Soft Lithography and Atomic Force Microscopy:
A Research Experience

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Team 1

May 5, 2004

Computers are everywhere. At the heart of every computer is a microprocessor, made from silicon. More than 220 billion silicon chips are produced every year (Chepesiuk, 1999). The constant push in consumer electronics is for smaller, faster, and cheaper products. With an increase in capabilities, there will also be an increase in demand. Thus, there is also a search for faster and cheaper manufacturing processes as well. As items become smaller, the realm of nanotechnology covers this manufacturing process.

Nanotechnology was first envisioned by Richard Fenyman in his paper "There's Plenty of Room at the Bottom." In this paper he outlines the principles behind creating objects on the very small scale. He talks about what was currently being studied at his time, where this was leading, and what the future could hold (*Nanotechnology*, n.d.). Since then, nanotechnology has expanded and now represents working in the 10 - 100 nanometer (10^{-9} m) range. At this size, one can recognize a fundamental change in the properties of matter. By taking advantage of these fundamental differences, researchers everywhere are striving for products never before imaginable. The hope is to be able to utilize some of these special properties in manufacturing.

There are two broad categories describing manufacturing on the nanotechnology scale (Whitesides & Love, 2001). The first is called top-down processing, and the other is called bottom-up. Top-down processing, in simple terms, is done through starting with something large and working with it, taking pieces away from it, in order to create something small. In top-down processing, a pattern is created and then shrunk in size. This pattern is used to create nanostructures on a larger substance, typically by removing material until the desired product is created. The bottom-up processing method is the fundamentally opposite of top-down. In bottom-up, one rearranges atoms and molecules individually and then builds them up in order to create nanostructures. By placing individual atoms or molecules, one has the power to control the very physical and chemical properties of a nanostructure (Whitesides & Love, 2001).

Many of the methods we use today are top-down processes, the making of something small out of something large. Photolithography is one such process. It uses ultraviolet light shown through a mask in order to create a pattern on a photo reactive surface. This process is very expensive and requires special equipment which is also expensive (Xia & Whitesides, 1998). As a commercial technique, this process is very financially demanding of a company. Another common top-down processing method is that of electron beam lithography (EBL). This process is similar to photolithography except that instead of using light, a beam of electrons is cast at an electron-sensitive surface to form the pattern. This too is an expensive and time-consuming process (Xia & Whitesides, 1998).

One of the most promising new techniques is called soft lithography. Soft lithography was developed by George Whitesides at Harvard University. The process resembles that of creating patterns using a simple rubber stamp (in fact, Whitesides first attempts were done with a conventional rubber stamp). A master with extremely small features is created using one of the common lithography methods (photolithography, EBL, etc.). A stamp is then created from the master and coated with "nano-ink". With the appropriate ink, a pattern can then be transferred to other materials. This process creates, on the stamped surface, a single layer of the molecules making up the ink (Xia & Whitesides, 1998).

The potential advantages of this method are quite astounding. First of all, unlike modern nanolithography, the polymer (a rubbery substance) stamp is flexible which allows it to print on non-planar surfaces (Xia & Whitesides, 1998). It will twist and turn to match the contours of the printed surface. There are also many more options for an "ink" or methods of transferring a pattern than with photolithography or EBL. With soft lithography it is no longer necessary to have a photo reactive surface in order to create a nanostructure (Xia & Whitesides, 1998). Another advantage of soft lithography is its resolution. The size of details created using soft lithography has been found to be smaller than that of photolithography in the laboratory setting (~30 nm compared to ~100 nm). Finally, soft lithography allows 2500 prints to be made from one master, as opposed to the modern process (photolithography or EBL) which makes only one print. As you can see, soft lithography has great potential for the manufacturing of nanostructures. But will it work?

The purpose of our experiment was to determine if soft lithography is a viable manufacturing process that could possibly replace our current methods. To test this, we performed a procedure similar to that described in Whitesides' paper, and then used an atomic force microscope to image—confirm—our results.

The first step in the soft lithography process is to prepare the substrate material and coat it with the photoresist. This substrate is the underlying material that will eventually be used as the master to create the stamps (Purdue University, n.d.). The most common substrate material is silicon (EU ESPRIT, n.d.). Silicon has been used extensively for photolithography because of its availability and its ability to be grown in the laboratory (Ottow, 2000). First, the substrate is cleaned with dichloromethane, acetone, and methanol. The surface finish of the substrate is extremely important to the outcome of the stamp because of the small surface dimensions (EU ESPRIT, n.d.). Next, the photoresist is applied by spraying or spin coating it onto the wafer. The goal is to apply a thin, even layer over the entire surface. Therefore, spin coating has proven to be more reliable and is now the method of choice for most applications. Finally, the substrate is put on a hot plate to be baked (Memsnet.org, n.d.).

There are two main types of photoresists. Positive photoresists, when exposed to ultraviolet light, structurally rearrange to become more soluble. When the developer is applied to the substrate, these areas wash away. Negative photoresists become insoluble when exposed to ultraviolet light, so they do not wash away when the developer is applied. Each type of photoresist has its advantages. Negative resists have been around longer and are cheaper to use, they have better photospeed, and adhere better to some substrate surfaces (Microcircuit Fabrication, n.d.). Two common negative resists are SU-8 and Bisarylazide (Photolithography, n.d). The biggest advantage positive photoresists have is the ability to produce higher resolution results (Microcircuit Fabrication, n.d.). Two common positive resists are Novolac-Diazoquinone and PMMA (Photolithography, n.d).

Once the photoresist is applied to the surface of the wafer, a mask must be created that will transfer the features to the master (Purdue University, n.d.). Care must be taken during this step. The most common defect to the surface of the substrate is caused when the substrate adheres to the mask. If the mask is removed improperly, it removes the photoresist as well, thereby ruining that step of the process (Mancini, Resnick, Screenivasan, & Wilson, 2001). The two main standards for creating masks are though optical lithography and electron beam lithography. Optical lithography is the more common of the two. It uses parallel processing to speed up the procedure, but its resolution is only 100 nm. Electron beam lithography is starting to gain popularity because of its higher resolution capability, but it is a slower process (EU ESPRIT, n.d.). After the mask is aligned to the substrate, ultraviolet light is used to cause a chemical change in the photoresist. Depending on the feature size, the surrounding environment needs to be pretty stringent. When working with moderate-size features, there is no need for a clean room environment. As the feature size decreases below 20 µm, the laboratory setting becomes more restrictive (Chou, Quake, Scherer, Thorsen, & Unger).

The third step of this process is exposing the photoresist to light in the mask aligner and developing it. The mask aligner is a machine used to position the mask on the photoresist/substrate correctly. The substrate/photoresist is placed in the mask aligner with markings (usually two pluses) that show where the mask should be placed. The mask is then aligned to these markings (*Layout*, n.d.). Once the mask and photoresist/substrate are aligned, the mask is exposed to ultraviolet light for a short amount of time—approximately 30 s for most SU-8 photoresists (Magnus, 2003). The minimum wavelength currently used in production is 250 nm (Uplaznik, 2002). After being exposed to light, the photoresist/substrate (template) is soft baked for 15-20 seconds at 100°C for every micrometer of photoresist thickness (Magnus, 2003). After cooling for 5 minutes, the template is developed in a bath of PGMEA (propylene glycol methyl ether acetate), IPA (isopropanol), or EGMEA (ethylene glycol monomethyl ether acetate) (Magnus, 2003; *SU-8 photo-resist*, 2003). It helps to use GBL (gamma-Butylacetone) as a rinse prior to the bath. GBL helps remove partially cross-linked SU-8 (*SU-8 photo-resist*, 2003). It is common to agitate the template during and before the development process to speed up development and assist in the removal of non-cross-linked SU-8 (*SU-8 photo-resist*, 2003; Bogdanov, n.d.). High frequency noise has been used prior to bathing, but does not seem to have a noticeable effect on development (Bogdanov, n.d.). However, stirring the bathing solution and agitating the template during bathing assists in the removal of non-cross-linked SU-8 (*SU-8 photo-resist*, 2003). Depending on whether you have a positive or negative resist, the pattern developed will be the same or the negative of your intended pattern (Magnus, 2003).

The most common resin to use in the creation of the master mold after development is PDMS. PDMS is rather resilient against destruction from non-polar solvents, but will swell and then shrink. If swelling is a large issue, Fluorosilicone (another resin) is an option. The resin is poured over the template at room temperature and spread by tilting the template in order to let the resin flow across the entire surface. Due to PDMS's chemical attributes, it can be cured at a wide range of temperatures. The cooler the temperature, the longer it takes to cure, but less shrinkage will occur. Likewise at higher temperatures, it takes less time to cure, but shrinkage is greater (Magnus, 2003). A low temperature, long duration curing atmosphere is ideal for PDMS. Given 24 hours at 25°C, the majority of the elastomer's strength will be present (Dow Corning Corporation, n.d.).

Once we had the PDMS stamp created, our next task was to apply the ink to see if we could pattern a gold substrate. The type of ink used was octadecanethiol, a type of alkanethiol. The term alkanethiol is used to describe any hydrocarbon attached to a thiol molecule. A 2 mM ethanol and octadecanethiol solution was used to soak the PDMS stamp (Xia & Whitesides, 1998). During this step, alkanethiol molecules would adhere to the surface of the stamp (see Figures 1-3). After letting the stamp sit for 5 minutes, we removed the stamp and dried it with nitrogen gas. The PDMS stamp was then pressed against the top of a gold substrate for a few minutes, allowing the alkanethiol molecules to transfer in the shape of the pattern.

To determine if our process was successful, we needed a way to image the surface of the gold substrate to see if any material had transferred. We decided to use a technique called atomic force microscopy (AFM). AFM is a type of scanning probe microscopy. Scanning Probe Microscopy was first developed in the 1980's by IBM (*Atomic Force Microscopy*, n.d.). To image the surface, an extremely sharp tip is used as the sensor. In AFM, the tip is moved across the surface of an object. As the tip encounters features, its height adjusts to the contour of the object, similar to a record player. This change in height is registered by the computer and a topographic image is created. In a certain AFM method, the twist or torque done on the tip by the surface is also measured which allows the computer to determine the amount of resistance to movement (friction) applied to the tip. Due to this nature of AFM, one of the advantages of AFM over Scanning Tunneling Microscopy is evident: its ability to image non-conductive surfaces (*Atomic Force Microscopy*, n.d.).

The key components of an atomic force microscope are the laser light source, the cantilever tip, and the light detecting diodes (Baselt, 1993). The laser projects a beam of light that reflects off of the back of the cantilever toward the light detecting diodes. As the cantilever tip encounters features on the surface, the tip will move up and down following the surface's contour, causing the laser to strike a slightly different part of the cantilever at a slightly different angle. This change in position and angle causes a change in intensity of the light at each diode. The computer looks at this change in order to create a topographic (height) and, in some cases, frictional (resistance to movement) image.

There are three different modes the atomic force microscope can use to image the surface: contact, non-contact, and tapping (*Atomic Force Microscopy*, n.d.). In contact mode, the cantilever tip is placed directly in contact with the surface being imaged. As the tip moves along the surface, the tip is affected by the repulsive van der Wall's forces of the atoms making up the surface. In non-contact mode, the tip is held slightly above the surface. As the tip moves, it is affected by similar attractive forces. The method is advantageous due to the fact that no actual contact is made with the surface being imaged. With tapping mode atomic force microscopy cantilever tip oscillates vertically. As it is oscillating, the tip is brought toward the surface being imaged and the computer registers where it first hits the surface. As it moves, the computer adjusts and records the height at which it touches the surface at the bottom of its oscillation (*Atomic Force Microscopy*, n.d.).

The most common of the three methods is contact mode, which is the method we used. One of the benefits of contact mode is its ability to measure the surface friction as well as the surface height

(Baselt, 1993). Surface friction measurement works along the same principle. As the tip is moved along the surface, the chemical properties of the surface also cause the tip to twist. The twisting causes the laser to be reflected to a different set of diodes. The amount of twist in the cantilever tip is directly related to the amount of friction that is being applied.

In our experiment we were working with a gold substrate. On the atomic level, gold has a very rough surface. Its surface's feature heights can differ between 2 and 3 nm. The alkanethiol layer we were trying to image has roughly the same height. Because of this similarity in feature size, it is nearly impossible to distinguish between the gold and alkanethiol using only a height image. Because gold and alkanethiol have different chemical compositions, however, the difference can easily be seen in the friction image (Kyung, 2004).

In order to better understand what we should be seeing, we used an optical microscope to view both the mask and the PDMS stamp that were used in making the nanostructure. The image of the mask was clearly defined and easy to see. When viewed through the optical microscope, it contained alternating black and white squares. The PDMS stamp on the other hand contained no noticeable features. Due to this we were unsure whether it even contained a pattern.

The images from atomic force microscope images also produced little results to our liking. Our images turned out very fuzzy and almost completely full of static. It was quite apparent that our pattern did not transfer to the gold surface. Neither the height map nor the frictional image contained any evidence of a nanostructure on the surface of the gold substrate.

After consulting additional resources in an attempt to explain our lack of results, we found a possible cause. By reviewing Whitesides' (1998) procedure in more detail, we found it included a step that we did not perform in our experimentation: silanization of the surface before applying the PDMS stamp. Silanization is a process that makes chemical groups in the SU-8 less active and thus makes the SU-8 surface less reactive. By not silanizing the silicon, the PDMS was able to stick to the residual SU-8 that still remained on the surface. When the PDMS stamp was removed, some of the SU-8 was stuck to it and thus removed as well (see Figure 4). This could have had two effects. First, the surface chemistry of SU-8 is different than that of PDMS, which could prevent some of the alkanethiol solution from adhering to it. Also, when the stamp was placed on the gold substrate, the SU-8 residual prevented the PDMS from making conformal contact. The gold has a naturally rough surface. One of the benefits of using PDMS is its flexibility. When it is applied to the substrate under normal conditions, it deforms and contours itself to the surface of the substrate, thus making contact at all points (see Figure 5). The roughness does not adversely affect the printing. In our case when the stamp was placed on the surface, some areas of SU-8, which is a lot more rigid than the PDMS stamp, came into contact with the surface. Because the SU-8 does not flex, it could not make conformal contact with the entire surface (see Figure 6).

Looking back at the experiment, there are some changes we would make. Before spin-coating the SU-8 onto the silicon, we would de-gas it. This removes all of the dissolved gas from the SU-8, leaving behind a pure, bubble-free, substance. We noticed that during spin-coating, small bubbles appeared which affected part of the surface where the pattern was to be created. We would also de-gas the PDMS resin before applying it to the silicon master. We noticed bubbles present in the PDMS as well, not only while we were applying the PDMS resin, but also in the finished PDMS stamp. The bubbles could have prevented the PDMS from conforming to the small features of the master. We would also lower the temperature of the PDMS and master while curing. The hardening of the PDMS is a temperature driven reaction, so by lowering the temperature, the process would take longer. Our hope is that this would allow the PDMS more time to fit into the grooves of the pattern and to make better contact with the silicon master.

During the transfer of the alkanethiol to the gold substrate, we did not pay careful attention to the time of contact. Review of Whiteside's (1998) procedure indicated that contact time should be about 10 – 20 seconds, and not exceed 30 seconds. A contact time longer than that can destroy the pattern. Finally, in order to know which parts of the experiment worked and which parts did not, we would like to have used the atomic force microscope on the surface of the silicon master, as well as on the surface of the

PDMS stamp. This would allow us to determine if a pattern was successfully created on the master, and then see if that pattern was successfully transferred to the PDMS stamp.

Through this experiment, we've concluded that soft lithography is a cutting edge process that has much promise in creating nanostructures starting from the molecule up. It is fast, easy, cheap and has many advantages over standard lithography procedures such as non-planar pattern creation. However, due to the results of our experiment, we feel soft lithography is not suitable for use as a commercial manufacturing process at this time. There is currently too great a chance for human error. Whitesides also pointed out other aspects of soft lithography that will need to be addressed before it becomes a viable nanomanufacturing process. These include the following: there is approximately a 1% shrinkage of the PDMS during curing; PDMS expands in non-polar solution; and sagging, and thus misprinting, can occur in patterns with widely-spaced features (Xia & Whitesides, 1998). Until these concerns are addressed, soft lithography will remain a process imprisoned to the laboratory.

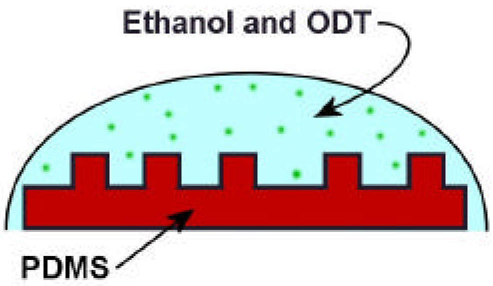

Figure 1 (Allen, W) - Step 1 of "inking." PDMS stamp is placed in Ethanol and ODT solution.

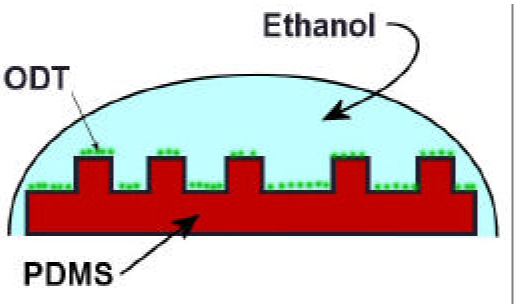

Figure 2 (Allen, W) - ODT from the solution settles down onto the PDMS stamp. Stamp now has ODT attached to it which acts as the

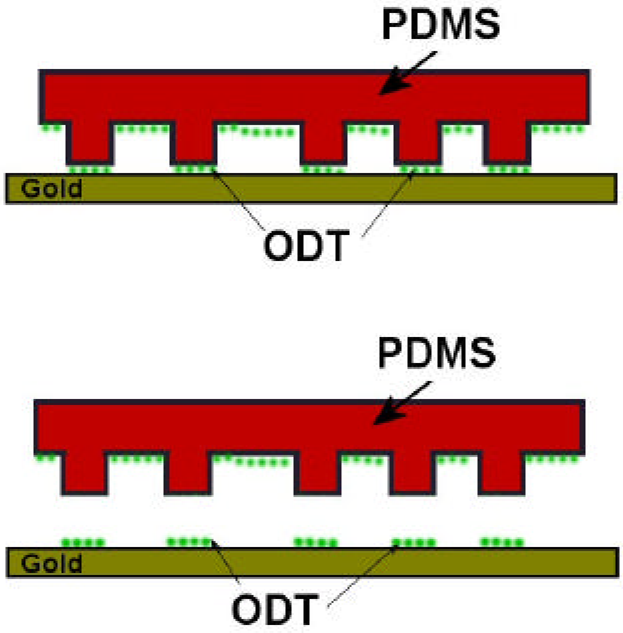

Figure 3 (Allen, W) - The PDMS stamp with the ODT is placed on the gold substrate. When the stamp is removed, the ODT in contact with the gold stays stuck to the gold. Thus the pattern from the stamp is transferred to the gold via the ODT "ink."

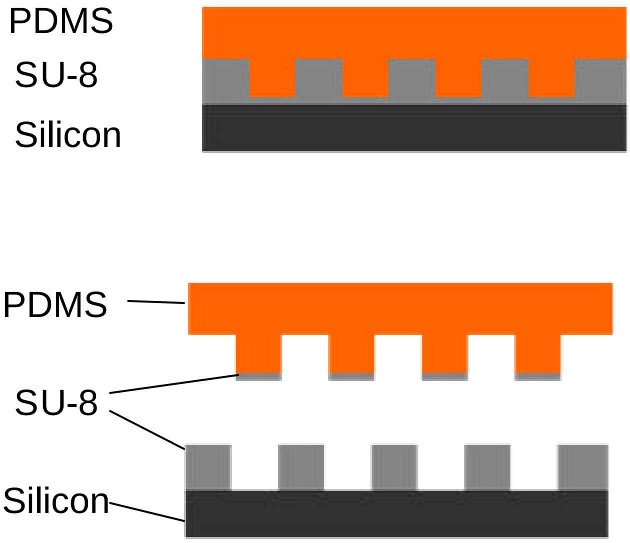

Figure 4 (Schroeder, R) – Because the SU-8 is so adhesive, some of it could have come up when we removed the PDMS molding from the master.

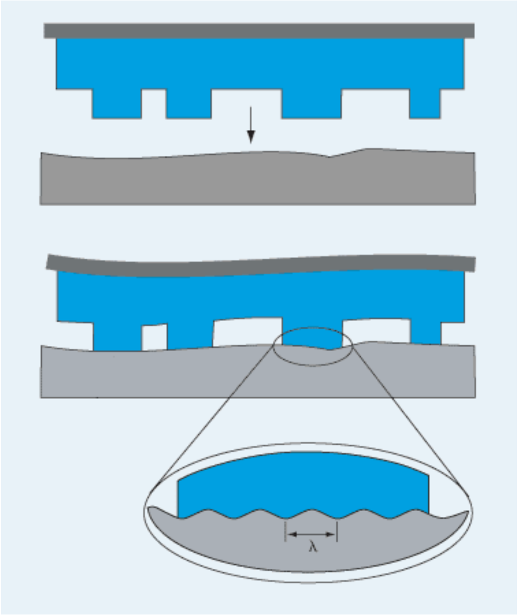

Figure 5 (Michel, B) – How PDMS conforms to the surface of the substrate

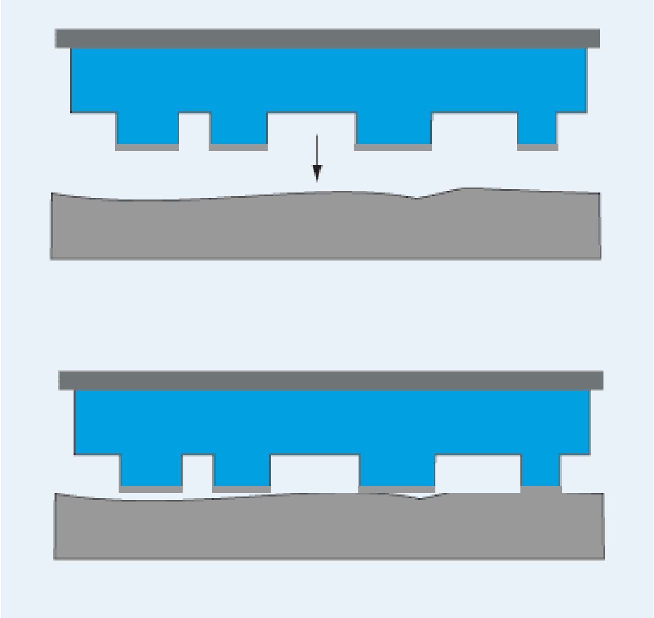

Figure 6 (adapted from Michel, B) – What would happen if SU-8 were attached to the PDMS stamp, making it unable to conform to the surface.

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