Microfabrication Teaching Laboratory

Option 1: Making a Diode or Photovoltaic Cell

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Overview.

This lab introduces students to the processes involved with fabricating micro devices, such as integrated circuits and micromechanical systems. Students reproduce the fabrication steps used in optical lithography, using simplified tools to carry out thin film deposition, patterning, etching, and doping. By following the procedure, students should be able to produce working examples of *p-n* junction-based devices, and perform electronic tests on these devices.

The lab is divided into five sections.
Section 1. Wafer cleaning and oxide growth. Students clean the wafers to remove fingerprints and dust, then use a high temperature furnace to grow an oxide layer on the silicon wafer.
Section 2. Patterning. Students print a simple mask on plastic film, spin-coat the wafer with photoresist (PR), expose the PR-covered wafer using the mask and a light source, and develop the PR to yield a patterned wafer.
Section 3. Etching. Exposed areas on the patterned wafer are etched away using a dilute acid solution.
Section 4. Doping. The active regions of the device are formed by adding boron in a liquid suspension to the wafer surface and driving the dopant into the exposed silicon regions using high heat.
Section 5. Finishing and device testing. Electrical contacts are added to the wafer. A simple current-voltage (I-V) is used to test the performance of the device.

Time Required

Prior to lab: Wafers must be oxidized by firing them for 14 hours. With temperature ramp-up and cool down, allow for 24 hours to prepare the oxidized wafers.
Patterning, etching, and doping: Two to three hours.
Post doping heat treatment: About six hours required to heat wafers and then cool to room temp.
Final device assembly: About one hour.
Device testing: About one hour.

Level: high school and undergraduate students. An introduction to solid state physics (*p*-n junctions) and some familiarity with acid-base chemistry is desirable.

Resources Needed

Equipment

- One or more hotplates, preferably with temperature readouts, preset to 105°C
- One 500mL beaker for mixing developer solution
- Four shallow trays to hold developer, etching bath, acetone, and water baths. Trays should be wide enough to immerse a 100mm wafer. Plastic food storage containers may be used.
- One or more desk lamps with a ~25 watt compact fluorescent bulb
- Optical microscope, preferably with digital camera
- Tweezers
- Digital timer

- Splash-proof safety goggles
- Chemical safety gloves

Special Equipment. See Appendix 1 for sources and ordering info.
- Tube furnace, large enough to accept 100mm wafers and capable of attaining 1100°C
- Quartz or ceramic tube
- Spin coater
- Clear plastic containment box, about 45x30x25 cm
- Current-voltage tester

Consumable Materials
- Gloves, light duty (for general wafer handling)
- Deionized water
- A source of clean, dry, particle-free compressed air
- Lint-free laboratory wipes
- Disposable plastic droppers
- Kapton tape or similar for masking the silver paste

Special materials, solvents, and chemicals. See below for sources and safety guidelines.
- Solvents: methanol, acetone, isopropyl alcohol
- Silicon wafers, pre-cleaned, 100mm diameter, doped n-type
- Photoresist: Microposit S1813. This must be stored in a dark-colored plastic bottle.
- Developer for the photoresist: Microposit 351. Dilute this concentrate by mixing one part 351 with 5 parts deionized or distilled water.
- Etchant: Rust Stain Remover (3% HF solution in water)
- Spin-on boron dopant: Borofilm 100
- Conductive silver or aluminum paste, for applying contacts to the device.

Safety
- Splash-proof safety goggles and light duty gloves are required when handling solvents, photoresist, and wafers.
- Heavier chemical-resistant gloves are needed for the etch chemical, which is a 3% solution of hydrofluoric acid. Concentrated HF can cause serious burns; this more dilute solution is safer to handle, but still requires the use of splash-proof chemical goggles and heavy gloves designed for caustic chemical handling (i.e., not light latex gloves). Wipe up spills immediately.
- Avoid contact with photoresist; use soap and water to remove any material that touches skin.
- The developer solution contains sodium hydroxide and is alkaline. Wear plastic gloves when handling.
- Solvents and the photoresist must be handled with adequate air circulation to avoid buildup of solvent vapor. Use of chemical fume hoods is recommended, but a well-ventilated laboratory may be acceptable.
- MSDS sheets for the chemicals used above are available at http://www.msds.com.
- These chemicals must be stored, used, and disposed of safely following your organization's chemical hygiene and hazardous waste disposal procedures.
- Use care when handling silicon wafers; they are fragile and may shatter into sharp fragments if dropped.

Procedure

Section I. Growing the thermal oxide layer

In this section the wafers to be processed have a thin film of oxide grown on their surface. This is done by heating the silicon wafer to 1050 C in air, which creates a layer of silicon dioxide (SiO_2) about 350-400 nm thick that will function as an insulator.

1. Place the wafers to be coated on a clean surface. If they wafers are not brand new, clean them by squirting a small quantity of isopropanol on each wafer and gently wiping with a dust-free wipe.
2. Place the wafers inside the quartz tube which is placed in the tube furnace.
3. Set the tube furnace temperature controls at 1050°C. Expose the wafer to this temperature for 14-16 hours to grow the oxide layer.
4. Shut down the furnace and allow the wafers to cool at least four hours.
5. Remove the wafers from the furnace and visually inspect them. Estimate the thickness of the silicon oxide layer by comparing wafer color to the color card. The wafers should have oxide layers of roughly 3500Å.

Section II. Optical Patterning

In this section the top oxide layer of the wafer is patterned using photoresist. At the end of this step, the pattern from the mask will have been transferred to the wafer. Any errors that occur at this stage can be corrected by removing the photoresist and re-doing the step.

1. Pre-clean the Wafer

a. Place wafers on a dry, clean wipe. Squirt a small quantity of isopropanol on each wafer and gently wipe with a clean room wipe. Allow the alcohol to dry from the wafers
b. Blow-dry the front of the wafers with particle-free compressed air.
c. Place the wafers on the hotplate set at 105°C for 60 seconds to drive off any remaining alcohol. Allow to cool.

2. Apply Photoresist

a. Place the spinner inside the containment box. Line the box with paper towels to catch excess photoresist.
b. Place a wafer on the spinner so that the flat of the wafer is next to a peg on the spinner disk. Rotate the wafer so that its outer edge is under all three pegs.
c. Position the spinner so that its center is directly under the hole in the lid of the containment box. Place the lid on the box to check alignment, and adjust if needed. With the lid on, turn the spinner on and allow it to run about 30 seconds to reach full speed.
d. While the spinner is spinning up to speed, open the bottle of photoresist. Withdraw enough photoresist into a disposable dropper to fill about 2-3 cm up from the bottom of the dropper tip.
e. When the spinner has reached full speed, insert the dropper into the hole in the box lid. Try to position the dropper directly over the center of the spinning wafer.

f. Squirt all the photoresist in the dropper onto the wafer in one continuous motion (i.e., don't stop and start but apply all the dropper contents at once to achieve an even coating). Allow the spinner to run 30 seconds, then shut it off and allow the spinner to spin down.
g. Place the wafer on the hotplate set at 105°C for 60 seconds. This helps to drive off excess solvent and prepare the photoresist for imaging.
h. Allow the wafer to cool for 1-2 minutes. Keep the wafers out of direct sunlight and strong room light during this time.

3. Expose and develop the photoresist

a. Place the wafer on a non-reflective surface.
b. Place the photomask directly on the wafer. The side on which the pattern is printed should be in the down position, closest to the wafer surface.
c. Position the compact fluorescent bulb about 12 cm above the mask.
d. Expose the wafer for 120 seconds.
e. Submerge the wafer in the developer solution and agitate for 45-60 seconds.
f. Submerge the wafer in deionized water for two minutes.
g. Dry the wafers using compressed air.
a. Inspect the wafer to ensure that the pattern was transferred accurately. If not, remove the photoresist by immersing the wafer in acetone. Rinse the wafer in isopropanol, then repeat steps 1-3

4. Hard Bake

a. The photoresist is relatively weakly bonded to the underlying oxide layer. When the wafer is immersed in the etching bath, the etchant will often diffuse under the photoresist and lift it off the wafer surface, causing an uncontrolled etch and degrading the pattern.
b. To prevent this, the wafer must be "hard-baked". Place the wafer in a lab oven set to 140°C, and allow the wafer to bake for 20 minutes. This bonds the photoresist more completely to the wafer surface and retards photoresist lift-off.

Section III. Etching

After the wafer is patterned with photoresist, it is ready for etching. Areas of exposed oxide are removed using a dilute solution of hydrofluoric acid. The HF solution requires the use of gloves and splash proof safety goggles.

1. Add the 3% HF solution to a plastic tray. DO NOT use a glass container for holding or storing the HF solution.
2. Place the patterned wafer in the HF solution. Leave the wafer in the etching solution for 25 to 30 minutes. The tray should be kept covered during this time to minimize evaporation.
3. At 10 minute intervals, observe the surface of the wafer in the etch bath. The photoresist will exhibit a pattern of cracking, but should remain on the wafer. If the resist appears to be coming off the wafer surface in flakes, the etch may be compromised and the sample may be over-etched.
4. After 25 minutes, withdraw the wafer from the etch bath, place in a water bath, and agitate gently. Then rinse the wafer under running water.
5. Test for etching completion: observe how water wets the surface of the wafer. Bare silicon is hydrophobic, and water should readily de-wet from a completely etched surface. The oxide is more hydrophilic, so water should evenly wet and sheet the oxide-covered regions.

6. Dry the wafer using compressed air.
7. Estimate the thickness of the oxide-covered regions using the SiO_2 film thickness color chart. They should be in the 1800 to 2500 Ǻ range.

Section IV. Doping

In this step the areas on the n-type wafer exposed by the previous etching step are coated with a p-type boron dopant. The boron is then diffused into the silicon matrix using high heat. This creates the *p-n* junction.

1. Apply the spin-on dopant.
   a. With the spinner inside the containment box, place the wafer on the spinner and attach it to the spinner as described in step II.2.b above.
   b. Position the spinner so that its center is directly under the hole in the lid of the containment box. With the lid on, turn the spinner on and allow it to run about 30 seconds to reach full speed.
   c. While the spinner is reaching running speed, fill a plastic pipette with about one ml of spin-on dopant.
   d. When the spinner has reached full speed, insert the dropper into the hole in the box lid. The dropper should be positioned directly over the center of the spinning wafer.
   e. Apply the dopant in the dropper onto the wafer in one continuous motion. Allow the spinner to run 30 seconds, then shut it off and allow the spinner to spin down.
   f. Remove the wafer from the spinner.
   g. Place the wafer on a hot plate or an oven at 200C for 15 minutes to remove excess solvent from the wafer.
2. Drive in the dopant at high temperature
   a. The dopant must be driven into the bulk silicon using high temperatures to speed up diffusion. However, these same high temps will re-form an oxide layer on the etched areas. To avoid this, the dopant is heated under nitrogen gas.
   b. Set up the furnace tube to receive a small controlled nitrogen flow.
   c. Place the wafer inside the quartz tube which is placed in the tube furnace.
   d. Set the tube furnace temperature controls at 1030°C. Expose the wafer to this temperature for 1-2 hours to diffusively drive the boron dopant into the open areas on the wafer.
   e. After 1-2 hours, shut off the nitrogen flow, shut down the furnace, and allow the wafers to cool at least three hours.
3. Since the dopant spread out over the whole wafer but does not need to be present on the oxide-covered areas, it needs to be etched from the latter.
   a. Place the wafer in the 3% HF bath for a few minutes to cleanup these areas.
   b. Rinse the wafer in DI water.
   c. Dry using compressed air or allow to air dry.

Section V. Applying Contacts

The wafer, now containing a *p-n* junction, must have metal contacts applied so that it can be tested. This is done by applying a conductive metal paste to the back of the wafer and in a thin trace to the front active area, allowing probes to be placed on either side of the junction. The exact placement of the conductors will depend on the device being made.

1. Clean the doped wafer with acetone and DI water and wipe it thoroughly.
2. Using the silver paste and the applicator, apply the past to the back side of the wafer, opposite to the active area on the front.

For a diode device:
3. Apply a thin trace (~1mm wide) to the window area on the front of the wafer. More than one trace can be placed across the window, but these should be connected into a common path.

For a photovoltaic device:
4. Mask the active region(s) using 0.5 mm kapton tape to form thin lines in between the active regions.
5. Carefully apply the silver paste in the active region unmasked by the tape. This forms thin lines of silver paint in the wafer that act as metal fingers to collect generated carriers by photogeneration.
6. Remove the tape with a tweezer and mask the end of the metal lines with the kapton tape.
7. Apply the silver paste in the horizontal direction to connect the vertical metal lines. This forms a series connection with the metal lines over the active solar cell region. This is the region where the device will be probed for further characterization.
8. While the paste is still wet, embed a small wire in the wet silver paste lines on both sides of the wafer. When dry, these wires will be the contacts to which probe clips can be attached.
9. Follow directions on the metallic paste as to drying. When dry, the device is ready to test.

Section VI. Device Characterization

The devices that can be made in this lab—diodes and photovoltaic cells—are characterized in terms of their current-voltage response, i.e., the I-V curve. Forward and reverse voltages are applied to the junction and the resulting current measured.

To test the I-V curve of the devices made in this activity, we recommend the ADAL M1000 tool from Analog Devices. With the aid of a simple external circuit, the M1000 can measure the I-V curve from diodes and transistors; it can collect the data, graph the results, and allow quantitative measurements of turn-on voltage, leakage current, and breakdown voltage.

Information on how to set up the circuit and use the M1000 can be found at Analog Devices' web site, wiki.analog.com/university/tools/m1k. See Appendix 1 for ordering information.

APPENDIX 1. Sources for materials and equipment

Materials

- Solvents may be obtained from Fisher Scientific (www.fishersci.com), Sigma Aldrich (www.sigmaaldrich.com), or other academic chemical supply houses.

- n-type silicon wafers may be purchased from several sources, including Polishing Corp of America (www.pcasilicon.com) and University Wafer (www.universitywafer.com). Wafers come in many grades; for this activity, specify n-doped test grade wafers. At this writing (spring 2017) these wafers cost about $12 each when purchased in quantities of 25.

- The Microposit 1813 photoresist and Microposit 351 developer can be ordered from MicroChem Corp., Newton, MA; tel: 617-965-5511, e-mail: sales@microchem.com. One liter of the S1805 photoresist costs about $160 at this writing, which should supply at least 100 experiments.

- The etchant in this activity is a commercial product called Rust Stain Remover, available in hardware and home improvement stores, and directly from the manufacturer at www.whink.com.

- The Borofilm 100 spin-on dopant can be purchased from Emulsitone Chemicals, LLC. Order at Emulsitone.com.

- High quality silver paste can be ordered from Ted Pella, Inc. (tedpella.com).

Equipment

- Spin coater. A simple device for spin coating photoresist may be constructed from a 120VAC 3" cooling fan with a 4” aluminum or plastic plate attached to the fan blades. Plans and a parts list for building the fan motor-based spin coater may be obtained from the Nano Center at the University of Minnesota, Minneapolis, MN. Call 612 624-8005 for more information.

- Containment box. Suitable clear plastic containment boxes may be found in the housewares section of a hardware store or similar outlets.

- Photomask. Inexpensive masks (~$50) can be obtained commercially from graphic printing shops. The design of the mask is quite simple, merely one or more open windows in a dark background. One possibility is illustrated in Appendix 2.

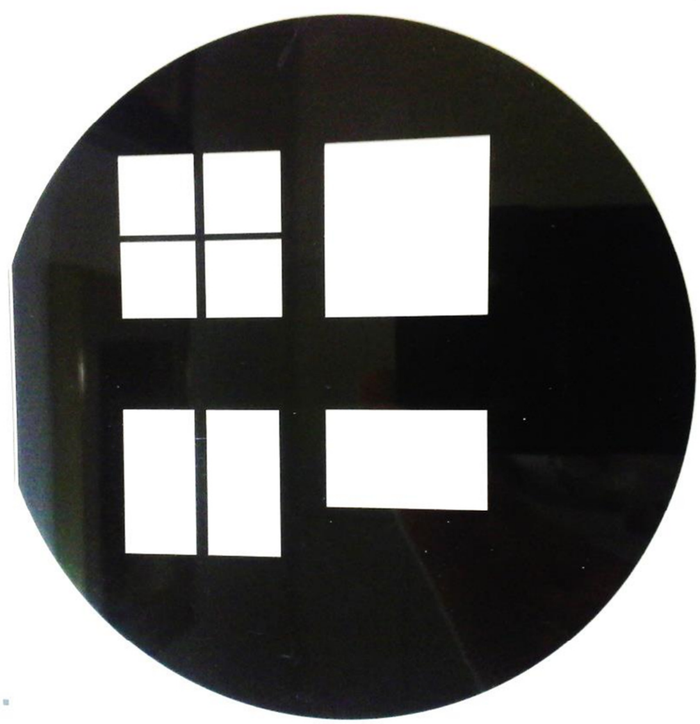
  Alternatively, a custom photomask may be designed on a computer drawing program, then printed on polyester transparency film using a high quality xerographic copier, or inkjet or laser printer. *NOTE:* When using some printers to produce these transparencies, the pattern may be insufficiently opaque to ensure a clean masking effect. To obtain a fully opaque pattern with an inkjet printer, repeated printing of the pattern on the same sheet of transparency is possible. By carefully aligning the paper guides, 5x overprinting without serious degradation of the image can be achieved. Allow the ink to dry fully (at least 5 minutes) between passes.

- Current-voltage tester. The devices made in this activity can be tested using the ADAL M1000 tool from Analog Devices. With the aid of a simple external circuit, the M1000 can measure the I-V curve from diodes and transistors. More information can be found at wiki.analog.com/university/tools/m1k . Ordering information is at: www.analog.com/en/design-center/evaluation-hardware-and-software/evaluation-boards-kits/ADALM1000.html#eb-overview

- Tube furnace and tube may be ordered from Fisher Scientific (www.fishersci.com), Sigma Aldrich (www.sigmaaldrich.com), or other academic supply houses. The tube must be large enough to accept 100mm wafers, which means the furnace cost may be over $5000.

  As an alternative to a laboratory tube furnace, an **art clay ceramics kiln** may be used. Remove all pottery debris and try to clean the loose ceramic powder inside the kiln, then place the silicon wafers on a ceramic support and fire to the cone corresponding to about 1100°C (2012°F).

APPENDIX 2. Photomask Template. This pattern may be used to make the open areas on the wafer that will become the photovoltaic surfaces.



APPENDIX 3. Silicon dioxide color card

Thin films of silicon dioxide will exhibit different colors according to how thick the layer is. Thus, the appearance of the oxide formed on silicon wafers is a guide to the thickness of the oxide layer. Use the color chart below to gauge the thickness of the oxide layer on your wafers.

SiO_2 Thickness Color Chart

Film Thickness (Å)	Color of Film (those shown are only indicative)
500	tan
700	brown
1000	dark violet to red violet
1200	royal blue
1500	light blue to metallic blue
1700	metallic to very light yellow-green
2000	light gold or yellow - slightly metallic
2200	gold with slight yellow-orange
2500	orange to melon
2700	red-violet
3000	blue to violet-blue
3100	blue
3200	blue to blue-green
3400	light green
3500	green to yellow-green
3600	yellow-green
3700	green-yellow
3900	yellow
4100	light orange
4200	carnation pink
4400	violet-red
4600	red-violet
4700	violet
4800	blue-violet
4900	blue
5000	blue-green
5200	green
5400	yellow-green
5600	green-yellow
5700	yellow to "yellowish" (at times appears light gray or metallic)
5800	light orange or yellow to pink
6000	carnation pink
6300	violet-red
6800	"bluish" (appears between violet-red and blue-green - overall looks grayish
7200	blue-green to green
7700	"yellowish"
8000	orange
8200	salmon
8500	dull light red-violet
8600	violet
8700	blue-violet
8900	blue
9200	blue-green
9500	dull yellow-green
9700	yellow to "yellowish"
9900	orange