Benchtop Nanoscale Patterning Using Soft Lithography

W

Viswanathan Meenakshi, Yelizaveta Babayan, and Teri W. Odom*
Department of Chemistry, Northwestern University, Evanston, IL 60208; **todom@northwestern.edu*

This paper describes nanoscale patterning experiments based on soft lithography that can be performed on the benchtop. These experiments are designed for undergraduate students at the beginning of their academic career (first- and second-year students). Because of the simplicity and inexpensive nature of the patterning methods, they can also be incorporated into advanced high school chemistry courses. We have demonstrated the feasibility of the labs by including them as part of a two-quarter, research-based course on nanoscience and technology at Northwestern University. The classroom size was limited to 12 students, although the experiments were intended to require only minimal supervision and can be scaled easily for larger class sizes. Prior to classroom implementation, these experiments were also tested in our laboratory by three undergraduate students.

We have developed these benchtop nanoscale experiments in response to the increasing need for laboratory exercises to supplement lecture-only courses on nanotechnology and to provide students with hands-on experience in nanopatterning techniques. Nanofabrication approaches generally fall into two categories: top-down and bottom-up. Top-down refers to the gradual reduction of size from the macroscale to the nanoscale, while bottom-up involves the assembly of larger structures from molecular building blocks. Although there have been reports of bottom-up experiments *(1, 2)*, top-down laboratories on lithography have only been limited to macroscale analogies, such as using:

1. PDMS stamps with mm-scale features for microcontact printing (μCP) of self-assembled monolayers (SAMs) *(3)*
2. Nylon spheres (1-in. diameter) in contact with photosensitive paper and a UV lamp to illustrate nanosphere lithography *(4)*
3. Projection lithography to create microscale circuits *(5)*
4. Photolithography to demonstrate the concept of microchip fabrication *(6)*

This paper is distinct from the examples above because it outlines experiments in which students use soft lithographic techniques to fabricate and replicate nanoscale (110 nm) features. The growing importance of nanofabrication in microelectronics, optoelectronics, and biomedical applications has prompted educational institutions to develop related undergraduate curricula; however, nanopatterning has not received attention in the form of labs because of the expense and expertise typically required in top-down microfabrication.

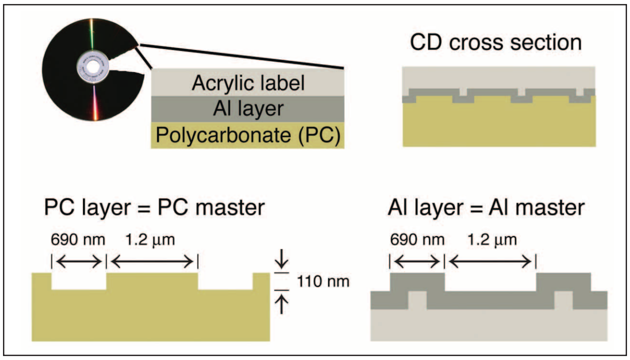

Figure 1. Schematic diagram of CD composition.

The nanopatterning techniques described here include replica molding (RM), micro-molding in capillaries (MIMIC), and μCP and etching *(7, 8)*. These methods can be used to generate both polymeric and metallic nanostructures using inexpensive materials such as compact discs (CDs), glass microscope slides, poly(dimethylsiloxane) (PDMS), and polyurethane (PU). If available, an atomic force microscope (AFM) or an optical microscope can be used to image the nanoscale patterns generated by these techniques. These instruments, however, are not necessary to determine whether the experiments were successful. A simple laser pointer can be used to visualize the diffraction pattern produced by the nanostructures, and in this way, macroscale tools can be used to determine indirectly the nanoscale patterns. Importantly, the experiments are supplemented by an online video manual that can be found at *http://www.nanoed.org/courses/nano_experiments_menu.html* (accessed Aug 2007).

Experimental Methods and Results

Nanoscale Masters and PDMS Molds

The first exercise in soft lithography is to fabricate a master. Masters are high-quality patterns that are typically fabricated using time-consuming and expensive techniques such as photolithography, e-beam lithography, and focused ion beam milling. We have found a simple and cheap alternative for obtaining masters with nanoscale features: CDs. CDs are composed of multiple layers, and two adjacent layers can be used as two *different* masters, in which one layer has features inverted to that of the other. For example, a Sony CD-R has a polycarbonate (PC)-surface with bumps that are 1.2 μm wide, 110 nm high, and spaced by 690 nm; the Al-surface has bumps that are 690 nm wide, 110 nm high, and spaced by 1.2 μm (Figure 1). Upon separation of the two layers using tweezers, two masters are obtained: a PC-master and an Al-master.

To produce a PDMS mold—the key pattern transfer element in soft lithography—from either master, students poured a pre-polymer of PDMS on the surface of the master, cured the PDMS, and then peeled off the mold. Figure 2A outlines this procedure starting from a PC-master. Figures 2B and 2C show AFM images of the PC-master from the CD and its PDMS mold; ~110 nm-tall features from the PC-master were transferred into ~110 nm-deep troughs in the PDMS mold. The fabrication of PDMS molds required about an hour (to cure the PDMS); once formed, the molds could be used repeatedly for all the soft lithographic techniques.

Replica Molding Technique

Replica molding (RM) can be easily used to produce polymeric structures with nanoscale features on a variety of surfaces. Interestingly, CDs are made by RM techniques. Students used RM to transfer the nanopatterns on the PDMS molds into polyurethane (PU), a flexible and optically transparent polymer that can be cured under UV light. Students placed a drop of PU on a clean microscope slide and then pressed down the PDMS mold onto the PU drop (Figure 3). After curing the PU and peeling off the PDMS mold, students produced a pattern in PU that was a replica of the master. For example, if the PDMS mold from the PC-master (Figure 2B) was used in RM, then a replica of the PC-master was produced in PU (Figure 3D). AFM images of the PU-patterns demonstrate that RM can produce replicas of the masters with high fidelity. RM is a practical and efficient method for transferring patterns into different polymeric materials and is limited only by the curing time of the polymer. The RM experiments took students 15–20 minutes to perform.

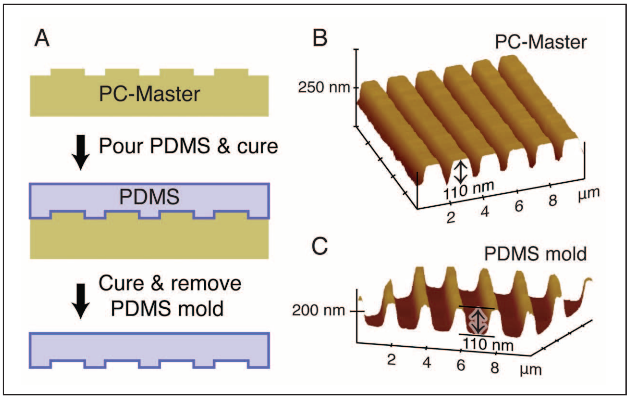

Figure 2. (A) Scheme to fabricate a PDMS mold from a PC-master. (B) AFM image of PC-master. (C) AFM image of PDMS mold formed from (B).

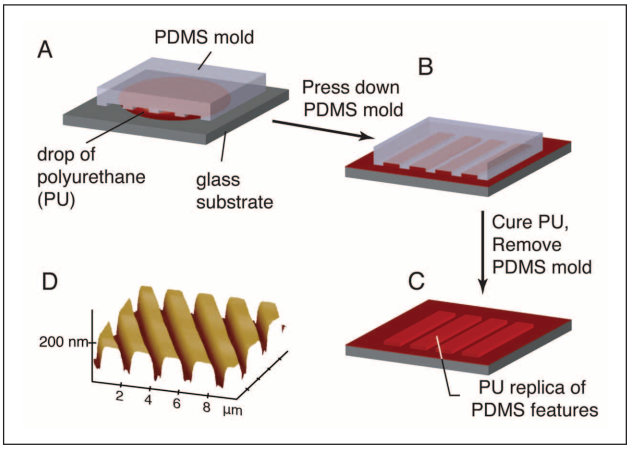

Figure 3. (A)–(C) Scheme of replica molding. (D) AFM image of the PU-replica, which is identical to the PC-master.

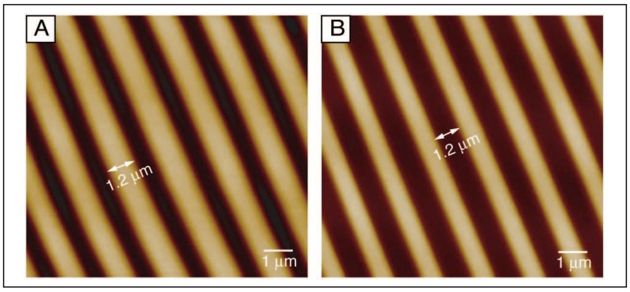

Figure 4. AFM images of (A) PDMS mold from aluminum layer and (B) PU-replica of the aluminum layer after MIMIC. Dark regions correspond to recessed features, and bright regions correspond to raised features.

Micro-Molding in Capillaries Technique

Micro-molding in capillaries (MIMIC) is based on the spontaneous filling of fluid into capillaries. Students constructed capillaries by placing the patterned side of the PDMS mold into conformal contact with a glass slide to form a network of channels. Then they placed a drop of PU pre-polymer at one of the open ends of the channels, and the channels were filled with PU by capillary action. After the PU was cured under UV light, the PDMS mold was peeled off to reveal a network of PU lines (same dimensions as channels in PDMS) on the glass slide. When a PDMS mold from the Al-master (Figure 4A) was used for MIMIC, then the PU-replica (Figure 4B) was a “mimic” of the original Al-master. MIMIC is slightly more challenging than RM because it takes time to fill the nanoscale channels with viscous fluid by capillarity; the smaller the channels, the harder they are to fill. It took students an hour to perform MIMIC using PDMS molds obtained from the Al-master, three to four times longer than RM.

Micro-Contact Printing and Etching Technique

Micro-contact printing (µCP) uses a PDMS stamp to “print” a chemical “ink” on a target substrate. (The word “stamp” is used for these experiments because the PDMS mold is now used to “print” molecules onto gold surfaces.) This technique has been widely used to pattern SAMs on gold because alkanethiol molecules can be transferred from a PDMS stamp to a gold surface to form patterns of SAMs (Figure 5). In these labs, students not only printed nanoscale patterns of SAMs, but also used the patterned molecules along with chemical etching to generate metallic nanostructures. SAMs can act as an etch resist to protect the underlying gold surface from chemical etching. Thus, when a gold film patterned with SAMs is placed into solution of cyanide-free gold etch (Transene), the exposed areas of gold are removed to reveal a pattern resembling the relief features of the PDMS stamp (Figure 5, top).

Archival-grade gold CD-Rs were used to produce more complex metallic nanostructures. First, students exposed the gold layer on the CD by treating the CD-Rs with nitric acid. *(Warning: Nitric acid is highly corrosive and can cause severe burns. Handle with care.)* Then, using a PDMS stamp from

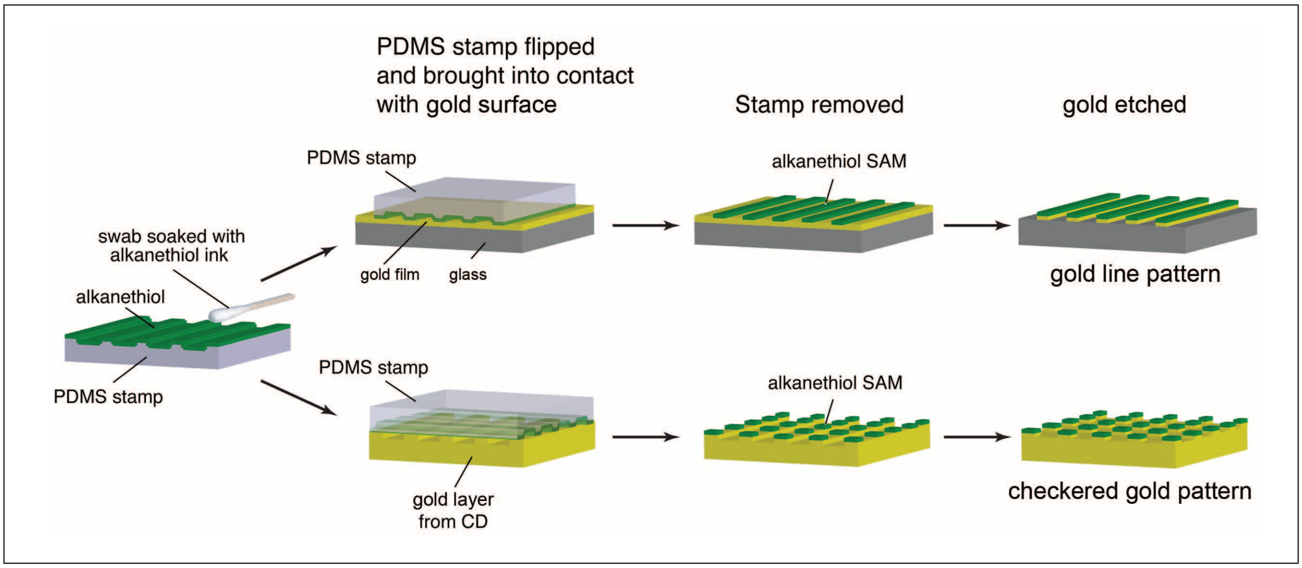

Figure 5. Procedure for micro-contact printing and etching of a gold film (top) and a gold-CD (bottom).

an Aluminum master, the students printed SAMs on the gold-CD surface. Molecules were transferred to the gold-CD only in the regions where the lines of the stamp were in contact with the lines on the gold-CD. When the lines on the stamp were nearly perpendicular to the lines of the CD, a checkerboard pattern of SAMs was produced. After students placed this substrate into the gold etch, the gold regions not protected by the SAM were etched away to reveal a checkerboard gold pattern (Figure 5, bottom).

Using macroscale diffraction methods, students visualized the nanopatterns on the gold-CD before and after etching by shining a laser pointer onto the unetched and etched gold surfaces (Figure 6). Because the gold layer is thin and fairly transparent, the best way to visualize the diffraction pattern is by shining a laser pointer through the sample onto a piece of white paper. In the case of the unetched gold-CD, where only lines were patterned, the diffraction pattern resulted in a single line of dots; when the laser was incident on the checkerboard pattern, a hexagonal diffraction pattern resulted. Depending on the angle of the PDMS stamp relative to the lines of the gold-CD, diffraction patterns with different symmetries (e.g., hexagonal, distorted, or square) could be produced.

Summary

With increasing interest in nanoscale science and technology, the development of new and inexpensive fabrication techniques to generate nanostructures has become an important scientific challenge. In this paper, we have demonstrated a series of simple benchtop nanopatterning procedures that have been successfully incorporated into an undergraduate-level course on nanoscale science. The experiments aim to introduce nanofabrication to undergraduate students and enable them to create nanoscale structures using simple and inexpensive tools.

Hazards

Students should wear rubber gloves and goggles for all the experiments described here to prevent contact with chemicals. Students should avoid looking directly at UV light or allowing their skin to be exposed to its radiation as the high intensity light is damaging to biological tissue after prolonged exposure. *Use concentrated* HNO_3 *with extreme care and only*

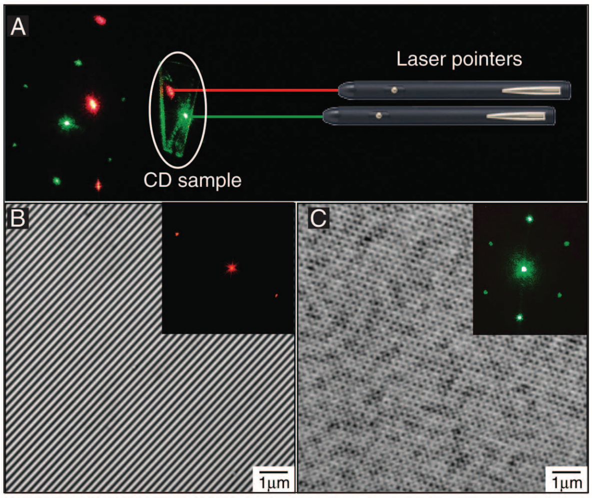

Figure 6. (A) Patterns on the CD can be visualized by shining a laser pointer onto the sample and observing the diffraction produced from the pattern. The top (red) laser pointer is incident on the unetched gold line pattern (B) and creates a linear diffraction pattern (B, inset). The bottom (green) laser pointer is incident on the etched checkerboard pattern (C) and creates a hexagonal diffraction pattern (C, inset). In the optical micrographs of (B) and (C), dark regions correspond to recessed features, and bright regions correspond to raised features.

in the fume hood. Never mix water and the acid while cleaning the substrates. The gold etchant should be handled carefully and only in a fume hood. All chemicals should be disposed of in labeled waste containers.

Acknowledgments

This work was supported by the National Science Foundation under the Nanotechnology in Undergraduate Education (NUE) Award (DMR-0407073) and the NCLT program (ESI-0426328) at the Materials Research Institute of Northwestern University. We would like to thank Northwestern undergraduates Laura Hughes, Numrin Thaitrong, and Scott Price for testing the experiments in the lab. TWO is a DuPont Young Professor, an Alfred P. Sloan Research Fellow, a Cottrell Scholar of Research Corporation, and a David and Lucile Packard Fellow.

[W]Supplemental Material

Introductory information, instructions for students, and instructions for teachers—including post-lab questions—are available in this issue of *JCE Online*. An online video manual designed for students is also available at *http://www.nanoed.org/courses/nano_experiments_menu.html* (accessed Aug 2007).

Literature Cited

1. Winkler, L. D.; Arceo, J. F.; Hughes, W. C.; DeGraff, B. A.; Augustine, B. H. *J. Chem. Educ.* **2005,** *82,* 1700–1702.
2. Bentley, A. K.; Farhoud, M.; Ellis, A. B.; Lisensky, G. C.; Nickel, A.-M. L.; Crone, W. C. *J. Chem. Educ.* **2005,** *82,* 765–768.
3. McKenzie, L. C.; Huffman, L. M.; Parent, K. E.; Hutchison, J. E.; Thompson, J. E. *J. Chem. Educ.* **2004,** *81,* 545–548.
4. Haynes, C. L.; McFarland, A. D.; Van Duyne, R. P.; Godwin, H. A. *J. Chem. Educ.* **2005,** *82,* 768A–768B.
5. Stelick, S. J.; Alger, W. H.; Laufer, J. S.; Waldron, A. M.; Batt, C. A. *J. Chem. Educ.* **2005,** *82,* 1361–1364.
6. Berkowski, K. L.; Plunkett, K. N.; Yu, Q.; Moore, J. S. *J. Chem. Educ.* **2005,** *82,* 1365–1369.
7. Xia, Y.; Whitesides, G. M. *Angew. Chem. Int. Ed.* **1998,** *37,* 550–575.
8. Gates, B. D.; Xu, Q.; Stewart, M.; Ryan, D.; Willson, C. G.; Whitesides, G. M. *Chem. Rev.* **2005,** *105,* 1171–1196.