Teacher’s Preparatory Guide

Small Scale Sculpting: Etch Lab

Overview This lab will help students understand some of the challenges of making semiconductor chips and waveguides—both of which are found in electronic circuits.

Purpose This lab is part 2 of a 2-part series of inquiry-driven labs designed to help students understand how materials are sculpted on a small, (nano)scale.

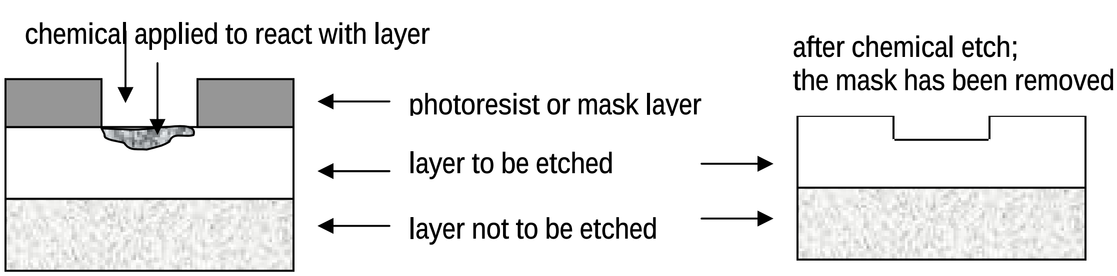
Time Required Two 45-minute periods (plus an optional third *enhancement* activity)

Level Middle school or high school

Teacher Background Improvements in technology often involve making computer chips smaller and faster. Computer chips are made of many layers of different materials that are connected electrically by an often complex maze of metal pathways. As computer chips approach the nanoscale (one billionth of a meter), the processes used to manufacture the chips have evolved to address the problems created by working with such small features.

One such process is the *etching* of materials. To *etch* means “to produce a pattern or design on a hard material by eating into the material’s surface.” In fact, the word origin can be traced back to the Old High German *ezzan*, which means “to eat[1]”. The technique of metal etching with acid was used to produce patterns in swords and other metal objects in the fifteenth century and was later applied to printmaking[2]. This old world technique is used even today in the fabrication of computer chips and other devices, which are on the forefront of electronic technology.

Though the size and scale of today’s computer chips are much smaller (10,000 times smaller!) than the works of art of the fifteenth century, the basic concept is still the same. A pattern is needed in a layer of metal or glass and a chemical reaction is used to “eat” away at the layer in specified areas while the rest of the layer is protected by a stencil. The stencil can be a patterned photoresist layer as introduced in the prior lab or a layer of another material that has been previously patterned by a photoresist. This patterned layer effectively serves as a mask for the subsequent etch and will be referred to as the mask layer. The diagram below shows a side view of a simple etching process in making a computer chip:



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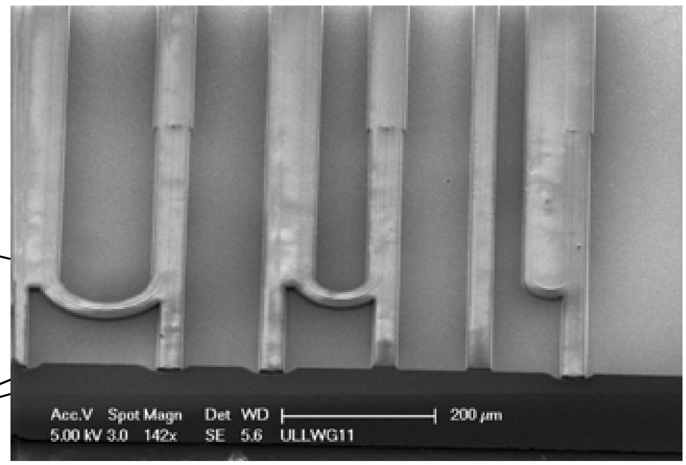
Various acids are used to etch away materials in the process of making devices. This process is called ***wet etching***, for the stenciled material is placed in a container of acid for a specified amount of time and temperature and then rinsed. On a computer chip, the areas to be etched are in the order of microns and nanometers in width and depth. One micron is 1 millionth of a meter and is the size of a hair on the eye of a bee.

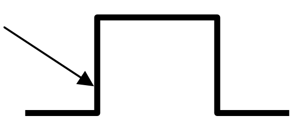
The trouble is, the new structures that are being designed involve widths and depths that are on the scale of 10 to 100 nanometers, which is 1/10 to 1/100 of a micron. At such small dimensions, the wet etching process quickly reaches its limits, for the acid is unable to reach into the micro to nano-scopic spaces to etch away evenly. A good etch method results in well-defined patterns. For novel devices, often more stringent criteria are necessary. This is why the processes involved with etching at the sub-micron level are carefully tailored and controlled to achieve the appropriate patterns and consistency, such as the waveguides shown below, with consistency.

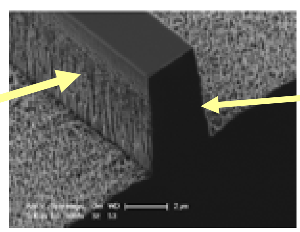
This diagram shows waveguide structures that are about 30 microns in width. (SEM photo courtesy of D. John)



Optical waveguides require smooth, vertical sidewalls to allow light to travel through the waveguide with minimal loss of light.

The pictures below show waveguides with sidewalls of varying roughness and verticality.





(SEM photos courtesy of D. John, UCSB)

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To solve this problem, new methods of etching have been developed. One such technique is called ***dry etching***.

One type of dry etching—called *Reactive Ion Etching (RIE)*—creates plasma with the reactive etching chemical and uses an electric field to accelerate the molecules in the plasma downward toward a layer. The ability to accelerate the molecules toward a layer allows control of force and direction of the etch. In a wet etch, the etching occurs in any direction in which the acid has contact with the material; however, in a dry etch, the ability to guide certain molecules (nanoscale) results in greater etching in one direction. These reactive chemicals bind with the molecules in the layer to be etched and a product is formed, which is swept away by a vacuum pump. One can also add non-reactive molecules to the plasma, such as Argon, and accelerate these molecules as well, which because of their large masses, then physically knock material from the layer. So RIE etches by **both** chemical and by physical means, as shown in the diagram.

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

The diagram above shows both the chemical and physical etching components of RIE.

Image source:
http://matthieu.lagouge.free.fr/microtechnology/microtech_pict/etching/rie-etching.png

The variables to consider in a dry etch method such as RIE are the:

- types and amount of etching chemicals used
- power of the electric field (which controls the acceleration of the etching chemicals)
- overall temperature
- chamber pressure (which also controls the acceleration of the etching chemicals)
- amount of non-reactive chemicals (which controls the amount of physical etching)

Due to the chemical nature of the etching process whether by wet etch or dry etch, many of the variables can be exemplified by a simpler chemical reaction that students can observe in class.

A wet etch can be simulated by this simple chemical reaction:

$$2HC_2H_3O_2 + CaCO_3 \rightarrow Ca(C_2H_3O_2)_2 + CO_2 + H_2O$$

Vinegar reacts with chalk to create a solid and gaseous product.

By ***stenciling*** parts of the chalk, thereby exposing certain areas to the vinegar, structures can be formed similar to the waveguides as discussed above. In the lab, the stencil will be formed from electrical tape positioned into patterns and will be referred to as the ***mask***. The students can then measure the depth of the etch with a caliper, by finding the difference of height between areas protected and unprotected by the mask. Dividing etch depth by the time of etch gives us the etch speed or ***etch rate***. Students can then vary the concentration of vinegar or the brand and type of chalk to see their effects on etch rate. Some brands contain more calcium carbonate and will etch faster. Other types of chalk are more porous, which will also etch faster. Using different

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types of chalk can serve as great analogies to the different materials and properties that are etched.

For example, when making a waveguide, the verticality of the sidewalls is a result of a controlled etch—if there are too many chemical reactions taking place, the sidewalls will be undercut (etched underneath the stencil). If the etch products are not removed, this may slow down etch rate and cause uneven etching. This phenomenon is illustrated by the roughened sidewalls of waveguides. It is also seen in the case of chalk and vinegar, for when there is less fresh chalk area exposed to the vinegar, the etch rate slows and the sidewalls of structures become rough and non-vertical. The temperature of the vinegar will also affect the etch rate. All these variables are those that exist not only with etching but also with most chemical reactions. A controlled etch is a result of much experimentation with the variables involved and occurs when a certain etch process is established and followed. Each material to be etched will have its own etch process. In this lab, the students will be given the opportunity to experiment with some of the etch variables and develop their own "etch process" for chalk.

Sources

1. Definition of *etch*—Merriam-Webster Dictionary
2. "Engraving and Etching—Origins And History Of Intaglio Printing" (accessed Aug. 6, 2009) http://science.jrank.org/pages/2515/Engraving-Etching-Origins-history-intaglio-printing.html

Materials per class of 36 students

- 5 boxes of Crayola™ blackboard chalk
- 1 gallon of white vinegar
- 3 rolls of electrical tape
- pH paper test strips 0–14 or 0–6 range
- hot plate
- 1 tray of ice cubes for ice bath
- 2 thermometers
- 2 shallow pans (8" × 8") of water to fit 9 beakers each
- 18 beakers (50 ml) that will sit in pans of water
- 500 ml of tap water
- 1 hole punch
- 3 black ink pads
- 3 dozen raw eggs (optional activity)
- 2 gallons of white vinegar (optional activity)
- 12 bottles of nail polish (optional activity)
- 1 box of large paperclips (optional activity)
- 36 pipettes or large droppers (optional activity)

Materials per lab group of 2 students

- 2 pieces of masked chalk of different patterns (Day 1)
- 2 pieces of masked "etch test" chalk of different patterns (Day 2)
- 2 pH paper test strips
- one 6 oz clear plastic cup to fill with tap water
- 1 plastic 6" caliper
- 1 digital stopwatch
- 50 ml beaker for the vinegar

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Advance Preparation Materials can be purchased from many educational supply companies. Vinegar and shallow pans can be purchased at a grocery store. The websites below are suggested places to start shopping.

Material	Website
6" plastic calipers	**Parts Express** (http://www.parts-express.com)
Color**pH**ast pH 0–14	**Science Kit Boreal** (http://sciencekit.com)

1. ***Mask the chalk into 2 patterns.***
For Day 1 activities, tape the chalk into the two designs shown below. Electrical tape works best. *Tape the bottom of each piece of chalk so that the vinegar won't seep in and weaken the chalk.* Prepare enough chalk pieces so each lab group receives both designs.

Mask #1 allows students to etch and measure a clear, large area, and will be used for calculating etch rates. Mask #2 is designed so that the resulting etch produces trenches so that students can observe the sidewall profiles.

2. ***Set up stations.***
For Day 1 and Day 2, stations should be set up so that factors that may affect etch rate can be tested:
Station 1: A hot plate with a water bath kept at a constant temperature hot enough to touch. This will allow students to place their cup of vinegar to be heated and kept at a warm temperature during the etch time. Place a thermometer in the warm bath so that the temperature can be recorded.
Station 2: Provide an ice bath. Place a thermometer in the ice bath so that the temperature can be recorded.
Station 3: Prepare 3 inkpads for printing at the end of the lab.
Other stations: To enhance the Independent Inquiry Lab, set up a station that allows students to dilute the vinegar solution.

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Station 1: warm bath

Station 2: ice bath

The warm bath and ice bath setups allow multiple groups to run their experiments at the same time. Place several beakers of vinegar in each pan and have the students use beakers as they become available. Limit the pieces of chalk to one per beaker. Beakers of vinegar can be reused. Students can walk up to the setup, place their masked chalk into an empty beaker and wait for the required amount of time.

3. ***Prepare "Etch Test" Chalk for Day 2.***
   The "etch test" chalk for the students will have features that they have not seen in Day 1. They are shown below. The dots were made with a hole-punch and the trench is as narrow as possible.

dot structures

narrow trench

Safety Information Keep the work area well ventilated—vinegar has fumes that may irritate in high concentrations. Inform students of the dangers of the hot plate and have a wash area set up in case of burns.

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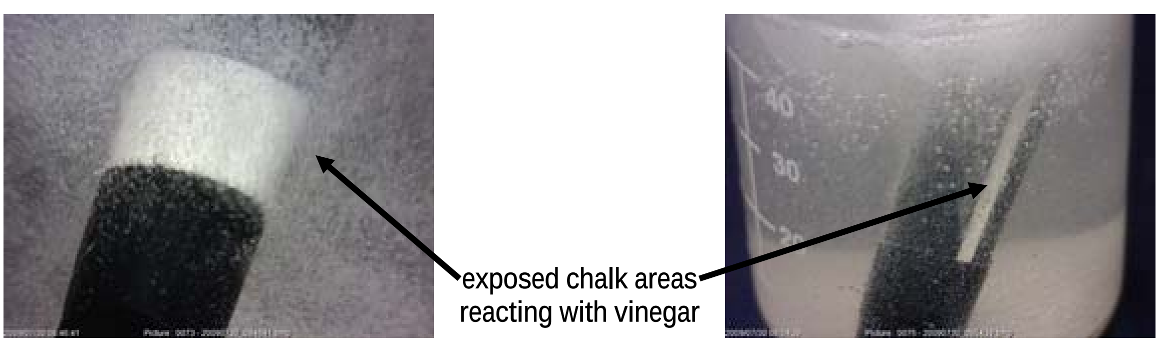
Instructional Procedure

Time	Activity	Goal
Day 1		
45 min	**Chalk and vinegar lab:** Students etch chalk for a given amount of time to determine etch rate. Then, with chalk masked along the axis, they etch to observe sidewall profile. Students experiment with variables given to begin formulating etch process. Have students complete Student Worksheet: *Small Scale Sculpting: Guided Inquiry I* (or follow Student Worksheet: *Small Scale Sculpting: Independent Inquiry I, Challenge #1*).	Etch rate. Factors that affect etch (chemical reaction). Vinegar is neutralized after etch.
Day 2		
45 min	**Design an etch process:** Given etch data collected during Day 1, students design an etch process to accomplish a certain etch rate or sidewall verticality. Have students complete Student Worksheet: *Small Scale Sculpting: Guided Inquiry II* (or follow Student Worksheet: *Small Scale Sculpting: Independent Inquiry I, Challenge #2*).	Assess understanding of variables that affect etch rate or type of etch. Can turn in resulting chalk piece to be graded.
Day 3 (optional)		
Enhancement **45 min (plus drying time and soaking time)**	**Etch an egg:** Students mask a raw egg in shell with nail polish leaving designed open areas, and then let egg sit overnight in vinegar following instructions on Student Worksheet: *Small Scale Sculpting: Independent Inquiry II*.	Reinforce etch and masking technique. Calcium carbonate can be found in living things.

Teaching Strategies

The two pieces of chalk used in Day 1 need to be etched sequentially. This allows Mask #1 to dry while Mask #2 is being etched. A wet piece of chalk tends to be weak and may break during the removal of the electrical tape. During the etch, draw attention to the bubbling on the exposed areas of the chalk such as shown below to discuss the etch products and what happens when the etch products get in the way of the etch.

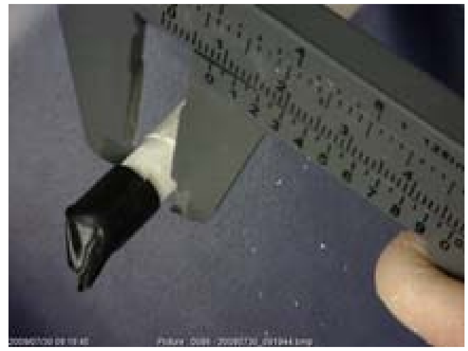


Mask #1 Mask #2

Review answers to the questions as a class at the end of each section to ensure that students understand the key concepts as they progress through the lab.

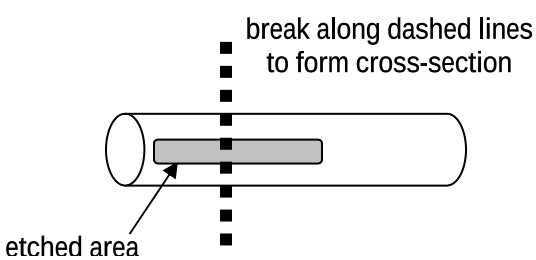
Students may not have seen a caliper. Prior to the lab, have students practice using the caliper and practice reading the correct measurement using the different scales.

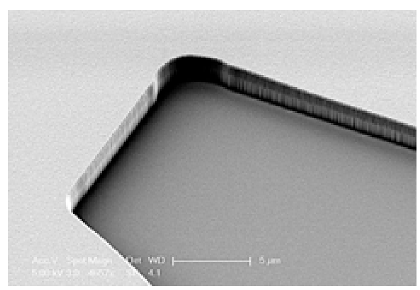
measurement of masked region



measurement of unmasked region

Model the measurement of the etch rate to the class. If possible, arrange to have a camera and projector to help the students see where the measurements should be taken as shown in the pictures above. The students need to do this on their own during the testing of the variables. Mask #2 was designed to etch a trench in order to observe profiles of sidewalls. Students can initially look along the trench, but to see the sidewalls more clearly, a cross sectional view is better. This is very similar to the process of analyzing waveguide structures. A cross-section allows the engineer to observe how the sidewalls look. Magnifying lenses may be useful for the students to take a closer look at the roughness and profiles of the sidewalls, but is not necessary. With the waveguides, a more powerful tool must be used to see the small features, such as the scanning electron microscope.





This picture shows an etched area in waveguide structure. Sidewall roughness can be observed. (Photo by D. John, UCSB.)

view along trench

view of cross-section of narrow trench

view of cross-section of wide trench

The cross-section pictures above show the typical sloped sidewalls of the trenches from a chalk etch. This is most likely due to the etch products (bubbles) that get in the way of the etching.

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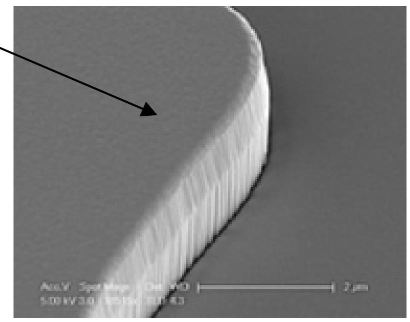
Students will be given the chance to explore two variables. For this, they must mask their own chalk. Hand each group 2 fresh pieces of chalk and 4 pieces of electrical tape. Have the students use the Mask #1 design so that etch rates can be calculated. The goal is to experiment enough so that on Day 2, they will apply their best etch process to a “test” piece of chalk. A good etch process will have the highest etch rate with the straightest sidewalls.

Keep the stations out for Day 2 for the students to use. Make sure that each group’s etch process is written and supported by sound reasoning before letting the groups try their etch. The “test” chalk is designed to have structures that present problems in etching similar to those that engineers face with their etching process. The very narrow trench structure has led engineers to create dry etch processes. The dots represent structures such as waveguides that need to have vertical and smooth sidewalls.

mask areas

The dot structures allow students to observe the profiles of sidewalls. The chalk piece to the left still has the mask layer and the waveguide structure to the right also has a mask layer.



This picture shows the dot structures with the mask removed. The sidewalls are very sloped.

This picture shows the very narrow trench. Evidence of how the etch products interfered with the etching is seen by the sloped walls and shallow etch depth.

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This is an example of a print made from the etched piece of chalk. Have the students carefully roll the piece of chalk on an inkpad then roll it onto their worksheet. Early printmaking was done in a similar fashion; however, in the case of intaglio printing (image is cut into the surface), the etched surface was metal and the ink was smeared into the etched lines of the metal. The paper was then placed on the metal to receive the image (as shown below on the right).

Above: A print and the piece of chalk from which the print was made.

Left: Rembrandt, The Virgin and Child with a Cat, 1654. Original copper etching plate above, example of the print below, with composition reversed. (Source: http://en.wikipedia.org/wiki/etching

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Etch an Egg:

This activity relates the chemical reaction and materials involved to the life sciences. Calcium carbonate is found in many living organisms as bone structures and shells. Have the students draw in pencil simple designs on a chicken egg. Because of the fragile nature of the shell when etched, keep the number of designs to 3 or 4 small shapes or outlines evenly spaced around the equator of the shell. Using nail polish as a quick drying mask, the students will paint the rest of the egg with a consistent coat of nail polish. Let the painted eggs dry for a couple of hours. Then soak the eggs in vinegar for about 8 hours. Adding salt to the vinegar will help keep the egg from bloating due to osmosis. The unmasked regions will etch away to the membrane as the pictures below indicate. After the etch is complete, have the students carefully poke holes in the top and bottom of the egg and after puncturing the egg yolk, blow out the egg with a pipette or large dropper. Rinse out eggs and let dry.

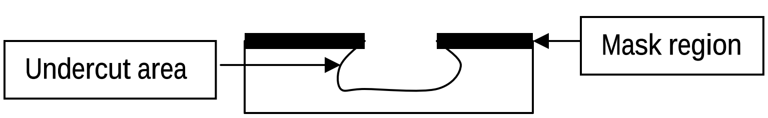
Materials needed:
- one egg per student
- paintbrush per student
- 12 bottles of nail polish (3 students per bottle)
- cups of vinegar with salt added—one per student
- paperclip
- large dropper or pipette

Masked eggs in vinegar show chemical reactions only in exposed areas.

The etch only occurs in the exposed areas and the membrane is left.

Guided Dialog *Before* beginning the lab, review the meaning of these terms:

Etch *To produce a pattern or design on a material by eating into the material's surface.*
Mask *A patterned material that is used to protect areas of a layer from an etch chemical.*
Etch rate *The amount of material etched per unit time.*
Sidewall profile *The slope of the sidewall of a structure.*
Undercut etch *An etch that has progressed underneath the masked region.*



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Etch products *Products of a chemical reaction that, if not removed, may get in the way of further etching.*

A nice opener for the etch lab is: "If I give each of you a grain of sand and tell you to sculpt it into a smiley face, what problems might you experience?" Answers may include needing small enough tools, seeing what I'm doing, needing a stencil to make the fine lines of the smiley face. This question is used in UCSB's chip camps (by A. Berenstein) to provoke discussion and is a great way to give perspective into the size constraints that semiconductor engineers encounter.

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

1. What happens during a *chemical reaction? Chemical reactions occur when the reactants (particles) come into contact with each other and form new products.*
2. What factors affect the rate at which a chemical reaction proceeds? *concentration of reactants; temperature of reaction; agitation of solution, surface area*
3. How does one use pH paper to identify acids and bases? *Acids will have a pH of 0–6 and Bases will have a pH of 8–14.*
4. How will adding an acid to a base affect the pH of the resulting solution? *An acid will neutralize a basic solution.*
5. What factors affect a chemical reaction? *The concentration of an acid will affect the chemical reaction.*

Last-minute Details

1. Clearly differentiate Mask #1 and Mask #2.
2. Make enough Mask #1 chalk to use for the activity on Day 2.
3. Remind/teach students how to use a caliper.

List any last-minute details that the students must remember, including reiterating all safety precautions. Now, begin the lab.

Cleanup Students should dump vinegar solutions down the drain, thoroughly rinse out their cups, and clean up their lab tables.

Enhancing Understanding Cover this section *after* the activity.

Research and show students the fabrication of Microelectromechanical Systems (MEMS) and the role of a great etch process in such structures. You may want to view the video on MEMS fabrication http://www.youtube.com/watch?v=PbF-hD5jnr0

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Going Further Students who have a good grasp of the content of the lab can be further challenged by asking questions to push the students' understanding. For example:

1. How would a dry etch improve upon the results from your etched dot structures and narrow trench structure? *The sidewalls of the dots should be more vertical and the trench would be deeper and the walls more vertical.*

Assessment: Students should be able to calculate etch rate, identify variables that affect the etch rate, and identify ways to test and improve upon etch processes.

Resources: You may wish to use these resources either as background or as a resource for students to use in their inquiry-based design.

- Microtechnology - Dry etching (a website written by a Doctoral student who nicely describes the processes used in his research):
  http://matthieu.lagouge.free.fr/microtechnology/dry_etch.html
- Etching Processes (an article that explains the difference between wet etching (traditional acid etch) and dry etching (methods like RIE)):
  https://www.memsnet.org/mems/processes/etch.html
- About MEMS and Nanotechnology
  http://www.memsnet.org/mems/
- About MEMS
  http://www.memx.com
- MEMS DVD - http://www.siliconrun.com/sr_mems.shtml

National Science Education Standards (Grades 5–8 and Grades 9–12)

Content Standard A: Science as Inquiry

- Abilities necessary to do scientific inquiry
- Understandings about scientific inquiry

Content Standard B: Physical Science

- Properties and changes of properties in matter

Content Standard E: Science and Technology

- Abilities of technological design

California Science Education Standards (Grade 8)

Physical Sciences, Content Standard 5: Reactions

7. Students know reactant atoms and molecules interact to form products with different chemical properties.
2. Students know how to determine whether a solution is acidic, basic or neutral.

Investigation and Experimentation, Content Standard 9

a. Plan and conduct a scientific investigation to test a hypothesis.
b. Evaluate the accuracy and reproducibility of data.
c. Distinguish between variable and controlled parameters in a test.

California Science Education Standards (Grade 9–12)

Chemistry, Content Standard 5: Acids and Bases

a. Students know the observable properties of acids, bases, and salt solutions.
d. Students know how to use the pH scale to characterize acid and base solutions.

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Chemistry, Content Standard 8: Reaction Rates

a. Students know the rate of reaction is the decrease in concentration of reactants or the increase in concentration of products with time.
b. Students know how reaction rates depend on such factors as concentration, temperature, and pressure.

Investigation and Experimentation, Content Standard 1

b. Identify and communicate sources of unavoidable error.
c. Identify possible reasons for inconsistent results, such as sources of error or uncontrolled conditions.
d. Formulate explanations by using logic and evidence.

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