 2	**Active vs. passive etching: Which works more effectively?**
15 min	Differentiate between *passive* and *active* chemical etching processes. Students prepare antacid tablets with a masked pattern.
20 min	Students perform passive and active chemical etching on prepared antacid tablets.
15 min	Students analyze the results and draw conclusions on *Part 2: Active vs. Passive Etching.*
5 min	Clean up.
Day 3	**Group oral presentation to the class**
5 min	Students analyze and organize results of both lab activities on a piece of paper. Students (as a group, with each member participating) prepare and present a 4-minute presentation of their findings to the class. Students make an outline on a sheet of paper of the information to be presented; this information will be transferred onto a “white board” during their presentation.
10 min	Each group prepares poster/white board with lab results to present to the class.
35 min	Each group presents their results to the class.
5 min	Each group will clean up white board or turn in their poster for display.

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Teaching Strategies: This activity works best in groups of 3 students, which facilitates more constructive collaboration by each student.

Guided Dialog *Before* beginning the lab, review the meaning of these terms with the class to clarify their understanding:

Acid *A substance that releases hydrogen ions when mixed with water. Has a pH <7.*
Substrate *In electronics, a supporting material upon which a circuit is formed or fabricated. Silicon is the most commonly used for electronics.*
Etching process *A process of cutting into the surface of something, such as a substrate by the action of acid or other type of substance.*
Wet etching process *A process utilizing chemicals to etch layers of atoms or molecules from the surface of a substrate. For example: glass being etched by hydrofluoric acid.*
Etching solution *A substance that etches (cuts) layers of atoms from the surface of a substrate.*
Anisotropic *Exhibiting properties with different values when measured in different directions.*
Isotropic *Exhibiting properties with same values when measured along x, y, and z axes in all directions.*
Undercutting *The removal of substrate material directly below the masked area.*

Ask students questions to provoke thought and review what they already know:

1. How do you know that a chemical reaction is occurring? *the formation of a gas, a change in odor, change in color, change in temperature, or emission of light*

Cleanup: Discard substrates and tape in the trash can. Wash liquids down the drain with excess water. Wash, rinse and dry Petri dishes, pipettes, and beakers.

Going Further: Students can compare and contrast what they did in this lab (wet etch process) with the process of erosion by writing a 250-word essay on the comparison of the processes, while stating examples that support their comparisons.

Assessment
Each group will prepare a poster board or white board and give a 4-minute oral presentation to the class to share their results. The white board or poster board should include:

White Board Requirement for Group Oral Presentation

<table>
<tr><td colspan="2">1. Title of Presentation: Lab Title</td></tr>
<tr><td rowspan="2">2. Abstract: Briefly describe the investigation, stating the scope of the investigation.
3. Prediction: What was expected from the investigation?
4. Vocabulary: List new terms.</td><td>5. Observations: Lab results.
6. Data analysis: Include graphs or drawings that facilitate their understanding of new concepts or vocabulary.</td></tr>
<tr><td>7. Conclusion: Restatement of prediction and state whether or not prediction was justified by the laboratory results. State reasons for experimental error.</td></tr>
</table>

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Students should be able to:

- accurately use new vocabulary terms introduced in the laboratory exercise in their presentation
- define wet etching
- identify the mask and the substrate *The tape is the mask and each tablet is the substrate.*
- differentiate between *isotropic* and *anisotropic* (They should be able to identify whether their shape was *isotropic* or *anisotropic*.)
- explain what caused the shape to be the way it was *The wet etching process for most substrates produces an isotropic pattern due to the equal removal of particles in all directions as the etching solution comes in contact with the substrate particles.*
- use the terms *reaction rate*, *surface area,* and *contact time* with the surface area to explain how the shape formed
- explain the difference between *active* and *passive etching*

Resources: You may wish to use this resource for further reading:

1. Intel's From Sand to Silicon- the making of a chip. Accessed at: http://newsroom.intel.com/docs/DOC-2476
2. Haixin Zhu, Mark Holl, Tathagata Ray, Shivani Bhushan and Deidre R Meldrum, "Characterization of deep wet etching of fused glass for single cell and optical sensor deposition." *Journal of Micromechanics and Microengineering* 19 (2009): 065013 (8pp) Stacks.iop.org/JMM/19/065013
3. Channel Intel procvies a variety of videos on chip making http://www.youtube.com/results?search_query=channel+intel

National Science Education Standards (Grades 5–8 and 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

Content Standard E: Science and Technology

- Abilities of technological design

Next Generation Science Standards

- MS-PS1-2. Analyze and interpret data on the properties of substances before and after the substances interact to determine if a chemical reaction has occurred.
- MS-ETS1-3. Analyze data from tests to determine similarities and differences among several design solution to identify the best characteristics of each that can be combined into a new solution to better meet the criteria for success.
- HS-PS2-6. Communicate scientific and technical information about why the molecular-level structure is important in the functioning of designed materials.
- HS-PS1-5. Apply scientific principles and evidence to provide an explanation about the effects of changing the temperature or concentration of the reacting particles on the rate at which a reaction occurs.

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