Development of Cellulose Derivative Mold for Imprint Lithography

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A cellulose derivative mold is used in imprint lithography and possesses great gas permeability. The gas permeable mold enables the minimization of the pattern failure caused by the accumulation of gas generated from imprinted material. This study aims to introduce a cellulose-based gas permeable mold for patterning UV-curable resin containing a volatile solvent. The measurement of the contact angles of the mold surface, dissolution test for the volatile solvent, and imprint lithography showed that the gas permeable mold has great imprinting repeatability and solvent resistance. We expect that imprint lithography using the gas permeable mold derived from the cellulose and materials containing volatile solvent will enable pattern failure reduction, repeatable imprinting, and decrease in the viscosity of the imprinted material.

Keywords: Imprint lithography, Gas permeable mold, Cellulose derivatives, Volatile solvent, Polydimethylsiloxane silicon elastomer

1. Introduction
The imprint lithography technique is a microfabrication technology. The patterns on the surface of the mold transferred onto the imprinted material upon depressing the fin patterned mold for filling imprinted material and demolding. [1-5] Imprint lithography has attracted attention as a next-generation microfabrication technology for manufacturing semiconductors and bio-tips owing to high-resolution and large-area patterning at a low cost. However, imprint lithography faces limitations of pattern failure caused by outgas. Outgas, such as air trapped during mold depression or oxygen generated from the imprinted material by chemical reaction, accumulates between the imprinted material and mold, causing a pattern failure from insufficient filling [6-9]. Herein, we demonstrate thermosetting cellulose derivatives used as mold materials for imprint lithography [10-13]. The mold derived from the cellulose derivatives has great gas permeability in comparison with conventional molds, such as quartz- or silicon-based molds. The outgas is discharged through the gas permeable mold. Figure 1 shows a comparison between the imprint lithography processes using a quartz-based mold and gas permeable mold. The removal of the accumulated gas enables the sufficient filling of the imprinted material into the mold patterns and imprint without a pattern failure.

Furthermore, the gas permeable mold is introduced into imprint lithography using imprinted material with an extra-volatile solvent. The volatile solvent is expected to decrease the viscosity of the imprint material and contribute toward the smooth filling in the mold-depressing process. A decrease in the viscosity of the imprinted material achieves the imprint for high-viscosity materials, such as epoxy novolak resins or silver nano-particle, which are limited for imprint lithography owing to their poor liquid properties, and expansion of the patterning area at one time [14,15]. Although the volatile solvent added in the imprinted material enhances the risks of pattern failure caused by solvent accumulation, the gas permeable mold enables the minimization of gas trapping. Furthermore, imprint lithography without a pattern defect is possible. The gas permeable mold derived from the cellulose derivatives is expected to imprint various types of materials and expand the patterning area for imprint lithography.
Herein, we synthesized thermosetting cellulose derivatives using cellulose derivatives and acrylic monomer and prepared a cellulose-based gas permeable mold. UV-curable resin containing a volatile solvent was patterned by imprint lithography using cellulose-based mold. By measuring the contact angles of the mold surface, dissolution test for the volatile solvent, and imprint lithography, the repeatability of the cellulose-based mold was evaluated by comparing it with the existing gas permeable mold, wherein polydimethylsiloxane (PDMS) silicon elastomer is used as a mold material [16-19].

Fig. 1. Imprint lithography using the gas permeable mold.

**2. Experimental**

2.1. Gas permeable mold materials

As shown in Fig. 2, the gas permeable mold material derived from the cellulose derivatives was synthesized using hydroxypropyl cellulose (HPC; Wako Pure Chemical) and 2-methacryloyethyl isocyanate (MOI; Showa Denko). The thermal cross-linkable cellulose derivatives (HPC–MOI) were formed through the chemical reaction of the isocyanate group of the MOI with hydroxy group of the HPC. The HPC was reacted with an acrylic monomer using methyl ethyl ketone as a solvent. Trimethylamine (Kanto Chemical) was added as a synthetic reaction catalyst. Subsequently, 3 wt% of 2,2’-azodiisobutyronitrile (AIBN; Tokyo Chemical) was added as a thermal radical polymerization initiator into the HPC–MOI solution.

The PDMS silicon elastomer (Fig. 3) used as a material of the existing gas permeable was obtained in a mixture at the rate of 10 parts the prepolymer base to one part the curing agent [20-23].

Fig. 2. Chemical reaction of HPC-MOI.

Fig. 3. Chemical structure of PDMS silicon elastomer, (a) Dimethyl siloxane, dimethylvinyl terminated, (b) Dimethylvinylated and trimethylated silica, (c) Tetra (trimethoxysilox) silane, (d) Dimethyl, methylhydrogen siloxane, (e) Tetramethyl tetravinyl cyclotetra siloxane. Pre-polymer base contains (a), (b), (c), and ethyl benzene. Curing agent contains (d), (a), (b), (e), and ethyl benzene.

2.2. Production of gas permeable molds

The gas permeable molds, i.e., HPC–MOI and PDMS silicon elastomer, prepared in Section 2.1 were formed through thermal imprint lithography using a simple type of imprint equipment (STIE-400; Litho Tech Japan). Figure 4 shows the manufacturing processes of the gas permeable molds. The gas permeable mold material, i.e., HPC–
MOI or PDMS silicon elastomer, was dispensed on a silicon substrate coated with under layer. The quartz master mold (NIPPON FALCON) was depressed at a pressure of 1 kgf for 2 min at room temperature. The thermal cross-linking of the gas permeable mold materials was baked at 130 °C at a pressure of 1 kgf for 60 min. The curing condition was usually used in the manufacturing process of the gas permeable molds using the PDMS silicon elastomer. The gas permeable molds with sub 2 µm line and space patterns were obtained by demolding the quartz master mold from the cured gas permeable mold material.

2.3. Imprint process using the gas permeable mold

UV-curable resin containing volatile solvent was patterned by UV lithography using the gas permeable mold. Cyclopentane, cyclopentanone, and acetone were used as a volatile solvent. The addition rate relative to the photo curable resin was 10 wt%. The UV-curable resin consisted of 16.0 wt% trehalose derivatives, 8.01 wt% glucose derivatives, 70 wt% isobornyl methacrylate, and 5.45 wt% 2-hydroxyl-2-methyl-1-phenyl-propane-1-ol. The gas permeable mold using HPC–MOI was coated by the mold release agent, Chem lease 70 (Chem trend), to increase the mold release property. The surface treatment of the gas permeable mold using HPC–MOI was expected to increase the number of the UV imprint lithography times along with using the PDMS silicon elastomer mold without surface treatment. Figure 5 shows the imprint lithography process. The photocurable resin containing 10 wt% volatile solvent was dispensed on a glass substrate. The gas permeable mold was then depressed on that. The photocurable resin was polymerized using a metal halide lamp system (SUN ENERGY DGM2501A-01) exposing 200 mW/cm² UV for 60 s. The gas permeable mold was then released from the cured resin. The UV imprint lithography processes were repeated to evaluate the repeatability of gas permeable molds for the imprinted material with the volatile solvent.

2.4. Measurement of the contact angle of the gas permeable mold materials

The contact angles for water, n-hexadecane, and diiodemethane of the gas permeable mold materials were measured using a dynamic contact angle meter (Dropmaster500z; Kyowa Interface Science). The contact angles for water, n-hexadecane, and diiodemethane were calculated using the θ/2 analysis method. The measurement time after dropping was 1.0 s.

2.5. Dissolution rate of the gas permeable molds for the volatile solvent

The dissolution test of the gas permeable molds prepared in Section 2.2 was performed by dipping in the volatile solvent. Cyclopentane, cyclopentanone, and acetone were used as the volatile solvent in the dissolution test. The thickness of the gas permeable mold using HPC–MOI and PDMS silicon elastomer was observed using a confocal microscope (Laser Tec OPTELICS H1200). The gas permeable molds were dipped in the volatile solvent at room temperature for 10 min.
The thickness of the gas permeable molds was then remeasured. The dissolution rate was determined as the difference between the initial and final thickness of the gas permeable mold layers in the process of manufacturing the gas permeable molds and dipping in the volatile solvent [24-27].

3. Results and discussion

3.1. Comparison of HPC–MOI and PDMS

Figure 6 shows the confocal microscope images of the line and space patterns of the imprinted material patterned by the gas permeable mold. The width of the line pattern formed in the 9th imprint lithography using the gas permeable mold of the PDMS silicon elastomer (Fig. 6(a2)) was narrower than that formed for the first time (Fig. 6(a1)). A decrease in the width of the line patterns was caused by the pattern expansion of the gas permeable mold during the UV imprint lithography process. The line edge roughness (LER) was also generated in the narrowed pattern; hence, the number of imprint times using the gas permeable mold of the PDMS silicon elastomer was limited under nine times at least. Comparing Fig. 6(a3) with Fig. 6(a2) and Fig. 6(a5) with Fig. 6(a4), the gas permeable molds of the PDMS silicon elastomer were similarly influenced by volatile solvent such as cyclopentanone and acetone. Meanwhile, in imprint lithography using the HPC–MOI mold, the width of the pattern formed in the 10th imprint lithography (Fig. 6(b2)) was the same as that in the first one (Fig. 6(b1)) when compared to that using the PDMS silicon elastomer mold. In the case of UV curable resin containing cyclopentanone and acetone, both of them were continuously formed without pattern failure, as shown in Fig. 6(b3), Fig. 6(b4), Fig. 6(b5), and Fig. 6(b6). The result indicated that the HPC–MOI mold had a great repeatability for imprint lithography using an imprinted material with a volatile solvent. Therefore, the gas permeable mold derived from the cellulose showed a good repeatable performance for imprinting the material.
with volatile content.

3.2. Contact angles of the HPC–MOI and PDMS molds

Table 1 shows the dynamic contact angles for water, n-hexadecane, and diiodomethane of the HPC–MOI and PDMS molds. On the HPC–MOI mold surface, the contact angles for water showed a huge different wettability from the PDMS mold surface. HPC–MOI had much of the hydroxy group (Fig. 2) even though some was substituted for the acrylic group for attaching the thermosetting property. We considered that the high wettability for water was presented by much hydroxy group in HPC–MOI. In addition, the presence/absence of the hydroxy group in mold a had great influence on the mold characteristics. The contact angles for water on HPC–MOI indicated better hydrophilicity and oil repellency in comparison with the mold from the PDMS silicon elastomer. We expected that the gas permeable mold derived from the cellulose will have low affinity to the volatile solvent using imprint lithography.

Table 1. Contact angle of the molds of HPC–MOI and PDMS.

| solvent       | HPC-MOI | PDMS |
|---------------|---------|------|
| Water         | 31.3    | 99.44|
| n-Hexadecane  | 42      | 41.12|
| Diiodomethane | 21.0    | 69.4 |

3.3. Dissolution rate of the HPC–MOI and PDMS molds

Table 2 shows the dissolution rate for three types of volatile solvent of the molds from HPC–MOI and the PDMS silicon elastomer. By dipping PDMS silicon elastomer in cyclopentane or cyclopentanone or acetone for 10 min, its mold thickness was the decreased by over 40%. Meanwhile, the final thickness of the HPC–MOI mold was the same as the initial thickness in the dissolution test. The result showed that HPC–MOI had good solvent resistance in the volatile solvent, and the mold was less affected by the imprinted material with the volatile solvent.

As mentioned in Section 3.2, cellulose is well known to have strong hydrogen bond and low affinity to the volatile solvent because of the hydroxy group in the cellulose. Therefore, the cellulose exhibited a slightly volatile solvent solubility and swelling property. Although HPC–MOI, which is a cellulose derivative of the 6-position hydroxy group, was substituted for the cross-linkable group, we expected that the cross-linked HPC–MOI also has enough hydrogen bond and low-volatile solvent affinity and does not cause dissolution or swelling for the volatile solvent like the cellulose. In imprint lithography, we considered that the poor volatile solvent solubility and swelling property of HPC–MOI inhibit the pattern expansion and LER caused by the volatile solvent.

4. Conclusion

Imprint lithography using the imprinted material containing a volatile solvent showed that the gas permeable mold had great repeatability without LER and pattern width change. The gas permeable mold using HPC–MOI tended to exhibit hydrophilicity and oil repellency and had great solvent resistance in cyclopentane compared to the mold from the PDMS silicon elastomer. We considered that the solvent resistance was obtained by the hydroxy group in the cellulose derivatives. The low-volatile solvent solubility and the swelling property were required to achieve repeatable imprinting of the materials containing the volatile solvent. We conclude that imprint lithography using the gas permeable mold derived from the cellulose and materials containing volatile solvent enable the reduction of pattern failure, repeatable imprinting, and decrease in the viscosity of the imprinted material.

Table 2. Dissolution rate of the molds of HPC–MOI and PDMS.

| solvent         | initial thickness (µm) | final thickness (µm) | dissolution rate (%) |
|-----------------|------------------------|----------------------|----------------------|
|                 | HPC-MOI | PDMS | HPC-MOI | PDMS | HPC-MOI | PDMS |
| cyclopentane    | 5.91    | 2.99 | 5.88    | 1.80 | -0.44   | -40  |
| cyclopentanone  | 21.3    | 14.0 | 22.1    | 5.98 | 3.6     | -57  |
| acetone         | 17.3    | 8.98 | 16.7    | 1.96 | -3.5    | -78  |
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References

1. S. Y. Chou, P. R. Krauss, and P. J. Renstrom, Appl. Phys. Lett., 67 (1995) 3114.
2. M. Colburn, S. C. Johnson, M. D. Stewart, S. Damle, T. C. Bailey, B. Choi, M. Wedlake, T. B. Michaelson, S. V. Sreenivasan, J. G. Ekerdt, and C. G. Willson, Proc. SPIE, 3676 (1999) 379.
3. M. A. Verschuuren, M. Megens, Y. Ni, H. van Sprang, and P. A. Hans, Adv. Opt. Technol., 6 (2017) 243.
4. S. C. Johnson, T. C. Bailey, M. D. Dickey, B. J. Smith, E. K. Kim, A. T. Jamieson, N. A. Stacey, J. G. Ekerdt, C. G. Willson, D. P. Mancini, W. J. Dauksher, K. J. Nordquist, and D. J. Resnick, Proc. SPIE, 5037 (2003) 197.
5. Y. Hirai, S. Harada, H. Kikuta, Y. Tanaka, M. Okano, S. Isaka, and M. Kobayasi, J. Vac. Sci. Technol. B, 20 (2002) 2867.
6. S. Nakajima, S. Takei, M. Hanabata, N. Sugino, T. Kameda, Y. Matsumoto, and A. Sekiguchi, Proc. SPIE, 10354 (2017)103541B.
7. S. Takei and M. Hanabata, Appl. Phys. Lett., 107 (2015) 141904.
8. M. Hanabata, S. Takei, K. Sugahara, S. Nakajima, N. Sugino, T. Kameda, J. Fukushima, Y. Matsumoto, and A. Sekiguchi, Proc. SPIE, 9777 (2016) 97771G.
9. N. Sugino, S. Takei, S. Nakajima, M. Hanabata, T. Kameda, and A. Sekiguchi, J. Photopolym. Sci. Technol., 30 (2017) 275.
10. S. Nakajima, S. Takei, S. Takamatsu, K. Mizui, T. Oka, Y. Matsumoto, A. Sekiguchi, and M. Hanabata, Jpn. J. Appl. Phys., 57 (2018) 086503.
11. K. Mizui, K. Kurematsu, S. Nakajima, M. Hanabata, and S. Takei, J. Photopolym. Sci. Technol., 31 (2018) 289.
12. S. Murayama, I. Motono, K. Mizui, K. Kondoh, M. Hanabata, and S. Takei, J. Nanomater., 2019 (2019) 5180460.
13. S. Takei, Appl. Phys. Express, in press (2019).
14. S. Takei, S. Nakajima, and M. Hanabata, Microelectron. Eng., 190 (2018) 68.
15. S. Takei and M. Hanabata, Appl. Phys. Express, 9 (2016) 056501.
16. C. Acikgoz, M. A. Hempenius, J. Huskens, and G. J. Vancso, Eur. Polym. J., 47 (2011) 2033.
17. S. Brittman, S. Z. Oener, K. Guo, H. Āboliņš, A. F. Koenderinka, and E. C. Garnett, J. Mater. Chem. C, 5 (2017) 8301.
18. T. Dattoma, A. Qualtieri, G. Epifani, M. De Vittorio, and F. Rizzi, Polymers, 11 (2019) 424.
19. A. I. M. Greer, I. Vasiev, B. Della-Rosa, and N. Gadegaard, Nanotechnology, 27 (2016) 155301.
20. V. Placet, and P. Delobelle, J. Micromech. Microeng., 25 (2015) 035009.
21. J. Liu, G. Zong, L. He, Y. Zhang, C. Liu, and L. Wang, Micromachines, 6 (2015) 855.
22. M. Wehner, R. L. Truby, D. J. Fitzgerald, B. Mosadegh, G. M. Whitesides, J. A. Lewis, and R. J. Wood, Nature, 536 (2016) 451.
23. B. Li, S. Dong, X. Wu, C. Wang, X. Wang, and J. Fang, Compos. Sci. Technol., 147 (2017) 52.
24. S. Takei, A. Oshima, A. Sekiguchi, N. Yanamori, M. Kashiwakura, T. Kozawa, and S. Tagawa, Appl. Phys. Express, 4 (2011) 106502.
25. S. Takei, Appl. Phys. Express, 11 (2018) 086501.
26. S. Takei, A. Oshima, T. Ichikawa, A. Sekiguchi, M. Kashiwakura, T. Kozawa, S. Tagawa, T. G. Oyama, S. Ito, and H. Miyasaka, Microelectron. Eng., 122 (2014) 70.
27. S. Takei, H. Maki, K. Sugahara, K. Ito, and M. Hanabata, AIP Adv., 5 (2015) 077141.