Unconventional Methods of Patterning Polymers

Dahl-Young Khang, Kahpyang Suh, Youngsang Kim, Hyunsik Yoon, and Hong H. Lee
School of Chemical Engineering, Seoul National University

Abstract: 미래의 집적 회로는 나노미터 수준의 소자를 제작할 수 있는 신뢰성 있는 기술을 요구한다. 노광공정은 현재 리소 그래피의 핵심 공정이고 앞으로도 그러할 것으로 예상되나 향후 100 nm 이하의 크기를 패턴하는 데에는 한계를 드러낼 것으로 보인다. 만약, 경제적인 문제만 아니라 전자범 리소그래피나 엑스레이 리소그래피, 탈착 리소그래피 등의 방법들이 이 미 사용 가능하나 기기 경쟁력에서 약점은 가지고 있다. 노광공정의 이러한 한계점 때문에 1990년대 중반부터 노광공정을 대체할 수 있는 비전통적인 방법들에 대한 연구가 진행되었다. 현재 부각되고 있는 비전통적인 패턴링 방법으로는 각인 방 법, 모세관 형상법, 미세 접착 프린팅법, 전기적 패턴 유도 방법 등 많은 종류가 있으나 여기서는 상온 각인법과 모세관 형상법에 대해 간단히 고찰해 보고자 한다.

Keywords: patterning, polymers, imprint lithography, capillary force lithography

1. Introduction

Future integrated circuits will require reliable techniques for fabricating nanometer-scale devices. Optical lithography or photolithography, which has been and will be the mainstay of lithography for the near future, is expected to be limited to ~100 nm resolution. Because of the limitations the photolithography has for sub-100 nm features, there have been extensive efforts made since mid 90s for the methods that can replace the photolithography. If the economics is not a major concern, there are technologies already available for sub-100 nm features such as electron-beam lithography, X-ray lithography, and scanning probe lithography, etc [1,2].

There emerging unconventional lithographies include nano-imprint lithography [3], capillary force lithography [4], micro-contact printing [5], and electrically induced structure formation [6]. Here, we introduce room-temperature lithography and capillary force lithography.

2. Unconventional Methods of Patterning Polymers

2.1. Room-temperature Imprint Lithography

Nano-imprint lithography generates resist relief patterns in a thermoplastic layer by physically compressing the resist that has been thermally softened, rather than by modifying the resist’s chemical structure by radiation [3]. In typical imprint lithography (hot-embossing lithography), a mold with nanostructures on its surface is pressed into a thin resist that has been heated above its glass transition temperature \((T_g)\) to endow the resist with fluidity. This fluidity enables the resist to conform to the mold pattern. After the resist is cooled below \(T_g\), the mold is removed. An anisotropic etching process, such as reactive ion etching (RIE), is used to remove the residual resist in the compressed region.

In this high-temperature process, clean release of the resist from the mold is one of the most important characteristics required. Usually, anti-adhesion agents have been used to achieve clean mold release [3]. Distortion of the imprinted structures or mold features due to the thermal cycle of heating followed by cooling is another problem to contend with.

Here, we demonstrate room-temperature imprint lithography based on plastic flow along with free-volume contraction and plastic deformation of the resist layer.
This room-temperature process has the unique features of enabling step-and-repeat and multiple imprinting, which is impossible in the conventional high-temperature imprint processes.

In amorphous polymeric materials, a certain number of vacancies, called free volume, must always be present due to the absence of long-range order and chain-like character with finite thickness and persistence. The vacant site fraction [8], \( f_v \), is given by

\[
f_v = \frac{\nu_v - \nu_v^0}{\nu_v}
\]

where \( \nu_v \) is the specific volume of the amorphous polymer and \( \nu_v^0 \) is the specific volume calculated from van der Waals radii. The value of \( f_v \) is in the range of 0.32−0.375 for typical amorphous polymer. The vacant volume, however, is not completely available for thermal motion since not all the vacant sites are accessible to monomeric units on conformational grounds. The volume available for motion, \( f_m \), is given by [8]

\[
f_m = \frac{\nu_v^0 - \nu_v^{00}}{\nu_v^{00}}
\]

where \( \nu_v^0 \) and \( \nu_v^{00} \) are the specific volumes of the amorphous and crystalline polymer, respectively, at 0 K. The value of \( f_m \) is in the range of 0.125−0.14 for most polymers. The pattern depth that can be obtained by free volume compaction, therefore, would be given by

\[
f_v^{1/3} h \sim f_m^{1/3} h
\]

where \( h \) is the original thickness of the polymer layer. For example, a polymeric film 100 nm thick can be compressed to a depth of 10−30 nm by the free volume compaction only. If the free volume compaction is completed and the applied stress exceeds the yield stress of the polymer, the pattern depth increases further due to plastic deformation of polymer.

Typical yield stress of inorganics such as Si or SiO\(_2\) is on the order of 1 GPa while that of organics (polymers) is 0.05 GPa, which is almost two orders of magnitude smaller than the yield stress of inorganics. The Young’s modulus of inorganics is about 150 GPa while that of polymer is about 1 GPa, which is also two orders of magnitude smaller than that of inorganics [9]. If the applied stress is in the range between the yield stress of polymer and that of the inorganic mold material, further imprinting of the mold features into the underlying polymer layer can be realized through the plastic deformation of polymer. Therefore more deeply imprinted pattern is left in the polymer when the plastic deformation is involved.

In typical experiments, the substrate was Si wafer ~ 2×2 cm\(^2\) in size and had a top layer of oxide 1 \( \mu \)m thick. The mold was prepared by electron beam lithography or photolithography. Polystyrene (PS), which was prepared by our anionic polymerization system, was used as the thermoplastic resist. It has a molecular weight of 100,000 g/mol with a polydispersity index of 1.02~1.05. Polystyrene has a very good etch-resistance, which is essential for the pattern transfer process such as reactive ion etching. The experimentally measured etch rate of SiO\(_2\) is six to ten times greater than that of PS under our etching conditions.

Prior to spin-coating onto a SiO\(_2\)/Si substrate with a PS/toluene polymer solution, the substrate was cleaned by nitrogen-blowing, ultrasonification for 5 minutes in trichloroethylene (TCE) and acetone, and then in isopropanol (IPA), rinsing by de-ionized water and blow-drying by nitrogen. The concentrations of polymer solutions in toluene are typically in the range between 0.5% and 10% polymer by weight. After spin-coating, the substrate with the polymer film was baked in vacuum oven at 150 to 200°C. The thickness of the dried resist layer thus formed on the substrate, as determined by ellipsometry, ranged from 50 nm to 550 nm depending on the coating conditions.

The PS/SiO\(_2\)/Si substrate was loaded and pressed at room temperature for a period of 5 to 20 seconds using a conventional hydraulic press, at a pressure between 30 and 150 MPa. When the pressure was released, the mold detached freely without being forced and no adhered polymer was found on the mold surface when examined by scanning electron microscopy (SEM) micrographs. This mold was re-used directly tens of times for the multiple or step-and-repeat imprinting with manual alignments.

One of the unique features of the room-temperature imprinting is the large area patterning capability by the step-and-repeat scheme, which is the major reason why photolithography has been the major lithographic tool. In the conventional high-temperature (above \( T_g \) of polymer) imprinting, the imprinting cannot be repeated sequentially on the same substrate, because the previously patterned features would be destroyed by the heating that follows for the next imprinting. In contrast, a desired pattern can be imprinted many times on the same substrate surface in the room-temperature imprinting without causing any distortion of the patterns that were formed previously.
Therefore, there is essentially no area limitation in the room-temperature imprinting.

Schematic diagram of the experimental procedure and an example of the pattern transfer by the two-step etching is shown in Fig. 1. For comparison purpose, SEM micrographs are shown of the master with which the pattern is imprinted, the pattern imprinted, and the pattern transferred into the underlying SiO₂ substrate (from top to bottom). It is noted in this regard that the indentation depth resulting from the imprinting ranges from 50 nm to 150 nm depending on the pressure applied. Since the height of the protruding lines is in excess of 500 nm, only a fraction of the height penetrates into the polymer upon pressing, which in this case is about 100 nm. The first step of etching polystyrene that was used as the polymer layer was carried out with CF₄ plasma. After the underlying SiO₂/Si layer had been exposed, the underlying SiO₂ was etched with CHF₃/CF₄ plasma to transfer the pattern into SiO₂. The cross-sectional SEM micrographs in Figure 1 show that a line and space pattern is well transferred to SiO₂ substrate by the two-step RIE process.

2. Capillary Force Lithography

Capillarity is one of useful concepts that can be used in the patterning of polymeric materials. When a liquid wets a capillary tube and if the wetting results in lowering the free energy, the wetting leads to the capillary rise of the liquid. This capillarity was used in a method called micromolding in capillaries [10]. To overcome a few shortcomings of the method, solvent-assisted microcontact molding was subsequently developed [11], which involves “softening” only a thin surface layer of the polymer film on a substrate by wetting the polymer surface with a suitable solvent for molding.

In the capillary force lithography presented here [4], the essential feature of the imprint lithography [3] of molding a polymer melt is combined with the prime element of microcontact printing [5] or soft lithography [2] of using an elastomeric mold. As a result, the advantage of the imprint lithography over the microcontact printing is retained in meeting the stringent pattern fidelity requirements in fabricating integrated circuits while eliminating the need to use an extremely high pressure that is needed in the imprint lithography. Furthermore, the etching step needed to open the windows after imprinting could be eliminated.

A schematic of the capillary force lithography is shown in Figure 2(a). We used polydimethylsiloxane (PDMS, Sylgard 184, Dow Corning) as an elastomeric mold and fabricated a PDMS master that has a planar surface with recessed or protruding patterns by casting PDMS against a complementary relief structure prepared by photolithography or electron-beam method. For the polymer, we used commercial polystyrene (PS) (molecular weight = 2.3 x 10⁵) and styrene-butadiene-styrene (SBS) block copolymer (molecular weight = 3 x 10⁵, styrene fraction = 0.3). Typically, silicon wafer (100) was used as the substrate, which can readily be expanded to other kinds of organic or inorganic substrate if the surface is planar enough to allow a conformal contact with the PDMS mold. Silicon wafer was cleaned by ultrasonic treatment in trichloroethylene and methanol for 5 minutes each and dried in nitrogen. Polymer films were spin-coated onto the Si substrate to 30 nm to 1.5 μm thickness and the PDMS mold was placed on the polymer surface. In spite of the spontaneous wetting property of the PDMS mold, care should be taken to avoid small gaps or bubbles between the mold and the polymer surface. The film was then annealed at a temperature above the glass transition temperature, Tg.
the mold was removed from the surface and the remaining polymer structure was examined by atomic force microscopy (AFM) and scanning electron microscopy (SEM).

Figure 2(b) shows the SEM images of various polymer patterns. When the polymer film is thick enough to completely fill the cavity of the mold, residual polymer remains on the substrate as shown in the figure. However, if the polymer film is thin and the interaction between the polymer and the substrate is sufficiently weak, no residual film remains and the substrate surface is exposed. In the latter case, a meniscus is observed at the protruding end of the polymer, which is the signature mark of the capillary rise. It is noted that initial wetting conditions are very crucial when the polymer does not completely fill the cavity of the mold. If the mold leans a little toward one side, an asymmetric structure results such that the meniscus is highly uneven. In this case, the polymer pattern along the channels is not uniform. Moreover, the annealing time should be chosen in such a way that instability of the polymer does not set in. For example, polymer films should be annealed less than about 15 hours at 120 °C for SBS. A longer annealing time leads to broken or isolated polymer structures. Features down to 100 nm can be replicated by CFL as shown in Figure 2 (right bottom). In the figure, the line features on the original mold were poor due to limited electron-beam capability, which is replicated in the lines formed.

The applicability to large area patterning has been tested. We found no defects or destruction of the polymer structure over an area as large as 4×4 cm² as long as the mold is in conformal contact with the polymer film.

The most important concept of CFL is that wetting of the wall of PDMS mold by polymer melt lowers the total free energy. If the interaction at the polymer/substrate interface is negligible and the polymer melt is liquid-like, the maximum height the polymer melt can rise to through a narrow channel of width L by the capillary action can be obtained by equating the capillary force to the resistant gravitational force, which gives [12]

$$h_{\text{max}} = \frac{2\gamma \text{polymer/air} \cos \theta}{\rho g L}$$

where $h_{\text{max}}$ is the maximum height, $\gamma \text{polymer/air}$ is the surface tension at the polymer/air interface, $\theta$ is the
contact angle at the polymer/mold interface, $\rho$ is the density of the polymer, and $G$ is the gravitational constant. From the meniscus of the cross-sectional SEM image, the contact angle is estimated to be about 85°. When we insert into Eq. (1) the surface tension ($\sim 30$ dyne/cm) and density (0.95 g/cm$^3$) of SBS and L of 300nm, a maximum height of 1.87 m is obtained, which indicates that the height of the patterned polymer can be made quite large. In fact, we were able to fabricate polymer structures with a step height as high as 5 $\mu$m for 80 $\mu$m line-and-space pattern. If we take into account the interaction at the polymer/substrate interface and the solid-like properties of the polymer melt, the theoretical maximum height would be reduced. For a more accurate model, further study would be required.

The time it takes for the polymer melt to fill up the void space between the mold and the polymer film can be estimated. If we neglect the effect of gravity, then the surface tension and viscosity of the polymer melt, and the size of the capillary determine the rate of flow such that the time is given by [13]

$$t = \frac{2\pi z^2}{R\gamma \text{polymer/(air)} \cos \theta}$$

(5)

where $z$ is the length of capillary to be filled, $t$ is the time, $\eta$ is the viscosity of the polymer melt and $R$ is the hydraulic radius (the ratio of the volume of the liquid in the capillary section to the area of the solid and liquid interface), which is approximately one half the width $L$. We observed that it took about 30 minutes for the SBS polymer to completely fill the void in the mold with a step height of 600 nm and a width of 400 nm at 100 °C. The viscosity of the SBS is about 10$^8$ (Pa×s) from the rheometrics spectroscopy (RMS) measurement at zero shear stress. When we use these values in Eq. (2), the time needed to fill the void in the mold is calculated to be 1377s ($\sim 23$ min), which is a little shorter than the observed value.

3. Conclusion

It has been demonstrated that the room-temperature imprint lithography introduced here has the unique features of allowing large area nano-patterning by step-and-repeat scheme, which is not possible with the conventional hot-imprint (or, hot-embossing) lithography. This room-temperature imprint lithography, which is based on a mechanism different from that for the conventional imprinting method, can lead to more versatile and practical nano-scale patterning.

Capillary force lithography (CFL) presented here is a simple and yet robust method for large-area patterning. With further development, the technique could become a strong candidate for an alternative to photolithography in fabricating large-scale integrated circuits.

References

※ 저자 소개

강달영
1987~1994년 서울대학교 화학공학과 공학사
1994~1996년 서울대학교 대학원 화학공학과 공학석사
1996~2000년 서울대학교 대학원 응용화학부 공학박사
2000.3~2000.10 성균관대학교 고문자 기술연구소 전임연구원
2001년~현재 (주)이누리텍 기술팀장

유현식
1992~1996년 서울대학교 화학공학과 공학사
1996~1998년 서울대학교 대학원 화학공학과 공학석사
1998년~현재 서울대학교 대학원 응용화학부 박사과정

서갑양
1992~1996년 서울대학교 화학공학과 공학사
1996~1998년 서울대학교 대학원 화학공학과 공학석사
1998년~현재 서울대학교 대학원 응용화학부 박사과정

이홍희
1966년 서울대학교 화학공학과 학사
1971~1977년 Westvaco Corporation 연구원
1977~1992년 University of Florida 화학과 교수
1992년~현재 서울대학교 공과대학 응용화학부 교수
1996~2001년 서울대학교 초미세소자 연구소 소장

김연상
1991~1995년 서울대학교 화학공학과 공학사
1995~1997년 서울대학교 대학원 화학공학과 공학석사
1997년~현재 서울대학교 대학원 응용화학부 박사과정