Fabrication of Replica Mold by Room Temperature Nanoimprinting using Organic Spin-on-glass

Makoto Okada^{1,3,4}, Masatoshi Maeda², Satoshi Shimatani²,
 Shoji Otaka², and Shinji Matsui^{1,3}

¹Graduate School of Science, LASTI, University of Hyogo
 3-1-2 Koto, Kamigori, Ako, Hyogo 678-1205, Japan

²Tokyo Ohka Kogyo Co., Ltd., 150 Nakamaruko, Nakahara, Kawasaki 211-0012, Japan

³JST-CREST, Sanbancho, Chiyoda-ku, Tokyo, 102-0075, Japan

⁴JSPS, 6 Ichibancho, Chiyoda-ku, Tokyo 102-8471, Japan

E-mail: m.okada@lasti.u-hyogo.ac.jp

Keywords: room temperature nanoimprinting, organic spin-on-glass, replica mold

1. Introduction

Nanoimprint lithography (NIL) can transfer the nano-patterns on the master mold into nanoimprint resin by physical contact. [1-3] It can be used effectively to fabricate nano-patterns with simple process and low cost and is therefore considered to be one of the most promising next-generation nano-patterning technologies.

A mold replication process with easy and low-cost is required to prevent the damage to a master mold. So far, the duplication of polymer molds from the master mold has been reported. [4] The polymer mold is also required a high mechanical strength because the pattern deformation of the polymer mold with a low mechanical strength is induced by a NIL with a high pressure.

Hydrogen silsesquioxane (HSQ) is a type of spin-on-glass material. As a technique to fabricate the nanostructure of the HSQ, room temperature (RT) NIL is reported. [5-8] The resin-thermal cycle and UV exposure is not needed in the RT-NIL, as shown in Fig. 1. However, we must apply a high pressure to the HSQ in this process. To reduce the imprinting pressure, the organic SOG (O-SOG) is produced from Tokyo Ohka Kogyo Co.. Although the O-SOG has the

organofunctional groups, the main chain consisted of -Si-O- bond. We therefore assume that the O-SOG has a higher mechanical strength than the polymer.

Fig. 1 Schematic of room temperature nanoimprint process.

In this study, we fabricated the replica mold of the O-SOG by RT-NIL and demonstrated the thermal nanoimprinting using the replica mold.

2. Replica mold fabrication using O-SOG

A SiO₂/Si mold was fabricated by electron beam (EB) lithography and reactive ion etching (RIE). Figure 2 shows the scanning electron microscopy (SEM) image of the line and space (L&S) pattern on the mold. The line- and space-width and height were 190, 300, and 150 nm, respectively. The L&S pattern area was 3.6 mm square on the mold.

Fig. 2 SEM image of L&S pattern on mold.

This mold was coated an antisticking layer by a dip coating. We used a silane-coupling agent with fluoropolymer (OPTOOL DSX: Daikin Industries) as the antisticking layer. [9] The dip coating process is as follows; (1) The mold is dipped into the 0.1 weight% OPTOOL DSX diluted by HD-TH (Daikin Industries) for 1min at room temperature in air atmosphere. (2) After dipping into the OPTOOL DSX, the mold is left in the high humidity atmosphere for 1h. (3) Then, to remove the multiple layers, the mold is rinsed by HD-TH for 5min.

We used OCNL540 (Tokyo Ohka Kogyo Co.) as the O-SOG. Figure 3 shows the chemical structure of O-SOG. This O-SOG has a methyl group in the polymer structure instead of the H group in the SOG. The curing speed of the OCNL540 is reduced by controlling the sol-gel reaction. The low curing speed induce to the low imprinting pressure.

Fig. 3 Chemical structure of OCNL540.

We fabricate the replica mold for thermal nanoimprinting by RT-NIL using O-SOG. The O-SOG

was spin-coated with 2000 rpm on the 15 mm square SiO₂/Si substrate. The O-SOG film thickness was about 200 nm in this case. We used the NM-0901SQ (MEISYO KIKO Co.) as a nanoimprinting system. The imprinting pressure and time were 15 MPa and 2 min, respectively. Figure 4(a) shows the SEM image of the L&S pattern on the O-SOG. The pattern was clearly imprinted

To demonstrate thermal nanoimprinting using the O-SOG replica mold, the replica mold was coated with the antisticking layer by above dip coating process. However, the imprinted O-SOG pattern was disappeared after leaving in the high humidity atmosphere. We assumed from this result that the imprinted O-SOG pattern was removed by the water because the O-SOG was not perfectly cured by RT-NIL. We therefore tried to dip the imprinted O-SOG pattern into the water.

(a)

(b)

Fig. 4 SEM image of (a) imprinted O-SOG pattern.
(b) post-baked O-SOG pattern.

As the result, the O-SOG pattern and layer were clearly removed. This indicates that the imprinted O-SOG pattern must be cured before the dip coating process of the antisticking layer. To resolve this issue,

we carried out post-baking at 120 °C for 2 min. The pattern shrinkage was not occurred by this baking process, as shown in Fig. 4(b). We confirmed that the post-baked O-SOG pattern was maintained after dipping into the water. This result indicates that the O-SOG was cured by post-baking. In fact, we were able to carry out the dip coating process of the antisticking layer for the post-baked O-SOG replica mold.

3. Thermal nanoimprinting using O-SOG replica mold

We next demonstrated the thermal nanoimprinting using the O-SOG replica mold. NEB-22 (Sumitomo Chemical Co.) was used as a thermal nanoimprint resin. The NEB-22 was spin-coated on the Si substrate and, then, this substrate was prebaked at 110 °C for 2 min. The mold and substrate temperatures increased by 150 °C during thermal nanoimprinting. The imprinting pressure and time were 20 MPa and 60 sec, respectively. After cooling process, the mold was demolded from the NEB-22/Si substrate. The L&S pattern was successfully transferred onto the NEB-22, as shown in Fig. 5(a).

Fig. 5 SEM image of (a) imprinted NEB-22 pattern by thermal nanoimprinting using O-SOG replica mold. (b) 40th imprinted NEB-22 pattern by step and repeat thermal nanoimprinting.

In the nanoimprinting process, the adhesion force between the O-SOG and SiO₂/Si substrate is an important factor because the replica mold must be in direct contact with the resin. If this force is small, the O-SOG pattern was separated from the substrate during nanoimprinting process. To evaluate the adhesion force between the O-SOG and SiO₂/Si substrate, we demonstrated step and repeat thermal nanoimprinting using the O-SOG replica mold. The imprinting pressure was 20 MPa. The mold and substrate temperatures were 180 and 90 °C, respectively. Figure 5(b) shows the SEM image of the 40th imprinted pattern. The pattern was clearly imprinted on the NEB-22. Furthermore, after 40 times of repeated nanoimprinting, the O-SOG pattern was not separated from the SiO₂/Si substrate. We confirmed from this result that the adhesion force between the O-SOG and SiO₂/Si substrate is sufficient to carry out the thermal nanoimprinting.

4. Conclusion

We proposed the replica mold fabrication using the O-SOG. The pattern was imprinted on the O-SOG with RT-NIL. We demonstrated thermal nanoimprinting using the O-SOG replica mold with the antisticking layer. The pattern was successfully imprinted on the NEB-22. In addition, we were able to carry out 40 times of repeated thermal nanoimprinting using the O-SOG replica mold.

References

- 1) S. Y. Chou, P. R. Krauss, and P. J. Renstrom: *Appl. Phys. Lett.* **67** (1995) 3114.
- 2) S. Y. Chou, P. R. Krauss, and P. J. Renstrom: *Science* **272** (1996) 85.
- 3) S. Y. Chou, P. R. Krauss, W. Zhang, L. Guo, and L. Zhuang: *J. Vac. Sci. Technol. B* **15** (1997) 2897.
- 4) Y. Kawaguchi, F. Nonaka, Y. Sanada: *Microelectronic Engineering*, **84** (2007) 973.
- 5) S. Matsui, Y. Igaku, H. Ishigaki, J. Fujita, N. Ishida, Y. Ochiai, M. Komuro, and H. Hiroshima: *J. Vac. Sci. Technol. B* **19** (2001) 2801.
- 6) S. Matsui, Y. Igaku, H. Ishigaki, J. Fujita, N. Ishida, Y. Ochiai, H. Namatsu, M. Komuro, and H. Hiroshima: *J. Vac. Sci. Technol. B* **21** (2003) 688.
- 7) K. Nakamatsu, K. Watanabe, K. Tone, T. Katase, W. Hattori, Y. Ochiai, T. Matsuo, M. Sasago, H. Namatsu, M. Komuro, and S. Matsui: *Jpn. J. Appl. Phys.* **43**

(2004) 4050.

8) K. Nakamatsu, K. Watanabe, K. Tone, H. Namatsu, and S. Matsui: *J. Vac. Sci. Technol. B* **23** (2005) 507.

9) Y. Hirai, S. Yoshida, A. Okamoto, Y. Tanaka, M. Endo, S. Irie, H. Nakagawa, and M. Sasago: *J. Photopolym. Sci. Technol.*, **14** (2001) 457