A Photolithography Laboratory Experiment for General Chemistry Students

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Optical lithography is the primary means of transferring complex microscopic patterns onto substrates in the manufacture of many types of microfabricated devices such as integrated circuits (ICs), micromachines, and other optoelectronic and electronic devices. The heart of the photolithographic process is a photochemical reaction that occurs when ultraviolet light reacts with a photoactive compound (PAC) incorporated into a carefully designed polymer system known as photoresist. The photoresist is spun-cast onto a substrate in thin film form. By placing a masking pattern over the substrate as the resist is illuminated, the pattern can be transferred. Subsequent deposition, etching, growth, and further lithographic processing is used to complete the device *(1)*.

Since lithography is relatively easy to demonstrate, it is an attractive model system to illustrate several topics of chemistry and materials science to undergraduate students (see for example the mechanical transfer of patterns using an elastomer recently reported by Campbell, et al., ref *2*). We have introduced photolithography to a second-semester general chemistry laboratory in order to infuse interdisciplinary concepts into the lower-division curricula. Gwozdz has reported a similar experiment through a National Science Foundation workshop that he calls a 'Paradigm Experiment' *(3)*. In his experiment, students are asked to design a mask, deposit photoresist onto a silicon substrate, expose the mask with UV radiation, and develop the pattern. We have extended Gwozdz's experiment to be more relevant to a chemistry audience by adding an investigation of the reaction kinetics. This addition enables students to develop an understanding of photochemical reactions as well as introduce them to materials science. Different UV light sources are used to photolyze the PAC and a diode-array UV–vis spectrometer operating in the kinetics mode is used to determine the rate constant of the photobleaching of the PAC as a function of time. Topics introduced in this laboratory include photochemistry, kinetics, spectroscopy, polymer chemistry, and microfabrication technologies.

Background of Photolithography

Photolithography is both the primary means for reproducing patterns onto substrates, and is one of the most pressing engineering challenges facing scientists and engineers in the drive to push ICs to smaller dimensions. This relentless drive to produce smaller and more powerful integrated circuits was first observed by Intel cofounder Gordon Moore in 1965, just five years after the planar IC was developed.

What has become known as Moore's Law posits that the number of transistors per IC doubles every 18 months *(4)*. Currently, minimum feature sizes of 0.18 µm are routinely produced using optical lithography. Since the theoretical resolution limit of optical lithography is determined by diffraction, the limit to the size of features using this approach is being rapidly approached. The resolution, R, is given by the Rayleigh equation as

$$R = \frac{k_1 \lambda}{\mathrm{NA}}$$

where λ is the wavelength of the light used, NA is the numerical aperture of the lens system, and k_1 is a constant that depends on the resist system. While the theoretical resolution given by the Rayleigh equation suggests that the ultimate resolution is approximately $\lambda/2$, the practical resolution limit is closer to λ *(5)*. This has required the continual development and improvement of shorter wavelength UV optical sources, higher numerical aperture lenses, better vibration isolation equipment, and cleaner production facilities. A typical fabrication process for advanced ICs requires lithography steps up to 30 times in the production of a single device. The demanding requirements of higher resolution and nanometer alignment of mask layers, known as registration, have pushed the cost of a single lithography exposure tool (called a stepper) to nearly $10 million today with next generation tools predicted to be up to $800 million of the cost required to build a $10 billion fabrication facility *(6)*. While there are other advanced lithography techniques that do not require UV radiation, such as electron beam, X-ray, ion beam, and even scanning probe, all of these have major hurdles to overcome in order to be considered a serious replacement for optical lithography.

Photoresist comes in two basic varieties depending on whether a mask pattern is transferred as is, or whether the negative of the mask is produced; the former type is called positive photoresist, and the latter is called negative photoresist. In other words, opaque regions of the mask are exposed and dissolve in the developer for positive resists and vice versa for negative resists. Positive resists work by increasing the solubility of the polymer in an aqueous, basic developer solution in regions that have been exposed to the light through the photochemical decomposition of the photoactive compound. In negative resists, the photochemical reaction results in cross-linking in the polymer, rendering the films less soluble in the developer in the exposed regions. Positive resists result in the highest resolution and are the most

commonly used resist in the IC industry. The standard type of positive resist consists of a phenol–formaldehyde polymer called novolak that does not photochemically degrade under UV illumination. The polymer is illustrated in Figure 1 *(7)*. The methyl group can be substituted in either the meta or para position depending on the resin. Typically, a relatively low molecular weight (1000–3000 amu) polymer with a large polydispersity is acceptable. The PAC is diazonapthoquinone (DNQ), which acts as both a strong dissolution inhibitor when unexposed and a dye-sensitizer after irradiation. Before irradiation, the DNQ slows the dissolution rate of the novolak in an aqueous base to 10–20 Å/s compared to the rate without DNQ of ~150 Å/s. After UV irradiation, the dissolution rate increases nearly 100-fold in the developer to a rate of 1000–2000 Å/s. The actual photochemical reaction mechanism of the DNQ is illustrated in Figure 2. The UV light releases the nitrogen to produce a radical on the carbon ring, which then undergoes a Wolff rearrangement to produce a ketene. This compound then reacts with water to generate an indene carboxylic acid photoproduct that dissolves in the basic developer to reproduce the mask pattern *(1, 7)*.

Overview of Procedures and Concepts Learned

Experimental Procedures

Students were divided into groups of four and were assigned to be "process engineers" at a semiconductor fabrication facility. Their first task was to design a mask that would generate a pattern onto a silicon wafer. To accomplish this, students produced a 2-cm × 2-cm black-and-white pattern using a computer graphics program and saved the design in a standard graphics format. These designs were then printed on transparency film using a 1200 dpi laser printer.[W]

The next task was to pattern silicon wafers with the mask designs. Wafers were placed on a hot plate set at 115 °C for 1 min prior to deposition of the resist to evaporate adsorbed water, which inhibits resist adhesion. Enough Shipley 1818 photoresist was deposited onto the stationary substrate to cover the surface of the wafer. The spin-coater was then accelerated to a speed of 3000 rpm for 60 s immediately followed by a 60 s post-deposition bake on the hot plate. This resulted in a resist film approximately 2 μm thick. Thickness calibration curves are provided in the resist literature to indicate the effect of spin speed upon film thickness. Students were then asked as a group to determine the optimal UV exposure time by creating an "exposure wedge". An opaque material was placed over a portion of the substrate for a specified time (for example, 5 s), while the remaining sample was exposed to light. The opaque material was then placed in a different position parallel to the first and illuminated for the same period of time. This was repeated several times, and then the entire wafer was immersed in the developer solution, thoroughly rinsed with deionized water, and dried using compressed N_2. The optimal exposure was determined by observation of the quality of the pattern transferred using an optical microscope. Students then used their own masks to pattern and develop pieces of silicon wafer using the optimized conditions. Finally students used an optical microscope to observe the pattern produced. An example is shown in Figure 3. The lighter region is the bare silicon surface and the

darker region is the area covered in photoresist. This figure illustrates that the best resolution using this mask technique is approximately 100 μm using a 1200 dpi printer.

Photochemical kinetics were studied using a diode array spectrophotometer. Two 1-cm × 1-cm glass slides were coated with photoresist thin films as described above, except that one of the films was not exposed to light prior to spectroscopy. The spectra of an overexposed sample (90 s UV exposure) and an as-deposited sample were compared; see Figure 4. The
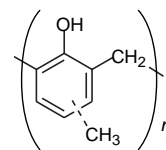
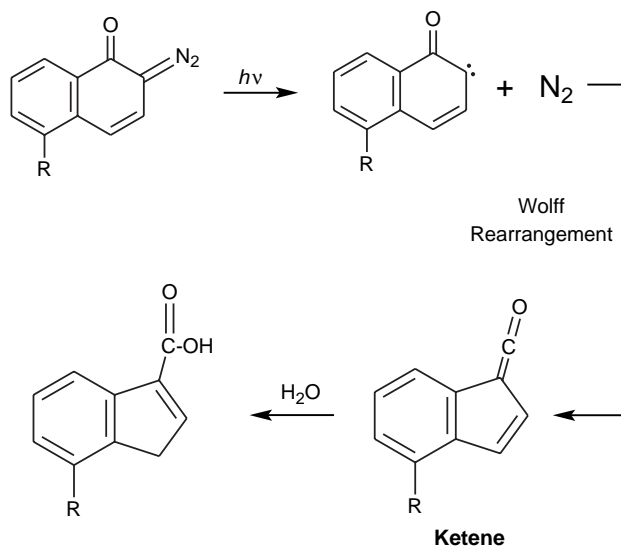Figure 1. Structure of novolak polymer. The methyl group may be in the meta or para position.

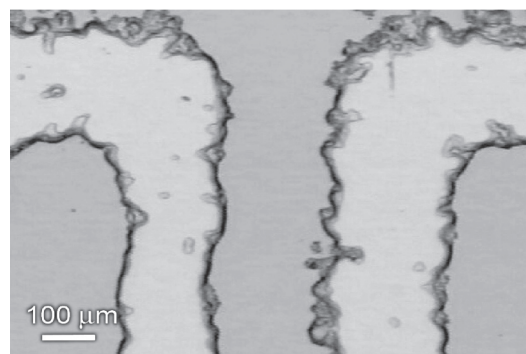Figure 2. Photochemical reaction of the diazonapthoquinone photoactive compound.

Figure 3. Optical micrograph of patterned and developed photoresist on a silicon substrate using laser transparency film photomasks. The lighter region is bare silicon; the darker region is photoresist. (A color version of this figure is printed on p 115.)

spectrophotometer was then run in the kinetics mode for 12 min with data being taken every 30 s at three wavelengths. Different groups were assigned one of three different sources of UV radiation to observe the photobleaching kinetics: (i) light from the spectrometer lamp with the room lights off, (ii) spectrometer light plus room light—there was no cover over the sample holder, and (iii) a 365 nm UV hand-held mercury lamp that was positioned at approximately a 45° angle relative to the surface of the glass substrate. The photobleaching of the 405 nm absorption peak for these three conditions is shown in Figure 5 with the normalized absorbance plotted as a function of time.

Summary of Evaluation Studies

We have used this experiment in the second semester of a general chemistry laboratory after the topics of kinetics and spectroscopy had been introduced in the lecture. This laboratory was used in a two-credit, special chemistry majors' laboratory section that we teach at JMU. Typically there are about 40 students in this lab, meaning a total of ten groups of students performed this experiment. Since this number of students was too large to accommodate in one laboratory meeting, we planned to have two experiments running simultaneously over the course of two weeks so that only 20 students performed this experiment in a given week. Of these, half performed the kinetics study and the other half produced a pattern at any given time. The groups then rotated stations to complete the study.

One of the primary discoveries made while performing this experiment was that a "bright field mask", that is, a pattern in which the background is predominantly white with the remaining design black, is superior to a "dark field mask".[W] The reason for this is that black portions of the mask produced by a laser printer are not completely opaque to the UV radiation. This leads to a pinhole effect in the photoresist. It is also important that the mask designs be either black or white and not have a gray-scale. Again, this leads to overexposure of the gray regions and poor contrast in the reproduced image. One can see from Figure 3 that the edge

resolution of the transferred patterns is relatively poor using masks produced from a laser printer. This is due to the pixelization from the toner deposited onto the transparency film. While we used a relatively high-resolution laser printer, the students could clearly see fuzzy edges by viewing the masks through the optical microscope.

There are other sources of masks that can be used. One can make masks using the negatives from 35 mm black and white photographic film as one would use to make slides of a computer screen in an instrument such as a Polaroid Digital Palette. We have previously reported that Kodak Kodalith film offers superior edge resolution for pattern production, but requires a dark room to develop the 35 mm film *(8)*. The negative is then used as the mask material producing excellent edge resolution with features as small as 80 μm. We have also used discarded microfilm donated from the campus library to pattern the page of a magazine article.[W]

In the kinetics portion of the experiment, Figure 5 suggests that the effect of exposure to the room light and the UV irradiation from the spectrometer are minimal over a 12 min time period, however, the use of a UV lamp dramatically increased the photobleaching observed. One could also use other sources such as a UV flash lamp or laser, given appropriate fixturing of the experiment. A rate plot of the ln (absorbance) as a function of exposure time is shown in the supplementary material for the data in Figure 5.[W]

List of Unusual Chemicals and Instruments

Shipley Microposit 1818 positive photoresist

Shipley Microposit 351 developer concentrate
(Both are available from MicroChem Corp. through their Web site at *http://www.microchem.com;* accessed Sept 2002)

Siliconsubstrates
(Virginia Semiconductor, Fredricksburg, VA)
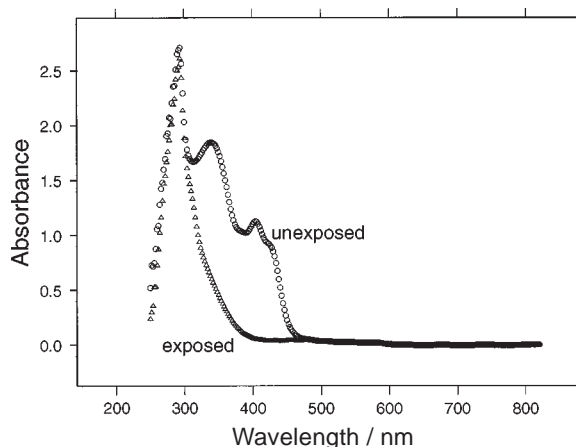
Spin-deposition system

UV exposure system

Figure 4. Absorption spectra of spun-cast thin films of photoresist on a glass substrate both unexposed (open circles) and exposed (open triangles) to a 365 nm Hg arc lamp irradiation for 90 s.
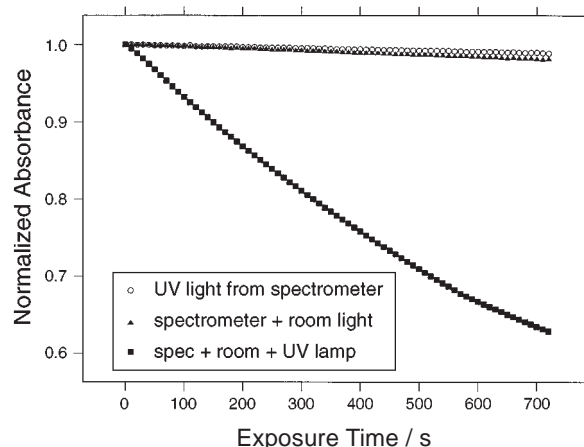

Figure 5. Normalized absorbance of the 405 nm absorption peak vs exposure time (s) for samples treated to three different UV light sources.

Hazards

Photoresist is an organic polymer dissolved in hexanes, and should be deposited and processed in a ventilated hood. The developer is a basic sodium hydroxide-based aqueous solution. Appropriate MSDS literature should be available for the photoresist and the developer prior to the lab, and salient safety features should be outlined. Spin coating involves the high-speed acceleration and deceleration of substrates (up to 5000 rpm). Any spin deposition system used must be mechanically rigid and the substrates must be shielded in case they break free from the substrate chuck.

Conclusions

Photolithography is an attractive system for demonstrating the principles of kinetics, photochemistry, polymer chemistry, and spectroscopy to lower-division chemistry students in a laboratory setting. Students learn about the production of microfabricated devices, and are introduced to the interdisciplinary field of materials chemistry through this experiment.

Acknowledgments

ᵂSupplemental Material

Instructions for the students and notes for the instructor are available in this issue of *JCE Online.*

Literature Cited

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