Durability and Transfer Properties of a Release-Agent-Free Replica Mold for Ultraviolet Nanoimprinting

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The durability and transfer properties of several replica molds were evaluated. Replica molds with patterns of holes or pillars were fabricated by ultraviolet nanoimprint lithography (UV-NIL) from an epoxy-type UV-curable resin. The resin had an antifouling effect, permitting the fabrication of replica mold without the use of a release agent. The transfer properties of the molds were evaluated by contact-angle measurements on the mold and by scanning electron microscopy of the UV-NIL transferred pattern. The error rates were calculated from the scanning electron micrographs and the values was used to assess the lifetimes of the replica molds. The thickness of the residual layer of the replica mold was controlled by changing the roll-press method. A replica mold with a thick residual layer showed a longer lifetime than one with a thin residual layer. In addition, the use of a cushion material was effective in improving the lifetime. Molds with hole patterns showed a longer lifetime than those with pillar patterns, and a lifetime of around 1000 repetitions was achieved.

Keyword: Ultraviolet nanoimprint lithography, photocurable polymer, release agent, replica mold, nanotechnology

1. Introduction

Nanoimprint lithography (NIL) is a powerful technique for the fabrication of nanoscale patterns [1]. In the case of ultraviolet-NIL (UV-NIL) [2], the presence of a release layer on the mold surface is important for preventing adhesion of the UV-curable resin [3–7]. A material for replica molds that does not require the use of a release agent is urgently needed for NIL and for roll-to-roll NIL-based technologies. In particular, a film-based replica material capable of transferring a master mold pattern by UV-NIL would have many advantages, such as a simpler pattern-transfer process, an improved ability to wrap around a roll mold, and better disposability. Available materials for the replica mold include poly(tetrafluoroethylene) [8], ethylene–tetrafluoroethylene copolymer [9], and polyurethane acrylate [10]. However, all these materials suffer from a lack of hardness of the cured resin, in that they have pencil hardness ratings in the range B to H and are therefore considered to be soft materials. Our previous study showed that the hardness of the cured resin of the replica mold is an important factor in the transfer of high-aspect-ratio nanoscale patterns [11]. Materials with greater pencil hardness are therefore needed. In another previous study, we developed an antifouling-effect UV-curable resin for fabricating antireflection structures [12]. This material was also sufficiently hard (pencil hardness 4H) to withstand touch or contact, making it suitable for use in replica molds. This UV-cured material, which is sufficiently hard and possesses an antifouling effect, is suitable for use in producing replica molds for UV-NIL. In addition,
we have introduced the error rate of the transferred dots patterns, determined by statistical analysis [13], as a means of quantifying the rate of deterioration of the replica mold. The resulting error rates have also been compared with other group error ratio results [14]. In this study, we evaluated the effects of the thickness of the residual layer of the replica mold and of the nature of the cushion material below replica mold on the durability and transfer properties of the replica mold.

2. Experimental Setup

The procedure for fabricating the replica molds is shown schematically in Fig. 1. The details have been reported elsewhere [11,12,15]. In this study, we used two silicon molds as master molds; one had a pattern of holes and the other had a pattern of pillars. The holes or pillars had a diameter of 230 nm, a pitch of 460 nm, and a height or depth of 200 nm. The molds were coated with 0.1 wt% OPTOOL DSX (Daikin Industries, Ltd., Osaka) as a release agent. The UV-curable resin was PARQIT OEX-028-X433-3 (hereafter referred to as X433-3; Autex Co., Ltd., Tokyo). This consists of a blend of a cationically polymerizable UV-curable resin and an epoxy-modified fluorinated resin. The base cationically polymerizable UV-curable resin comprises a blend of several alicyclic epoxy resins. The antifouling component of X433-3 segregates to the surface of the cured resin after heat treatment, imparting an antifouling effect at the surface and permitting it to perform as a release-agent-free replica mold [15]. A characteristic of cationic UV-cured epoxy systems is that they form hard cured resins. The process for fabricating the replica patterns from X433-3 was as follows. First, a portion of X433-3 was placed on the silicon mold and covered with a polyester film substrate (Cosmoshine A4300; Toyobo Co. Ltd., Osaka) [Fig. 1(1)]. The layer of X433-3 was pressed onto the mold by the weight of the polyester film [Fig. 1(2)] and the assembly was irradiated with UV radiation at a wavelength of 365 nm and a dose of 3000 mJ/cm² [Fig. 1(3)]. The cured layer of X433-3 was released from the mold [Fig. 1(4)] and baked at 85 °C for 30 min to induce the antifouling effect [12] [Fig. 1(5)]. This procedure gave X433-3 replica molds with hole or pillar patterns and an antifouling effect [Fig. 1(6)].

Using these fabricated X433-3 replica molds, we performed the UV-NIL process repeatedly to examine the rate of deterioration of the replica mold. At this stage we used a UV-curable resin (PAK-01CL; Toyo Gosei Co. Ltd., Tokyo) as the transfer resin. First, a layer of PAK-01 CL was applied to the replica X433-3 mold and covered by a layer of polyester film. The assembly was then pressed at 0.5 MPa in a parallel-plate-type UV-NIL machine and exposed to UV radiation at a dose of 120 J/cm². The PAK-01CL layer was then released from the X433-3 mold. The X433-3 replica mold was used repeatedly until the PAK-01 CL resin began to adhere to the surface of the X433-3 as a result of repeated use of the mold.

The evaluation methods that we used are shown in Fig. 2. The water contact angle of the replica X433-3 molds was measured at constant intervals by using contact-angle-measurement equipment (DropMaster DM-701; Kyowa Interface Science Co., Ltd, Niiza City). Surfaces with a high contact angle were sufficiently hydrophobic to prevent adhesion of the UV-curable resin. We also examined samples of the transferred patterns at constant intervals by means of scanning electron microscopy (SEM) (Elionix Co. Ltd, Tokyo). The error rate was calculated from the population proportion. In this study, we measured more than 100,000 replicated dots on the UV-curable resin, and this measurement gave a 95% confidence interval. To ensure that errors in the replicated pattern were easily identifiable, we choose molds with patterns of holes or pillars. The measurement method was as follows. First, a scanning electron micrograph at a magnification of 4000× was obtained. Then we counted each error, such as that shown by the red circle in Fig. 2. Next, the SEM field was relocated by a given distance, a further micrograph was taken, and the errors were counted as before. We measured 30 fields of replicated dots patterns for each imprint and we counted the total
number of errors. These 30 fields of replicated dot patterns contained a total of 114,570 individual dots.

The statistical analysis of the error rate was performed by using the following expression:

\[
\frac{m}{N} - 1.96 \sqrt{\frac{m(1-m)}{N^2}} \leq p \leq \frac{m}{N} + 1.96 \sqrt{\frac{m(1-m)}{N^2}}
\]

where \( m \) is the number of errors, \( N \) is number of samples (in this case, 114,570), and \( p \) is the error rate. The resulting error rate is expressed as a 95% confidence interval [14].

![Fig. 2 Methods for evaluating the replica mold surface and the transfer pattern. The transferred patterns were observed by SEM, and the error rates were calculated.](image)

3. Results and Discussion

3.1. Durability and Transfer Properties of the Replica Molds

The X433-3 replica molds with patterns of holes or pillars made were evaluated in repetitive UV-NIL. The contact angles and error rates were measured at constant intervals, and the results are shown in Fig. 4. In this case, the diameter of the holes or pillars was 230 nm and their depth/height was 200 nm. Each transfer test was performed twice to investigate the reproducibility. The error rate for the pillar mold in the second test was not calculated because too many errors were present. The pillars pattern molds showed adherence to the UV-curable resin at midstream, at which stage we stopped the transfer. The mold with the holes pattern was reused 1000 times before we stopped the transfer.

![Fig. 3 Procedure for the fabrication of the replica mold by the roll-press method](image)
Replica molds with patterns of holes therefore have a longer lifetime than those with patterns of pillars. The trends in the contact angles for both molds showed similar curves, but those for the error rates were different. An error rate of more than 0.0001% is considered to be the limit for the lifetime of a mold, so the replica mold with the pattern of holes in the first-round test showed the longest lifetime, permitting about 600 cycles of the imprinting process. Because of the error rate, the pillar pattern had a shorter lifetime. The results can be explained as follows. PAK-01 CL shows volume shrinkage after UV curing. In the case of the hole-replica X433-3 patterns, the PAK-01 CL formed pillar patterns and, because these shrank, they could be easily removed from the X433-3 mold. On the other hand, in the case of pillar-replica pattern, the shrinkage motion acted on the pillar pattern of the X433-3 replica mold and the forces of this shrinkage motion were focused on the pillar parts of the X433-3, producing outwardly directed forces in the direction of the pillar diameters, inducing breakage of some of the pillars. Our results show a need for an improvement in durability. We therefore examined the effects of the thickness of the residual layer on the transfer properties. To investigate the effect of the thickness of the residual layer, we developed a roll-press method for fabricating replica molds with a controlled thickness of the residual layer.

3.2. Transfer properties of replica molds with controlled thicknesses of the residual layer

Fabricated X433-3 replica molds with various thicknesses of the residual layer are shown in Fig. 5. The thickness of the residual layer was determined as the distance between the polyester film and the bottom of the pattern features.

Replica molds with thick residual layers were fabricated at a roll pressure of 1.0 MPa. This gave a 6-μm-thick residual layer for the replica mold with a pattern of holes and a 10-μm-thick residual layer for the replica mold with a pattern of pillars. Production of replica molds with thin residual layers required higher pressures. Replica molds with patterns of holes and pillars having residual layers of thickness 0.6 μm and 0.8 μm, respectively, were fabricated by using roll pressures of 7.5 MPa and 15 MPa, respectively. We evaluated the durability of these X433-3 replica molds from their contact angles and error rates, as shown Fig. 6.

![Fig. 5 The thickness of the residual layer of the X433-3 replica mold with a pattern of (a) holes and (b) pillars. The micrographs on the left- and right-hand sides correspond to thick and thin residual layer, respectively.](image)

![Fig. 6 The durability and transfer properties of X433-3 replica molds with various thicknesses of the residual layer](image)
These results showed that molds with a thicker residual layer have a longer lifetime. However, the effect of changing the thickness of the residual layer varied, resulting in a poor reproducibility, similar to that shown in Fig. 4. Furthermore, the lifetime of each replica mold in Fig. 6 was shorter than that of the corresponding mold in Fig. 4. This is because finer patterns tend to produce more transfer errors; in particular, the pillar shaped molds were severely affected.

Pattern replica molds with broken holes are shown in Fig. 7. We halted repetitions of the UV-NIL when we observed adhesion of UV-curable resin or breakage of the replica mold.

Fig. 7 Breakage of the holes-pattern replica mold for residual layers of various thicknesses.

In the case of the thick residual layer, no breakage was observed, but the scanning electron micrographs showed that some areas were removed and buried. Other areas remained intact, but, on the basis of the error rate, we judged that the lifetime of this replica mold was 600 cycles of UV-NIL. In the case of the thin residual layer, we observed adhesion after 400 repetitions of UV-NIL, and the scanning electron micrograph also showed adhesion of resin.

Pattern replica molds with broken pillars are shown in Fig. 8.

Fig. 8 Breakage of pillars in replica pattern molds for residual layers of various thicknesses.

In the case of the thick residual layer, considerable breakage was observed after 27 cycles of UV-NIL. Scanning electron micrographs also showed removal of the replica mold surface and losses of the pillar patterns. In the case of the thin residual layer, breakage was observed after 15 cycles of UV-NIL, and this was confirmed by SEM. Therefore, even in the case of the pillar-pattern replica mold, increasing the thickness of the residual layer is effective in increasing the lifetime of the mold, even though the lifetime is still short. In an attempt to ameliorate this problem, we used a cushion material under the replica mold substrate because we believe that a thicker residual layer acts as cushion during the imprint motion and release motion.

3.3. Durability and transfer properties of a replica mold with a thick residual layer and a cushion material

We used double-side adhesive tape made of poly(dimethylsiloxane) (PDMS; NSA-100, NIPPA Co., Ltd, Suita City) to attach the replica mold to the NIL stage. The tape consisted of a soft rubber-like material and was 100-μm thick. By using this arrangement, we fabricated replica molds with hole or pillar patterns and a thick residual layer. The durability and transfer properties of these molds are shown in Fig. 9.

The lifetimes of both replica molds were longer than previously (Fig. 6), showing that the use of a soft cushioning material is effective in improving the lifetime of the replica mold. The lifetime of replica molds with a pillar pattern showed a marked improved, breaking only after 240 cycles of UV-NIL, at which stage the process was halted and the products were examined by SEM.

Fig. 9 The durability and transfer properties of X433-3 replica molds with a cushion material
In the case of the replica mold with a holes pattern, the error rate became greater than 0.0001% after 1000 cycles of UV-NIL, corresponding to a lifetime of about 1000 cycles. This is an adequate figure for a replica mold. The contact angle after 1000 cycles (83.0°, Fig. 9) was almost identical to that in Fig. 6 (82.4°). Therefore, contact-angle evaluation alone is not adequate for characterizing the lifetime of the mold.

The breakage of the replica molds is shown in Fig. 10.

Fig. 10 Breakage of hole- and pillar-pattern replica molds with a cushion material

For the holes pattern, breakage was observed after 2800 cycles. As shown in the Figure, the replica mold was removed and a crack was generated. On the other hand, the pillar-pattern replica mold was broken after 240 cycles, when partial removal and losses of pillars were observed. Further development of the materials is therefore required to achieve longer lifetimes for pillar-pattern replica molds.

4. Conclusion

We examined the durability and lifetime of replica molds produced from X433-3, a release-agent-free material. The lifetime can be evaluated measuring the error rate of the transferred pattern. A thick residual layer and the use of a cushion material are effective in improving the lifetime of the replica mold. However, replica molds with patterns of pillars have markedly shorter lifetimes than those with patterns of holes. Furthermore, replica molds with finer pattern features have shorter lifetimes than those with larger pattern features.

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