Non-Residual Layer Transfer of High Viscous Ultraviolet Photocurable Resin Using Liquid Transfer Technique

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Ultraviolet-nanoimprint lithography (UV-NIL) is a next-generation lithographic technology. However, its usefulness is negatively affected by the formation of an extra resin layer between the curable resin pattern and the substrate, which is known as the residual layer (RL). Liquid-transfer imprint lithography (LTIL) is a promising technique for reducing the RL. However, it is difficult to ensure a thin RL with LTIL when using a high viscous UV curable resin. A technique combining LTIL and roll press can be used to overcome this drawback. High viscous UV curable resins generally possess high selectivity for dry etching and can exhibit various refractive indices. In this study, master molds were prepared with a patterned design and varying line and space values. The pattern ratio was 1:2, and the line widths were 990 nm, 540 nm, and 270 nm. UV curable resins with viscosities of 2900 mPa·s and 13090 mPa·s could be used to transfer the line and space patterns of three nanoscale widths to eliminate the RL, by using a repeated roll-press and LTIL technique and parallel plate UV-NIL.

Keywords: Ultraviolet-nanoimprint lithography, Liquid-transfer imprint lithography, High viscous ultraviolet curable resin, Residual layer

1. Introduction

Nanoimprint lithography (NIL) [1] is expected to serve as a next-generation lithographic technology for manufacturing nanoscale patterns, particularly in the semiconductor industry. Ultraviolet nanoimprint lithography (UV-NIL) [2] involves the use of a resin cured with UV light and can produce nanoscale patterns with high throughput.

A problem with UV-NIL is that an extra resin layer called the residual layer (RL) [3-6] is generated between the curable resin pattern and the substrate. This RL must be removed before the dry etching process, so a thin or nonexistent RL is desirable in the UV-NIL process. Several methods for removing the RL have been proposed [7-10]. Liquid-transfer imprint lithography (LTIL) [11] is a promising technique for reducing the RL, and it involves the use of a replica mold and a dummy substrate. The replica mold is separated from the liquid-phase UV curable resin on the dummy substrate. Then, a thin liquid UV curable layer remains on the replica mold surface. The replica mold is then contacted with the new substrate, and UV-NIL is carried out. After UV-NIL, the thin RL pattern can be transferred onto the substrate. With this LTIL technique, it is difficult to prepare a thin RL when using a high viscous UV curable resin. Resin spirit cannot reduce the RL when using a high viscous UV curable resin. A solvent is usually used to reduce the resin viscosity, but in this case, air bubbles tend to be trapped in the resin. Our previous study [12] revealed that a uniform thin RL could be achieved using the roll-press LTIL method, even on curved surfaces. The merit of the roll-press method is that it reduces the RL of the liquid-phase UV curable resin by applying a high pressure.

High viscous UV curable resins generally exhibit high selectivity for dry etching [13] and various refractive indices [14]. The combination of the latter benefit with lab-on-a-chip [15-17] technology is expected to result in great progress in
biology [18] and chemical engineering [19]. A thin RL is necessary when using high viscous UV curable resins for dry etching masks. In the current study, high-pressure roll-press LTIL was used to achieve a nonexistent RL with a high viscous UV curable resin.

2. Experimental

Figure 1 shows the process used to fabricate the master mold. An electron beam resist (ZEP520A, diluted 1:1 in ZEP A, Zeon Co., Ltd., Japan) was deposited on a Si substrate by spin coating at 2000 rpm for 20 s (Fig. 1(a)). The ZEP 520 A solvent was then removed by baking in an oven at 180 °C for 20 min (Fig. 1(b)). Electron beam writing was carried out using a 10 kV system (ERA 8800 FE, Elionix Co., Ltd., Japan). The resolution of the electron beam lithography (EBL) system was 27 μC/cm² when using an accelerating voltage of 10 kV (Fig. 1(c)). A line and space pattern was fabricated. The pattern ratio (i.e. line: space ratio) was 1:2, and the line widths were 990 nm, 540 nm or 270 nm. The samples were soaked in the developer (ZED-N50, Zeon Co., Ltd., Japan) for 60 s (Fig. 1(d)). A 30-nm-thick Cr layer was deposited by vacuum evaporation (VPC-260F, Ulvac Kiko Inc., Japan) (Fig. 1(e)). The samples were then lifted off (ZDMAC solution, Zeon Co., Ltd., Japan) for 1 h (Fig. 1(f)). The exposed Si substrate was etched using an inductively coupled plasma (ICP) system (EIS-700, Elionix Co., Ltd., Japan) (Fig. 1(g)) for 1 min. The etching conditions were as follows: gas flow rate, 20 sccm/20 sccm (C₆F₆/SF₆); ICP radio frequency (RF) power, 600 W/400 W; sample RF power, 100 W/0 W. A pillar patterned master mold was thus formed (Fig. 1(h)).

The master mold was soaked in a release agent, Optool DSX 0.1% (Daikin Industries Ltd., Japan), for 6 h (Fig. 2(a)) and then baked at 120 °C for 5 min (Fig. 2(b)). A UV curable resin (PAK-01-CL, Toyo Gosei Co., Ltd., Japan) was deposited onto the master mold, and a polyethylene terephthalate (PET) film substrate (Cosmoshine A4300, Toyobo Co., Ltd., Japan) was set on the PAK-01-CL resin layer (Fig. 2(c)). The sample was then exposed to UV light (10 mJ/cm²) (Fig. 2(d)), and the PAK-01-CL layer on the PET film substrate was released from the master mold. A hole patterned replica mold was thus formed (Fig. 2(e)), and is hereafter referred to as the first replica mold. The first replica mold was sputter-coated (ESC-101, Elionix Co., Ltd., Japan) with Pt (Fig. 2(f)) and subjected to the process steps depicted in Figs. 2(a) and (b). A UV curable resin (OEX-028-X433-3, AUTEX Co., Ltd., Japan) was deposited onto the first replica mold, and a PET film substrate was set on this X433-3 resin layer (Fig. 2(g)). The first replica mold was used in order to avoid the risk of breaking the master mold while fabricating replicas in X433-3. Preliminary experiments indicated that the PAK-01-CL pattern fractured at high pressure, so a high hardness X433-3 was used. The sample was exposed to UV light (6000 mJ/cm²) (Fig. 2(h)). The X433-3 layer on the PET film substrate was released from the first replica mold (Fig. 2(i)). X433-3 reportedly becomes fluorinated when subjected to heat treatment [20,21]. X433-3 on the PET film substrate was baked at 85 °C for 30 min (Fig. 2(j)). The pillar patterned replica mold was thus formed (Fig. 2(k)), and is hereafter referred to as the second replica mold. The pattern height of the second replica mold was observed by atomic force microscopy (AFM, SPM-9600, Shimadzu Co., Kyoto, Japan), and the widths of the second replica mold were measured by scanning electron microscopy (SEM, ERA 8800 FE, Elionix Co., Ltd., Japan).
The roll press apparatus used in the next experiment is shown in Fig. 3. The roller and sample table are made of stainless steel and aluminum, respectively. Transfer materials are pressed by the roller and the sample table, and the resin from the sample can be pushed out by rotating the roller. In order to calculate the pressure, the pressure width is measured by using a FULIFILM PRESCALE film (FUJIFILM Co., Japan). Initially, this film is white in color, but when pressure is applied, the area of application assumes a red color. The roll-pressed widths are measured using the width of the red-colored area of the PRESCALE films that were overlaid with the second replica mold film and sandwiched between the roller and the sample stage. The results obtained from the colored PRESCALE films under various loads and the calculated pressures are shown in Fig. 4.

Fig. 3. Overview of roll press apparatus.

Fig. 4. Pressure width and pressure.

A high viscous UV curable resin (MY-133-V2000, MY POLYMERS Ltd., Israel) was used [22]. The viscosity of the MY-133-V2000 resin was 2900 mPa·s. MY-133-V2000 was deposited onto the Si substrate by spin coating at 10000 rpm for 120 s (Fig. 5(a)). The second replica mold was set onto the Si substrate (Fig. 5(b)). The sample was pressed by a roller at a pressure of 15.0 MPa (the contact area of the roller was 60 mm², the load was 900 N, and the substrate was Si) and a roll speed of 1.6 mm/s (Fig. 5(c)). When more than 15.0 MPa pressure was applied, defects were formed during transfer. The second replica mold was then carefully peeled off the liquid resist layer (Fig. 5(d)). After the second replica mold was set onto the Si substrate, MY-133-V2000 was filled into the second replica mold, using parallel plate UV-NIL equipment (2.2 MPa, 1 min) (Fig. 5(e)) [23]. While filling, the sample was exposed to UV light (75 J/cm²) (Fig. 5(f)). The second replica mold was then released from the Si substrate (Fig. 5(g)) [24]. It was impossible to observe the results of this process by cross-sectional SEM imaging because the viscoelasticity of the cured MY-133-V2000 was very high. Thus, the pattern heights and film thicknesses of MY-133-V2000 were observed by AFM. The widths of the patterned MY-133-V2000 resin were observed by SEM.

Fig. 5. Process for roll-press liquid transfer when the viscosity was 2900 mPa·s.

A second, high viscous UV curable resin (OEX-009-S6-N-1, AUTEX Co., Ltd., Japan) was used [25]. The viscosity of OEX-009-S6-N-1 was 13090 mPa·s, which is higher than that of MY-133-V2000. It was necessary to repeat the roll press and LTIL processes because the residual resin could not be removed by a single application of roll pressing and LTIL. Thus, the modified process was as follows. OEX-009-S6-N-1 was deposited onto the Si substrate by spin coating at 10000 rpm for 120 s (Fig. 6(a)). The second replica mold was set onto the Si substrate (Fig. 6(b)). The sample was pressed by a roller at a pressure of 15.0 MPa and a roll speed of 1.6 mm/s (Fig. 6(c)). When more than 15.0 MPa of pressure was applied, the patterns of the second replica mold collapsed. The second replica mold was then carefully peeled off the liquid resist layer (Fig. 6(d)). The second replica mold was then set onto the PET film substrate. The sample was pressed by a roller at a pressure of 15.0 MPa (the contact area of the roller was 60 mm², the load was 900 N, the substrate was PET film) and a roll speed of 1.6 mm/s (Fig. 6(e)).
When more than 15.0 MPa of pressure was applied, the patterns of the second replica mold collapsed. The second replica mold was then carefully peeled off the liquid resist layer (Fig. 6(f)). The second replica mold was then set onto a new Si substrate, and the sample was pressed by a roller at a pressure of 4.0 MPa (the contact area of the roller was 50 mm², the load was 200 N, the substrate was Si) and a roll speed of 1.6 mm/s (Fig. 6(g)). When more than 4.0 MPa pressure was applied, defects occurred during transfer. OEX-009-S6-N-1 was filled into the second replica mold using parallel plate UV-NIL equipment (2.2 MPa, 1 min) (Fig. 6(h)). While filling, the sample was exposed to UV light (75 J/cm²) (Fig. 6(i)). The second replica mold was then released from the new Si substrate (Fig. 6(j)). The pattern heights and widths of OEX-009-S6-N-1 were observed with SEM.

![Fig. 6. Process for roll-press liquid transfer when the viscosity was 13090 mPa·s.](image)

### 3. Results and discussion

The line widths of the second replica mold were measured for each pattern with SEM. The measured imprint width for the pattern with a ratio of 1:2 and line width of 990 nm (first replica mold) was 889 nm (second replica mold). The measured imprint width for the pattern with a ratio of 1:2 and line width of 540 nm was 407 nm. The measured imprint width for the pattern with a ratio of 1:2 and line width of 270 nm was 149 nm. The line width shrank due to curable shrinkage since the pattern was transferred twice from the master mold. The height of the second replica mold was measured to be 644 nm by AFM.

The thickness of the film that had been UV cured after spin coating (see Fig. 5 (a)) was 4.13 μm. The UV curable resin with 2900 mPa·s viscosity could not be thinned by spin coating alone. An SEM image of the line width of the MY-133-V2000 surface is shown in Fig. 7.

![Fig. 7. SEM image showing MY-133-V2000 pattern line width.](image)

A line width of 990 nm could be transferred with the UV curable resin having 2900 mPa·s viscosity. The line width spread by 18 nm when the MY-133-V2000 resin was used to transfer the pattern from the second replica mold. The line width spread was attributed to the collapse of the pattern height. An AFM height profile depicting the thickness of the MY-133-V2000 film is shown in Fig. 8. The portion without a pattern was cut with a cutter.

![Fig. 8. AFM height profile of MY-133-V2000 film thickness.](image)

An AFM height profile of MY-133-V2000 is shown in Fig. 9.

![Fig. 9. AFM height profile of MY-133-V2000 pattern.](image)
The MY-133-V2000 film thickness and pattern height were 623 nm and 623 nm, respectively. Since the MY-133-V2000 pattern was a hole pattern, the RL was considered to be zero.

A cross-sectional SEM image showing the thickness of the OEX-009-S6-N-1 after spin coating (see Fig. 6 (a)) is illustrated in Fig. 10.

The thickness of the film that had been UV cured after spin coating, was 8.08 μm. The UV curable resin with 13090 mPa·s viscosity could not be thinned by spin coating alone. The RL that remained cured after a single LTIL step (Fig. 6 (d)) is shown in Fig. 11.

The cured RL after a single LTIL process was 1.42 μm. The RL could not be thinned by a single LTIL procedure, so the LTIL procedure was carried out twice. An SEM image of the line width of the OEX-009-S6-N-1 surface is shown in Fig. 12.

A line width of 990 nm could be transferred with the UV curable resin of 13090 mPa·s viscosity. The line width spread by 18 nm when OEX-009-S6-N-1 was used to transfer the pattern from the second replica mold. Again, this spread was attributed to the collapse of the pattern height. Cross-sectional SEM images of the line width and pattern height of the MY-133-V2000 resin are shown in Fig. 13.

The RL became smaller each time the LTIL process was applied.

4. Conclusion

High viscous UV curable resins with viscosities of 2900 mPa·s and 13090 mPa·s could not be thinned solely by spin coating. The second replica mold with a line and space pattern ratio of 1:2 was used, with line widths of 889 nm, 407 nm, or 149 nm. The UV curable resin with 2900 mPa·s viscosity yielded no RL following a single LTIL and roll-press procedure. The UV curable resin with 13090 mPa·s viscosity yielded no RL following two LTIL and three roll-press procedures. The high-pressure roll-press LTIL method is useful for transferring nanoscale patterns via high viscous UV curable resins. These resins, which are compatible with dry etching and exhibit various refractive indices, could potentially be
applied to lab-on-a-chip technology. Dry etching masks could be obtained using high viscous UV curable resins.

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