Durability Evaluation of Antireflection Structure Replica Mold using High Hardness and Antifouling UV-curable Resin

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Moth-eye-structure replica mold was fabricated from a glassy carbon master mold by UV-NIL. New UV curable resin with high hardness and antifouling property was used. The moth-eye-structure was duplicated from the replica mold by use conventional UV curable resin for UV-NIL. Compared with the replica mold by use of a conventional release-agent-free UV curable resin, the moth-eye-structure of new replica mold had superior imprint durability. The reflectance of the imprinted film was below 1% for the 350th imprint. It was that the antifouling property was very important for prolonging life time of replica mold.

Keywords: UV-NIL, Antireflection structure, UV-curable resin, Lifetime

1. Introduction

Ultraviolet nanoinprint lithography (UV-NIL) is an efficient technique used to obtain nanoscale patterns on films or other substrates by dropping a UV-curable resin onto a nanoscale-patterned mold and irradiating it with UV light [1-3]. One of the applications of this technique is the fabrication of anti-reflective structures. These structures are particularly important in the smartphone and portable electronics field. Typical antireflection structures are multilayer films, which are time-consuming to produce and are limited in terms of the wavelengths and angles at which reflection can be suppressed. By contrast, moth-eye structures can be made of a single film and can realize low reflectance for a wide range of wavelengths and angles [4]. However, moth-eye structures are fragile and also take a long time to fabricate, which hinders their widespread application [5]. Moreover, these structures are fabricated on glassy carbon, which is impenetrable to light, meaning that it needs to be transferred by UV-NIL to polyester films, which are optically transparent [6]. Therefore, we hypothesized that it is might be possible to reduce the number of times the glassy carbon master mold was used by making a replica mold with high-hardness resin from the master mold and using it for transcription [7-9].

In this study, we used a newly developed, high-hardness UV-curable resin to make a replica mold from a glassy carbon master mold with a moth-eye structure. We then used this replica mold instead of the glassy carbon master mold in UV-NIL. The replica mold had substantially improved durability than the master mold.

The resin that we used for the replica mold was a newly developed, cationically curable multifunctional epoxy resin with a sulfonium salt as the initiator. It has high hardness (pencil hardness of 9H) and toughness after UV curing, and also contains an antifouling component [10-13]. Because of these mechanical properties, it is not necessary to use a release agent with this resin [14-16]. We prepared the resin with and without the antifouling component, and investigated the influence of the antifouling properties on the imprints.

2. Experimental

The glassy carbon master mold was fabricated using an ECR-type ion-shower machine. The moth-eye structure was produced by applying a voltage to the glassy carbon and performing oxygen plasma etching. The master mold was processed under an...
accelerating voltage of 400 V, an etching time of 50 minutes and an oxygen flow rate of 3.5 sccm. The processed master mold had a low reflectivity of about 0.1% in the visible-light region (400–700-nm wavelength). The glassy carbon used in this experiment was a square (2 cm × 2 cm).

Figure 1 shows the scanning electron microscope (SEM; Elionix Co., Ltd.) images of the master mold. The diameter, pitch and height of the moth-eye structure of the master mold were 51 ± 2 nm, 79 ± 5 nm and 610 ± 6 nm. Because the master mold was impenetrable to light, we transferred it by UV-NIL to an optically transparent polyester film (Cosmoshine A4300, Toyobo Co., Ltd.).

To prevent degradation of the pattern with repeated imprinting, we used a replica mold instead of the master mold. The replica mold is made by UV-curable resin for experiment. To prepare the replica mold, we first coated the master mold with a 30-nm layer of chromium using chemical vapor deposition [17-20]. The master mold was then immersed in a release agent (1.0% Optool DSX; Daikin Co., Ltd.) for 1 hour, before the being treated with the same release agent in the gas phase for 12 hours. To remove excessive water in the release agent, the master mold was baked on a hot plate at 120 °C. Next, the master mold was rinsed with NOVEC7300 (3M Japan Co., Ltd.) for 1 minute to remove dust on the surface.

Figure 3 shows the fabrication method of the replica mold. First, the master mold was dropped in the resin, covered with the polyester film and exposed to UV radiation at 50 J/cm² with baking at 80 °C under a pressure of 0.011 MPa (Figs. 3(a,b)). Curing of the high-hardness resin is promoted by baking during UV irradiation. The replica mold was released from the master mold (Fig. 3(c)) and the cured pattern was baked at 100 °C for 30 minutes (Fig.3(d)). To bake the replica mold, the antifouling component contained in the resin was precipitated on the surface [15]. A replica mold without antifouling properties was then fabricated using the same procedure in Figs. 3(a)-(c).

First the hardness of the flat UV cured resins were measured. The measurements were carried out using a dynamic ultra-micro-hardness tester (DUH-211; Shimadzu Corp., Kyoto). After the resins were UV-irradiated and baked on a hot plate. Table 1 shows the martens and pencil hardness values of the resin with and without antifouling properties, which are higher than those of the conventional resin Parquit OEX-028-X433-3(Autex Co., Ltd., hereafter, X433-3). Next, the replica molds were fabricated according to the fabrication process shown by Fig. 3.

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**Fig. 1.** Moth-eye structure of the glassy carbon master mold. (a) Top view, (b) tilted view at 75°.

**Fig. 2.** The reflectance of GC master mold.

**Fig. 3.** Fabrication of the replica mold.
The SEM images are shown in Fig. 4, (a) the newly developed resin replica mold with antifouling properties, and (b) without antifouling properties. The diameter, pitch and height of the moth-eye structure were 70 ± 6 nm, 106 ± 5 nm and 362 ± 7 nm, and 68 ± 4 nm, 95 ± 3 nm and 234 ± 10 nm, with and without antifouling properties, respectively.

![Fig. 4. Replica mold (a) with and (b) without antifouling properties.](image)

**Table 1. Hardness of the UV-curable resins.**

| UV-curable resin                  | Martens hardness [N/mm²] | Pencil hardness |
|-----------------------------------|--------------------------|----------------|
| PARQUET-OEX-028-X433-3            | 170                      | 5H             |
| Newly developed resin             | 231                      | 9H             |
| Newly developed resin without antifouling | 213                      | 9H             |

Imprinting was conducted using a fully automatic parallel-plate-type UV-NIL machine (Mitsui Electric Co., Ltd.) [15]. The UV curable resin used for this machine was PAK-01-CL(TOYOGOSEI Co., Ltd.). The pressure, filling time and UV dose were 0.078 MPa, 15 s and 360 mJ/mm², respectively. To evaluate the durability of the replica mold, we measured the contact angle of the replica mold during repeated imprinting. To evaluate the moth-eye structure of the transcripts prepared from this replica mold, we measured the reflectance and transmittance (Solidspec-3700; Shimadzu Corp., Kyoto) of the imprint, and observed the structure by SEM. The allowable range of the reflectance of the imprinted film was set under 1.0%.

**3. Results and discussion**

To evaluate the contact angle in the mold, we fabricated flat and pillar-patterned (diameter 200 nm, pitch 400 nm, height 200 nm; scivax Co., Ltd. [15]) replica molds with and without antifouling properties. Table 2 shows the contact angles of the convention and the new, high-hardness resin in each pattern. The high-hardness resin with the antifouling component has a high value of 143° and 149° in the pillar pattern and moth-eye structure, respectively.

The contact angle without antifouling is lower than that with antifouling because the surface energy was larger than that with antifouling. Moreover, the high contact angle is also due to the higher surface roughness, as described by the Cassie–Baxter model [21-23]. The moth-eye structure is extremely small compared to the pillar pattern at its tip; hence, a high contact angle is obtained. Figure 5 shows the contact angle of each replica mold with the moth-eye structure as a function of imprint number.

**Table 2. Contact angles of resins for different patterns.**

| UV-curable resin                          | contact angle [°] | flat pattern | pillar pattern | moth-eye structure |
|------------------------------------------|-------------------|--------------|----------------|-------------------|
| PARQUET-OEX-028-X433-3                   | 102               | 132          | 140            |
| Newly developed resin                    | 111               | 143          | 149            |
| Newly developed resin without antifouling | 99                | 140          | 140            |
Fig. 5. Contact angle of replica molds with a moth-eye structure.

For a replica mold made using conventional resin (X433-3), the contact angle was gradually decrease as increasing the number of imprints, and the reflectance increased to 1.0% after the 200th transcript [5]. The surface energy of the replica mold must be increased by the imprint resin adhesion to the replica mold as increasing the number of imprints. The contact angle of one replica mold without the antifouling component rapidly decreased with repeated transcription. The reflectance of the transcript exceeded 1.0% after the 100th transcription. For the replica mold without the antifouling component, a larger release force was applied to the pattern during release, which increases the likelihood of defects occurring in the replica mold [11]. This replica mold with antifouling maintained a high contact angle with repeated imprinting (130° after the 400th imprint) and the reflectance of the imprinted films remained below 1% until the 350th imprint. Thus, to maximize the transfer durability of the replica mold, not only a high resin hardness of the replica mold, but also an antifouling component are essential. We repeated the experiment several times under the same conditions and confirmed the replicability of reported transfer durability.

Figure 6 shows the reflectance of our replica mold with antifouling properties and the imprinted films. The replica mold has a reflectance of about 0.5% before the 1st transfer. The reason why the replica mold had a higher reflectance than the first imprint is probably because the resin slightly discolored owing to heating during the production of the replica mold. The reflectance of the 350th imprint is within 1% in the visible-light region (400–700 nm), but the reflectance of the 400th transcript exceeds 1%.

Figure 7 shows the transmittance of imprinted films made from our replica mold with antifouling properties. In general, when the patterned structure of the moth-eye mold is damaged (for example, by repeated transfer), the transmittance decreases, which may increase the reflectance. However, for our mold, there was little difference between the transmittance of the 1st and 350th transcripts. Thus, imprinted films made from our replica mold maintain transparency and their antireflective function.

Figure 8 shows SEM images of the 1st and 100th imprinted films of our replica without antifouling properties. The diameter, pitch and height of the moth-eye structure of the 1st and 100th imprinted films are 90 ± 3 nm, 105 ± 5 nm and 154 ± 2 nm, and 101 ± 2 nm, 112 ± 4 nm and 132 ± 4 nm,
respectively. Notably, the height of the first imprint is lower than that of the replica mold. In addition, the diameter increases and the height decreases after repeated transfer.

Figure 9 shows SEM images of the 1st and 350th imprinted films of the replica mold with antifouling properties. The diameter, pitch and height of moth-eye structure of the 1st and 350th imprinted films are $89 \pm 3$ nm, $109 \pm 5$ nm and $311 \pm 4$ nm, $100 \pm 7$ nm, $127 \pm 2$ nm and $188 \pm 3$ nm, respectively. The height of 1st imprint is high but the height of the 350th imprint is about a half that of the replica mold. Similar to the replica mold without antifouling properties, the diameter and pitch increased after repeated transfer.

In the 350th imprinted film by the replica mold with the antifouling properties, needle structure can be seen more clearly than the 100th imprinted film without the antifouling properties. It was found from the experiments of two replica molds that the height of the needle of moth-eye structure is reduced by increasing imprint times, so it seems that the antifouling properties reduced by the adhesion of the transfer resin (PAK-01-CL).

Although the moth-eye structure of the 350th imprinted film was clearly degraded for the replica mold with the antifouling property, the contact angle remained constant irrespective of the number of imprint in Fig. 5. Therefore, the contact angle data does not provide good information on the shape of the structure.

Therefore, we compared the height and aspect ratio (i.e. height/diameter) of moth-eye structure of imprinted films from replica mold with antifouling properties, as shown in Fig. 10.

The aspect ratio decreases sharply after the 250th imprint. With repeated imprinting, the antifouling component on the mold surface is consumed and the releasability decreases. As a result, the transfer resin remains in the mold, and the height and aspect ratio of the imprinted films decreases.

4. Conclusion

We fabricated a replica mold with a moth-eye structure using a new high-hardness resin, and compared its transfer durability to that of a conventional resin. We prepared the new resin with
and without antifouling properties to study how this affects imprinting. Imprinted films made from our mold with antifouling properties maintained a high contact angle and reflectance within 1% until the 350th transfer, demonstrating far superior durability than the mold without the antifouling component and the mold made from conventional resin.

The long time is necessary to manufacture moth-eye structure on GC, but to use the replica mold with antifouling property, it can replicate the structure easily. A film with a moth-eye structure for use in a smartphone requires a larger area. Although it is possible to create a large number of transparent films with moth-eye structures using our replica mold, it is difficult to transfer a large film area. Therefore, an important future research direction will be to device strategies to increase the area of the replica mold.

From this experiment, the newly developed resin having an antifouling properties showed high usefulness as a replica mold material. In the future, it will be possible to produce patterns efficiently by using not only moth-eye structure but also replica molds of various patterns with this resin.

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