Electronic Materials Letters, Vol. 4, No. 3 (2008), pp. 141-145

Characterization of Etch Resistance Property of Imprinting Resin

Seon-Yong Hwang[1], Ho-Yong Jung[1], Ki-Yeon Yang[1], Jun-Ho Jeong[2], Kyung-Woo Choi[3], and Heon Lee[1,*]

[1]Department of Materials Science and Engineering, Korea University, Seoul 136-701, Korea
[2]Nano-Mechanical Systems Research Center, Korea Institute of Machinery and Materials, Yuseong-gu, Daejeon 305-343, Korea
[3]Korea Institute of Nuclear Safety, Daejeon 305-600, Korea

Nanoimprint lithography has been intensively researched since it can fabricate nano-scale patterns on large area substrates. Thermal nanoimprinting, using a monomer-based resist has gained more interest due to its shorter process time and lower process temperature, compared to the conventional hot embossing process. A near-zero residual layer imprint process can also be done using monomer-based imprint resin, due to its low viscosity. However, the poor etch resistance of monomer-based imprint resin limits its possible applications. In this study, Methacryloxypropyl terminated Poly-Dimethylsiloxanes material was added to a monomer-based thermal imprint resin, and its effect on etch resistance and imprintability was investigated.

Keywords: nanoimprint lithography, imprint resin, etch resistance, M-PDMS (methacryloxypropyl terminated poly-dimethylsiloxanes), bi-layer imprint, benzylmethacrylate

1. INTRODUCTION

Micro- to nano-scale patterns can be formed on large area substrates using nanoimprint lithography. Thus, this technique has been intensively studied for use in semiconductor device fabrication, for the formation of photonic crystal patterns for light emitting diodes, and for applications in various MEMS and NEMS devices.[1-6] Nanoimprint lithography can be categorized into two groups, based on the imprint resin.[7-9] Hot embossing lithography uses a solid-phase thermoplastic polymer resin and patterns can be made by heating the resin above its glass temperature and pressing the imprint template on the resin layer. UV and thermal nanoimprint uses a liquid-phase monomer based imprint resin. The patterns can be formed by pressing the imprint template on the liquid-phase resin and the resin is solidified by UV illumination or heating. Because a liquid-phase resin is used, the imprint pressure can be drastically decreased, and thus near-zero residual imprinting can be done. However, a monomer-based resin has an inherently poor etch resistance compared to a polymer-based resin, and thus intensive work is being made to improve the etch resistance of imprint resin.[10]

Nano-scale metal patterns can be fabricated using nanoimprint lithography by either a direct etching method or a lift-off method.[11-12] Compared to the direct etching of a metal layer with imprinted resin, as in an etch mask, a lift-off process can make the metal patterns easily, especially with non-etchable metals. The lift-off process can be either a single-layer lift-off or a bi-layer lift-off processes. Since the undercut structured resist patterns, which assure a defect-free lift-off pattern, cannot be made by nanoimprint lithography, lifted-off metal patterns often show rabbit ear shaped defects due to a sidewall deposition of the metal. In order to avoid such a defects, the bi-layer imprint process has often been used.[13-14] In a bi-layer imprint process, the under-layer is coated on the substrate and then the imprint resin layer is coated over the under-layer. To make an undercut profile, the top imprinted resin layer must have a higher etch resistance, especially to oxygen plasma, than the under-layer.

Generally, a monomer-based imprint resin has a relatively poor etch resistance. In this study, a lift-off process, based on a bi-layer thermal imprint process, was developed. To improve the etch resistance of the imprint resin, which was based on a BMA (benzylmethacrylate) monomer, M-PDMS (Methacryloxypropyl terminated Poly-Dimethylsiloxanes) material was added, and the effects of the M-PDMS addition to etch resistance and imprint process were investigated. M-PDMS has a lower viscosity compared with other PDMS-based polymeric materials and the same reaction mechanism of the BMA. For these reasons, it was found to improve etch resistance, while near-zero residual imprinting could be achieved.

2. EXPERIMENTS

Tables 1 and 2 summarize the composition of the mono-

*Corresponding author: heonlee@korea.ac.kr

Table 1. Composition of BMA based thermally curable monomer resin

Reagent	Base Thermal Monomer Resin
Benzylmethacrylate	90%
Poly Benzylmethacrylate	7%
Trigonox 21 (thermal radical generator)	3%

mer based imprint resin used in this study and the concentration of M-PDMS, respectively. BMA was chosen as a base monomer and poly benzylmethacrylate was added to suppress the vaporization of base monomer. As a thermal-radical generator, commercially available Trigonox 21 (Akzo Nobel Polymer Chemicals Co.) was used.[15] In order to increase the etch resistance of this thermally curable monomer based imprint resin, M-PDMS was added from 0% to 15%. The imprint process used a Si template containing a pillar array 380 nm diameter and 250 nm in height, which was fabricated using DUV photolithography and a reactive ion etching process. To assure the smooth detachment of the imprint template, the template surface was coated with a hydrophobic antistiction SAM layer by dipping the template into the solution of heptadeca-fluoro-1,1,2,2-tetra-hydrodecyl trichlorosilane diluted with 1000:1 normal hexane. The details of the SAM layer coating process are explained elsewhere.[16] The imprinting process was done via a pressure vessel type imprinting system, as described elsewhere,[16] in order to achieve uniform pressing over a large area.

Figure 1 shows the developed bi-layer imprint process based on a monomer-based imprint resin. The Si wafer substrate was cleaned with a piranha solution and DI water. Then, 200 nm thick LOL™2000, made by Shipley, was spin-coated on the Si wafer and baked at 140°C for 3 min. The monomer-based imprint resin, containing varying amounts of M-PDMS, was dispensed on the surface of the baked LOL™2000. Imprinting was done at 25 atm of imprinting pressure at 120°C for 10 min.

3. RESULTS AND DISCUSSION

In order to characterize the fluidity of the imprint resist containing M-PDMS as an etch resistant agent, an imprinting process was performed using a Si wafer coated with an LOL™2000 under-layer. A Si master template containing 250 nm height submicron-sized dot array patterns and coated with an anti-stiction SAM layer was used as an imprint template. Figure 2 shows top-view and cross-sectional view SEM micrographs of the Si master template and imprinted resist patterns with varying M-PDMS addition from 0% to 15%. Regardless of M-PDMS addition from 0% to 15%, the surface protrusion patterns of the Si master template were

Table 2. Composition of imprint resins, containing varying amount of M-PDMS for etch resistance, used in this study

Reagent	Resin 1	Resin 2	Resin 3	Resin 4	Resin 5
Thermal Monomer Resin	100%	97%	95%	90%	85%
Methacryloxypropyl Terminated PolyDimethylsiloxanes	0%	3%	5%	10%	15%

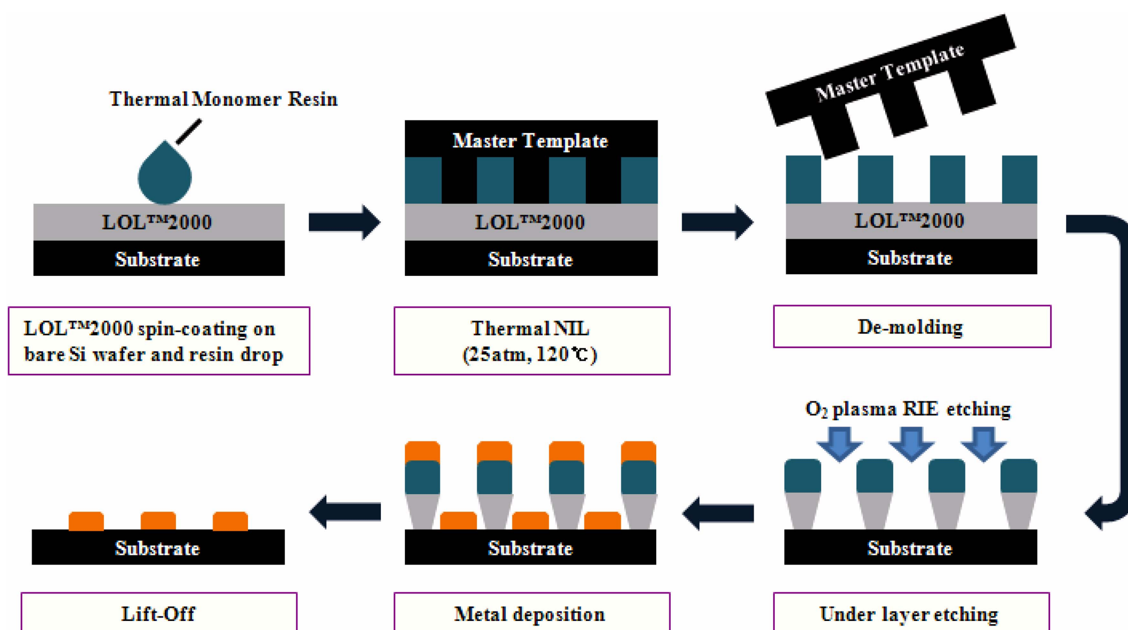

Fig. 1. Overall process procedure of bi-layer imprint process and lift-off process.

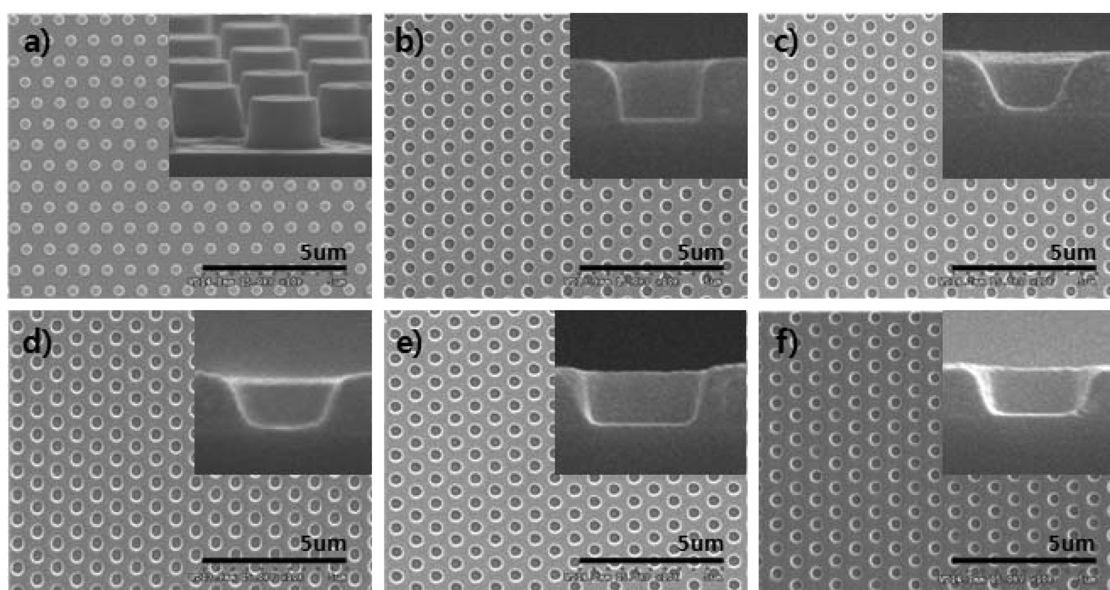

Fig. 2. SEM micrographs of a) Si Master template imprinted resist patterns of varying M-PDMS, b) 0 wt% M-PDMS, c) 3 wt% M-PDMS, d) 5 wt% M-PDMS, e) 10 wt% M-PDMS, f) 15 wt% M-PDMS.

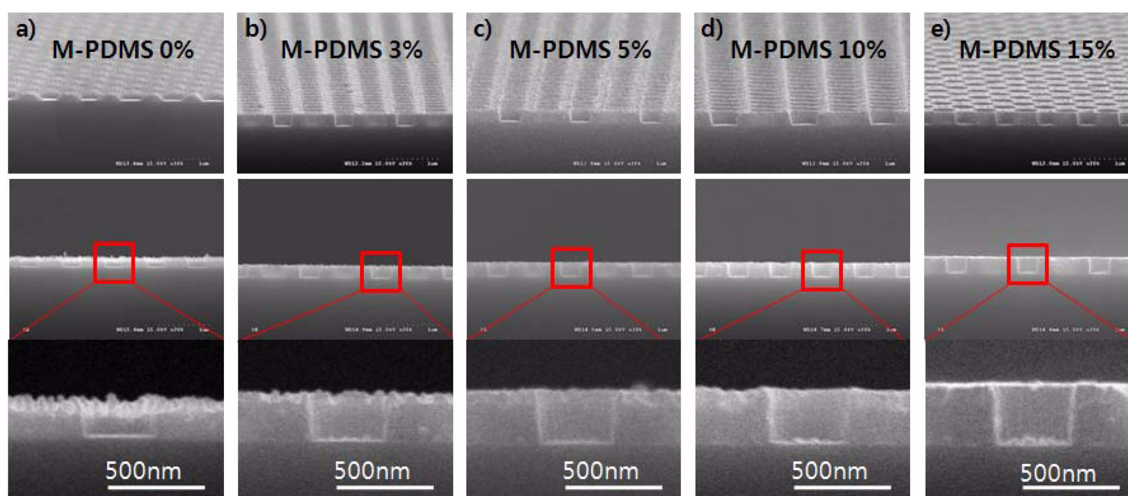

Fig. 3. Effects of M-PDMS content on etch resistance of imprinted resist pattern to oxygen plasma (100 W, 40 sccm, 40 mTorr, 50 sec). As the content of M-PDMS increases, the etch resistance to oxygen plasma is improved.

transferred to the imprinted resin layer with high fidelity and the fluidity of the imprinted resin containing M-PDMS up to 15% was sufficiently high to achieve a near zero-residual layer. This implies that the addition of M-PDMS up to 15% did not degrade the imprintability of the resin.

Etch resistance of the imprinted resin containing M-PDMS, against oxygen plasma was investigated. The oxygen reactive ion etch process was followed using a home-made RIE (Reactive Ion Etching) system and was defined as 100 W of plasma power, 40 mTorr of pressure and 40 sccm of oxygen flow rate. The etch time was fixed at 50 sec. SEM micrographs of the imprinted resist patterns formed using 0% to 15% of M-PDMS content and after the oxygen RIE process are shown in Fig. 3. It can be seen from the figure that the etch resistance of the imprinted resist pattern against oxygen plasma increased with increased M-PDMS content. The surface of the imprinted resist containing 0% M-PDMS was severely eroded. However, etching of the imprinted resist was drastically reduced with the addition of M-PDMS. Figure 4 also shows the etch rate of the imprint resin against oxygen plasma as a function of M-PDMS content. Gradual decrease of the etch rate of the imprinted resin was observed with increasing M-PDMS.

Since PDMS-based polymeric material contains Si, the element and Si can be easily oxidized with oxygen plasma and the oxidized Si can act as an etch barrier by blocking the

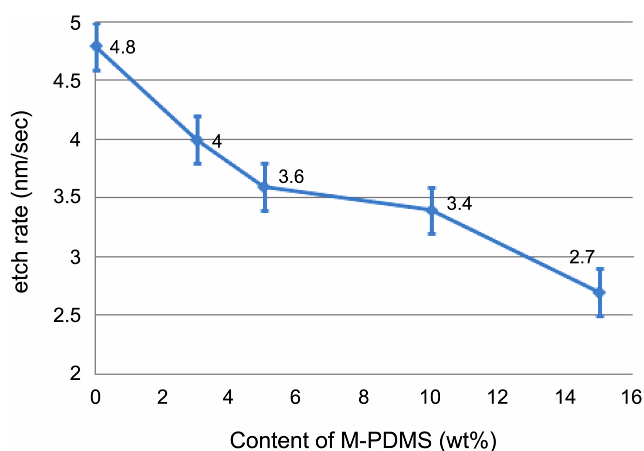

Fig. 4. Etch rate of imprint resin against oxygen plasma (100 W, 40 sccm, 40 mTorr, 50 sec) as a function of M-PDMS content.

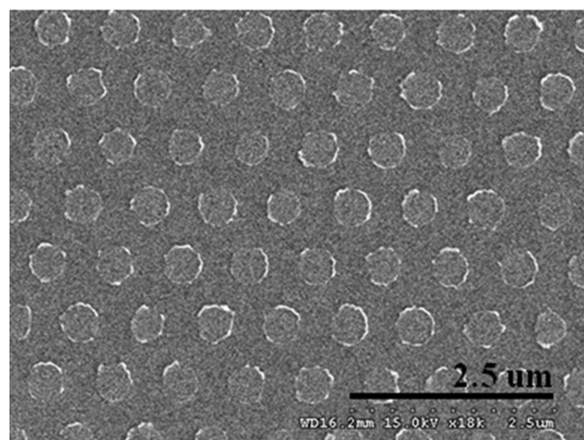

Fig. 6. SEM micrograph of lifted-off Mo metal patterns, using bi-layer imprint process. Micro-pattern of Si master template was successfully transferred to Mo metal patterns.

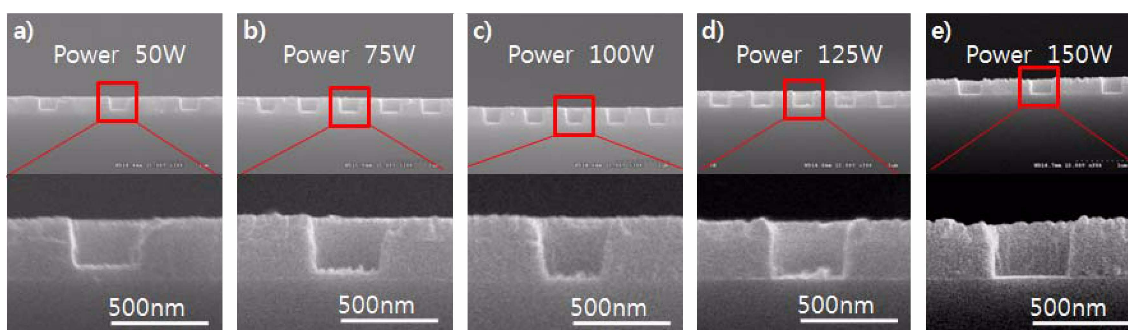

Fig. 5. The effect of plasma power on the etch rate of imprint resin with 15% of M-PDMS as an etch resistant agent. The etch rate of imprint resin, containing 15% of M-PDMS was unchanged as plasma power increases.

oxygen plasma.[17] Thus, etch resistance of the imprint resin was increased with increasing M-PDMS addition. However, imprint resin containing more than 15% of M-PDMS, the polymerization of imprint resin was impeded and, thus, M-PDMS concentration was limited to 15% in this study.

The effect of plasma power on the etch rate of the imprint resin with 15% of M-PDMS as an etch resistant agent is shown in Fig. 5. While the plasma power varies from 50 W to 150 W, the etch rate of the imprint resin was not influenced by the plasma power. While the imprint resin is not affected by the plasma power, the etch rate of LOL™2000 under-layer linearly increased with an increase of plasma power. The oxygen plasma condition was fixed as 40 mTorr of pressure and 40 sccm of oxygen flow rate for 40 sec. This result implies that the etch rate of the imprint resin was fortified by adding M-PDMS. Since the LOL™2000 under-layer can be fast etched with increased plasma power, the selectivity of the imprint resin to the LOL™2000 under-layer is increased with an increase of plasma power. In Figure 6, SEM micrograph of the lifted off Mo metal pattern is shown. A bi-layer imprint process was used. A monomer-based imprint resin containing 15% of M-PDMS was chosen as an imprint resin and LOL™2000 was selected as an under-layer. With a bi-layer imprint process, the micro-pattern of the Si master template was successfully transferred to Mo metal patterns. After imprinting, the LOL™2000 under-layer was removed via an oxygen plasma using 125 W of plasma power, which assures high selectivity to imprint resin.

4. CONCLUSIONS

An imprint resin with a high etch resistance to oxygen plasma is essential to make micro- to nano-sized metal patterns using a bi-layer imprint and a lift-off process. For an effective lift-off process, the formation of an undercut structure after imprinting is very important to transfer metal patterns with high fidelity without rabbit ear shaped defects. Such an undercut structure can be made using a high etch-resistant imprint resin. In this study, the etch resistance of a BMA monomer based imprint resin was increased by adding M-PDMS. The concentration of M-PDMS was optimized to obtain a high etch resistance to oxygen plasma and to assure high fidelity imprinting with good fluidity.

ACKNOWLEDGMENTS

This research was supported by a grant (no. 08K1401-00210) from the Center for Nanoscale Mechatronics & Manufacturing, which is one of the 21st Century Frontier Research Programs, which are supported by the Ministry of Education, Science, and Technology, Korea, and partially funded by Korea University.

REFERENCES

1. H. Lee, S. H. Hong, K. Y. Yang, and G. Y. Jung, *Microelectron. Eng*. **84**, 573 (2007).
2. V. Malyarchuk, F. Hua, N. H. Mack, V. T. Velasquez, J. O. White, R. G. Nuzzo, and J. A. Rogers, *Opt. Express* **13/15**, 5669 (2005).
3. K. J. Byeon, S. Y. Hwang, and H. Lee, *Appl. Phys. Lett*. **91**, 091106 (2007).
4. G. Luo, I. Maximov, D. Adolph, M. Graczyk, P. Carlberg, S. Nilsson, D. Hessman, T. Zhu, Z. Liu, H. Q. Xu, and L. Montelius, *Nanotechnology* **17**, 1906 (2006).
5. Y. C. Tung and K. Kurabayashi, *Appl. Phys. Lett*. **86**, 161113 (2005).
6. M. J. Lee and Y. S. Kim, *Electron. Mater. Lett*. **3**, 155 (2007).
7. S. H. Hong, J. H. Lee, and H. Lee, *Microelectron. Eng.* **84**, 977 (2007).
8. H. Lee, S. H. Hong, and K. Y. Yang, *Appl. Phys. Lett.* **88**, 43112 (2006).
9. W. C. Liao and S. L. C. Hsu, *Nanotechnology* **18**, 065303 (2007).
10. L. Jay Guo, *Adv. Mater.* **19**, 495 (2007).
11. N. V. Le, W. J. Dauksher, K. A. Gehoski, K. J. Nordquist, E. Ainley, and P. Mangat, *Microelectron. Eng*. **83**, 839 (2006).
12. K. Nakamatsu, K. Tone, and S. Matsui, *Jpn. J. Appl. Phys*. **44/11**, 8186 (2005).
13. X. Sun, L. Zhuang, W. Zhang, and S. Y. Chou, *J. Vac. Sci. Technol. B* **16/6**, 3922 (1998).
14. G. Y. Jung, W. Wu, S. Ganapathiappan, D. A. A. Ohlberg, M. Saif Islam, X. Li, D. L. Olynick, H. Lee, Y. Chen, S. Y. Wang, W. M. Tong, and R. S. Williams, *Appl. Phys. A* **81**, 1331 (2005).
15. H. Lee, S. H. Hong, K. Y. Yang, and K. W. Choi, *Microelectron. Eng*. **83**, 323 (2006).
16. H. Lee and G.-Y. Jung, *Microelectron. Eng.* **77**, 168 (2005).
17. H. Ge, W. Wu, Z. Li, G. Y. Jung, D. Olynick, Y. Chen, J. Alexander Liddle, S. Y. Wang, and R. Stanley Williams, *Nano Lett.* **5/1**, 179 (2005).