Introduction to Photolithography: Preparation of Microscale Polymer Silhouettes

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Much of today's information technology relies on microchips developed by the semiconductor industry. These microchips are the brains behind most electronic devices such as personal computers, cell phones, and CD players. Although microchip function is typically described in terms of physics and engineering, the underlying process for the fabrication of these complex electronic devices, photolithography, is rooted in polymer chemistry *(1).* Developed in 1959, photolithography is a process that uses high-intensity light and a photomask to prepare a polymer network on a silicon wafer *(2, 3).* The polymer network is formed through a physical change to a photoresist, which contains a light-sensitive compound and a mixture of polymers that becomes soluble or insoluble when exposed to UV light. The patterned polymer network acts as a guide for the chemical etching of the silicon wafer, much as a canyon channels a river's flow and causes it to carve away the underlying soil. The terms given to the different types of photoresists, positive and negative, depict the resulting polymer "image" that is displayed. A positive photoresist is composed of an insoluble polymer that degrades into a soluble polymer when exposed to UV light, while a negative photoresist is composed of monomers or polymers that polymerize or crosslink to form insoluble polymers upon UV exposure. Previously, Christenson and coworkers reported an experiment for undergraduates that mimics the process of microchip construction using a positive photoresist *(4).* This article describes an easy procedure based on a negative photoresist process that is designed for junior high or high school students, which will introduce them to the key terms and concepts of photolithography. The experiment allows the students to visualize the fundamental process behind microchip fabrication, observe the rapid prototyping enabled by such a technique, and appreciate its versatility by fabricating polymer thin film objects in virtually any shape they choose, including their own polymer silhouettes, all within minutes.

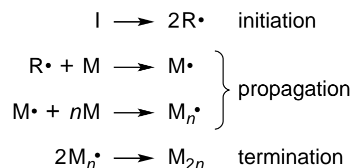
Principles

Polymerization

As stated earlier, the fabrication of many electronic devices is based on the formation or degradation of polymers. A polymer is a substance that contains a chain of many repeating molecules called monomers. A polymer can be visualized as a string of pearls, with each individual pearl representing a monomer. The process of combining monomers to form polymer is polymerization. An excellent resource for a background on polymer science can be found online *(5).* In this experiment, all polymers will be formed through radical polymerization, which is a type of polymerization that occurs through the reactivity of an unpaired electron species, or radical, and involves three processes: initiation, propagation, and termination (Scheme I) *(5).* In the initiation step, a radical species (R·) is produced when a molecule called an initiator (I) is exposed to a trigger such as heat or light. This radical species reacts with a monomer (M) and transfers its radical character to that monomer. The reactive monomer then adds a second monomer, thereby transferring its radical reactivity to the new monomer, and increases the chain length by one. The continuous addition of monomer to a growing polymer chain is called propagation. When the radical species at the end of the polymer chain combines with a second radical species, the polymer becomes inactive and further propagation is inhibited through a process called termination.

Photopolymerization

When light is used as the trigger to produce the reactive radical species during initiation, the process is called photopolymerization. Photopolymerization occurs through the use of a photoinitiator, which is a molecule that contains a bond easily broken by light to produce a radical. The photoinitiator used in this experiment is 2,2-dimethoxy-2-phenyl acetophenone (DMPA). When DMPA is exposed to UV light, it breaks down into reactive radical species (Figure 1) and then combines with a monomer to initiate polymerization. The molecular weight of the polymer formed through the photopolymerization process depends on factors such as the type and concentration of the monomers, the concentration of the photoinitiator, and the intensity of the UV light *(6–9).*



Scheme I. Mechanism of radical polymerization.

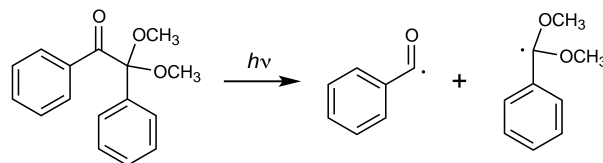


Figure 1. DMPA fragments into two radicals (shown) that can further break down into other radicals or initiate the polymerization of monomer.

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Crosslinking Density

If a monomer contains just one group that is capable of reacting with growing polymer, linear polymers will result. When a monomer that contains two or more polymerizable groups is used, two linear polymer chains may be connected to create a crosslinking junction, forming a polymer network. A monomer with two or more polymerizable groups is called a crosslinker. To visualize crosslinking, think of the crosslinker as a person with two arms. Each reactive group is a hand that can grab onto a polymer chain, therefore combining two polymer chains into one branched polymer chain. The degree of crosslinking junctions present in the polymer network is called the crosslinking density. The crosslinking density is an important factor that dictates the structure and the properties of a polymer and can be controlled by altering the quantity of crosslinker used. A difference in crosslinking density can make a polymer that is normally soluble in a suitable solvent become completely insoluble in that same solvent. Figure 2A depicts a mixture of polymers that are lightly crosslinked and therefore soluble in a suitable solvent. In contrast, Figure 2B shows a mixture of polymers that are highly crosslinked and therefore insoluble in the same solvent *(10, 11)*. The two monomers used in this experiment are isobornyl acrylate (IBA), which contains one polymerizable group ($-CH{=}CH_2$), and bisphenol-A-glycidyldimethacrylate (bis-GMA), which contains two polymerizable groups ($-C(CH_3){=}CH_2$) (Figure 3).

Photolithography

The most appealing aspect of photopolymerization is its ability to control the location of the polymer network. This control can be accomplished through photolithography, a process that utilizes light and a photomask to form or degrade a polymer network in a specific geometric shape. A photomask is a device that allows light to pass through predetermined areas to project an image on a surface. When applied to the construction of microchips, photolithography is used to form or dissolve photoresist on a silicon wafer. The main steps of photolithography involving a negative photoresist are shown in Figure 4. The process begins with the preparation of a silicon wafer with an oxidized (SiO_2) surface. A thin layer of photoresist is spin-coated onto the surface with a typical thickness of 1 μm, which is approximately 1/70 the thickness of a human hair (Figure 4A). A photomask with the desired structural feature is positioned above the photoresist, and UV light is focused onto the photoresist through the photomask (Figure 4B). The light that passes through the photomask (clear area) causes the photoresist to polymer-

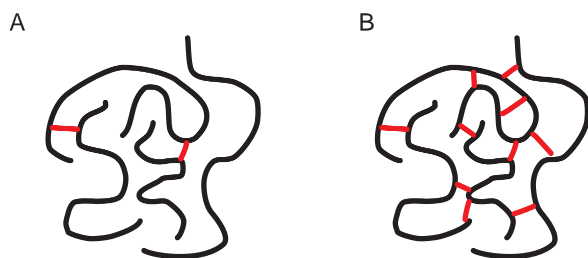

Figure 2. The difference in crosslinking density between a lightly crosslinked, soluble polymer (A) and a highly crosslinked, insoluble polymer network (B).

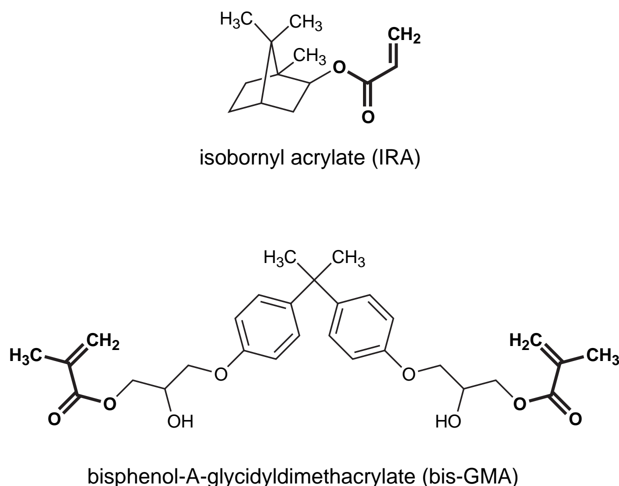

Figure 3. Monomer and crosslinker used for the photoresist. The polymerizable portions of the molecules are highlighted.

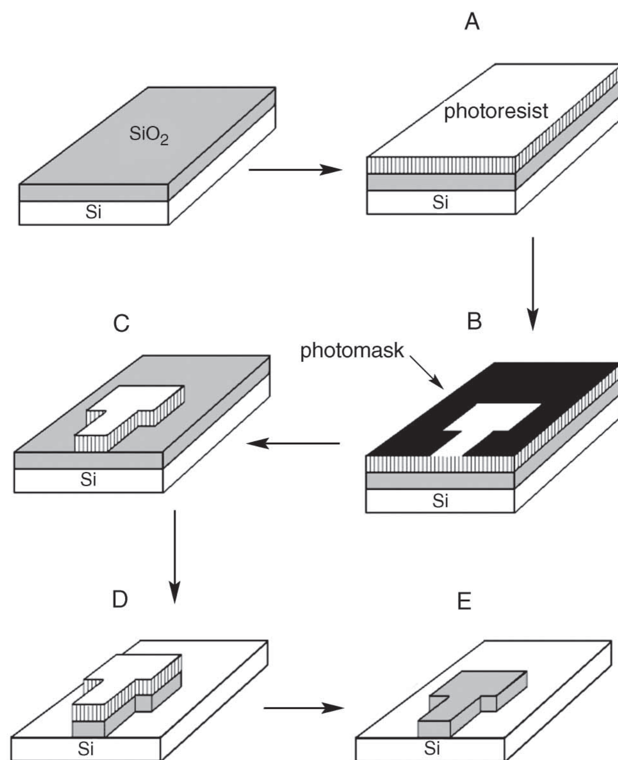

Figure 4. The process of photolithography used in microchip construction. A photoresist is spin-coated onto the oxidized surface of the silicon wafer (A) and a photomask is aligned on top (B). The unit is subjected to UV light, the photomask is removed, and the unpolymerized photoresist is rinsed away (C). Finally, the exposed, oxidized surface of the silicon wafer is etched away (D), and the remaining polymer is removed (E) to result in a silicon chip patterned in the negative image of the photomask.

ize and thus become insoluble. The area that is covered and protected by the dark area of the photomask does not polymerize and can therefore be dissolved away (Figure 4C). After a polymer pattern is present on the SiO_2 substrate, all of the SiO_2 that was not covered with the patterned polymer is etched away (Figure 4D). Finally, the remaining polymer is removed from the surface of the wafer, resulting in a SiO_2 layer that is a negative image of the photomask (Figure 4E) *(1)*.

Experimental Procedures

Materials

Isobornyl acrylate (Aldrich), 2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]propane (bis-GMA, Polysciences, Inc.), 2,2-dimethoxy-2-phenyl-acetophenone (DMPA, Aldrich), oil blue (solvent blue 14, Aldrich), oil red (solvent red 27, Aldrich), and fluorescent yellow 3G (solvent yellow 98, Aldrich) are used without purification. Fisherbrand microscope slides (75 × 50 × 1 mm), Corning cover glass slides (22 × 50 mm, No. 1), and transparency paper are purchased from Fisher Scientific. The light source used is a handheld, long wavelength (365 nm) UV lamp (Spectroline ENF-240C, Fisher Scientific). The sonicator used is a Branson model 1210.

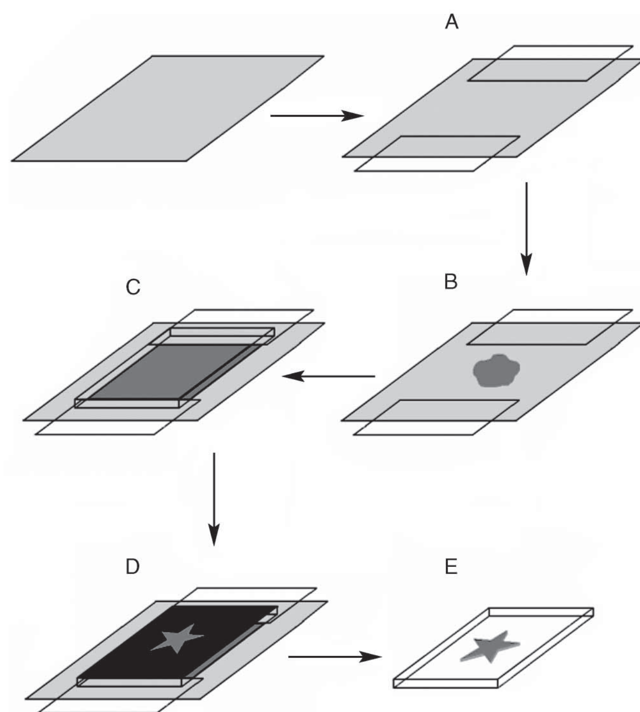

Figure 5. Overview of the fabrication process. Two coverslips are placed at the top and bottom of a transparency (A) and prepolymer solution is dropped in the center (B). A thick, glass slide is positioned on top of the prepolymer solution, allowing it to rest on the coverslips, and causing the prepolymer solution to flow and fill the gap (C). A photomask is aligned on top of the glass slide (D), a second glass slide is placed over the photomask to keep it in place, and the exposed photoresist is polymerized using UV light. After rinsing, an insoluble, patterned polymer results (E).

Preparation of Photoresist

A prepolymer mixture is prepared by combining the monomers, isobornyl acrylate (3.5 g) and bis-GMA (2.0 g), into an amber vial containing the photoiniator DMPA (0.18 g). The mixture is sonicated for 30 min or until a homogeneous solution is formed. For blue, red, or yellow prepolymer solutions, a milligram of oil blue, oil red, or fluorescent yellow 3G, respectively, is added to the mixture and subsequently sonicated for 5 min. A vortex mixer or prolonged, vigorous shaking and stirring may be used if a sonicator is unavailable. Both the monomers and photoinitiators are light sensitive, therefore an amber glass vial fitted with a screw-on eye dropper is recommended for easy storage and application. A clear vial wrapped with aluminum foil is also suitable.

Preparation of Photomask

Designs for photomasks are created using Microsoft Paint, Microsoft Word, or Adobe Photoshop. In Microsoft Word, a 3 × 3 in. black box is formed and used as a background template for all photomask designs. Six boxes should be prepared on one page for efficient use of transparency film. To design a text-containing photomask, a text box is created and formatted for white characters. This text box is then centered inside the 3 × 3 in. black box so that at least 0.5 in. of black is present on all sides of the text. To design a picture-containing photomask, shapes are manipulated in Microsoft Paint by forming a black background, pasting a white design on it, and then copying this figure to fit inside of the 3 × 3 in. black box in Microsoft Word. The photomasks are printed onto standard transparency film using a black and white desktop printer at a resolution of 600 dpi or higher.

Preparation of Polymer Patterned Glass Slide

A transparency slide is cut into fourths to prepare equal pieces of 5.5 in. × 4.25 in. One of these transparency pieces is placed flat on a table and two coverslips (22 × 50 mm, No. 1) are placed at the top and bottom of the transparency (Figure 5A). These coverslips act as spacers between the transparency and the glass slide that is patterned. Approximately 15–30 drops of the prepolymer solution are applied to the middle of the transparency, about 2.5 in. from each coverslip (Figure 5B). A glass slide (75 × 50 × 1 mm) is then placed in the center of the transparency, allowing its top and bottom to rest on the spacer coverslips (Figure 5C). Upon placing the glass slide on the coverslips, the prepolymer solution flows to uniformly cover the entire area. After the entire space between the transparency and the glass slide is filled by prepolymer solution, a photomask is placed on top of the glass slide (75 × 50 × 1 mm) at the desired location (Figure 5D). A second glass slide (75 × 50 × 1 mm) is placed on top of the photomask to keep it flat. The exposed regions of prepolymer solution are polymerized by holding a handheld UV lamp (365 nm) 0.5 in. above the photomask for 20 seconds. The photomask is then removed and the glass slide is carefully peeled away from the transparency paper to expose the polymer image, which forms on the bottom of the glass slide (Figure 5E). The nonpolymerized monomer is washed off the glass slide into a beaker with ethanol and the patterned

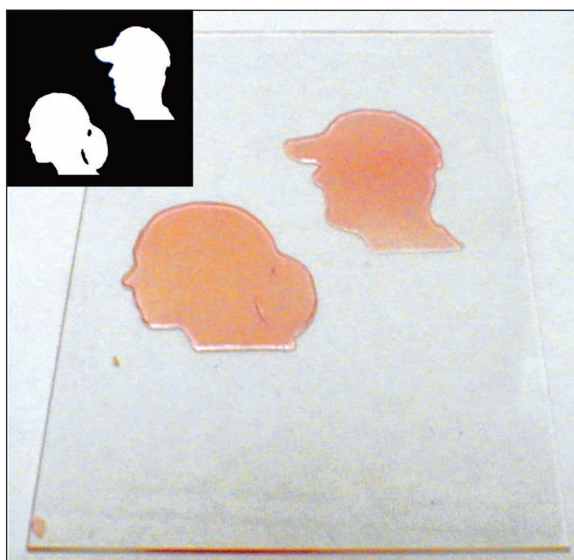

Figure 6. Student polymer silhouettes. A digital camera is used to capture a picture of the student's shadow. A negative of this image is used as the photomask.

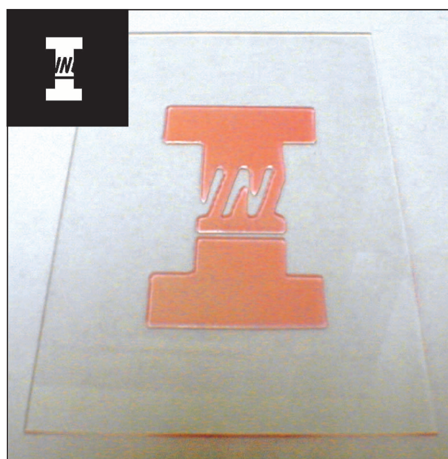

Figure 7. Multicolored polymer structures produced using complementary photomasks and different colored photoresists.

glass slide is dried by gently dabbing it with a paper towel. Smaller glass slides such as thin coverslips can also be patterned if a less expensive method is desired, but extra care should be taken as the coverslips have a high tendency to break.

Advanced Experiments

As stated earlier, the integrity of the polymer network that forms as a result of the photopolymerization process depends on factors such as the concentration of the monomer, crosslinker, and photoinitiator. These concepts can easily be demonstrated by preparing a series of prepolymer solutions containing varying quantities of monomer, crosslinker, and photoinitiator, and undertaking the process of irradiating the solutions through a detailed photomask. The quality of the subsequent polymer structure can be qualitatively determined by the resolution of the resulting image. Severe changes to the optimal composition of the prepolymer solution will lead to loss of resolution, delamination, or incomplete polymer formation.

Just for Fun

Fabricating "polymer silhouettes" of individuals is also possible using this same technique. A silhouette is first obtained by having the subject positioned between an overhead projector and a projection screen so that his or her shadow is prominent. A picture is then taken of the shadow of the subject's silhouette using a digital camera, and the image is rendered black and white with software such as Adobe Photoshop. This image is cropped to exclude everything but the head and neck of the subject's shadow, and then inverted to produce a white subject on a black background. The contrast is manipulated until a sharp distinction is evident between the white polymer portrait and the black background. This file is then transferred onto the 3 × 3 in. black box in Microsoft Word and printed as normal. The finished product is shown in Figure 6.

Multicolored polymer images can also be produced using several photomasks in succession with photoresists of different colors. Figure 7 depicts an example of this technique by showing the formation of a bicolored University of Illinois logo. Following the same experimental procedure as described above, one colored photoresist was polymerized and washed with ethanol. Resubjecting the same glass slide to a second color and polymerizing the photoresist through a properly aligned, second photomask with subsequent rinsing produced the multicolored design.

These experiments may also be performed outside using the UV light produced by the sun. The polymerization time will depend on several factors, including the time of year, the time of day, and the degree of cloud cover. Comparison between the rate of polymerization using the light from a fluorescent classroom light (very slow) and the sun can be a great demonstration of the quantity of UV light that we are exposed to outside every day. Our experiments have shown that on a bright, sunny day, the prepolymer mixture will actually polymerize faster outside than under a handheld UV lamp!

Hazards

Students should wear goggles and disposable gloves to prevent contact with the photoresist and washing solutions. Students should avoid looking into the UV light or allowing their skin to be exposed to its radiation because the high intensity light is damaging to biological tissue after prolonged exposure. Liquid waste should be collected and disposed of as nonhalogenated waste. The monomer, crosslinker, and photoinitiator are irritants and should not be allowed to contact the skin. The stock solutions of the photoresist may be prepared by a supervisor before the lab begins to minimize student exposure of the chemicals. The resulting polymer is safe to handle after all residual monomer is washed away.

Summary

This laboratory experiment describes a simplified version of the generic process of photolithography, which is appropriate for junior high or high school students and can be used to process hundreds of polymer images quickly. In this experiment, a glass slide is substituted for the silicon wafer and a prepolymer solution containing monomer (IBA), crosslinker (bis-GMA), and photoinitiator (DMPA) acts as the photoresist. The photomask is a transparency film containing the negative of a computer-generated image and the light source is a handheld UV lamp. This laboratory allows the visualization of photolithography, while demonstrating important concepts in polymer chemistry, such as photopolymerization and the effects of UV intensity, UV exposure time, crosslinking density, and photoinitiator concentration on the properties of the resulting polymer.

Acknowledgments

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[W]Supplemental Material

Instructor notes, chemical information, hazards' information, experiment overview, student procedure, photomask template, troubleshooting tips, suggested questions with answers, and a glossary for this article are available in this issue of *JCE Online*.

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