Study on UV / EB Nanoimprint Lithography Using Nano-/ Micro-fabricated Crosslinked PTFE Mold

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Nano-/ micro-scale structures of crosslinked polytetrafluoroethylene (RX-PTFE) have been directly fabricated by focused ion beam (FIB). In this study, the nano-/ micro-fabricated RX-PTFE were attempted to be applied for the polymeric molds of nanoimprint lithography (NIL). The ability of the RX-PTFE mold for electron beam NIL (EB-NIL) was evaluated by the imprinted patterns, and compared with ultraviolet NIL (UV-NIL) method. The RX-PTFE molds and the imprinted structures obtained by UV- / EB-NIL were observed by a field emission scanning electron microscope (FE-SEM) and a scanning electron microscope (SEM). The height of imprinted structures was 860 nm, and the thinnest line width achieved in the experiments showed 180 nm with EB-NIL process. The estimated aspect ratio was 4.8.

Keywords: Crosslinked PTFE, Nanoimprint lithography, EB, UV, TMPTA

1. Introduction

Nanoimprint lithography (NIL) is a technique for duplicating nano-/ micro-scale structures with higher throughput and lower cost than the conventional photolithography.

Generally, it is well-known that there are two types of methods for the NIL: the thermal and UV light curing. The molds for thermal-NIL are mainly made of metals or ceramics, such as Ni, Au, Si, and SiO₂, and the thermoplastic polymer or thermos curable monomers are used. It has a widely choice of the imprinted matrix. However, it takes a long time for heating and cooling them, because it often carried out at high pressure and high temperature which would be over the glass transition temperature or melting temperature of them.

On the other hand, quartz is often used as the molds for UV-NIL, because they must have the high transmittance of UV light (e.g. 254 nm, 365 nm). There is a requirement of the photo-initiator in the curable monomer. The UV-NIL can be carried out at mild condition such as lower temperature and lower pressure, compared with the thermal-NIL.

By the way, an electron beam (EB) irradiation can directly cure the monomer without any photo-initiators, and then immediately induce polymerization. In addition, EB irradiation can easily cure the monomer, which compounds the colorants such as carbons, titanium, leads and zinc, although the UV light exposure can hardly do.

The crosslinked polytetrafluoroethylene (RX-PTFE) is well-known for its excellent properties, such as the highest chemical stability of all polymers, the radiation resistance (half value of mechanical properties: 1~2 Mgy), thermal durability, low adhesive property and so on [1-4].

In our recent studies, the nano-/ micro-scale structures of various perfluorinated polymers, such as PTFE and RX-PTFE, were fabricated by focused ion beam (FIB) irradiation with maskless direct etching technique [5-8].

In this study, the nano-/ micro-fabricated RX-PTFE obtained by FIB irradiation were attempted to be used as the polymeric mold for NIL. In the case of the RX-PTFE molds for NIL, it
is expected that the release materials would not be needed to coat the molds, because the RX-PTFE has very low adhesion property. The ability of the RX-PTFE mold for EB-NIL was evaluated by imprinted pattern, compared with UV-NIL.

2. Experimental procedure

The UV- / EB-NIL patterning process for this study is schematically shown in Fig. 1. These processes consist of three steps. The first step is the nano- / micro-scale fabrication of RX-PTFE by FIB direct etching. The second step is UV light exposure or EB irradiation for the curing. The final step is removal of the cured resin from the RX-PTFE mold.

2.1 Materials

PTFE dispersion (FLUON® XAD911, average diameter: 0.25 μm, 60 wt%, ASAHI GLASS Fluoropolymers) was used for the experiments. PTFE dispersion with about 100 μL was coated on silicon wafers (N-type, 525 μm, 4 inch, Shin-Etsu Chemical), which were cut into 1.5 × 1.5 cm² squares, with a spin-coater (SPINCOATER 1H-DX2, MIKASA). The heat treatment was carried out at 360 °C for 30 min for obtaining the sintered PTFE. Then the samples were crosslinked by the EB irradiation (Curetron®, NHV Corp., accelerating voltage: 200 kV, beam current: 1 mA, installed at RISE, Waseda University) with a dose of 600 kGy at 335 ± 5 °C under N₂ gas atmosphere. Thus the spin-coated RX-PTFE was obtained on the silicon wafers.

Trimethylolpropane-triacrylate monomer (TMPTA, ARAKAWA Chemical) with three double bonds (-C=CH₂) was used for the NIL processes. 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 a photo-initiator for UV curing.

2.2 FIB fabrication process

The nano-/micro-scale polymeric molds of the RX-PTFE was fabricated by FIB (SMI2050, SII-NIT, ion source: Ga³, accelerating voltage: 30 kV, installed at ISIR, Osaka University) equipment. The samples were set in the vacuum chamber perpendicularly to the FIB. Figure 2 shows the image map of fabrication pattern, and Table 1 summarizes the line and the space widths. FIB was irradiated on the black regions of Fig. 2. The beam current was 9 pA (beam size: φ13 nm, FWHM), and the irradiated fluence was 5E+15 ions cm⁻². From the estimated etching rate of the RX-PTFE [6,8] the selected fluence could completely etch the thickness of 3 μm.

![Fabrication pattern image map of FIB irradiation](image)
2.3 NIL process

2.3.1 UV-NIL process

The UV curable resin was prepared by mixing TMPTA (95 wt%) and IRGACURE® 907 (5 wt%). The UV curable resin was dropped with amount of about 1 µL on the RX-PTFE mold. The glass (18 × 18 mm², 100PCS, MATSUNAMI) with the thickness of 150 µm was covered the resin on the mold. The prepared samples were exposed by UV light (HB100A-1, SEN LIGHTS) in ambient condition. The center wavelength of the UV light is 365 nm, and the exposure dose is 670 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.

2.3.2 EB-NIL process

To evaluate the yields of polymerization by EB irradiation for EB-NIL process, TMPTA was irradiated up to 30kGy at room temperature (25°C) under N₂ gas atmosphere [10]. After EB irradiation, the irradiated TMPTA were analyzed by FT-IR spectroscopy (JEOL, JIS-6000).

TMPTA was dropped with the amount of about 1 µL on the FIB fabricated RX-PTFE mold. Polyethylene-terephthalate (PET, S-10, TORAY) film with the thickness of 16 µm, which was cut into 1 × 1 cm² squares, was covered on the dropped TMPTA on the RX-PTFE mold. To cure the TMPTA, the assembled samples were irradiated by EB (accelerating voltage: 200 kV, beam current: 1 mA) with a dose of 15kGy at room temperature under N₂ gas atmosphere. Then, the cured TMPTA was removed from the RX-PTFE molds, and the imprinted structures were obtained on the PET film.

2.4 Measurements

The FIB fabricated RX-PTFE molds and the imprinted structures obtained for EB- and UV-NIL were observed by a field emission scanning electron microscope (FE-SEM, S-4500S, HITACHI) and a scanning electron microscope (SEM, S-3000N, HITACHI).

3. Results and discussion

3.1 FIB fabrication

Figure 3 shows the FE-SEM images of the RX-PTFE molds fabricated by the FIB maskless direct etching. The controlled fine structures of nano / micro scale line and space patterns were obtained on the spin-coated RX-PTFE. It was found that the RX-PTFE was completely etched down to the silicon wafer substrate. This means that the bottom of the mold is silicon and its sidewall is RX-PTFE. Table 2 summarizes their widths of the fabricated lines and their spaces. The height of fabricated RX-PTFE molds was 860 nm. The line widths of fabricated structures were about 100-200 nm larger than the pattern map of fabrication image, as shown in Fig. 2 and 3.

This spread of line width could be due to the low density Ga⁺ ions which would distribute around the set beam diameter (φ13 nm, FWHM). The low density Ga⁺ ions outside the beam diameter were irradiated to the surrounding areas of fabrication patterns. Thus, it is considered that the low density Ga⁺ ions would distribute within 200 nm around the beam diameter. Hence, if the line widths less than 200 nm are fabricated by FIB, it would be necessary to prepare the thinner RX-PTFE film to avoid the influence of surrounding low density Ga⁺ ions.

3.2 UV-NIL

Figure 4 shows the FE-SEM images of the imprinted structures on the glass sheet obtained with UV-NIL process. The curing period of UV-NIL were 2 minutes, and the temperature of sample positions showed about 60 °C, because the temperature was elevated by UV-light exposure.

The clear block structures were obtained with
UV-NIL. The blocks on glass sheet 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 smooth. Table 3 summarizes the line and the space widths of UV-NIL imprinted structures. The height of imprinted materials showed the 860 nm, which was as same as the height of the RX-PTFE molds, i.e., it was indicated that UV-resin could reach the bottom of the RX-PTFE molds due to low viscosity less than 100 mP·s at 60 °C. However, the line widths of the imprinted TMPTA structures were 5 - 15 % smaller than those of the RX-PTFE molds. And also, the space widths were 5 - 15 % wider than those of the RX-PTFE molds. This reason would be explained by the shrinking amount of TMPTA. The shrinking of TMPTA is known as about 12 % under this condition.

Therefore, UV-NIL process using nano-/micro-fabricated RX-PTFE polymeric molds was succeeded without the release materials.

Figure 4. The FE-SEM images (tilt 30 °) of the imprinted structures with UV-NIL using the RX-PTFE molds. The SEM images (tilt 0 °) of those using the RX-PTFE molds. The photographs (a), (b), (c), (d), (e), and (f), are taken under the conditions of 1, 3, 5, 6, 7, and 8 for the numbers sited in Table 2, respectively.

Table 3. The measured sizes of the imprinted structures with UV-NIL using each RX-PTFE mold.

<table>
<thead>
<tr>
<th>No.</th>
<th>Line X [µm]</th>
<th>Space Y [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1040</td>
<td>850</td>
</tr>
<tr>
<td>2</td>
<td>700</td>
<td>890</td>
</tr>
<tr>
<td>3</td>
<td>620</td>
<td>900</td>
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<tr>
<td>4</td>
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<td>6</td>
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<tr>
<td>7</td>
<td>1000</td>
<td>430</td>
</tr>
<tr>
<td>8</td>
<td>1050</td>
<td>240</td>
</tr>
</tbody>
</table>

3.3 EB-NIL

After EB irradiation, the amounts of polymerization for irradiated TMPTA were analyzed by FT-IR spectroscopy. TMPTA has three double bonds (-C=CH₂), and the absorbance corresponding to the double bonds at 1400 cm⁻¹ was evaluated by FT-IR spectroscopy.

Figure 5 shows the relationship between EB dose and the absorbance at 1400 cm⁻¹. The absorbance at 1400 cm⁻¹ decreased with increasing of EB dose until 10kGy, and then tended to saturate. That is, the -C=CH₂ double bonds in TMPTA decreased with increasing of EB dose. These results indicate that the TMPTA was polymerized by EB irradiation very effectively.

In our previous work [10], in the case of EB irradiation under vacuum, TMPTA was easily polymerized by irradiation with the dose of 1kGy.

For the complete TMPTA curing by EB irradiation, assembled samples were irradiated with the dose of 15kGy at room temperature under N₂ gas atmosphere.

Figure 5. The relationship between the EB dose and the absorbance at 1400 cm⁻¹. EB irradiation was carried out at room temperature in nitrogen atmosphere.

Figure 6 shows the FE-SEM images of the imprinted structures on the PET film obtained with EB-NIL process. The widths of lines and spaces obtained by EB-NIL were summarized in the Table 4. The height of imprinted materials showed the 860 nm, which was as same as those for the RX-PTFE molds. That is, it was indicated that TMPTA would adequately reach the bottom of the RX-PTFE molds. However, the line widths of the imprinted TMPTA structures were 5 - 20 % smaller than those of the RX-PTFE molds. This reason was explained by shrinking rate of TMPTA, like in UV-NIL process.

The thinnest line width in the experimental conditions showed 180 nm by EB-NIL process, and the estimated aspect ratio was 4.8.

The relationship between the line / space widths of FIB fabricated RX-PTFE molds and imprinted EB / UV-NIL was evaluated by SEM images, as seen in Fig. 4 and 6. The imprinted line widths of
about 200 nm lines were obtained both for EB- and UV-NIL processes. It was not found that the difference of imprinted line width between EB-NIL and UV-one.

In the case of EB-NIL, when the space of fabricated RX-PTFE molds was 200 nm, a part of polymeric molds would be released from cured TMPTA, as shown in Fig. 6 (f). In this case, it is considered that the RX-PTFE would be contacted with thinner cross-section of silicon wafer, and TMPTA monomer may be reacted with the RX-PTFE molds. As the results, a part of molds would be removed from silicon wafer due to low adhesive properties of the RX-PTFE to Si wafer. Thus, to obtain the imprinted pattern with more thin space, it is necessary to improve the adhesion between the substrate materials and the RX-PTFE mold.

EB-NIL process using nano-/micro-fabricated RX-PTFE polymeric molds was succeeded without the release materials and the photo-initiator. Moreover, the curing period by EB-NIL were less than 2 seconds, and shorter process than UV-NIL one. It was thought that the energy efficiency of EB-NIL process would be higher than that of UV-NIL one.

4. Conclusion
Nano / micro scale structures of the RX-PTFE were fabricated by FIB direct etching. The obtained structures of the RX-PTFE were attempted to be used as the polymeric molds for EB- and UV-NIL. The RX-PTFE molds and EB/UV-imprinted structures with EB- and UV-NIL were observed with FE-SEM. When the RX-PTFE molds with lines larger than 200 nm were imprinted, clear structures were obtained by both EB- and UV-NIL. The differences of EB- and UV-NIL could not be observed in the view point of line widths. The height of both imprinted structures was 860 nm, and the thinnest line width showed about 180 nm by EB-NIL process. The aspect ratio of each imprinted pattern has been achieved 4.8.

Acknowledgement
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