Bilayer, nanoimprint lithography

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Nanoimprint lithography has been shown to be a viable means of patterning polymer films in the sub-100 nm range. In this work, we demonstrate the use of a bilayer resist to facilitate the metal liftoff step in imprinter fabrication. The bilayer resist technology exhibits more uniform patterns and fewer missing features than similar metal nanoparticle arrays fabricated with single layer resist. The bilayer resist relies upon the differential solubility between poly(methyl methacrylate) and poly(methyl methacrylate methacrylic acid copolymer). Evidence is presented that shows the technique has a resolution of better than 10 nm. © 2000 American Vacuum Society.

I. INTRODUCTION

Due to the inevitable transition from the microelectronic to the nanoelectronic age, the demand for sub-100 nm feature sizes in lithographic techniques will increase greatly. As current devices rapidly approach the 100 nm barrier, the microelectronics industry is considering several technologies to overcome this hurdle. Clearly there is an urgent need for fast, reliable, and cost-effective nanolithography. Nanoimprint lithography shows promise in meeting this need.

Nanoimprint lithography is a relatively new lithographic technique that has received considerable attention in recent years.1–3 It is relatively straightforward. First, an imprinter (mask) is made with the desired sub-100 nm features raised from the surface. Next, the imprinter is coated with a very thin layer of mold release compound to protect it and prevent sticking during the imprinting process. The substrate to be patterned is then coated with a thin film of thermoplastic polymer. The elastomer is heated above its glass transition temperature ($T_g$) where it becomes viscoelastic. The imprinter is then pressed into the polymer and the system is cooled back down below the polymer’s $T_g$, freezing the pattern into the polymer. The mask is then removed and the trenches are cleaned with either an O$_2$ plasma or with solvents to remove any residual polymer that may remain in the trenches. The imprinter can be reused numerous times thereby providing cost-effective, sub-100 nm lithography.

There are several challenging problems associated with nanoimprint lithography.4 One critical area is to perform the next level of processing while maintaining the same resolution demonstrated in the polymer resist layer. The formation of patterned metal layers is one application. Finely patterned metal layers are used as interconnects in integrated circuits. They can also be used as catalysts for subsequent layer growth. If the subsequent metal layers cannot readily be etched, e.g., due to crystalline dependent etching rates, an additive approach such as liftoff is desirable. However, single layer resists are problematic when transferring the pattern via metal liftoff. The nonvertical sidewalls resulting from the imprinting process result in tearing and detachment of the metal film during liftoff. Nonvertical sidewalls occur in imprint lithography if the imprinting element does not have vertical sidewalls. Even if the imprinter does have vertical sidewalls, nonvertical sidewalls are formed in the imprinted film due to a descumming step necessary to remove residual polymer from the bottom of the imprinted feature. Therefore, a technique is required that minimizes the problems associated with metal liftoff using single layer resists.

In this work, we address this issue by considering the fabrication of nanometer-scale metal arrays. We use a bilayer resist technique to provide undercutting that dramatically improves the metal liftoff. We demonstrate high resolution arrays of particles, lines, and crosshatches fabricated from metal liftoff after nanoimprint lithography using a bilayer resist.5

II. EXPERIMENT

Figure 1 shows a schematic drawing of the imprinting process. The experimental steps involve imprinter (mask) preparation, sample preparation, imprinting, postprocessing, metalization, and liftoff.
A. Sample preparation

After suitably cleaning a silicon wafer, the bilayer resist is spun on. There are a wide range of thermoplastic elastomer polymers available that should work well for bilayer resists. We chose poly(methyl methacrylate) (1% 495k PMMA in chlorobenzene) and poly(methyl methacrylate methacrylic acid copolymer) [2.2% 73k P(MMA-17.5%MAA) in glycol ether] for this work. These polymers are used as electron beam lithography and x-ray lithography resists and have consistent formulations that spin on uniformly.

To produce the bilayer resist the PMMA is first spin coated onto the wafer (2000 rpm, 60 s) and soft baked to drive out the solvent (170 °C for 60 min). Next, the P(MMA-MAA) copolymer is spin coated (6000 rpm, 60 s) onto the PMMA film and soft baked in the same manner. This results in each layer being approximately 50 nm thick for a total film thickness of approximately 100 nm. It has been shown that these two layers mix neither during the soft baking process nor when heated above their $T_g$’s.6,7

B. Mask preparation

Nanoscale imprint lithography requires a suitable mask or imprinter. This is a crucial component of the imprinting process and the fabrication of the imprinter is covered in Ref. 5. It is sufficient to note that our imprinters have been fabricated in both silicon and silicon dioxide, using e-beam lithography and plasma etching. For the work presented here, the imprinter is fabricated in a 500 nm layer of thermally grown silicon dioxide on a silicon wafer.

Prior to use, the imprinter must be coated with a mold release polymer such as the hyperbranched perfluorinated polymer used in this study. A 2 mg/ml solution of the mold release polymer dissolved in chloroform is drawn into a pipette and enough solution is expelled onto the imprinter to form a meniscus (i.e., the entire surface of the imprinter is covered with mold release polymer solution). Since the mold release solution evaporates rapidly, the imprinter is immediately spun at 6000 rpm for 30 s before the concentration on the imprinter has had time to increase significantly. Atomic force microscopy measurements of the resulting film have shown that the thickness is 5–10 nm. The chloroform solvent is removed by placing the imprinter in a vacuum chamber and pumping the chamber down below 50 mTorr.

C. Imprinting

The imprinting apparatus consists of aluminum plates, guide pins, and alignment structures. See Fig. 2. We used carbon tape to fix the sample with respect to the imprinter. This tape serves the dual purpose of holding the sample in place and providing leveling during imprinting. The soft, plastic nature of the tape helps ensure that the imprinter and sample are parallel by deforming to compensate for any macroscopic area pressure gradients. The tape was replaced after every five imprintings due to gradual degradation at the elevated temperatures.

The next step is patterning the bilayer resist polymers. The bilayer-coated substrate is attached to the bottom piece of the imprinting apparatus via the double-sided carbon tape. The entire apparatus is placed into an oven heated to 180 °C. Then the sample and imprinter are brought into intimate contact. A specific amount of force is applied to achieve a desired imprint depth. The force is applied until the oven atmosphere (air) reaches 170 °C. The apparatus is flash cooled and the imprinter is removed. Figure 3 shows a set of scanning electron microscope (SEM) micrographs taken after imprinting. The imprinted sample is now ready for postprocessing.
D. Postprocessing

After the imprinter is retracted, a small amount of residual polymer remains at the bottom of the trenches. This must be removed if quality reproductions are to be obtained. The residual polymer can be removed by means of a short oxygen plasma etch or by a wet solvent etch. It should be noted that even if the elements of the imprinter have perfectly vertical sidewalls resulting in trenches with perfectly vertical sidewalls, this descumming step will round the edges of the indented structure, resulting in slightly beveled sidewalls. This can lead to the errors already mentioned for single layer resists. The use of an anisotropic oxygen plasma as the descumming agent will reduce this problem somewhat. The bilayer resist is much less sensitive to this effect and can function even when descumming is done using isotropic techniques.

We used two different postprocessing techniques. In the first method, a high pressure is applied during the imprinting process such that the imprinting elements create deep trenches in the bilayer resist. The trench is deep enough to cause considerable compression of the lower PMMA layer. Before the sample can be descummed, any residual mold release polymer must be removed from the surface of the sample so it does not prevent descumming of the thin P(MMA-MAA) film. This is accomplished with a 5 s rinse in toluene. The mold release polymer is very soluble in toluene and a 5 s rinse is more than sufficient. Longer times should be avoided as the toluene will also etch away the lower PMMA layer in areas in which it is exposed. Immediately after rinsing the imprinted sample it was dried with a stream of dry nitrogen.

After removing the residual mold release polymer, there is a thin membrane of P(MMA-MAA) covering the inside of the trench. This thin membrane must be removed otherwise undercutting will be impaired. The membrane can be removed by soaking the imprinted sample in methanol for approximately 5 s and then immediately drying with dry nitrogen. The methanol will etch the P(MMA-MAA) polymer while leaving the lower PMMA polymer unaffected. This is an isotropic etch that not only eliminates the thin P(MMA-MAA) membrane in the trench, but also reduces the thickness of the top layer of the bilayer resist. The final step in preparing the sample for metal deposition and liftoff is to descum the PMMA from the bottom of the trenches while simultaneously creating undercut in the bottom layer. This goal was accomplished by soaking the imprinted sample in a chlorobenzene solution. The chlorobenzene attacks the lower PMMA layer while leaving the upper P(MMA-MAA) unaffected. Typical soak times are 45–60 s.

The second postprocessing technique is used for dense structures in which capillary action upon removal of the imprinter after a deep imprinting results in damage to the poly-
mer films. This damage can be prevented with a shallow imprint. This method will also work with less dense patterns, but is slightly more complex. This technique uses only enough pressure to make indentations that are from 30 to 35 nm deep. After imprinting, the mold release polymer is removed with toluene as described earlier. The pattern must now be transferred deeper into the bilayer resist without the benefit of the imprinter. This is achieved with an anisotropic plasma etch that cuts the pattern deeper into the resist. It is crucial that the final trench depth extend into the bottom layer and that 20–30 nm of P(MMA-MAA) remain. Etching was implemented at the Cornell Nanofabrication Facility using the PlasmaTherm 72 Reactive Ion Etcher. Imprinted samples were etched at a chamber pressure of 15 mTorr, 100 W of power, with gas flows of CF$_4$ = 42 sccm and H$_2$ = 15 sccm for 65 s (the etch rate of this plasma chemistry was found to be 29 nm/min). The choice of CF$_4$/H$_2$ chemistry was primarily due to its availability in the chamber. It is likely that the primary etch mechanism is sputtering and an inert gas could be used instead. However, the degree to which any polymer deposition may be influencing the etching process will require further study. Oxygen plasmas were also employed, but the etch rate was much higher, making the etching of precise depths difficult.

The final step of this postprocessing method is identical to that of the previous method. A slightly longer soak time in chlorobenzene is needed to ensure that the lower layer PMMA is etched down to the silicon surface. Typical soak times are around 60 s.

E. Metallization

The final step to validate the results is to transfer the pattern imprinted into the resist into a second processing step. We chose to metalize the substrate. Metal evaporation was done using a CVC SC4500 thermal evaporator equipped with a crystal thickness monitor (Cornell Nanofabrication Facility.) The 16 in. throw distance minimizes heating of the substrate which can damage the polymer resist layers.

Once the metal film has been evaporated onto the imprinted sample, liftoff must be done to remove all of the unwanted metal and resist polymers. Liftoff is achieved by soaking the metal-coated sample in a 1:1 mixture of acetone and methylene chloride for 30 min followed by sonication for 3 min. Further sonication in a clean solution of 1:1 acetone:methylene chloride may be required if optical inspection reveals incomplete liftoff.

III. RESULTS AND DISCUSSION

In this work, we have seen that the quality of imprinting depends on the density of the patterns on the imprinter. As patterns become more dense, there is an increasing tendency for the polymer layers to adhere to the imprinter upon removal. This capillary action is reduced with the use of a mold-release polymer, but in dense patterns, it is not eliminated. As discussed in Sec. II, the tendency for the polymer layers to adhere to the imprinter can be reduced by doing a shallow imprint followed by a solvent rinse. The shallow imprint is controlled by the pressure applied to the imprinter. Figure 4 shows the imprint depth as a function of applied pressure.

![Fig. 4. Imprint depth as a function of applied pressure in a bilayer resist consisting of 50 nm of 495k PMMA (bottom layer) and 50 nm of 73k P(MMA-17.5%MAA)(top layer).](image)

Figure 5 shows the polymer thickness removed as a function of time for various solvents. Note that the 495k PMMA is quite soluble in chlorobenzene whereas the 73k P(MMA-17.5%MAA) is essentially insoluble in chlorobenzene.

![Fig. 5. Polymer thickness removed from a polymer film as a function of time for various solvents.](image)
friction between the rods and the top plate (see Fig. 2) in the imprinting apparatus. The entire imprinting apparatus is brought up to 170 °C before entering the cooling cycle. For the highest pressure shown in Fig. 4, the time to reach 170 °C was approximately 85 min, whereas for the lowest pressure, the imprinting temperature was reached in 40 min. The difference between these times is due to the method we used to apply the pressure. It was simply a set of weights on the top plate of the imprinter apparatus. More pressure requires larger weights, which in turn take longer to heat up. The most striking feature in the data is the nearly constant depth of imprint given by the first four data points. These points cover a wide range of pressures. This phenomenon is most likely a surface effect with several contributing factors. The orientation of the polymer at the surface is almost always different from the interior. In addition, small molecules such as oxygen and water can diffuse deep into the polymer surface due to the large free volume of amorphous polymers. Furthermore, surface oxidation or contamination can exist. For example, P(MMA-MAA), which is the top layer, contains electrolyte side chains which readily attract and react with water molecules creating a contamination layer. Since the imprints are done at a relatively high temperature the diffusion of contaminants into the polymer can be large, resulting in a fairly thick contamination layer.

Very recently it has also been found that the glass transition temperature at the surface of a polymer can be much higher than that for the bulk polymer.9–11 In addition, in most polymers the surface skin can be from a few nanometers thick to tens of nanometers thick12 and this can be a sizable fraction of the 50 nm P(MMA-MAA) layer. To complicate matters further, bulk polymers are known to have a skin in the rubbery flow regime due to surface tension effects,12 but how this skin would manifest itself and what effect it would have upon nanoscopic thin films is uncertain.

It is likely that the relatively constant imprint depth of 35 nm for pressures less than 1400 MPa is due to some combination of the above-mentioned effects. Above 1400 MPa, the surface layer yields to the imprinter elements and they punch through. The yielding pressure is likely to be highly depen-
dent upon the shape and geometry of the imprinting elements, such that a sharp cone like element would easily puncture the surface layer while a flat cylinder like element (a pillar for instance) would have more difficulty. After the surface layer has been compromised the imprinting elements quickly pass through the remaining liquid like PMMA-MAA layer and reach the soft elastic PMMA layer below (it is assumed the PMMA layer is in the soft elastic region due to the slope of Fig. 4 coupled with the observation that single layer PMMA films do not show flow upon compression). The rubbery PMMA layer is then compressed with the applied stress from the imprinting elements as shown by the monotonically increasing imprint depth with increasing pressure after 1600 MPa.

Figure 4 demonstrates that one can control the depth of imprinting to a certain extent by controlling the applied pressure. In particular, the two depths (35 and 100 nm) considered in Sec. II are easily obtained by controlling pressure. Note that although the bilayer was nominally 100 nm thick, there is approximately 20% uncertainty in this value resulting in the high-pressure imprint depths exceeding 100 nm.

It is well known that liftoff can be considerably improved when a certain amount of undercutting is produced in the structure. This proves to be the great advantage of using a bilayer resist for imprint lithography. Electron beam lithography and photolithography naturally produce undercutting (in positive resists) due to diffraction spreading effects for photolithography and electron scattering and secondary electron production in the resist for electron beam lithography. In imprint lithography, undercutting must be produced in another way. We achieve this with a bilayer resist. The two polymers used for the bilayer resist, PMMA and P(MMA-MAA), have considerably different chemical properties. There are a wide range of solvents that will attack PMMA, but not P(MMA-MAA) and vice versa (see Fig. 5). The 495k PMMA is highly soluble in chlorobenzene and toluene but quite insoluble in isopropanol and methanol. In contrast, the 73k P(MMA-17.5%MAA) exhibits a high solubility in methanol and low solubility in chlorobenzene, toluene, and isopropanol. After imprinting, the sample is exposed to a solvent that will attack the bottom PMMA layer but not the upper P(MMA-MAA) layer. In this way, undercutting can be produced in the imprinted features and the vapor deposited metal film will not form a continuous film as long as the thickness of the metal is less than that of the bottom layer. The degree of undercutting is easily controlled by timing the solvent rinse. Figure 6 is a series of SEM micrographs showing undercutting in a bilayer resist imprinted with 250-nm-diam holes. The solvent was chlorobenzene and rinse times ranged from 0 to 240 s. Figure 6(a) represents an imprint in which no postprocessing has been done other than a toluene rinse. Figure 6(b) shows a sample that has been soaked in chlorobenzene for 30 s. The undercut and discontinuity in the
sidewalls is now apparent. In Fig. 6(c), the sample has been soaked for 60 s. The undercut is now very noticeable. Figures 6(d) and 6(e) represent samples soaked in chlorobenzene for 120 and 240 s, respectively. In both cases the undercut is extreme. Finally, in Fig. 6(f), in which the sample has been soaked for 240 s, the degree of undercutting is so extreme that the upper, unaffected P(MMA-MAA) layer has collapsed onto the substrate, possibly due to the capillary forces present during solvent evaporation.

One measure of the performance of the bilayer imprinting technique is how well metal liftoff occurs. There were three basic types of patterns originally produced on imprinters — dot arrays, parallel lines, and crosshatch patterns. The first of these patterns is shown in Fig. 7. Figure 7 compares the single layer imprint lithography [Figs. 7(a) and 7(b)] with the bilayer imprint lithography [Figs. 7(c) and 7(d)]. For the case with the single layer of 495k PMMA resist, the dots are very nonuniform in both size and shape. Additionally, it can be seen in Fig. 7(a) that many of the dots have been completely pulled from the substrate during the liftoff process. Finally, many of the dots appear to have tails which are created by metal breaking at an intermediate place on the sidewalls of the trenches.

Figures 7(c) and 7(d) show nickel metal array produced
by imprinting completely through the bilayer resist. It is im-
portant to note the high uniformity in size and shape of the
60-nm-diam dots. An additional point can be seen from Fig.
7(c). Our imprinter had an error in the dot array caused by a
pattern generator error in the Leica VB-6 electron beam li-
thography machine. This error produced a subset of the im-
printing elements with a spacing of less than 10 nm. As can
be seen in the right half of Fig. 7(c), bilayer nanoimprint
lithography is capable of distinguishing the two imprinting
elements, suggesting that bilayer nanoimprint lithography
has a resolution of 10 nm or better.

Two other patterns were evaluated. Figure 8 shows 50-
nm-wide parallel lines spaced 500 nm apart. Imprinting was
done using the shallow imprinting method and liftoff was
performed after thermal evaporation of chromium (20 nm). Figure 9 shows a crosshatch pattern with 50-nm-wide lines
spaced 500 nm apart. Shallow imprinting and chromium lift-
off were used to fabricate this pattern. In both of these fig-
ures, a perspective view is provided to orient the reader and
an overhead view is then used to measure the width of the
lines. For both the parallel lines and the crosshatch pattern,
very few errors can be seen in the SEM images.

IV. CONCLUSIONS

In this work, we demonstrated the advantages of a bilayer
resist for nanoimprint lithography. Metal nanoparticle arrays
can be fabricated using thermal evaporation and metal liftoff
when an appropriate bilayer resist is used. In comparison to a
single layer resist, the metal arrays exhibit more uniform
patterns and fewer missing features. The bilayer resist relies
upon the differential solubility between PMMA and
P(MMA-MAA). While gross errors are associated with
single layer nanoimprint lithography, bilayer nanoimprint li-
thography produces much higher quality metal patterns when
using liftoff.

We have also demonstrated a shallow imprinting tech-
nique in which the bilayer resist is used in conjunction with
shallow imprinting to reduce film damage when imprinting
dense feature patterns.

Finally, there is evidence that the bilayer resist technique
has a resolution of better than 10 nm if an appropriate im-
print mask is fabricated. This high resolution coupled with
liftoff technology opens up new opportunities for nanoscale
research.

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