Photolithography – Version A
Cover Sheet

This version of the photolithography experiment is meant for Introductory/High School students.

The major difference compared to Version B is that in Version B, students prepare their own prepolymer photoinitiator solution. As well, suggestions are given in the references for other extension experiments from the original JChEd article involving varying the prepolymer composition to determine effects on the resulting polymer.

Instructors are directed to read the original JChEd article and Supplemental material before utilizing this lab. See Instructor's Guide.

Note: The lab prep sheet included in the Instructor's guide is different from Version B.

Seattle's Hub for Industry-driven
Nanotechnology Education – May 2016

NSF –DUE Award #1204279

Name________________________

Photolithography – Version A
Pre-Lab Assignment

Pre-Lab Assignment

- This pre-lab assignment is worth 5 points.
- This part of the pre-lab assignment is due *at the beginning* of the lab period, and must be done individually *before you come to lab!*

I. Background Preparation

1. **Read this experiment thoughtfully**
   Mentally note any procedural questions and plan how you and your partner will complete all experiments efficiently during the three-hour lab period.

2. View the following YouTube videos on the lithography process. These videos demonstrate the basis upon which are based the photolithography experiments you will perform in this lab.
   - https://youtu.be/NeIuYLaw9ks
   - https://youtu.be/nUXDltQfqSA

II. Safety Hazards/Precautions

1. Complete the following table. Use the MSDSonline link on your lab web page. Be sure to follow and specific search instructions from your instructor and be sure the chemical name matches precisely.

Materials	GHS Pictograms (Circle all that apply)	Hazard Statements (Check and list all that apply)
NOTE: The following 3 chemicals are ingredients of the pre-mixed “photoresist prepolymer” that will be distributed to students in a single dropper bottle. You should be aware of the safety hazards of the 3 ingredients of this mixture.		
isobornyl acrylate		☐ Corrosive ☐ Toxic ___________________ ☐ Flammable ☐ Reactive _________________ ☐ Irritant ☐ Other? __________________

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Materials	GHS Pictograms (Circle all that apply)	Hazard Statements (Check and list all that apply)
2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]propane (bis-GMA)		☐ Corrosive ☐ Toxic __________________ ☐ Flammable ☐ Reactive ________________ ☐ Irritant ☐ Other? _________________
2,2-dimethoxy-2-phenyl-acetophenone (DMPA)		☐ Corrosive ☐ Toxic __________________ ☐ Flammable ☐ Reactive ________________ ☐ Irritant ☐ Other? _________________
Waste Disposal	Identify (briefly) how you will dispose of waste materials from this experiment.	

2. **Workplace/Personal Cleanup Notes** (indicate what you will do to clean up yourself and your lab space before you leave the lab):

Pre-Lab Questions

1. What is a “substrate”?

2. What is the purpose of “photoresist” in the photolithography process?

3. When a mask is placed over the photoresist and exposed to UV light, a chemical change occurs in the photoresist polymer that changes it wherever it was exposed to light. Later, a chemical “etchant” is used to wash away part of the photoresist. Which part of the photoresist is washed away, the exposed or unexposed portion?

4. Why do you want the transparency mask to have a black background with the image in white?

5. Actual integrated circuits on silicon computer chips are made using a similar photolithography process. However, the dimensions of the components on the chips are nanometers in scale. What additional steps must be performed in making nano-sized components on computer chips that you will not do in this experiment (i.e. how are the nano-sized “masks” created?)?

6. What precautions must be taken when working with UV lamps?

7. Prepare a brief outline or flow chart of the steps you will use in this experiment.

Name_______________________

Photolithography – Version A

Questions of the Day

- What is photolithography?
- How is photolithography used to make micro- and nanoscale patterns on computer chips?
- How can we make simple patterns using a photolithography type process?

Introduction

Lithography was a term originally used to define a type of printing process invented in the 1700s in which a pattern was transferred onto a flat stone or surface. Alois Senefelder invented the printmaking process of lithography in 1798. From its beginning, according to the College of Technology's Digital Media Program article The History of Lithography, it has become one of the largest industries in the United States – a part of the Printing Industry, which is the third largest manufacturing industry in the United States. Alois Senefelder started out his career as a successful playwright. Several of his works were published; however, he found it expensive to reproduce copies of his plays. In an attempt to reduce the publication cost, he tried to produce his own copperplate engravings. In the late 1700s copper plates were mostly used in printing, but it was a difficult process to create images and text to be printed in reverse. In order to reduce cost and time, Senefelder decided to practice his engraving on slabs on Bavarian limestone instead of expensive copper. To correct mistakes made on the limestone, he found that a mixture of wax, soap, lamp-black and rainwater were efficient.

Through experimentation, Senefelder discovered that when he drew on the limestone with the correction fluid, the drawn image would repel water (hydrophobic), while the surface of the stone where no image was drawn would hold water (hydrophilic). That is, the hydrophilic stone itself, which held water, would repel the ink, while the correction fluid, which is greasy and repels water (hydrophobic), would accept more ink. "He found he could first wet the entire stone then apply ink, with a roller, to the entire stone to replenish the ink left only on the image". The hydrophilic bare stone (no image) would repel ink. Since lithography is based on a chemical principal, Senefelder decided the call the process chemical printing.

Today, lithography is also a term used to describe how structures such as computer chips are designed. Features, including fluid channels and electrical circuits, can be made by adding light (**photo**lithography). *A diagram and description of the process is given after the following description. It may be helpful to refer to the diagram as you read this description.

Step 1) A silicon wafer (the "substrate") is first coated with a light-sensitive chemical called a "photoresist". In a way, the photoresist is similar to the emulsion of photographic film. When exposed to light (typically UV light), the exposed areas are chemically changed ("developed") and can be washed away.

Step 2) A **mask** is created with the pattern that is desired to be etched into the silicon wafer (substrate). Light is shone through the mask onto the substrate. Wherever light passes through the mask and onto the substrate, the photoresist is "exposed" and a copy of the original mask pattern is produced in the photoresist.

Step 3) Next, the exposed pattern of the photoresist is developed, and then the exposed area is washed away using chemicals that remove only exposed photoresist but leave the unexposed areas untouched. At this point, the mask pattern has now been reproduced physically in the photoresist on the surface of the substrate.

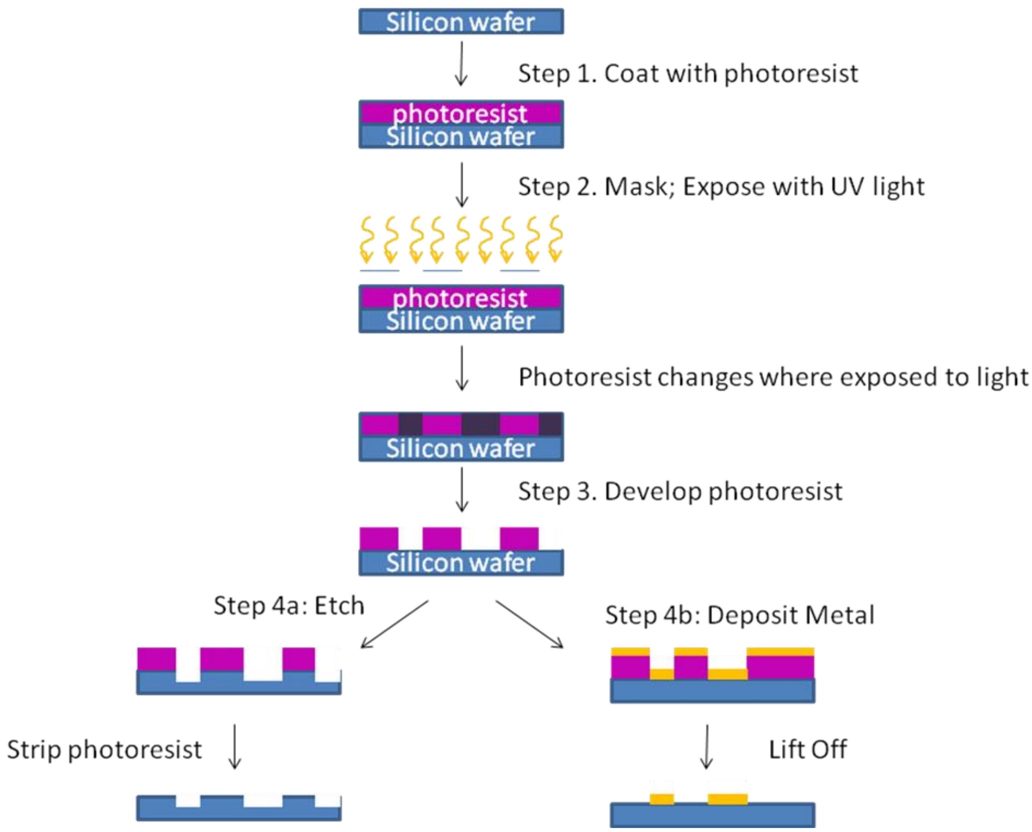
Step 4) The last step is to use a "chemical etch" solution to wash over the photoresist. This chemical etchant will etch the pattern into the substrate only where the exposed areas of the photoresist have been washed away. Thus, the mask pattern has been physically and chemically etched into the substrate.

Until recently, lithography was only used to make structures that were at most only a few layers thick. The size of the materials presented problems with aligning lithographic layers as well as the precision of focus. Current technology has allowed lithographic techniques to be used to 3-D print nano- and micro-scale objects.

Importantly, incredibly small details, such as the billions of components and circuits on a microchip, can effectively be made using photolithography, to a high degree of precision. But how is the original mask made, if the final circuit is to be on the nanometer scale? To achieve this, engineers design the microchip circuit on normal computers at a regular scale. A mask is then produced at somewhat reduced scale. In the chip making process, the light is shown through the reduced mask, and then using camera optics, the image is reduced in size down to the micro- and nanoscale. The limiting factor in using this process is the physical fact that once the dimensions of the final circuit on the chip are similar to the wavelength of light being used to produce the image (UV light), the light is not able to produce a "sharp" image on the substrate (this is called the "diffraction limit"). It is not a characteristic of the quality of the camera/projection lenses, but rather a result of the wave nature of light. Objects (or patterns) that are about the same size as the wavelength of light cause it to bend ("diffract") around the edges of the pattern, causing fuzziness in the image. Current technology uses UV light that is short enough to allow minimum feature sizes of around 50 nm.

All modern electronics are made using photolithography. Typically, silicon wafers are used as the substrate due to their conductivity properties and the availably of the material.

Figure 1. Steps of the photolithography process.



STEP 1. Coat a substrate with a photosensitive material, called a photoresist.

STEP 2. Cover the substrate and photoresist with a mask, which will block light in certain areas. Expose the substrate with light, which will cause a chemical change to occur in the exposed areas of photoresist (where the light is not blocked by the mask).

STEP 3. Develop the photoresist. In positive photolithography, the EXPOSED areas of photoresist are dissolved away in the developer. In negative photolithography, the UNEXPOSED areas of photoresist are dissolved away in the developer.

STEP 4. Now you have a substrate with a pattern of photoresist on it. You can then do one of two processes:

a. Etch – the substrate is etched away in areas not protected by the photoresist
b. Lift-Off – a metal is deposited over the entire substrate. The photoresist is then removed, leaving behind metal only in the areas not covered by the photoresist.

In either case, you now have a permanent pattern remaining on your substrate. The photolithography process may be repeated more than 20 times to create all of the layers in a computer chip.

Overview of this Experiment[1]

An overview of the steps you will take in today's experiment are as follows:

The following experiment demonstrates the concepts behind microchip construction through photolithography and simple polymer chemistry (Figure 1). First, two glass coverslips are positioned at the top and bottom of a piece of transparency film that is lying on a flat surface (a). Several drops of pre-polymer solution are then applied to the center of the transparency film (b). A glass microscope slide, which represents the "microchip", is placed on top of the prepolymer solution, allowing it to rest on the glass coverslips (c). These coverslips act as spacers between the transparency paper and the "microchip" to give depth to the resulting polymer. A photomask is then placed on top of the glass slide (d) and a second glass slide is also placed on top of the photomask to hold it in place. The sample is illuminated with UV light (365 nm) to polymerize the exposed pre-polymer solution and the unpolymerized (unexposed) photoresist is rinsed away. An insoluble polymer patterned in a shape predetermined by the photomask results on the bottom of the glass slide (e). You will have thus printed an image using light and chemistry!

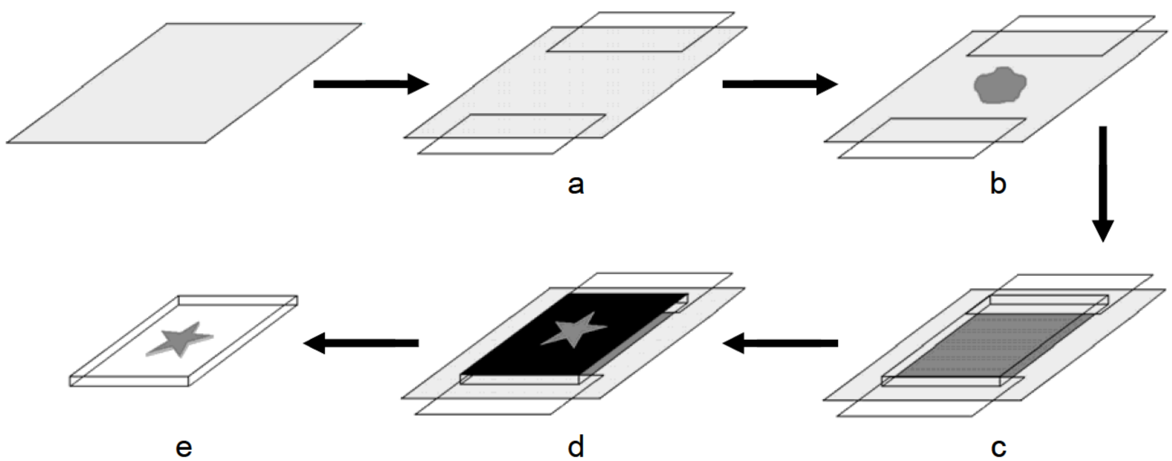


Figure 1. Overview of the fabrication process. Two coverslips are placed at the top and bottom of a transparency (a) and pre-polymer solution is dropped in the center (b). A thick, glass slide is positioned on top of the pre-polymer solution, allowing it to rest on the coverslips, and causing the pre-polymer 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 on top of the photomask to keep it in place, and the exposed photoresist is polymerized using UV light. After rinsing, an insoluble, patterned polymer results (e).

[1] Berkowski, Plunkett, Yu and Moore (2005). Introduction to Photolithography: Preparation of Microscale Polymer Silhouettes *J. Chem. Ed.*, *82*(9), 1365-1369.

Safety Precautions

- ***Gloves should be worn during this lab at all times.***
- *Experiment must be performed in a well-ventilated or hooded area.*
- *Take care using the UV lamp and never look into the light or expose to the body.*
- *IBA, Bis-GMA, and DMPA are slightly irritating to the eyes and skin. No significant signs or symptoms occur through skin absorption or inhalation. These chemicals may be hazardous if large quantities are ingested.*
- *Ethanol is irritating to the eyes and skin and causes nausea, vomiting, and inebriation upon ingestion.*
- *Oil blue, oil red, and fluorescent yellow 3G (contained within the photoresist prepolymer) are slightly irritating to the eyes and skin and are toxic upon ingestion.*

Waste Management

- <u>All</u> waste solutions must be disposed of in the appropriate organic waste collection container in the lab. No chemicals can go down the drain.

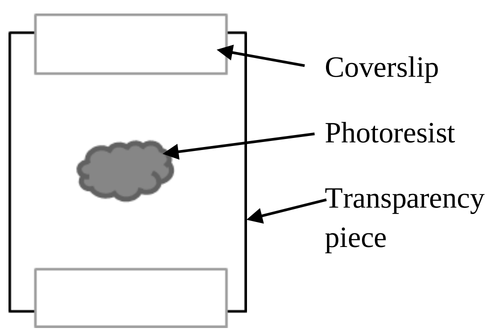
Procedure - Creating the Lithographic Image

1. Obtain the following materials as directed by your instructor:

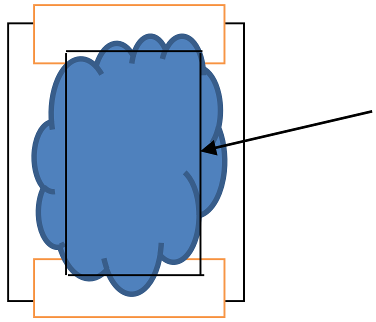
- Photoresist prepolymer solution (in amber-colored dropper vial)
  - Note hazard precautions above
- UV lamp (365 nm wavelength)
- Photomask - (1 ¾” x 1 ¾” image in a 2” x 2” black square printed on a transparency)
- 4.25” x 5.5” transparency piece
- 2 coverslips (22 x 50 mm) or transparency piece (22 mm x 50 mm)
- 2 glass microscope slides (75 x 50 x 1 mm)
- 100-mL beaker
- Ethanol rinse bottle

NOTE: Depending on the circumstances, your instructor may have you create your own mask. If so, follow your instructor’s directions.

2. Place one transparency piece (4” x 3.5”) flat on the lab bench.
3. Place two coverslips on top and bottom of transparency slide. The coverslips act as spacers between the transparency piece and the patterned glass slide that will go on top.
4. Drop approximately 15-30 drops of the photoresist solution in the middle of the transparency piece, about 2.5 inches from each coverslip.



5. Place a glass slide in the center of transparency piece, resting on the coverslips; wait until the entire space under the glass slide is filled with the photoresist solution. See figure on next page.



6. Place the photomask on top of glass slide so that you can read or view the image correctly.

7. Place a second glass slide on top of the photomask to hold the mask in place.

8. Hold the UV lamp approximately 0.5" above the photomask and turn on for 20 seconds to expose the pattern (polymerizing the exposed regions of the photoresist). ***Make sure you do not look into the UV light.***

9. Remove the second slide and the photomask.

10. Carefully, peel away the first glass slide with the photoresist sticking to it from the transparency piece. The exposed polymer photoresist image should be on the bottom of the glass slide.

11. Rinse the glass slide into a waste beaker with ethanol to remove the unexposed material.

12. Air-dry the resulting polymer image, or dry by gently dabbing it with a paper towel.

Extension Experiments

Extension 1: Polymer silhouettes

Equipment: Overhead projector, projection screen or white wall, digital camera, Adobe Photoshop or similar software

1. Position the subject (person) between an overhead projector and projection screen so the shadow of his or her profile is prominent. A blurry shadow will become sharp by adjusting the distance of the subject from the projection screen.
2. Take a picture of the subject's shadow with the digital camera. Make sure that the subject's head does not overlap his or her shadow in the picture.
3. Download the image into a program such as Adobe Photoshop or MS Paint and crop the picture so only the shadow of the subject's head and neck remain.
4. Invert the image to produce a white profile on a black background.
5. Adjust the contrast of the picture until a sharp distinction is evident between the white profile and the black background.

6. Paste this image on the photomask template in MS Word as provided by your instructor and print on transparency paper (see the photomask template as an example). Your instructor may have specific instructions for completing this step.
7. Prepare a photolithographic polymer image based on your silhouette as you did in the **original procedure.**

Extension 2: Multicolored images

Equipment: Same materials as the **original procedure** except obtain a photoresist prepolymer solution that is of a *different* color.

1. Prepare or obtain two photomasks that are complementary to one another (your instructor may give you prepared masks or show photomask templates as examples).
2. Polymerize one color photoresist with one of the photomasks as described in the **original procedure** and rinse away the unpolymerized photoresist with ethanol.
3. Repeat Steps 2-5 of the **original procedure** using the second (different) color photoresist.
4. Place the half-patterned glass slide (from Step 2) on top of the photoresist using the thin, coverslips as spacers. The second color photoresist should flow around the polymerized image from Step 2 of this part.
5. As done in Steps 8-12 of the **original procedure**, align the second photomask in the desired position, polymerize, and rinse to produce a multicolored polymer image.

Extension 3: Substitution of sunlight for a handheld UV lamp

Equipment: Transparency paper; scissors; thin, glass coverslips (22 x 50 mm, No. 1); thick glass slides (75 x 50 x 1 mm); dropper or pipette; watch or timer; 1000 mL beaker; paper towels; a stiff piece of paper such as cardboard or a folder, a dark-colored folder, tape, four identical photomasks

Optimization of Polymerization Time:
1. Cut a transparency paper into four equal pieces of 5.5 in. x 4.25 in. and tape all four pieces to a single, stiff piece of paper such as a folder.
2. For each of the four transparency papers, follow steps 3-7 of the **original procedure**, using identical photomasks for each sample.
3. Cover all of the samples with a dark-colored folder or opaque paper to prevent premature exposure to sunlight.
4. Take covered samples and a watch or timer outdoors.
5. Remove the dark-colored folder or paper that is covering the samples to expose them to sunlight and start the timer.
6. Cover the first sample after a specified time interval. Cover each additional sample after subsequent timed intervals. For example on a bright, sunny day,try covering the first sample after 10 s, the second sample after 20 s, the third sample after 30 s, and the fourth sample after 40 s. These time intervals will vary depending on the time of day, the season, and the amount of cloud cover.

7. After all the samples have been covered, take everything back indoors and follow steps 9-12 of the **original procedure**. After optimizing the polymerization time for the specific day, time, and cloud cover, compare it with the polymerization time required with the handheld UV lamp.

References

This experiment and instructor's guide are adapted, in part, from

- Berkowski, Plunkett, Yu and Moore (2005). Introduction to Photolithography: Preparation of Microscale Polymer Silhouettes *J. Chem. Ed.*, *82*(9), 1365-1369.

General References on Lithography

- http://www.ece.gatech.edu/research/labs/vc/theory/photolith.html

"Photolithography." *School of Electrical and Computer Engineering at the Georgia Institute of Technology*. Web. 12 July 2016. <http://www.ece.gatech.edu/research/labs/vc/theory/photolith.html>.

- http://www.metmuseum.org/toah/hd/lith/hd_lith.htm

Ives, Colta. "Lithography in the Nineteenth Century." *Heilbrunn Timeline of Art History: The Metropolitan Museum of Art*. Metropolitan Museum of Art, 2004. Web. 12 July 2016. <http://www.metmuseum.org/toah/hd/lith/hd_lith.htm>.

- http://www.cnf.cornell.edu/cnf_process_photo_resists.html

"Photolithography Resist Processes and Capabilities." *CNF - Cornell NanoScale Science & Technology Facility*. Web. 12 July 2016. <http://www.cnf.cornell.edu/cnf_process_photo_resists.html>.

News/Research Articles

- http://www.newscientist.com/article/dn18613-for-smaller-chips-borrow-18thcentury-tricks.html

Barras, Colin. "For Smaller Chips, Borrow 18th-century Tricks." *New Scientist.* Reed Business Information Ltd., 2010. Web. 12 July 2016. <http://www.newscientist.com/article/dn18613-for-smaller-chips-borrow-18thcentury-tricks.html>..

Videos

- http://www.youtube.com/watch?v=-GQmtITMdas&feature=related – how a computer chip is made

"From sand to chip - How a CPU is made." *YouTube.* Web. 12 July 2016. <https://youtu.be/NeIuYLaw9ksd>.

- http://www.youtube.com/watch?v=NeIuYLaw9ks&feature=related – art lithography

"Lithography process explained in conjunction with Chuck Close Prints exhibition at the First Center." *YouTube*. Web. 12 July 2016. <http://www.youtube.com/watch?v=NeIuYLaw9ks&feature=related>.

- https://www.youtube.com/watch?v=nUXDltQfqSA – art lithography

"Pressure + Ink: Lithography Process." *YouTube*. Web. 12 July 2016. <https://youtu.be/nUXDltQfqSA>

Name________________________

Photolithography – Version A
Report Sheet

Creating the Lithographic Image

Observations

A. Record and describe any observations as you prepared and developed your photolithographic polymer image.

B. Record and describe any observations as you prepared and developed your photolithographic polymer image.

Extension Experiments

Extension 1: Polymer silhouettes

A. Record and describe any observations as you prepared and developed your photolithographic polymer image.

B. Draw a diagram/image of your final photolithographic polymer silhouette image.

Extension 2: Multicolored images

1. Record and describe any observations as you prepared and developed your photolithographic polymer image.

2. Draw a diagram/image of your final photolithographic polymer multicolor image. Be sure to label which colors you used for each part of the image.

Extension 3: Substitution of sunlight for a handheld UV lamp

A. Record and describe any observations as you carried out the polymerization time optimization experiment.

B. Describe the results for each timed sample in the table below.

Atmospheric conditions at time of experiment (sunny, cloudy, windy, etc.): Ambient outdoor temperature (if known):	
Sample 1 exposure time:	Sample 2 exposure time:
Sample 1 result:	Sample 2 result:
Sample 3 exposure time:	Sample 4 exposure time:
Sample 3 result:	Sample 4 result:

Analysis

Creating the Lithographic Image

1. Why would the photoresist solution polymerize (develop) if it was not stored in a vial protected from sunlight?

Extension 3: Substitution of sunlight for a handheld UV lamp

2. What was the optimal exposure sunlight exposure time as determined by your experiments?

3. Explain how you determined the optimal sunlight exposure time.

4. Describe any other experiments you performed and results obtained.

Instructor's Guide

Primary Reference for this Experiment

Explicit and extensive instructor information, including troubleshooting notes, material preparation notes, templates, etc., is provided in the supplemental material to the original article in the Journal of Chemical Education.

*It is highly recommended instructors using this experiment in their course to review this lab documentation.

- **Introduction to Photolithography: Preparation of Microscale Polymer Silhouettes**
  Kimberly L. Berkowski, Kyle N. Plunkett, Qing Yu, and Jeffrey S. Moore
  Journal of Chemical Education **2005** *82* (9), 1365
  DOI: 10.1021/ed082p1365

The supplemental material is attached to the end of this document.

Other References

**A different, simple photolithography procedure for High School where students use a similar process (photoresist) and chemically etch patterns into a copper-clad circuit board.

- http://www.nisenet.org/catalog/photolithography (accessed 7/12/2016)

- *NOTE: in the NISE documentation, the link for the copper-clad board no longer works (as of 7/122016.) Find the sensitized boards at:
  - http://www.mgchemicals.com/products/prototyping-and-circuit-repair/presensitized-boards/positive-presensitized-600-series/
  - This company has an excellent set of FAQs about preparing photolithography prototype boards that would easily fit into a lab experiment. Start here:
    - http://www.mgchemicals.com/tech-support/instructional-guides/prototyping-positive-faq/#boards

A procedure appropriate for General Chemistry students, creating photolithographic structures on a silicon substrate using a commercial photoresist is given in:

- **A Photolithography Laboratory Experiment for General Chemistry Students**
  Thomas C. DeVore, Brian H. Augustine, Adora M. Christenson, and Gregory W. Corder
  Journal of Chemical Education **2003** *80* (2), 183
  DOI: 10.1021/ed080p183

Learning Outcomes

- To understand how photolithography is used to make electronic and biomedical devices and nano- and micro- scale 3D printed objects
- To make simple patterns using photolithography type processes

Washington EALR Alignment

9-11 PS2F All forms of life are composed of large molecules that contain carbon. Carbon atoms bond to one another and other elements by sharing electrons, forming covalent bonds. Stable molecules of carbon have four covalent bonds per carbon atom.

9-11 PS2G Chemical reactions change the arrangement of atoms in the molecules of substances. Chemical reactions release or acquire energy from their surroundings and result in the formation of new substances.

9-11 PS2H Solutions are mixtures in which particles of one substance are evenly distributed through another substance. Liquids are limited in the amount of dissolved solid or gas that they can contain. Aqueous solutions can be described by relative quantities of the dissolved substances and acidity or alkalinity (pH).

Oregon Content Standards Alignment

H.2 P.1 Explain how chemical reactions result from the making and breaking of bonds in a process that absorbs or releases energy. Explain how different factors can affect the rate of a chemical reaction.

Lab Prep Sheet per class of 40 students (20 pairs)

Photolithography – Ver. A

SPECIAL NOTE: Extension experiments
This lab contains 3 potential extension experiments to be done at the instructor's discretion.
The prep list below is provided as for doing the main experiment with NO Extensions.
- NOTE: Each extension, if done as a class, requires additional quantities of the chemicals and equipment as listed below for the original procedure. If doing extensions, alter prep-sheet accordingly (see ADDITIONAL Extension prep under "Equipment Glassware and Models" section below

CHEMICALS & SOLUTIONS

Chemical	Amount/ Concentration	Distribution Notes
Photoresist Solution – Mixture below will suffice for ~20 glass slides **Detailed preparation instructions follow in the Lab Tech Notes below**		
isobornyl acrylate (**IBA**) CAS# 5888-33-5 (Aldrich)	3.5 g	These quantities when mixed as described below will suffice for ~ 20 glass slide preparations Depending on number of students and how many slides they each will make, bottle and distribute the appropriate quantities of the photoresist as appropriate Note: it will not be efficient to have only one supply bottle of the photoresist available to larger classes. Divide into bottles for every 1-3 students as appropriate.
2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]propane (**bis-GMA**; Polysciences, Inc.)	2.0 g	
2,2-dimethoxy-2-phenyl-acetophenone (**DMPA**, Aldrich)	0.18 g	
oil blue (solvent blue 14, Aldrich)	1 mg	
oil red (solvent red 27, Aldrich)	1 mg	
fluorescent yellow 3G (solvent yellow 98, Aldrich)	1 mg	

Lab Tech Notes:

Photoresist solution preparation steps:

A. Use a spatula to mass approximately 2.0 g of Bis-GMA into an amber vial. Bis-GMA is extremely viscous and sticky and you may need an additional spatula to push it to the bottom of the vial.
B. If some of the Bis-GMA sticks to the sides or top of the vial, tightly screw on the vial lid and completely submerge the vial in a beaker full of hot tap water until the Bis-GMA flows to the bottom.
C. Add approximately 3.5 g of IBA to the vial containing Bis-GMA.
D. Add approximately 0.18 g (3% wt) of DMPA to the vial containing IBA and Bis-GMA.
E. Sonicate the mixture for 30 min. (see note below re: not having a sonicator)
F. Swirl the solution to make sure it is homogeneous. If all components are not dissolved, sonicate the solution for an additional 10 min.
G. Repeat F until the solution is homogeneous.
H. Add the appropriate color dye (1 - 1.5 mg or a small spatula tip) to the resulting photoresist.
I. Sonicate this solution for 5 -10 min.
J. Store the photoresist in an amber **dropper** vial with a screw-top dropper in a chemical refrigerator, if available. A clear **dropper** vial wrapped with aluminum foil may also be used.

A vortex mixer or prolonged, vigorous shaking and stirring may be used if a sonicator is unavailable.

To prevent premature polymerization of the photoresist, **store it in an amber dropper vial or a clear vial wrapped with aluminum foil in a chemical refrigerator**, if available, and minimize its exposure to light.

EQUIPMENT, GLASSWARE & MODELS

	Quantity	Equipment / Model	Distribution Notes
❑	20	photomasks - see instructions in Lab Tech Notes below *prepare several patterns	1 mask per student/pair
❑	20	transparency sheet cut into four equal pieces of 5.5 in. x 4.25 in. Each student/pair needs 1 square	1 square per student/pair
❑	40	coverslips (22 x 50 mm, No. 1, Corning)	2 per student/pair
❑	40	thick glass microscope slides (75 x 50 x 1 mm)	2 per student/pair
❑	20	scissors	
❑	20	Handheld UV lamp (**365 nm wavelength**)	ideally 1 per student/pair – decide on how many you have available and divide among class
❑	20	100-mL beaker	1 per student/pair
❑	1	sonicator (for photoresist prep)	
	20	ethanol wash bottles	
	Extension experiment equipment – necessary only if Extension experiments 1, 2 and/or 3 are performed - NOTE: Each extension, if done as a class, requires an entirely new set of chemicals and equipment as listed above for the original procedure. If doing extensions, alter prep-sheet accordingly		
	Extension 1		
	1 (or more)	digital camera	
	1 (or more)	overhead projector, projection screen	
	1	Adobe Photoshop or paint or similar software	
	1 set	requires **another complete batch of all chemicals and equipment**	
	Extension 2		
		2 photomasks that are complementary to each other (see the University of Illinois logo on the photomask template as an example).	
		requires **another complete batch of all chemicals and equipment**	
	Extension 3		
	20	Stiff, opaque cardboard or a folder, etc.	
		requires **another complete batch of all chemicals and equipment**	

Lab Tech Notes:

Photomask preparation (this step may be assigned as pre-lab homework, an example is provided at the end of this prep sheet).

Equipment: Word processing program (Microsoft Word), a design program (Microsoft Paint) and Adobe Photoshop are also recommended, transparency film, black and white printer

A. Create a 3 x 3 in. black box in Microsoft Word to use as a template.

B. Copy and paste six of these black boxes on a single page to create multiple photomasks.

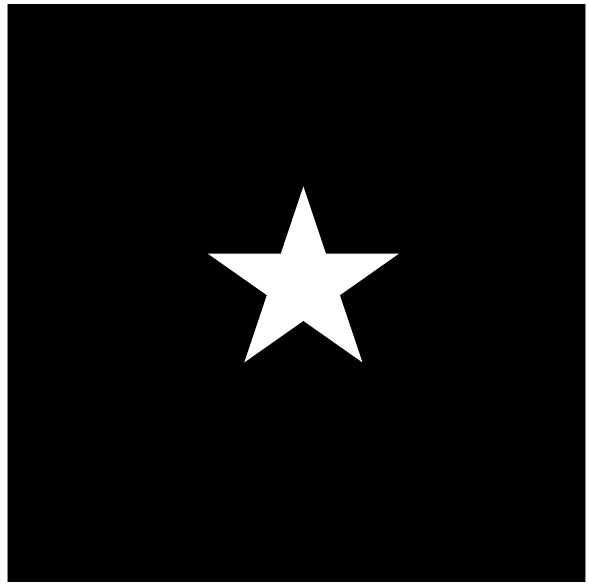
C. Text containing photomasks - create a text box, format it for white font and no fill, and center the text box inside the black box to allow at least a 0.5 in. black border surrounding the text.

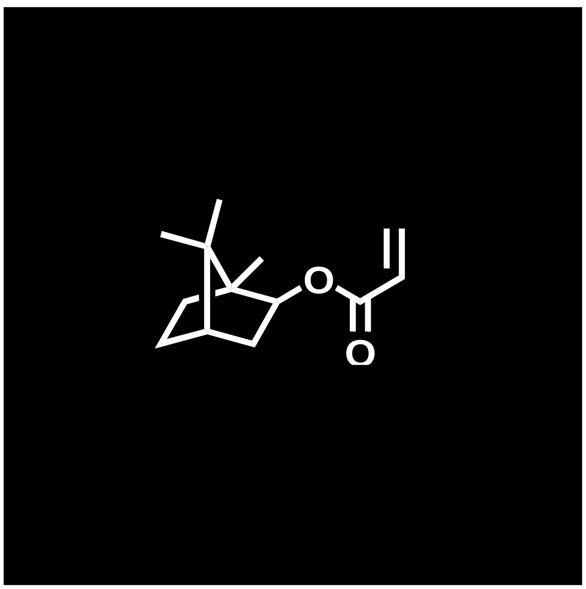
D. Picture containing photomasks – manipulate shapes in Microsoft Paint by pasting a white shape on a black background and copy this figure to the center of the black box on your template.

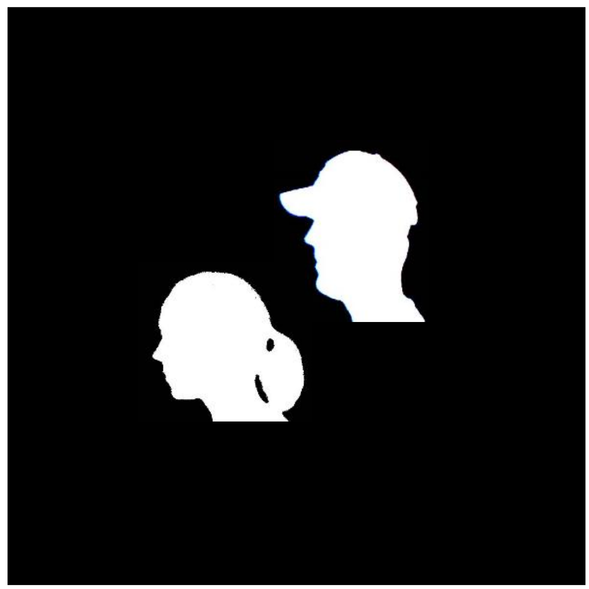
E. Print the photomasks on transparency paper using a black and white printer at a resolution of 600 dpi or higher.

❑ WASTE CONTAINER(S)
Non-Halogenated organics waste collection jug

Lab Prep Sheet







LAB DOCUMENTATION

INTRODUCTION TO PHOTOLITHOGRAPHY – PREPARATION OF MICROSCALE POLYMER SILHOUETTES

*Kimberly L. Berkowski, Kyle N. Plunkett, Qing Yu, and Jeffrey S. Moore**

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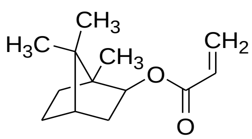
Notes for the instructor:

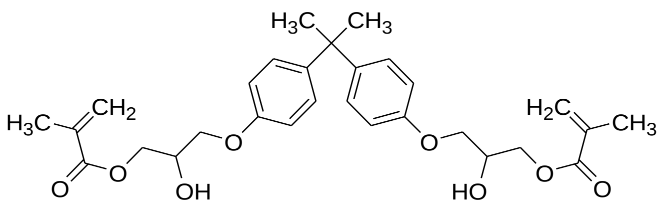
A vortex mixer or prolonged, vigorous shaking and stirring may be used if a sonicator is unavailable. To prevent premature polymerization of the photoresist, store it in an amber vial or a clear vial wrapped with aluminum foil in a chemical refrigerator, if available, and minimize its exposure to light.

Chemical Information:



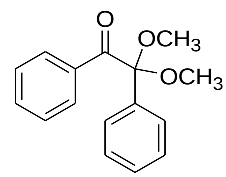
Isobornyl acrylate (IBA)

CAS# 5888-33-5



Bisphenol-A-glycidyldimethacrylate (Bis-GMA)

CAS# 1565-94-2



2,2-Dimethoxy-2-phenyl acetophenone (DMPA)

CAS# 24650-42-8

Dyes:

Oil Red O (Solvent Red 27), CAS# 1320-06-5

Oil Blue N (Solvent Blue 14), CAS# 2646-15-3

Fluorescent Yellow 3G (Solvent Yellow 98), CAS# 12671-74-8

Hazards:

IBA, Bis-GMA, and DMPA are slightly irritating to the eyes and skin. No significant signs or symptoms occur through skin absorption or inhalation. These chemicals may be hazardous if large quantities are ingested. Ethanol (64-17-5) is irritating to the eyes and skin and causes nausea, vomiting, and inebriation upon ingestion. Oil blue, oil red, and fluorescent yellow 3G are slightly irritating to the eyes and skin and are toxic upon ingestion. Eye contact and prolonged skin contact with UV light is damaging to biological tissue. Liquid waste should be collected in a non-halogenated waste container and appropriately disposed.

Overview of Experiment:

The following experiment demonstrates the concepts behind microchip construction through photolithography and simple polymer chemistry (Figure 1). First, two glass coverslips are positioned at the top and bottom of a piece of transparency film that is lying on a flat surface (a). Several drops of pre-polymer solution are then applied to the center of the transparency film (b). A glass microscope slide, which represents the "microchip", is placed on top of the pre-polymer solution, allowing it to rest on the glass coverslips (c). These coverslips act as spacers between the transparency paper and the "microchip" to give depth to the resulting polymer. A photomask is then placed on top of the glass slide (d) and a second glass slide is also placed on top of the photomask to hold it in place. The sample is illuminated with UV light (365 nm) to polymerize the exposed pre-polymer solution and the unpolymerized photoresist is rinsed away. An insoluble polymer patterned in a shape predetermined by the photomask results on the bottom of the glass slide (e).

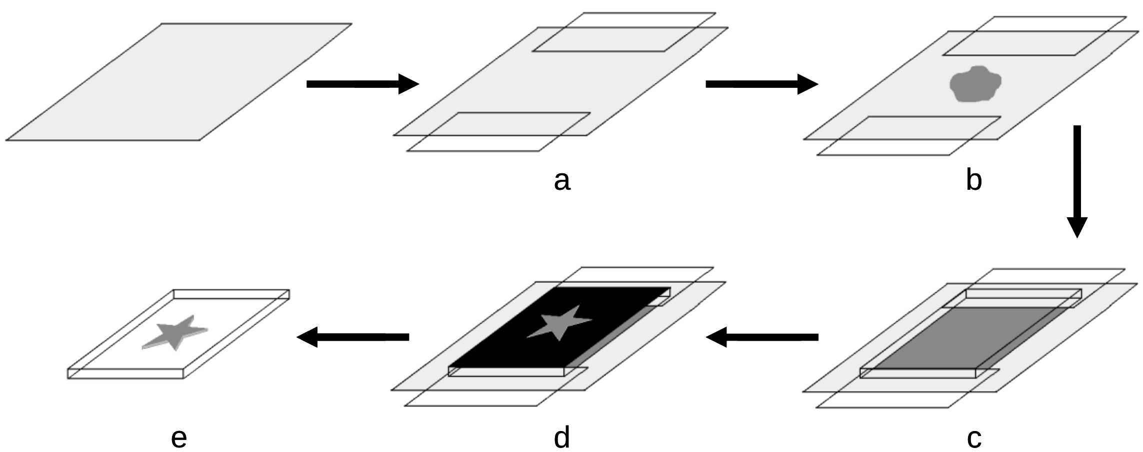


Figure 1. Overview of the fabrication process. Two coverslips are placed at the top and bottom of a transparency (a) and pre-polymer solution is dropped in the center (b). A thick, glass slide is positioned on top of the pre-polymer solution, allowing it to rest on the coverslips, and causing the pre-polymer 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 on top of the photomask to keep it in place, and the exposed photoresist is polymerized using UV light. After rinsing, an insoluble, patterned polymer results (e).

PROCEDURE:

Safety: *Wear safety glasses and disposable gloves at all times and work in a well-ventilated area. Do not look directly into the UV light and avoid its prolonged exposure to your skin. Collect chemical waste in appropriate containers. Do not rinse any chemicals down the sink.*

Step 1. Photoresist preparation (This step should be performed in bulk ahead of time by the instructor to conserve time and to minimize student exposure to the chemicals. The suggested amounts produce enough photoresist to pattern approximately 20 glass slides).

Chemicals: IBA, Bis-GMA, DMPA, dye (oil red, oil blue, or fluorescent yellow 3G)

Equipment: spatula, disposable pipette and bulb, sonicator, amber vial with screw-top dropper

A. Use a spatula to mass approximately 2.0 g of Bis-GMA into an amber vial. Bis-GMA is extremely viscous and sticky and you may need an additional spatula to push it to the bottom of the vial.

B. If some of the Bis-GMA sticks to the sides or top of the vial, tightly screw on the vial lid and completely submerge the vial in a beaker full of hot tap water until the Bis-GMA flows to the bottom.

C. Add approximately 3.5 g of IBA to the vial containing Bis-GMA.

D. Add approximately 0.18 g (3% wt) of DMPA to the vial containing IBA and Bis-GMA.

E. Sonicate the mixture for 30 min.

F. Swirl the solution to make sure it is homogeneous. If all components are not dissolved, sonicate the solution for an additional 10 min.

G. Repeat F until the solution is homogeneous.

H. Add the appropriate color dye (1 - 1.5 mg or a small spatula tip) to the resulting photoresist.

I. Sonicate this solution for 5 -10 min.

J. Store the photoresist in an amber vial with a screw-top dropper in a chemical refrigerator, if available. A clear vial wrapped with aluminum foil may also be used.

Step 2. Photomask preparation (this step may be assigned as pre-lab homework, an example is provided in this procedure).

Equipment: Word processing program (Microsoft Word), a design program (Microsoft Paint) and Adobe Photoshop are also recommended, transparency film, black and white printer

A. Create a 3 x 3 in. black box in Microsoft Word to use as a template.

B. Copy and paste six of these black boxes on a single page to create multiple photomasks.

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E. Print the photomasks on transparency paper using a black and white printer at a resolution of 600 dpi or higher.

Step 3: Polymer patterning.

Chemicals: Prepared photoresist, wash bottle containing ethanol, waste container

Equipment: Transparency paper; scissors; thin, glass coverslips (22 x 50 mm, No. 1); thick glass slides (75 x 50 x 1 mm); prepared photomask; dropper or pipette; hand-held UV lamp; watch or timer; 1000 mL beaker; paper towels.

A. Cut a transparency paper into four equal pieces of 5.5 in. x 4.25 in. and place one of these flat on the table.

B. Align two thin, glass coverslips (22 x 50 mm) on the top and bottom of the transparency.

C. Apply 15-30 drops of the photoresist to the center of the transparency leaving about 2.5 in. between each coverslip and the liquid photoresist.

D. Cover the photoresist with a thick, glass slide (75 x 50 x 1 mm) by placing the slide in the center of the transparency and allowing its top and bottom to rest on top of the thin coverslips.

E. Wait until the entire space between the thick glass slide and the transparency is filled with photoresist.

F. Place the photomask on top of the thick glass slide and make sure that photoresist is visible through all parts of the photomask.

G. Place a second thick, glass slide on top of the photomask to keep it in place.

H. Polymerize the exposed photoresist by shining UV light (365 nm) from the hand-held lamp 0.5 in. above the sample for 20 s (time may be dependent on the UV lamp).

I. Remove the photomask and carefully peel away the bottom transparency from the thick, glass slide.

J. Wash away the unpolymerized photoresist into a beaker with a wash bottle containing ethanol.

K. Dry the resulting polymer by gently dabbing it with a paper towel.

Just For Fun: Polymer silhouettes

Equipment: Overhead projector, projection screen or white wall, digital camera, Adobe Photoshop or similar software

A. Position the subject between an overhead projector and projection screen so the shadow of his or her profile is prominent. A blurry shadow will become sharp by adjusting the distance of the subject from the projection screen.

B. Take a picture of the subject's shadow with the digital camera. Make sure that the subject's head does not overlap his or her shadow in the picture.

C. Download the image into a program such as Adobe Photoshop and crop the picture so only the shadow of the subject's head and neck remain.

D. Invert the image to produce a white profile on a black background.

E. Adjust the contrast of the picture until a sharp distinction is evident between the white profile and the black background.

F. Paste this image on the photomask template and print as normal (see the photomask template as an example).

Just for Fun: Multicolored images

A. Prepare two photomasks that are complementary to one another (see the University of Illinois logo on the photomask template as an example).

B. Polymerize one color photoresist with one of the photomasks as described above and rinse away the unpolymerized photoresist with ethanol.

C. Apply the second color photoresist to a new transparency and place the half-patterned glass slide on top of the photoresist using the thin, coverslips as spacers.

D. Align the second photomask in the desired position, polymerize, and rinse to produce a multicolored polymer image.

Just for Fun: Substitution of sunlight for a handheld UV lamp

Equipment: Transparency paper; scissors; thin, glass coverslips (22 x 50 mm, No. 1); thick glass slides (75 x 50 x 1 mm); dropper or pipette; watch or timer; 1000 mL beaker; paper towels; a stiff piece of paper such as cardboard or a folder, a dark-colored folder, tape, four identical photomasks

Optimization of Polymerization Time:

A. Cut a transparency paper into four equal pieces of 5.5 in. x 4.25 in. and tape all four pieces to a single, stiff piece of paper such as a folder.

B. For each of the four transparency papers, follow steps B-G in **Step 3: Polymer Patterning**, using identical photomasks for each sample.

C. Cover all of the samples with a dark-colored folder to prevent premature exposure to sunlight.

D. Take covered samples and a watch or timer outdoors.

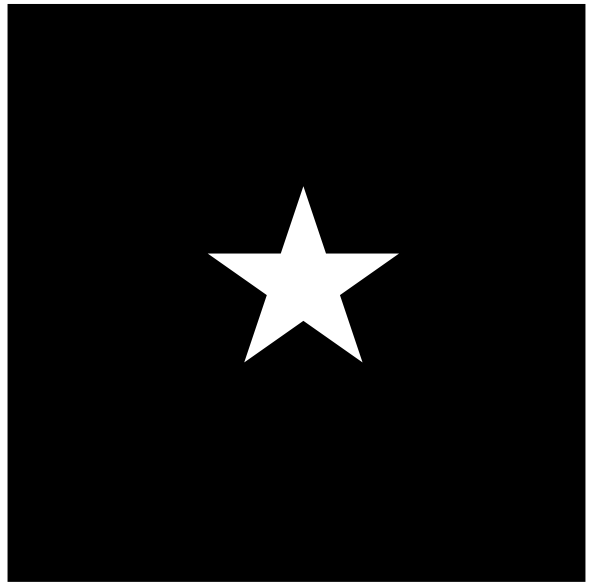
E. Remove the dark-colored folder that is covering the samples to expose them to sunlight and start the timer.

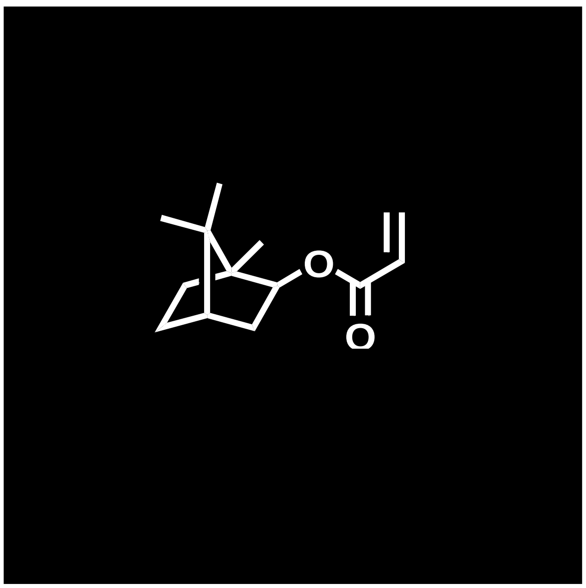
F. Cover the first sample after a specified time interval. Cover each additional sample after subsequent timed intervals. On a bright, sunny day, we covered the first sample after 10 s, the second sample after 20 s, the third sample after 30 s, and the fourth sample after 40 s. These time intervals will vary depending on the time of day, the season, and the amount of cloud cover.

G. After all the samples have been covered, take everything back indoors and follow I-K in **Step 3: Polymer Patterning**. After optimizing the polymerization time for the specific day, time, and cloud cover, compare it with the polymerization time required with the handheld UV lamp.

Examples of patterned glass slides:


CHEMISTRY
ROCKS!

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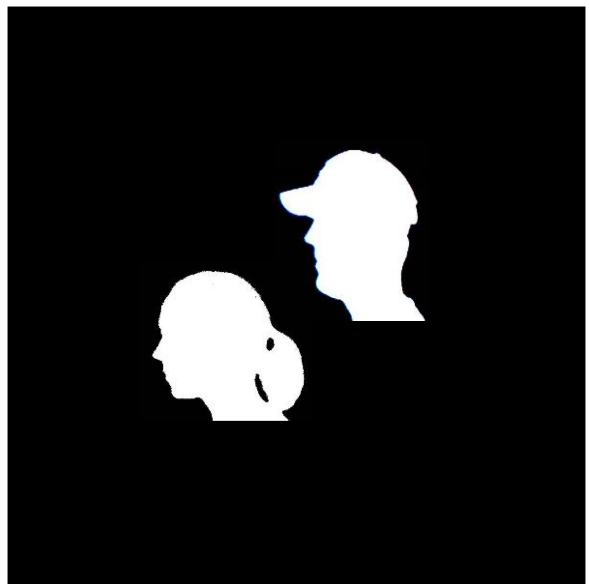
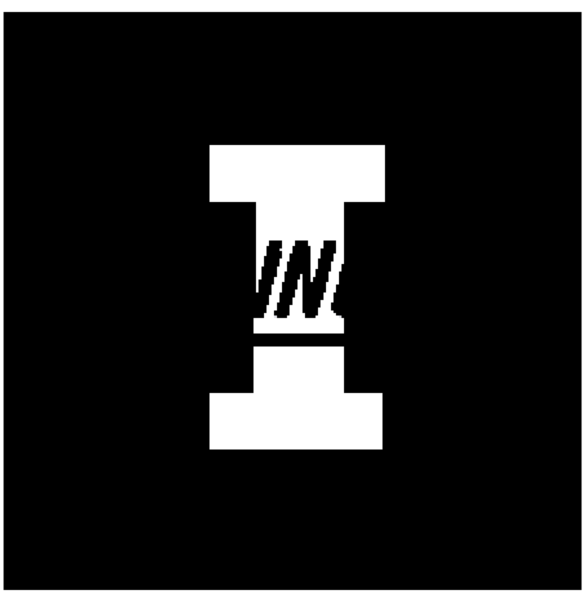
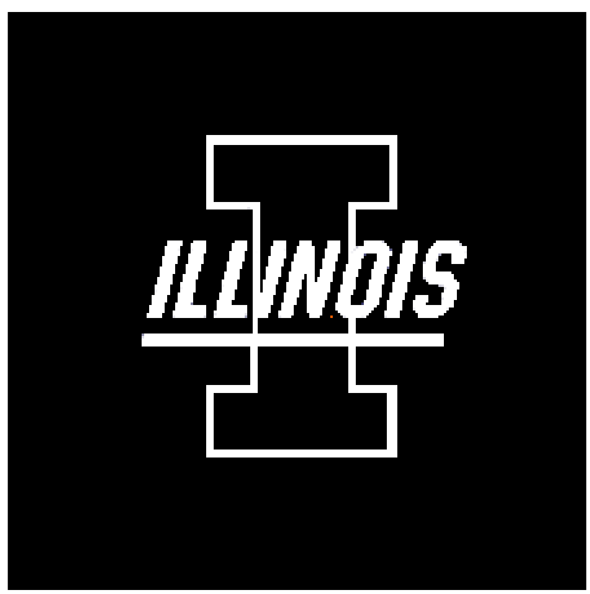





ILLINOIS

Troubleshooting:

1. Photoresist solution is not homogeneous – increase sonication time

2. Photoresist solution polymerizes in container – store in an amber container or a container wrapped with aluminum foil in a chemical refrigerator, if available.

3. Photoresist does not flow to edges of glass slide or polymer pattern is too thin – increase the initial amount of pre-polymer solution on the transparency film

4. Bubbles form in the polymer product
   a. Poke away all bubbles with a pipette tip when photoresist is dropped on the transparency
   b. Carefully place the glass slide on top of the photoresist

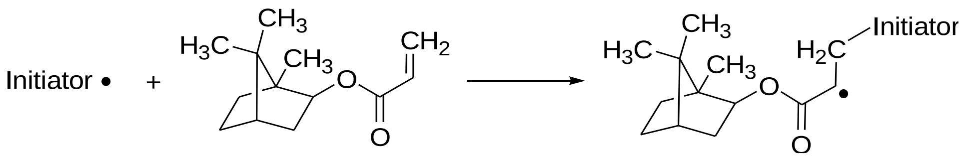
5. Incomplete or no polymerization upon exposure to UV light
   a. Increase UV exposure time
   b. Increase crosslinker concentration (Bis-GMA)
   c. Increase photoinitiator concentration (DMPA)
   d. Decrease amount of dye

6. Brittle or delaminating polymer structures.
   a. Decrease UV exposure time
   b. Decrease crosslinker concentration (Bis-GMA)
   c. Decrease photoinitator concentration (DMPA)

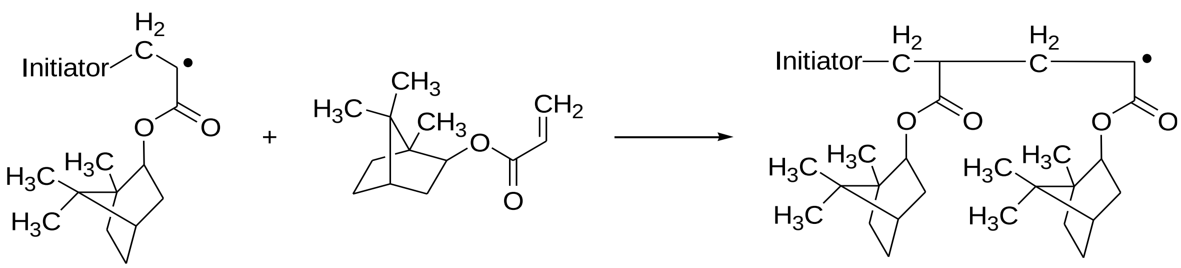
7. Polymer forms in areas that were not exposed to UV light.
   a. Decrease UV exposure time
   b. Increase space between structures and letters on photomask
   c. Blacken dark areas of photomask with a marker to suppress light transmission

Suggested Questions with Answers (some of these questions may be omitted or adapted to reflect the level of the students).

1. Show the initiation of IBA polymerization using the given radical initiator.



2. Show the propagation of IBA polymerization.



3. Show some of the possible termination combinations using the following radicals as the initiator and growing polymer chain:

Initiator• Polymer•

Initiator—Initiator

Initiator—Polymer

Polymer—Polymer

4. How and why do you think the properties of the resulting polymer would change when:

a. More Bis-GMA is added to the photoresist?

Tougher, more insoluble polymer. If too much is added, the polymer will become brittle.

b. Less Bis-GMA is added to the photoresist?

Less rigid polymer that may become more soluble in a solvent.

c. More photoinitiator is added to the photoresist?

More polymer chains with less molecular weight. May not form a rigid structure if too much initiator is added.

d. Less photoinitiator is added to the photoresist?

Longer polymer chains will form with more entangling, which may increase the toughness of the polymer. Too little photoinitiator may not fully polymerize monomer mixture.

e. The photoresist is illuminated with UV light for less time?

Full polymerization may not occur causing the polymer to have poor physical properties.

5. Why would the photoresist solution polymerize if you did not store it in a vial protected from sunlight?

Sunlight contains UV light that would initiate the polymerization of the photoresist.

Glossary:

Bisphenol-A-glycidyldimethacrylate (Bis-GMA) – crosslinker used in this experiment

Crosslinker – a monomer with two or more polymerizable units

Crosslinking density – the degree of crosslinking in a polymer network

2,2-Dimethoxy-2-phenyl-acetophenone (DMPA) – photoinitiator used in this experiment

Etching – cutting into the surface of something, typically by chemical means

Free radical - an atom, molecule, or ion that has one or more unpaired electrons

Initiation – The step in a chain reaction that produces a reactive species that can start the propagation steps of polymerization

Insoluble – unable to be dissolved in the surrounding medium

Isobornyl acrylate (IBA) – monomer used in this experiment

Microchip – a small crystal of a silicon semiconductor fabricated to carry out electrical functions in an integrated circuit

Monomer – a substance of relatively low molecular mass that is used to make a polymer

Negative photoresist – polymer that becomes insoluble upon exposure to UV light

Photoinitiator – a substance that contains a bond easily broken by light to initiate a radical chain reaction and start a polymerization

Photolithography – the process of transferring geometric shapes on a photomask to the surface of a silicon wafer

Photomask – a mask that allows the passage of light through predetermined areas

Photopolymerization – a polymerization that is triggered by light

Photoresist – an organic polymer used in the semiconductor industry that contains a light sensitive substance, which allows it to become soluble or insoluble when exposed to UV light

Polymer – a substance containing repeating monomer units

Polymerization – a chemical reaction that converts monomer into a polymer

Positive photoresist – polymer that degrades or becomes soluble upon exposure to UV light

Pre-polymer mixture – solution containing monomer, crosslinker, and photoinitiator that is able to form polymer when triggered

Propagation – the step in the chain reaction in which a reactive product binds to a monomer and increases its chain length

Semiconductor – a substance that is capable of conducting electricity, although not as well as a metal

Silicon wafer – a substance used for the fabrication of a microchip

SiO_2 – silicon dioxide, the oxidized surface of a silicon wafer

Soluble – able to be dissolved in the surrounding medium

Termination – the step in the chain reaction in which a reactive species needed for chain propagation reacts with another radical rendering it useless for continued propagation or polymer growth

UV light – light with a wavelength of 200-400 nm