Transparent Crosslinked PTFE Mold Fabrication and Nano-/Micro-Pattern Transfer to Photo-Curable Resin

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Nano-/micro-scale structures of transparent crosslinked polytetrafluoroethylene (RX-PTFE) mold have been fabricated by combined process which is thermal and radiation process for fabrication of RX-PTFE (TRaf process). The nano-/micro-fabricated RX-PTFE were attempted to be applied for the transparent polymer molds of UV nanoimprint lithography (NIL). The ability of the RX-PTFE mold for UV-NIL was evaluated by the imprinted patterns. The RX-PTFE molds and the imprinted structures obtained by UV-NIL were observed by a field emission scanning electron microscope (FE-SEM). As a result, imprinted structures of photo-curable resin (Trimethylolpropane-triacrylate: TMPTA) by UV-NIL using RX-PTFE mold were successfully obtained. The nano-scale L&S patterns, square (410 nm × 410 nm) and hole (φ 170 nm) array patterns were clearly obtained.

Keywords: Crosslinked PTFE, UV-NIL, Transparent polymer mold, TRaf process

1. Introduction

Nanoimprint lithography (NIL) technique has been realized for duplicating nano-/micro-scale structures with higher throughput and lower cost than the conventional photolithography [1]. Generally, it has been well-known that there are three types of methods for the NIL: the thermal, UV light curing and electron beam curing and modification. The molds for thermal-NIL are mainly made of metals or ceramics, such as Ni, Si, SiO2 and Al2O3, and the thermoplastic polymer or thermo curable monomers are used. It has a wide choice of the imprinted matrix. However, it takes a long time for heating and cooling treatment of them, because it is often carried out at high pressure and high temperature which would be over the glass transition temperature or melting temperature of them [2-4].

On the other hand, quartz is often used as the molds for UV-NIL, because they must have the good UV light (e.g. 254 nm, 365 nm and 436 nm) transmittance. It also requires the photo-initiator in the resin. The UV-NIL can be carried out at mild condition such as lower temperature and lower pressure, compared with the thermal-NIL [5-7]. EB-NIL can cure the monomer (or oligomer) without photo-initiator, and can modify the characteristics of polymer. Moreover, it does not need any requirements, as is the case of UV-NIL, for the mold materials [8, 9]. Poly(tetrafluoroethylene) (PTFE), have been widely applied for various industrial fields because of its excellent characteristics, such as high chemical stability, thermal durability, and low adhesive property, and so on. Furthermore, it is confirmed that the crosslinked PTFE (RX-PTFE) has been obtained with irradiation of ionizing radiation such as electron beam (EB) and γ-rays under its molten state under oxygen-free atmosphere [10-12]. The properties were very much improved by network formation, which showed the high optical transparency and high abrasion durability, and so on [13]. For example in the case of crosslinking dose with 3MGy, RX-PTFE shows high transparency more than 90% from ultra-violet (300 nm) to near infrared (900 nm) region.

In this study, the nano-/micro-fabricated RX-PTFE obtained by combined process, which is

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thermal and radiation process for fabrication of RX-PTFE (TRaf process [14]) was attempted to be used as the transparent polymeric mold for the UV-NIL.

2. Experimental procedure

The UV-NIL patterning process for this study is schematically shown in Fig. 1. The process consists of three steps. First step is the nano-/micro-scale fabrication of RX-PTFE using TRaf process. Second step is UV light exposure for the resin curing. Final step is removal of the cured resin from the RX-PTFE mold.

![Fig. 1 UV-NIL process](image)

2.1 RX-PTFE molds fabricated by TRaf process

PTFE dispersion (FLUON® XAD911, average diameter: φ 250 nm, 60 wt%, ASAHI GLASS Fluoropolymers) was used for the experiments.

The nano-/micro-scale transparent RX-PTFE molds were fabricated by TRaf process [14]. This process consists of three steps. First step is spin-coating of PTFE dispersion on fabricated Si mold which were fabricated by EB lithography technique and RIE. The fabricated patterns of the structure on Si mold are line & space, square, dot/hole patterns. The spin-coating speed for PTFE dispersion and duration time were 800 rpm and 60 s, respectively. Second step is the crosslinking treatment of PTFE and the fabricating of nano-/micro-structures using EB irradiation. The irradiation was carried out using low energy EB accelerator (Curetron®, NHV Corp., accelerating voltage: 200 kV, beam current: 1 mA, installed at RISE, Waseda University), as described in our previous paper [15]. Final step is removing nano-/micro-patterned RX-PTFE from Si mold.

2.2 UV-NIL process for TMPTA

Trimethylolpropane-triacrylate monomer (TMPTA, ARAKAWA Chemical) with three double bonds (C=C=CH2) was used for the UV-NIL process. The viscosity of TMPTA monomer is reported to be about 100 mP·s at 25 °C. In the case of UV-NIL process, it is necessary to add a photo-initiator in TMPTA. IRGACURE®907 (Chiba Japan) was selected as the photo-initiator for UV curing. The UV curable resin was prepared by mixing TMPTA (95 wt%) and IRGACURE®907 (5 wt%). The prepared resin was dropped with amount of about 1 µL on the RX-PTFE mold. The glass (18 x 18 mm², 100PCS, MATSUNAMI) with the thickness of 150 µm was covered the resin on the mold. The samples were exposed by UV light (HB100A-1, SEN LIGHTS) in the ambient condition. The center wavelength of the UV light was 365 nm, and the exposure dose was 1095 mJ cm⁻². After the exposure, the cured resin was removed from the RX-PTFE molds, and imprinted structures were obtained on the glass sheet.

2.3 Measurements

To evaluate the transparent polymeric mold for UV-NIL, the optical transparency of spin-coated RX-PTFE was measured by Ultra Violet - Visible light spectroscopy (UV-vis spectrometer, V-630, JASCO).

Si molds, RX-PTFE molds fabricated by Traf process and the imprinted structures fabricated by UV-NIL were observed by a field emission scanning electron microscope (FE-SEM, S-4500S, HITACHI) for measuring line edge roughness (LER) and shrinking ratio of imprinted structures. The LER means that how rough the straight line against to the structure. LER is determined with three times amount of root-means-square (3r) deviation. Furthermore, as the space (line) width of imprinted structures correspond to line (space) one of the RX-PTFE mold, the shrinking ratio was defined by line shrinkage ratio between the space width of the molds and line width of imprinted structures.

3. Results and discussion

3.1 RX-PTFE molds fabricated by TRaf process

Figs. 2 and 3 show the FE-SEM images of Si molds and RX-PTFE molds fabricated by TRaf process, respectively. The controlled fine structures of nano-/micro-scale patterns were obtained on the RX-PTFE molds.

In the case of line and space (L&S) patterns shown in Figs. 2 and 3, the depth of fabricated Si mold (Fig. 2 (a) and (b)) is corresponding to the height of the fabricated RX-PTFE (Fig.3 (a) and (b)). Both the depth and height showed about 250 nm. Table 1 shows the list of the obtained values including the LER for the Si mold and the fabricated RX-PTFE mold using TRaf process. For the Si mold (Fig.2 (a)), the L&S widths show 800
nm and 600 nm, respectively. As seen in Figs 2(a) and 3(a), both pitch sizes of Si mold and fabricated RX-PTFE mold of were about 1400 nm. In case of the corresponding L&S widths of fabricated RX-PTFE were about 860 nm and 540 nm, respectively. Moreover, as seen in Fig 2 (b), L&S widths of Si show 820 nm and 360 nm, respectively. Moreover, as seen in Fig 2 (b), L&S widths of RX-PTFE were 840 nm and 320 nm, respectively, and both pitch sizes of Si and RX-PTFE are 1180 nm. By TRaF process, it was found that RX-PTFE shrink ratio was about 10%.

On the other hand, for square and hole matrix patterns, the depth of fabricated Si mold (Fig 2 (c) and (d)) were 160 nm and 110 nm respectively, and the height of RX-PTFE (Fig.3 (c) and (d)) showed also 160 nm and 110 nm, respectively. Average square size of Si mold (Fig.2 (c)) was 430 nm × 430 nm, and average diameter of Si mold (Fig.2 (d)) was 170 nm. From Fig.3 (c) and (d), square size and dot diameter of fabricated RX-PTFE were 410 nm ×410 nm, and 170 nm, respectively. It is found that fabricated dot structure on RX-PTFE mold which is smaller than average diameter of PTFE powder (250 nm) could be fabricated by TRaF process successfully.

3.2 Transparent RX-PTFE mold

Fig. 4 shows UV-vis spectra of PTFE and prepared RX-PTFE (EB dose for crosslinking: 600 kGy). The thicknesses of PTFE and RX-PTFE were about 1 μm. It is found that optical transparency of the RX-PTFE is higher than that of PTFE from 200 nm to 600 nm. Then, UV light (i-line: 365 nm) went through a RX-PTFE (600 kGy) adequately. Thus, the RX-PTFE which was made of PTFE dispersion could be used as a transparent polymeric mold for UV-NIL. Due to the thickness of 1 μm, the interference effect of light occurred at near IR region (900 nm) as shown in Fig. 4.

3.3 UV-NIL

Fig. 5 shows the FE-SEM images of the imprinted structures on the glass substrate obtained by UV-NIL process. The curing period of UV-NIL was 5 minutes, and the temperature of sample showed about 60 °C. The temperature was elevated by UV-light exposure. The nano-scale L&S patterns, square and hole patterns were obtained by the UV-NIL. The nano-scale patterns on glass substrate were the cured polymer based on TMPTA. There is no crack in the imprinted structures. It is found that the profiles of obtained structures were very smooth.

Fig.2 Si molds (a) wide line & space pattern, (b) narrow line & space pattern, (c) square pattern, (d) hole pattern

Fig.3 RX-PTFE molds (a) wide line & space pattern, (b) narrow line & space pattern, (c) square pattern, (d) dot pattern

Fig.4 UV-vis results for PTFE and RX-PTFE (600 kGy) films fabricated by EB irradiation.
For the L&S patterns, the depths of imprinted TMPTA structures by UV-NIL (Fig. 5 (a) and (b)) were 250 nm, which was as same as the height of the RX-PTFE molds, i.e., it was indicated that photo-curable-resin could reach the bottom of the RX-PTFE molds due to low viscosity less than 100 mP·s at 60 °C. Table 2 summarizes their widths of lines and their spaces, shrinking ratio and LER of RX-PTFE molds and imprinted TMPTA structures by UV-NIL.

The L&S widths of imprinted TMPTA show 850 nm and 550 nm, respectively, as seen Fig.5 (a) and shown in Table 2. Pitch size of imprinted TMPTA is 1400 nm, as same as those of Si and RX-PTFE. Furthermore, L&S widths of imprinted one show 850 nm and 330 nm, respectively, as seen in Fig. 5 (b), and pitch size is 1180 nm, as equivalent to those of Si and RX-PTFE. These values are corresponding to L&S widths of RX-PTFE mold. By the UV-NIL process, it is evaluated that TMPTA shrinking ratio was about 1.2 %.

In the case of square and hole matrix patterns, the depth of imprinted TMPTA were 160 nm and 110 nm respectively, as seen in Fig. 5 (c) and (d). The depth corresponds to the height of RX-PTFE were same values. The square size and hole diameter of imprinted one were 410 nm × 410 nm, and 170 nm, respectively. For square structure, it is found that TMPTA shrinking ratio was about 4.7% by the UV-NIL process. The shrinking ratio of square pattern is larger than that of L&S patterns. On the contrary, in the case of hole structure, TMPTA hardly observes the shrinking. Thus, the shrinking ratio might be depended on mold structure.

Thus, the UV-NIL process using transparent nano-/micro- RX-PTFE molds fabricated by TRAf process was succeeded without any the release materials on the surface of the mold.

4. Conclusion
Nano-/micro-scale structures of Si mold were fabricated by EB lithography technique. After that, nano-/micro- scale structures of the RX-PTFE were fabricated by TRAf process. The obtained structures of RX-PTFE were attempted to be used as the transparent polymeric molds for UV-NIL. It is found that nano-/micro- structure of transparent RX-PTFE

![Fig.5 imprinted structures obtained with UV-NIL process. (a) wide line & space pattern, (b) narrow line & space pattern, (c) square pattern, (d) hole pattern](image)

Table 1 Widths of line & space, shrinking rate and LER of Si molds and obtained RX-PTFE mold.

<table>
<thead>
<tr>
<th>Pattern</th>
<th>Space Width (nm)</th>
<th>Line Width (nm)</th>
<th>Pitch (nm)</th>
<th>Shrinking ratio (%)</th>
<th>LER (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a)</td>
<td>600</td>
<td>800</td>
<td>1400</td>
<td>-</td>
<td>20</td>
</tr>
<tr>
<td>(b)</td>
<td>360</td>
<td>280</td>
<td>1180</td>
<td>-</td>
<td>20</td>
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<tr>
<td>RX-PTFE</td>
<td></td>
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<td></td>
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<tr>
<td>(a)</td>
<td>540</td>
<td>860</td>
<td>1400</td>
<td>10.0</td>
<td>20</td>
</tr>
<tr>
<td>(b)</td>
<td>320</td>
<td>860</td>
<td>1180</td>
<td>11.1</td>
<td>20</td>
</tr>
</tbody>
</table>

*RX-PTFE line/space values are divided by Si space/line values.

Table 2 Widths of line & space, shrinking rate and LER of RX-PTFE and imprinted TMPTA structures by UV-NIL.

<table>
<thead>
<tr>
<th>Pattern</th>
<th>Line Width (nm)</th>
<th>Space Width (nm)</th>
<th>Pitch (nm)</th>
<th>Shrinking ratio (%)</th>
<th>LER (nm)</th>
</tr>
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<tr>
<td>RX-PTFE</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a)</td>
<td>540</td>
<td>860</td>
<td>1400</td>
<td>-</td>
<td>20</td>
</tr>
<tr>
<td>(b)</td>
<td>320</td>
<td>860</td>
<td>1180</td>
<td>-</td>
<td>20</td>
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<tr>
<td>(a)</td>
<td>550</td>
<td>850</td>
<td>1400</td>
<td>1.2</td>
<td>20</td>
</tr>
<tr>
<td>(b)</td>
<td>330</td>
<td>850</td>
<td>1180</td>
<td>1.2</td>
<td>20</td>
</tr>
</tbody>
</table>

*TMPTA space/line values are divided by RX-PTFE line/space values.
could be as applied as a mold for UV-NIL. The nano-scale L&S patterns, square and hole array patterns were clearly obtained using UV-NIL. There is no crack in the imprinted structures and also no release materials. It is found that the profiles of obtained structures were very smooth.

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Reference