Lifetime amelioration of antireflection structure molds by means of partial-filling ultraviolet nanoimprint lithography

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Abstract

Release coating layer (RCL) becomes an important element in ultraviolet nanoimprint lithography (UV-NIL) for preventing the adhesive resin from adhering to the surface of antireflection structures (ARS) mold. However, complete filling the resin of a high-aspect-ratio ARS mold during UV-NIL generates a strong release force (RF) that deteriorates the RCL and affects the lifetime of the ARS mold. In this paper, we proposed a technique of partial-filling UV-NIL in order to reduce the RF and consequently, ameliorate the lifetime of the ARS mold. The release and optical properties of the ARS were measured to determine the lifetime of the mold, and complete-filling UV-NIL was also executed for comparison. By means of partial-filling UV-NIL, we successfully fabricated ARS films with excellent performance up to the 150th imprint, i.e., reflectivity of $0.25 \pm 0.15\%$ and transmittance of $94.0 \pm 0.50\%$ at visible wavelengths, compared to complete-filling UV-NIL up to the 50th imprint.

Keywords: Ultraviolet nanoimprint lithography (UV-NIL), Lifetime, Partial filling, Release force, Contact angle

1. Introduction

Ultraviolet nanoimprint lithography (UV-NIL) [1] is expected to be an effective technique for the mass fabrication of antireflection structure (ARS) films. ARS films play a pivotal role in enhancing the performance of electronic devices such as solar cells, light emitting diodes, and displays. However, lengthening the lifetime of ARS molds is a challenge for their mass fabrication. Even if a release coating layer (RCL) is applied to the ARS mold, there are still unresolved problems such as the resin filling failure, resin adhesion, and imprint flaws. These occur due to the degradation of the RCL by mechanical [2] and chemical [3] factors. Our previous investigation [4] showed that complete filling of the resin for a high-aspect-ratio mold results in a strong release force (RF), which degrades the RCL rapidly and consequently limits the lifetime of the ARS mold. We also discussed the correlation between the resin filling behavior and the vitality of the RCL at various filling pressures in [5]. Considering the concept of partial filling in [6-9], we assumed from the results in [4, 5] that partial filling the resin during UV-NIL can reduce the RF and lower the aspect ratio of the replicated ARS film. Thus, prolongs the lifetime of the ARS mold.

In this study, the idea of partial-filling UV-NIL is associated with the presence of capillary force (P_c) that acts on the substrate owing to the difference of surface energy and the formation of fine nanostructures [10, 11] that affects the filling behavior. The needlelike ARS shape in our study is identical to the shape of the capillary, thus, the equation of P_c that we used in elucidating the phenomenon of resin fillings as following [12];

$$P_c = \frac{2\gamma \cos \theta}{a} \quad (1)$$

Here, a is pitches of the needlelike AR structures, γ is the surface tension of the resin, and θ is contact angle (CA) in the capillary. The illustration of resin filling behaviors of ARS mold is elucidated in Fig. 1. In normal cases, with an uncoated hydrophilic ARS mold in Fig. 1(a), the positive value of $\cos\theta$ and the narrow pitches of the needlelike ARS structures generates a positive value of P_c for pulling the resin downward. Otherwise, when ARS molds with an RCL, i.e., hydrophobic molds (Fig. 1(b)), $\cos\theta$ is negative and generates a negative value of P_c for pushing the resin upward. This negative value of P_c has been confirmed at nano-scale feature size mold with RCL in [13]. The presence of RCL and ARS on molds lowers the surface energy and exacerbates the capillarity that complicates the fillings. Thus, a sufficient filling pressure equivalent to P_c is required to assist the resin filling process. This phenomenon gives merit to the development of the partial-filling UV-NIL technique. Furthermore, the shrinkage effect [14, 15] also plays a role in shaping the fine replicated pattern.

Therefore, we established a technique to ameliorate the lifetime of the ARS mold by means of partial-filling UV-NIL (Fig. 1(c)); complete-filling UV-NIL (Fig. 1(d)) was also performed for comparison. The release properties, i.e., the RF, CA, and optical properties of the fabricated partial- and complete-filled ARS films are evaluated to determine the lifetime of the ARS molds.

2. Experimental apparatus and procedure

2.1 ARS mold fabrication

We prepared two mirror-finished glassy carbon (GC; Tokai Carbon Co., Ltd.)

substrates, 15 mm $\times$ 15 mm in size as the master molds for the purpose of partial- and complete-filling cases; named as GC *A* and GC *B* molds, respectively. The mold fabrication procedure is briefly illustrated in Fig. 2. Needlelike ARSs were fabricated on top of the GC substrate by oxygen ion-beam-reactive dry etching (Fig. 2(a)) [16]. An EIS-210ER (Elionix, Inc.) ion-beam apparatus equipped with an electron-cyclotron-resonance-type ion source was used. In this work, the ARS was self-assembled on the GCs at low acceleration voltage of 300 V for 60 min of etching condition; details are given in [17]. Fabricated molds at low acceleration voltage can possibly generate small RF during UV-NIL owing to the formation of the narrow pitches and effective heights on the molds. To form a robust ARS, the fabricated molds were finished by a 30 nm chromium deposition and then treated by 1 wt% Optool DSX (Daikin Co.) as the RCL (Fig. 2(b)). The coating conditions were as follows: a 24-h dipping time, 100-°C baking temperature, and 3-min baking time [4, 18]. To obtain the same initial condition of both molds, GCs were simultaneously etched and treated with release agent in the same condition and time.

2.2 Repetitive UV-NIL of ARS mold

A parallel-plate-type UV-NIL machine (Mitsui Co. Ltd.) was used to repeatedly imprint the ARS onto a polyester (PES) film (thickness = 100 μ m; Toyobo Cosmoline A4300). This machine provides uniform pressing and releasing. Also, it assists in the dissolution of air bubbles. To compare the trend of the ARS mold lifetime, the filling pressures to initiate both partial and complete filling of the resin were investigated; the applied pressures were 0.017 and 0.050 MPa, respectively. The UV-NIL conditions were a

15-s filling time, 620-mJ/cm² UV dose, and a 5-s irradiation time; the UV-photocurable resin was PAK-01-CL (62.4 mPa-s viscosity at 25 °C and 30.6 mN/m of surface tension; Toyo Gosei Co., Ltd. [19]). Fig. 3 briefly outlines the repeated UV-NIL mechanism. The ARS mold was aligned to be parallel with the load cell equipped with the high-intensity UV source ($\lambda = 365$ nm) and was fixed onto the sample stage using adhesive tape. In this case, the gap between the PES film and ARS mold was 0.75 ± 0.25 mm. The PAK-01-CL was dispensed onto the PES film by the resin dispenser and subsequently moved to be above the center of the ARS mold. The jig was then pushed upward by the sample stage, and the load cell pressed the PES film onto the ARS mold with the desired pressure. After the UV exposure, the jig pulled the stage downward to separate the mold and film at a release speed of 200 $\mu\text{m/s}$.

2.3 Lifetime evaluation

The RF during release and the CA of the ARS mold after release were measured by employing an RF measurement tool [4] and a CA instrument (DM-701, Kyowa Interface Science Inc.), respectively. The RF measurement tool provides peeling motion in one direction to give accurate values of the RF. The distilled water droplet was used for CA. The RF and CA values are to indicate the durability of RCL on the ARS molds. The RF and CA were measured every 10th imprint of the UV-NIL process until the 50th and then at every 25th imprint. Repetitive partial- and complete-filling UV-NIL were halted when the resin adhered to the ARS mold. The reflectivity at a 5° incident light angle and the transmittance of the partial- and complete-filled ARS films were evaluated using a UV–visible–near-infrared spectrophotometer (SolidSpec-3700, Shimadzu) over a spectral range of 300–1000 nm. The

analysis of optical properties is used to determine the lifetime of the ARS molds. The morphologies of the ARS mold (before and after UV-NIL), replicated partial-filled ARS, and complete-filled ARS films (PAK-01-CL) were also observed using a scanning electron microscope (SEM; ERA-8800FE, Elionix Co.); both top view and 75° tilted view images were obtained.

3. Results and discussion

Fig. 4 shows top and 75° tilted views of the ARS molds as master molds. The aspect ratios, reflectivities and surface areas of needlelike ARS of GC *A* and GC *B* were 7.75 and 7.94 which are relatively high (>1), 0.18 ± 0.08 and 0.15 ± 0.07 % at visible wavelengths, and 15.6×10^{-4} and $15.4 \times 10^{-4} \text{ m}^2$, respectively. The detailed calculation of surface area is elucidated in [20]. The application of the RCL changed the surface from hydrophilic ($\text{CA} = 6 \pm 2^\circ$) to superhydrophobic ($\text{CA} > 152 \pm 1^\circ$) for both molds. These features shows that the ARS molds conforms to the prescribed definition of an effective ARS [21] and has an excellent anti-sticking property for repetitive UV-NIL.

Fig. 5 shows the dependence of the RF and CA on the number of imprints in the case of partial- and complete-filling UV-NIL. From the graph, it is apparent that the RF increased and the CA decreased as the number imprints increased for both filling cases, and the partial-filling RF values were smaller than the complete-filling values up to the lifetime of the ARS mold. In the case of partial and complete filling, the RF increased from 63.8 to 217 N/cm^2 until the 350th imprint and from 79.7 to 165 N/cm^2 until the 100th imprint, respectively. The CA of the ARS mold after partial and complete filling decreased from 153

to 29.3° until the 350th imprint and from 153 to 92.4° until the 100th imprint, respectively. We believe that the release agent (1 wt% Optool DSX) on the ARS mold was imbibed to the PAK-01-CL during UV-NIL, leading to the increase in the RF and decrease in the CA. We also assumed that the tendency of rapid ripped off of RCL from the ARS mold is higher in complete-filling UV-NIL compared to partial-filling UV-NIL due to the strong RF. These results indicate that partial-filling UV-NIL prolongs the lifetime of the ARS mold compared to complete-filling UV-NIL.

Fig. 6 shows selected SEM images of partial-filled ARSs (150th, 250th, and 350th imprints) and complete-filled ARSs (50th, 75th, and 100th imprints) of PAK-01-CL. The selection criterion of SEM images is based on the difference in quality of replicated ARS for both partial- and complete-filling UV-NIL. Details of the morphologies are summarized in Table 1. From the SEM images, it can be seen clearly that defects occurred at the 250th and 75th imprints in the case of partial- and complete-filling UV-NIL, respectively. These defects corresponded to defects on the ARS mold. The heights of the replicated PAK-01-CL features decreased, while the pitches and diameters of the features increased as the number of imprints increased. These resulted in lower aspect ratios. This type of analysis is essential for detecting defects in the replicated PAK-01-CL and precisely evaluating the lifetime of the ARS mold. From the morphological study (Fig. 4 and Fig. 6), we also conclude that partial-filling UV-NIL reduced the anchor effect [22] during release of replicated PAK-01-CLs from the high-density surface area of ARS molds. In the case of complete-filling UV-NIL, the replicated surface area of complete-filled of PAK-01-CLs was higher compared to

partial-filling UV-NIL. The presence of anchor effect during release also disrupted the durability of RCL on the ARS mold.

The optical properties, i.e., the reflectivity and transmittance, of selected partial-filled ARSs (150th, 250th, and 350th imprints) and complete-filled ARSs (50th, 75th, and 100th imprints) of PAK-01-CL over the spectral range of 300–1000 nm are shown in Fig. 7(a) and (b), respectively. We found that the reflectivity increased and the transmittance decreased as the number of imprints increased. This shows the deterioration trend in optical properties of replicated partial- and complete-filled ARS of PAK-01-CL as the patterns in ARS molds degraded. The graph also shows that partial-filling UV-NIL produces ARS films that maintain an excellent performance until the 150th imprint, i.e., films with a reflectivity of $0.25 \pm 0.15\%$ and a transmittance of $94.0 \pm 0.50\%$ at visible wavelengths. Though the defect of ARS of PAK-01-CL was observed at the 250th imprint for partial-filled UV-NIL, it still exhibited good optical properties (reflectivity; $\approx 0.5\%$, and transmittance; $\approx 93.5\%$ at the spectral range of 300 nm– 750 nm). In comparison, ARS films with good optical properties are obtained up until the 50th imprint with complete-filling UV-NIL. Furthermore, the decrease on the aspect ratio of replicated PAK-01-CL due to the degradation of ARS mold, opposed the prescribed effective AR property (pitch; $p < 150$ nm, and height; $200 \text{ nm} < h < 300$ nm) [21], thereby leading to the poor performance of the optical properties of replicated PAK-01-CLs. Fig. 8 shows the SEM image of ARS mold after the 350th imprint of partial-filling UV-NIL. From the top view of SEM image, we can see the adhesion of resin in the interstices of the ARS mold. Whereas from the 75° tilted view, the damaged area on the

surface of ARS mold and the condition of the needlelike structures of ARS can clearly be observed. The reflectivity of ARS mold after repetitive of partial-filling UV-NIL was $1.50 \pm 0.75 \%$ in the spectral range of 300–1000 nm.

We carried out this experiment twice, and in both cases, we observed the same trend of experiment results. We target to achieve 1000 of ARS film imprints per mold by means of partial-filling UV-NIL. Fabricated ARS from GC material is brittle and RCL has a limitation. It becomes a pressing need to fabricate ARS molds that free from RCL and from a material that will offer antisticking effect, antifouling effect, and a tested durability. Our future work will be focused towards this goal.

4. Conclusions

We have achieved lifetime amelioration of ARS molds by means of partial-filling UV-NIL. We successfully fabricated ARS films with excellent performance until the 150th imprint, i.e., reflectivity of $0.25 \pm 0.15\%$ and transmittance of $94.0 \pm 0.50\%$ at visible wavelengths, compared to complete-filling UV-NIL, i.e., until the 50th imprint. We examined the resin filling behavior that affects the lifetime of the ARS mold and found that the durability of the RCL plays an important role in maintaining the lifetime of the ARS mold during repetitive UV-NIL. However, different resin fillings lead to different RFs. A strong RF will lead to rapid deterioration of the RCL and consequently affect the mold lifetime. Thus, we have demonstrated an effective technique for the mass fabrication of ARS films that offers simplicity and cost-effectiveness. We also believe that our proposed technique has a great advantage in improving the roll-to-roll nanoimprint lithography (R2R UV-NIL) technique.

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Figure captions

Fig. 1. Phenomenon of resin filling behaviors in UV-NIL: (a) Positive value of capillary force that attracts resin filling in hydrophilic ARS mold denotes as P_c ; (b) Negative value of P_c that against the resin filling in hydrophobic ARS mold denotes as P'_c . (c) Partial filling with filling pressure P_1 i.e. $P_1 < P'_c$ and its replicated result. (d) Complete filling with filling pressure P_2 i.e. $P_2 \geq P'_c > P_1$ and its replicated result.

Fig. 2. (a) Fabrication of ARS on top of GC by etching process. (b) Fluorine coating to construct a robust ARS mold.

Fig. 3. Repeated fabrication of ARS film by parallel-plate-type UV-NIL machine.

Fig. 4. SEM image of the master molds.

Fig. 5: RF and CA as a function of the number of imprints in the case of partial- and complete-filling UV-NIL.

Fig. 6: SEM images of ARS film replicated by PAK-01-CL: (a) partial-filled ARS film, and (b) complete-filled ARS film.

Fig. 7: Reflectivity at 5° incident light angle and transmittance of partial- and complete-filled ARS films at visible wavelengths.

Fig. 8: SEM image of the ARS mold after the 350th imprint of partial-filling UV-NIL.

Table 1. Morphologies of partial- and complete-filled ARS films.

Type of film	Number of imprints	ARS morphologies				
		Height, h [nm]	Diameter, d [nm]	Pitch, p [nm]	Aspect ratio	Surface area [$\times 10^{-4}$ m ²]
Partial-filled ARS	150	209 ± 2	57 ± 1	69 ± 2	3.67	8.07
	250	197 ± 4	74 ± 2	85 ± 5	2.66	6.29
	350	156 ± 3	101 ± 3	125 ± 3	1.54	4.97
Complete-filled ARS	50	400 ± 1	61 ± 5	72 ± 3	6.56	16.3
	75	350 ± 4	80 ± 3	100 ± 4	4.38	9.96
	100	325 ± 2	93 ± 5	122 ± 2	3.49	9.71

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Filling behaviors of resins

Normal phenomenon

(a) Capillary force P_c denotes as a positive value in hydrophilic mold

(b) P_c denotes as a negative value of P_c in hydrophobic mold

$P_1 < P_c$
(c) Development of partial filling of resin

$P_2 \geq P_c > P_1$
(d) Development of complete filling of resin

Partial-filling UV-NIL ameliorates the lifetime of ARS molds during repetitive UV-NIL