Nanoimprint lithography

Stephen Y. Chou,[a] Peter R. Krauss, and Preston J. Renstrom
NanoStructure Laboratory, Department of Electrical Engineering, University of Minnesota, Minneapolis, Minnesota 55455

(Received 20 June 1996; accepted 17 August 1996)

Nanoimprint lithography, a high-throughput, low-cost, nonconventional lithographic method proposed and demonstrated recently, has been developed and investigated further. Nanoimprint lithography has demonstrated 25 nm feature size, 70 nm pitch, vertical and smooth sidewalls, and nearly 90° corners. Further experimental study indicates that the ultimate resolution of nanoimprint lithography could be sub-10 nm, the imprint process is repeatable, and the mold is durable. In addition, uniformity over a 15 mm by 18 mm area was demonstrated and the uniformity area can be much larger if a better designed press is used. Nanoimprint lithography over a nonflat surface has also been achieved. Finally, nanoimprint lithography has been successfully used for fabricating nanoscale photodetectors, silicon quantum-dot, quantum-wire, and ring transistors.

I. INTRODUCTION

One of the major road blocks in developing nanostructures is the lack of a low-cost, high-throughput manufacturing technology. This problem is particularly serious for structures with a size below 0.1 μm. Numerous technologies are under development to solve this problem.[1–6] One year ago, we proposed and demonstrated another possible solution to nanostructure manufacturing, namely a new nonconventional lithographic method called nanoimprint lithography.[7] The key advantage of this lithographic technique is the ability to pattern sub-25 nm structures over a large area with a high-throughput and low-cost. Therefore, nanoimprint lithography is a manufacturing technology. In this article, we will present recent progress in developing this lithographic technique.

II. PRINCIPLE OF IMPRINT LITHOGRAPHY

Nanoimprint lithography has two basic steps as shown in Fig. 1. The first is the imprint step in which a mold with nanostructures on its surface is pressed into a thin resist cast on a substrate, followed by removal of the mold. This step duplicates the nanostructures on the mold in the resist film. In other words, the imprint step creates a thickness contrast pattern in the resist. The second step is the pattern transfer where an anisotropic etching process, such as reactive ion etching (RIE), is used to remove the residual resist in the compressed area. This step transfers the thickness contrast pattern into the entire resist.

During the imprint step, the resist is heated to a temperature above its glass transition temperature. At that temperature, the resist, which is thermoplastic, becomes a viscous liquid and can flow and, therefore, can be readily deformed into the shape of the mold. The resist's viscosity decreases as the temperature increases.

Unlike conventional lithography methods, imprint lithography itself does not use any energetic beams. Therefore, nanoimprint lithography's resolution is not limited by the effects of wave diffraction, scattering and interference in a resist, and backscattering from a substrate. Furthermore, imprint lithography is fundamentally different from stamping using a monolayer of self-assembled molecules.[8] Imprint lithography is more of a physical process than a chemical process. It is conceivable that in the future, the mold used in imprint lithography can be made using a high-resolution but low-throughput lithography, and then imprint lithography can be used for low-cost mass production of nanostructures.

III. MOLDS, RESISTS, AND PROCESS CONDITIONS

In our experiments, silicon dioxide and silicon were used as the mold materials. Certainly other materials such as metals and ceramics could also be used. The mold was patterned with dots and lines with a minimum lateral feature size of 25 nm using electron beam lithography and RIE. Polymethyl methacrylate (PMMA) was our primary resist, although we have had success with AZ and Shipley novlak resin-based resists as well. The PMMA showed excellent properties for imprint lithography. PMMA has a small thermal expansion coefficient of $\sim 5\times 10^{-5}$ per °C and a small pressure shrinkage coefficient of $\sim 3.8\times 10^{-7}$ per psi.[9] Mold release agents were added into the resists and worked well to reduce the resist adhesion to the mold. The pressure and temperature for the imprint process depend on the resist used. For PMMA, which has a glass-transition temperature of about 105 °C, the imprint temperature used in our experiments is typically between 140 and 180 °C, and the pressure is from 600 to 1900 psi. For that temperature and pressure range, the PMMA thermal shrinkage is less than 0.8% and the pressure shrinkage is less than 0.07% (a smaller volume at a higher pressure), therefore, the shape of the PMMA should conform with that of the mold. To reduce air bubbles, the imprint process should be done in a vacuum. The gas used in the RIE pattern transfer, which also depends on the resist used, was oxygen for PMMA.

[a]Electronic mail: chou@ee.umn.edu

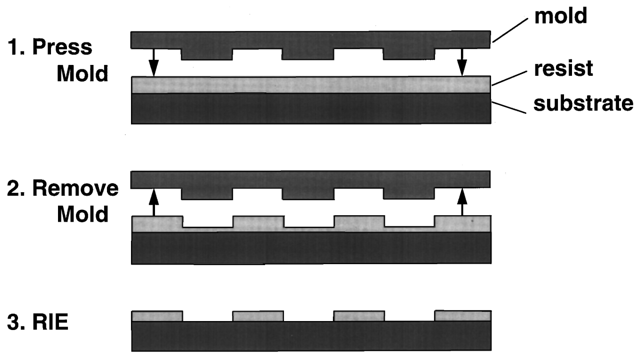

FIG. 1. Schematic of nanoimprint lithography process: (1) imprinting using a mold to create a thickness contrast in a resist, (2) mold removal, and (3) pattern transfer using anisotropic etching to remove residue resist in the compressed areas.

Typically, the intrusion of the mold is from 40 to 200 nm and the aspect ratio for the smallest mold features is 3:1. The thickness of the resist is from 50 to 250 nm. The resist was kept thicker than the mold intrusion to prevent the mold from contacting the substrate. This is essential to prolong the lifetime of the mold.

IV. RESULTS AND DISCUSSION

A. Imprint

Various nanostructures have been imprinted into PMMA including 25 nm diam holes with a 120 nm period and 30 nm wide trenches with a 70 nm period. Figure 2 shows a scanning electron micrograph of imprinted PMMA strips before RIE. The strips, which are 70 nm wide and 200 nm deep, have very smooth (a roughness less than 3 nm) and vertical sidewalls, and nearly 90° corners. The spacing between the strips was intentionally made large to allow for examination of the sidewalls. The terminal face of the PMMA strips is not from cleaving, but directly from imprinting. As shown later, the small bend at the end of the PMMA strips is actually due to curvature in the mold.

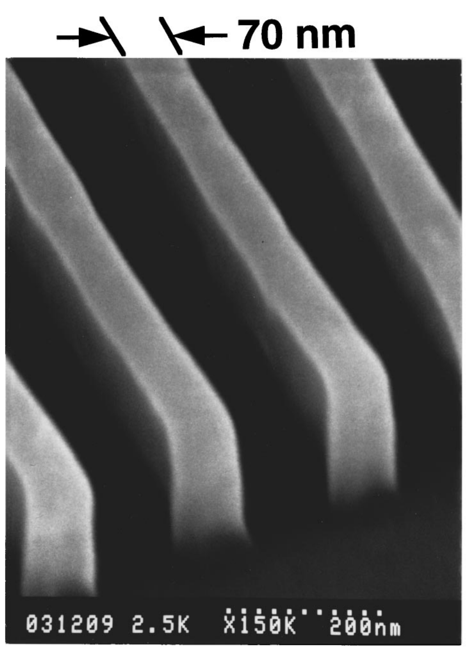

FIG. 2. SEM micrograph of a perspective view of strips formed into a PMMA film by imprint. The strips are 70 nm wide and 200 nm tall, have a high aspect ratio, a surface roughness less than 3 nm, and nearly perfect 90° corners.

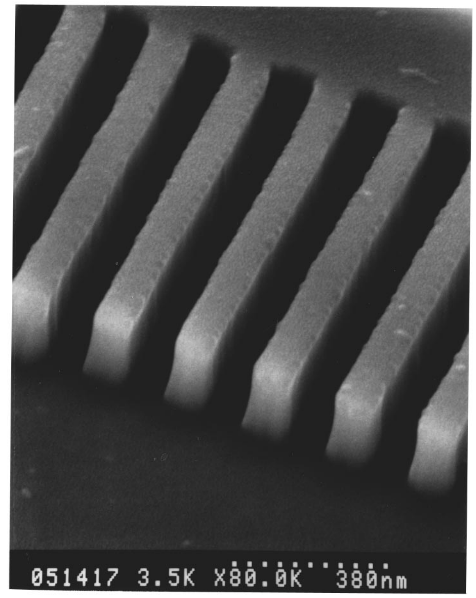

FIG. 3. SEM micrograph of the mold that was used to imprint the PMMA strips shown in Fig. 2.

B. Comparison with mold

To compare the imprinted resist profile and the profile of the mold features, we examined the mold using a scanning electron microscope (SEM) as shown in Fig. 3. The PMMA profile shown in Fig. 2 comes from the closed end of the mold fingers; therefore, a precise comparison between the mold shape and the PMMA profile is not feasible. However, comparison of the general features, such as the linewidth, heights, and slight bending at the end of each line, indicated that the PMMA profile conformed to the mold.

C. Effect of RIE on lateral dimension of imprinted PMMA patterns

To examine the effects of the oxygen RIE pattern transfer step on removing the residue resist in the compressed areas and on changing the lateral dimension of the PMMA features, the PMMA resist structures created by imprint lithography were used as the template for a lift off of metals. The RIE process was done with a power of 400 W and a pressure of 90 mTorr using oxygen gas. In the lift-off process, 5 nm Ti and 15 nm Au were first deposited onto the entire sample, and then the metal on the PMMA surface was removed when the PMMA was dissolved in acetone. We compared the SEM image of the imprinted PMMA template before the oxygen

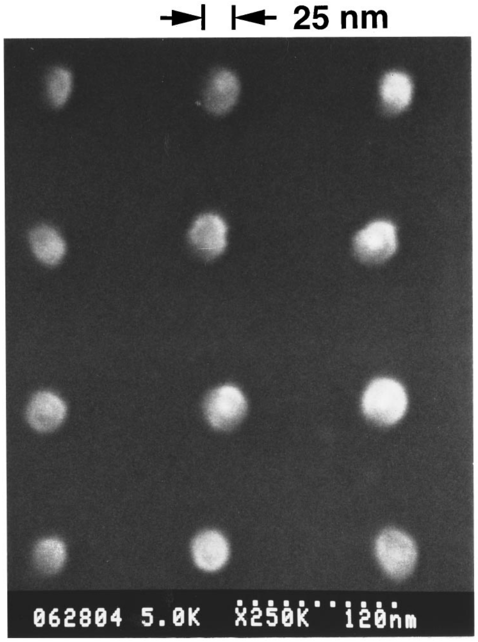

FIG. 4. SEM micrograph of 25 nm diameter and 120 nm period metal dots fabricated by imprint lithography and a lift-off process.

RIE transfer step to that of the metal patterns after the lift off. Figure 4 shows 25 nm diam dots with a 120 nm period lifted off from the PMMA template of 25 nm diam holes made by imprint lithography. Figure 5 shows 30 nm linewidth and 70 nm pitch metal lines lifted off from a PMMA template fabricated using imprint lithography. Comparing these metal features with the imprinted PMMA templates before RIE, there are no noticeable differences between the

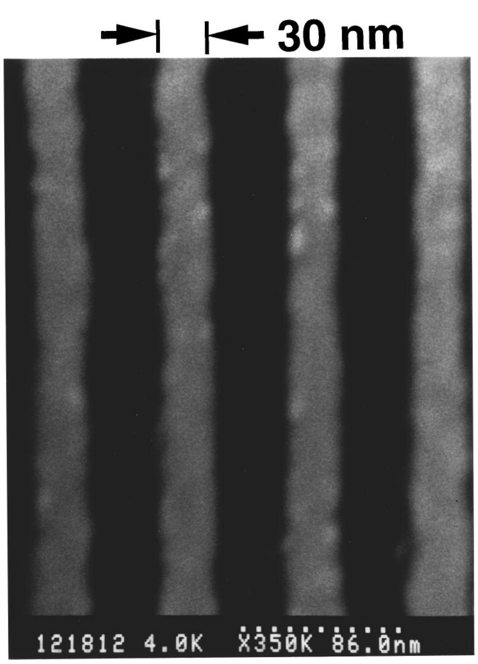

FIG. 5. SEM micrograph of 30 nm wide and 70 nm period metal lines fabricated by imprint lithography and a lift-off process.

lift-off metal structures and the PMMA patterns. This indicates that during the oxygen RIE process, the compressed PMMA areas were completely removed while the lateral size of the PMMA features experienced little change.

D. Estimation of ultimate lithography resolution

The minimum feature size of imprint lithography shown in the previous section is limited by the minimum feature size on the mold. Further experiments have shown that a few nanometer variation on the mold can be successfully transferred into the sidewalls of the PMMA, as shown in Fig. 6(a). This means that if the polymer has sufficient mechanical strength, imprint lithography should be able to produce 10 nm feature size in the polymer.

E. Process repeatability and mold durability

Imprint lithography process repeatability and mold durability are two key issues in making imprint lithography a manufacturing technology. We have used the same mold to imprint PMMA over 30 times and examined the mold and the PMMA profile every time. We did not observe any noticeable changes in either the PMMA profile or the mold. Although over 30 times imprinting is hardly considered a repeatability and durability test, we should expect the process to have a good repeatability and mold durability. This is because mold release agents gave a good release, the PMMA held above glass-transition temperatures is very soft, and the mold intrusion does not touch the substrate.

F. Uniformity

To examine the uniformity of this process, arrays with 30 nm wide strips and a 150 nm pitch were fabricated at the four corners and the center of a mold that had a size of 15 mm by 18 mm. After imprint lithography in PMMA, a lift-off process left 30 nm wide metal lines with a 150 nm pitch on the substrate, as shown in Fig. 7. Figure 7 clearly shows that even though the press we used is very primitive, imprint lithography can be very uniform over a significantly large area. We are quite confident that with a better designed press, good uniformity over a much larger imprint area can be achieved.

G. Imprint lithography over a nonflat surface

There are at least two ways to approach the problem of imprint lithography over a nonflat surface. The brute force method is to use a thick resist, create a large thickness contrast, and etch the PMMA very deep in the vertical direction. An example is given in Fig. 6 where a 75 nm step in the substrate was covered with a 300 nm resist. Then a 200 nm thickness contract was created in the PMMA and about 150 nm of PMMA was removed during the pattern transfer. As shown, the 75 nm step can be seen clearly after etching. However, due to prolonged etching, the linewidth is reduced from 60 to 40 nm.

A better approach would be to use a thick resist to create a flat surface first. After the imprint step, a material that is

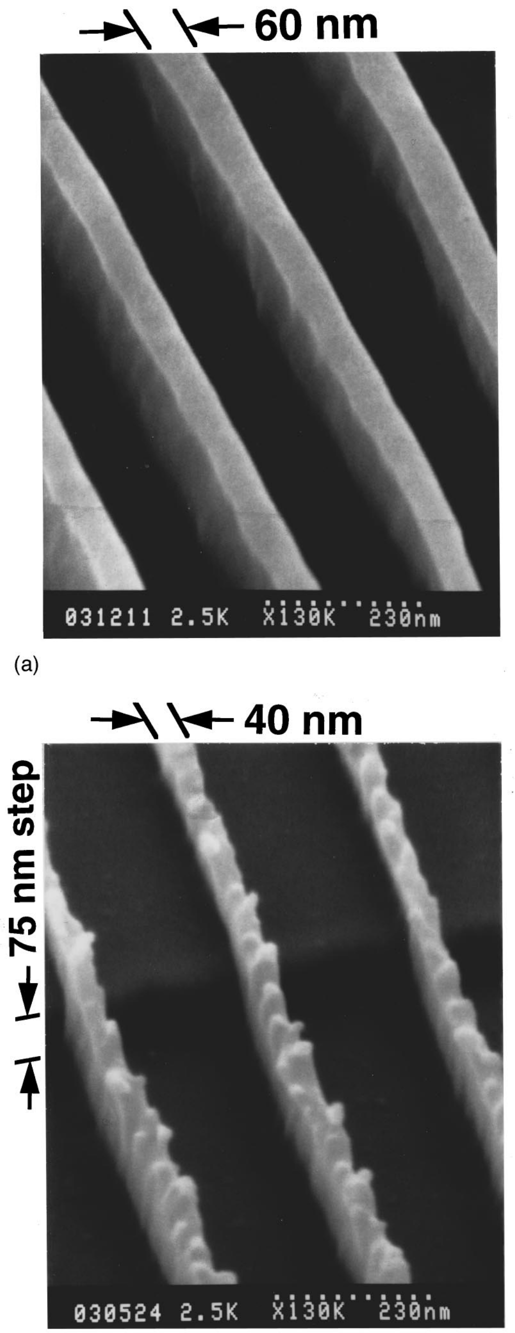

FIG. 6. The PMMA lines imprinted over a 75 nm step (a) before RIE pattern transfer and (b) after. Due to the deep vertical etch required, the PMMA linewidth was reduced from 60 to 40 nm.

very resistant to RIE is coated only on the top surface of the imprinted pattern. Then the coated material is used as a RIE mask in transferring the pattern into the entire resist. We are currently developing this technology.

H. Fabrication of nanodevices using imprint lithography

In parallel with developing imprint lithography, we have used imprint lithography to fabricate nanodevices. One example is metal–semiconductor–metal photodetectors fabricated using imprint lithography and optical lithography. In addition, we fabricated quantum-wire, quantum-dot, and ring transistors in silicon using imprint lithography and RIE of silicon. Quantum effects and single electron effects were observed in these devices, which will be reported elsewhere.[10]

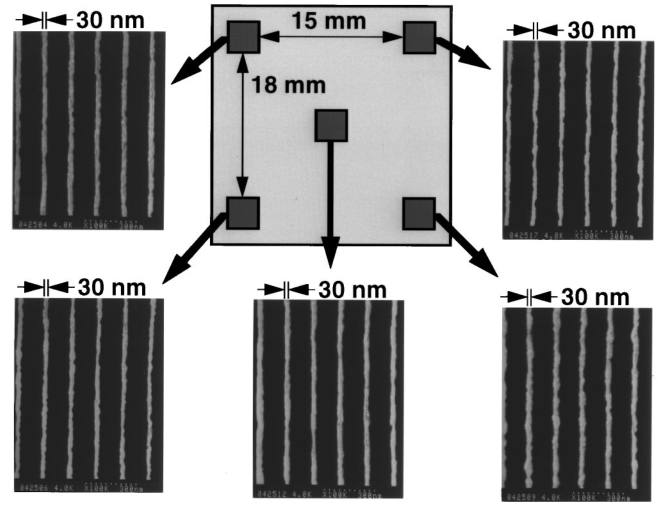

FIG. 7. SEM micrographs of 30 nm wide metal gratings with a 150 nm period fabricated using imprint lithography and lift off. The five pictures come from the four corners and the center of a mold that has a size of 15 mm by 18 mm.

V. FUTURE IMPROVEMENT AND CHALLENGES

No doubt, imprint lithography is still at its infancy and further investigations are needed to make it a manufacturing technology. Currently, we have not fully characterized and fully understood imprint lithography. The press we used is rather primitive. The surface sticking problem, which has been greatly reduced in our current work, still needs more improvement. Molding conditions are not optimized yet. The effect of thermal expansion on lithography resolution has not been studied. Molds with smaller feature size are needed to explore the ultimate resolution. We also need to prove that the area for a single imprint can be much larger than 1 sq in. Finally, multilevel alignment is one of the biggest challenges. However, since the first report on imprint lithography a year ago, many groups have started looking into this technology. We should expect significant progress in the near future.

VI. CONCLUSION

We have demonstrated that imprint lithography can achieve 25 nm feature size and 70 nm pitch, vertical and smooth sidewalls, nearly 90° corners, and uniformity over an area of 15 mm by 18 mm in a single imprint. Our study indicates that imprint lithography can potentially have a 10 nm resolution over an area much greater than 1 sq in., and can have good repeatability and durability. Therefore, imprint lithography has high-throughput and low-cost. With further development, imprint lithography can become the technology for manufacturing nanostructures, and can have a significant impact in many areas such as integrated circuits, biology, and chemistry. No doubt, the current study of imprint lithography is preliminary. Yet, the future of imprint lithography seems very promising.

ACKNOWLEDGMENT

The authors would like to thank other members of the NanoStructure Laboratory whose efforts have profoundly affected the current work.

[1]A. N. Broers, J. M. Harper, and W. W. Molzen, Appl. Phys. Lett. **33**, 392 (1978).
[2]D. Flanders, Appl. Phys. Lett. **36**, 93 (1980).
[3]K. Early, M. L. Schattenburg, and H. I. Smith, Microelectron. Eng. **11**, 317 (1990).
[4]M. A. McCord and R. F. P. Pease, J. Vac. Sci. Technol. B **4**, 86 (1986).
[5]J. W. Lyding, T. C. Shen, J. S. Hubacek, J. R. Tucker, and G. C. Abelin, Appl. Phys. Lett. **64**, 2010 (1994).
[6]T. R. Albrecht, M. M. Dovek, C. A. Lang, P. Grutter, C. F. Quate, S. W. J. Kuan, C. W. Frank, and R. F. W. Pease, J. Appl. Phys. **64**, 1178 (1988).
[7]S. Y. Chou, P. R. Krauss, and P. J. Renstrom, Appl. Phys. Lett. **67**, 3114 (1995); Science **272**, 85 (1986); P. R. Krauss and S. Y. Chou, the 39th EIPB, Scottsdale, AZ, May 30–June 2, 1995 [J. Vac. Sci. Technol. B **13**, 2850 (1995)].
[8]A. Kumar and G. M. Whitesides, Appl. Phys. Lett. **63**, 2002 (1993).
[9]I. Rubin, *Injection Molding* (Wiley, New York, 1972).
[10]L. J. Guo, P. R. Krauss, and S. Y. Chou, Appl. Phys. Lett. (submitted).