Thermal roll-to-roll nanoimprinting using a replica mold without release agent

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Received: 10 April 2018; Revised: 27 July 2018; Accepted: 19 August 2018

Abstract

Thermal roll-to-roll nanoimprint (T-R2RNIL) using a flexible replica mold made of a special UV-curable resin was demonstrated. This UV-curable resin is able to be used for the nanoimprint process without a release agent. In this study, we examined the relationship between the hardness of the UV-curable resin and the transfer performance using flexible replica molds made of three types of UV-curable resins. The experimental result found that one special resin is a good candidate for fabrication of a replica mold for T-R2RNIL because of its high hardness and good release properties.

Keywords : Thermal roll-to-roll nanoimprint, Replica mold, UV-curable resin, Release agent-free, Thermoplastic pattern

1. Introduction

Ultraviolet nanoimprint lithography (UV-NIL) (Haisma et al., 1996) and thermal nanoimprint lithography (T-NIL) (Chou et al., 1996) are expected to be the patterning techniques of the next generation for fabricating nanopatterns with high throughput. The UV-NIL method uses UV-curable resins and permits a very high throughput [e.g., 18 m/min with UV roll-to-roll NIL (R2RNIL)] at a nanoscale resolution (Yoshikawa et al., 2013). This is possible because of the short curing time of the UV-curable resin. On the other hand, the material cost of the UV resins is expensive, and there is little flexibility in the material design. In contrast, thermal NIL (T-NIL), in which thermoplastics are used as transfer substrates, permits the fabrication of nanopatterns at low cost because thermoplastics are much cheaper than UV resins. Furthermore, unlike the case of UV-curable resins, a wide choice of thermoplastics with desirable properties such as superior transparency, chemical durability, or high hardness is available. In the case of the T-NIL process, the master molds that are normally used are made from silicon or quartz substrates because of their high resolution (Guo, 2004; Landis et al., 2006; Zhao et al., 2009; Park et al., 2009). However, the cost of fabricating such master molds is high, because it typically involves complex processes such as electron-beam lithography, metal deposition and lift-off, and dry etching. In addition, silicon and quartz substrates are not flexible, so it is difficult to perform thermal R2RNIL (T-R2RNIL) by using the master mold. Therefore, replica molds produced by nickel electroplating are used in the T-R2RNIL process to permit high-throughput nanopatterning (20 m/min) (Mäkelä et al., 2011). Although nickel replica molds are widely used (Maury et al., 2011; Ogino et al., 2013; Wu et al., 2013) because they have a high resolution and do not require any release agent, the time for the electroplating process is comparatively long.

In this study, we performed T-R2RNIL by using a replica mold made of a special UV-curable resin [PARQIT OEX-028-X433-3 (AUTEX, INC; referred to hereafter as X433)]. We previously reported that a replica mold fabricated from X433 shows a high performance in a UV-NIL process using heating gun (Moro and Taniguchi, 2015). The UV-cured resin has a high hardness (pencil hardness 4H), and the fluorinated component present in X433 segregates at the surface of the cured resin after heat treatment, permitting its use in a release-agent-free NIL process.

We examined T-R2RNIL by using three types of UV-curable resin [X433, PAK-01-CL (Toyo Gosei Co.; hereafter PAK) and ETAX-003XC (AUTEX, INC; hereafter ETAX)], and we investigated the relationship between the hardness

of the UV resin and the transfer performance. As a result, it became clear that X433 is a good candidate for the T-R2RNIL process, because of its high hardness and good release properties.

2. Experimental apparatus and procedure

2.1 Hardness testing of the UV-curable resins with a nanoindenter

Figure 1 shows the method for preparing samples for a hardness test with a nanoindenter (DUH-211, Shimadzu Co.). First, a silicon wafer and a glass slide were cleaned with acetone and ethanol in an ultrasonic bath. The cleaned silicon wafer was subsequently coated with a release agent (Optool DSX, Daikin Industries Ltd.) and the test resin was poured on the coated silicon wafer [Fig. 1(a)], pressed against the glass slide at 125 N [Fig. 1(b)], and cured by UV irradiation. Finally, the glass slide with the attached layer of cured resin was released from the silicon wafer [Fig. 1(c)]. We prepared approximately 6- μm -thick cured layers of X433, PAK, and ETAX on glass slides and measured their Martens hardness with a nanoindenter at a loading rate of 0.488 mN/s [Fig. 1(d)]. The test force was set to 0.1 or 0.3 gf, so that the tip of nanoindenter did not reach the glass surface.

Fig. 1 Method for the preparation of samples for hardness testing with the nanoindenter. The thickness of the layer of UV-curable resin was about 6 μm .

2.2 Thermal nanoimprinting with replica molds made of UV-curable resins

Figure 2 shows the process for fabrication of replica molds made of UV-curable resins. By using a silicon master mold produced by electron-beam lithography, a transparent mold was fabricated from PAK. At first, PAK was poured onto the silicon master mold [Fig. 2(a)] and covered with a polyester film. Next, UV-NIL was carried out [Fig. 2(b)] at a force of 125 N for 1 cm^2 and a UV dose of 400 mJ/cm^2 . After UV curing, the polyester film was released from the mold along with the duplicated patterns of cured PAK [Fig. 2(c)]. At this stage, the silicon mold was coated with a release agent. We also prepared self-standing films of X433 by placing a drop of X433 between polypropylene films [Fig. 2(a')] and pressing the X433 layer at 125 N [Fig. 2(b')]. After curing the layer of X433 at a UV dose of 3000 mJ/cm^2 , the polypropylene films were both carefully released [Fig. 2(c')] to give a self-standing film of X433. Finally, UV-NIL was carried out by using the fabricated transparent mold on the self-standing film of X433. As a result, a self-standing replica mold consisting solely of X433 was obtained [Figs. 2(d)–(f)]. The shrinkage coefficient during UV-curing of a bulk film made of X433 is 4–5 % that is similar to a conventional UV curable resin. We prepared two line-and-space (LS) patterns, one with a space width of 0.68 μm , and a line width of 0.37 μm (nanoscale mold), and the other with a space width of 1.2 μm , and a line width of 0.70 μm (micronscale mold). The patterned area of the LS patterns measured 450 $\times$ 580 μm . We similarly fabricated replica molds made of PAK or ETAX.

Fig. 2 The fabrication process for replica molds made of UV-curable resin. UV-NIL was carried out on a self-standing film made of the same resin, so that a self-standing replica mold consisting exclusively of UV-curable resin was obtained.

Fig. 3 T-NIL process using the replica mold on a 20-μm-thick nickel film. The self-standing replica mold was attached to the nickel film by using an adhesive agent.

Fig. 4 Measurement three points by using AFM of the mold and the obtained pattern. We examined ten heights at each measurement point and the total AFM data of 30 were used to calculate the average height.

Next, the resulting replica mold was fixed to a 20- μm -thick nickel film by using an adhesive agent, and we performed T-NIL as shown in Fig. 3. First, an adhesive agent was poured onto a nickel film and pressed against a glass slide at 125 N. The adhesive agent was then dried for 10 minutes at room temperature and T-NIL was performed by using the resulting sample and a 125- μm -thick film of poly(methyl methacrylate) (PMMA). The conditions for the T-NIL process were as follows: force, 715 N per 1 cm^2 of nickel film; temperature, 120 $^{\circ}\text{C}$; process time, 5 min. In the case of the X433 film, the replica mold was not coated with any release agent. The pattern obtained on the PMMA film was examined by atomic-force microscopy (AFM; SPM-9600, Shimadzu Co.) and by scanning electron microscopy (SEM; ERA-8800FE, ELIONIX Inc.) We measured the height of the imprinted pattern ten times at three different areas by using AFM. Figure 4 shows the measurement points for AFM. The average height was then calculated using 30 AFM data in this study.

2.3 Thermal roll-to-roll nanoimprinting by using a replica mold fixed to a thin nickel substrate

T-R2RNIL was examined by using replica molds, in a similar manner to the planar T-NIL process. Figure 5 shows our T-R2RNIL equipment, which consisted of a heating roll, a backside press roll, and a driving unit for the plastic web (Mäkelä et al., 2011, Unno et al., 2014). Both rolls were 66 mm in diameter and 60 mm wide. In this study, the upper roll was heated by an internal electrical heater, whereas the lower roll was unheated. The nickel film carrying the replica mold made of the UV resin was wrapped on the upper roll. A constant driving speed was maintained by a motor installed in the upper roll, and the lower roll rotated following the upper roll. The imprinting force was applied by an air cylinder that pressed the lower roll against the upper roll. Since the glass transition temperature (T_g) of X433 was almost 166 $^{\circ}\text{C}$, we examined T-R2RNIL at various surface temperatures below 150 $^{\circ}\text{C}$ of the wrapped nickel film with both the PMMA film and a 90 μm -thick film of cellulose acetate (CA). Since the T_g of PMMA and CA were lower than that of X433, it was possible to perform T-R2RNIL using a replica mold made of X433 in this study.

Fig. 5 Schematic view of our T-R2RNIL equipment. The upper roll was heated by an internal electrical heater, whereas the lower roll was unheated. The nickel film with the replica mold was wrapped on the upper roll.

3. Results and discussion

Table 1 shows the hardness of X433, PAK, and ETAX as measured the nanoindenter. We measured the hardness at test forces of 0.1 and 0.3 gf, and Fig. 6 shows the typical force curves. The hardest UV resin was X433, followed sequentially by PAK and ETAX. As shown in the figure, the depth of indentation was less than the thickness of the UV resin; we therefore believe that the obtained hardness were reasonable values and that similar trends would be observed even if the pattern width of the UV resins was at the nanoscale.

Table 1 Hardness of X433, PAK, and ETAX, as measured with a nanoindenter. The hardest UV resin was X433, followed successively by PAK and ETAX.

UV-curable resins	Martens hardness[N/mm ²]	
	Test force [gf]	
	0.1	0.3
ETAX-003XC	1.6 ± 0.1	3.5 ± 0.1
PAK-01-CL	82.3 ± 2.7	78.9 ± 3.5
PARQIT OEX-028-X433-3	162.2 ± 3.9	161.2 ± 1.5

Fig. 6 Typical force curves measured by the nanoindenter. The tip of the indentation did not touch to the substrate, as the maximum penetration depth was ~5 μm.

Figure 7 shows cross-sectional views of the replica molds before and after the planar T-NIL process. Although X433 does not require the release coating, we coated all the replica molds with a thin layer of platinum and a release agent (Yoshikawa et al., 2013) because identical conditions were required for the purpose of a comparative test. In this technique, the obtained pattern made of a UV curable resin by UV-NIL is coated with the platinum layer of 10 nm. The platinum surface is then coated with a release agent (Optool DSX, Daikin industries, LTD.) After baking at 120 °C for 15 min, the coated surface has a good release property in the UV-NIL process. The height of the PAK molds decreased to almost a half after T-NIL, whereas that the X433 molds changed by only about 8%. In contrast, the ETAX mold was stretched after the T-NIL process. It appeared that the ETAX mold was too soft and deformed easily.

Fig. 7 Cross-sectional AFM views of the replica molds before and after the planar T-NIL process. The height of X433 molds changed by only about 8%.

Figure 8 shows the patterns on PMMA obtained by using each mold and the patterned height on the PMMA film with the X433 mold was higher than that with the PAK mold or the ETAX mold. Let us focus on the heights of imprinted patterns using the three replica molds. With the ETAX mold, although there was no deformation before and after T-NIL process, the height of imprinted pattern was less than half of the height of the ETAX mold. This is because the ETAX mold was deformed when the pressure was applied in the imprint process. After unloading the imprint pressure, the height of ETAX mold was able to be recovered because of its softness. With the PAK mold, the height of imprinted pattern was also lower than the height of PAK mold and it appeared that the PAK mold was also deformed in the imprint process. Since the X433 mold has a higher hardness than the PAK mold, in contrast, the imprinted pattern with the X433 mold was higher than that with the PAK mold. In this study, the height variation of the pattern height is observed resulting from the height of master mold.

Fig. 8 The PMMA patterns obtained by using each mold in a planar T-NIL process. The X433 replica mold showed a good performance in pattern transfer.

Consequently, it became clear that the hardness of the replica mold is very important in relation to the T-NIL process and that X433 is a good candidate for this process. However, the linear expansion coefficient of X433 at bulk state is $2.3 \times 10^{-4} \text{ K}^{-1}$, which is larger than that of nickel. Therefore, although the mold design considering the thermal expansion will be needed when X433 was used, we believe that it is possible because the obtained pattern width in the planar T-NIL test by using the X433 mold did not greatly differ from the mold pattern width.

Next, we examined T-R2RNIL by using the X433 replica molds with micro- and nanospaced LS patterns. The driving speed was controlled at a constant 0.2–0.3 m/min and the imprinting force was 600 N in this case. Figure 9 shows the relationships between the surface temperature and the patterned features on the PMMA film with X433 replica molds. We did not heat up the process temperature to the T_g of PMMA in this study. We have already reported that the mold was not filled completely with a plastic film when the process temperature was much lower than the T_g of a plastic film (Unno et al., 2014). Figure 9 also shows that the height of the obtained pattern was less than that of the mold. Moreover, the height was increased with increasing the process temperature. Note that the thermal expansion of PMMA was not main reason of the height change. As a result, the patterned features on the PMMA film was obtained using with X433 replica molds without any release agent. Except for the case of 130 °C, the pattern height increased with increasing surface temperature.

Fig. 9 Relationships between the surface temperature and the patterned features on the PMMA film with X433 replica molds: (a) nanoscale space mold, (b) microscale space mold.

Figure 10 shows Dynamic mechanical analysis (DMA) of the PMMA film. E' , E'' and $\tan \delta$ represents the storage modulus, loss modulus and loss tangent, respectively. The hardness of a material depends on E' and $\tan \delta$ is a factor of viscoelasticity. When the temperature was rise up to 130 °C, the slope of E' was changed and $\tan \delta$ reached its peak. This is probably because the transfer property of the obtained pattern was not linear at 130 °C. We intend to examine details of this phenomenon in our future work. The line and space widths were almost constant when the surface

temperature was less than 133 °C. However, the line and space widths changed at temperatures close to 147 °C, probably as a result of reflow of the PMMA pattern after releasing the mold. The heights of the X433 mold before and after the T-R2RNIL process were 570 ± 3 nm and 560 ± 3 nm, respectively. As a result, the X433 replica mold was still usable after about 100 imprints at 150 °C, as shown in figure 11.

Fig. 10 Dynamic mechanical analysis (DMA) of the PMMA film. It appears that the trend changed at about 130 °C, which is close to the peak of the loss factor ($\tan \delta$, blue line).

Fig. 11 AFM image of the X433 replica mold after 100 imprints.

Figure 12 shows the relationships between the surface temperature and the patterned features on the CA film with X433 replica molds and no release agent. It is clear that the pattern height decreased markedly at 134 °C. We had already observed this phenomenon when using a nickel replica mold and the CA film (Unno et al., 2014), and the cross-section of the resulting CA patterns in this study showed a similar trend, as shown in Fig. 13. The temperature at

which a decrease in the pattern height was observed was shifted upwards when the X433 mold was used, possibly as a result of the difference in thermal conductivity of nickel and X433. Although the process temperature of the X433 mold was increased compared with that for the nickel replica mold and the height of the transferred pattern was not equal to the mold height, we nevertheless succeeded in fabricating a nanoscale LS pattern, because the X433 replica mold was tolerant to high temperatures up to 150 °C in this study. Further optimization of T-R2RNIL conditions will be needed to increase the pattern height.

Fig. 12 Relationships between the surface temperature and the patterned features on the CA film with X433 replica molds: (a) nanoscale space mold, (b) microscale space mold. The patterned height decreased markedly at 134 °C.

Consequently, we used one replica mold made of X433 to investigate the transfer characteristics of the T-R2RNIL process. Although the pattern height of the X433 mold was decreased by 8 %, it seemed that the mold was not broken after the T-R2RNIL examination at the temperature of below 160 °C (over 20 imprints). In the future, we will investigate what mainly causes the deformation of the X433 mold: heat shrinkage or imprint pressure. Moreover, the durability and reproducibility of the X433 mold should be investigated.

Fig. 13 AFM cross-section of the CA patterns obtained in this study. At near the glass-transition temperature, the pattern height decreased, as observed in our previous study with a nickel replica mold (Unno et al., 2014).

4. Conclusion

We examined T-NIL with replica molds made by three types of UV-curable resin: X433, PAK-01-CL, and ETAX. When we examined the relationships between the hardness of the UV resin and the transfer performance, it became clear that X433 is a good candidate for the T-R2RNIL process, because of its high hardness and the good release properties without any release agent. We also performed T-R2RNIL by using an X433 replica mold and showed that it was still usable after ~100 imprints at 150 °C. Although the process temperature of the X433 mold was higher than that for the nickel replica mold, we nevertheless succeeded in fabricating a nanoscale LS pattern by the T-R2RNIL process using a replica mold made of the UV-curable resin. We believe that our technique will be helpful in reducing costs of molds for T-R2RNIL.

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