Microelectronic Engineering 141 (2015) 81–86

Contents lists available at ScienceDirect

Microelectronic Engineering

journal homepage: www.elsevier.com/locate/mee

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

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ARTICLE INFO

Article history:
Received 29 October 2014
Received in revised form 12 January 2015
Accepted 27 January 2015
Available online 7 February 2015

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

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 ± 0.15% and transmittance of 94.0 ± 0.50% at visible wavelengths, compared to complete-filling UV-NIL up to the 50th imprint.

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.

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http://dx.doi.org/10.1016/j.mee.2015.01.035
0167-9317/

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 × 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.

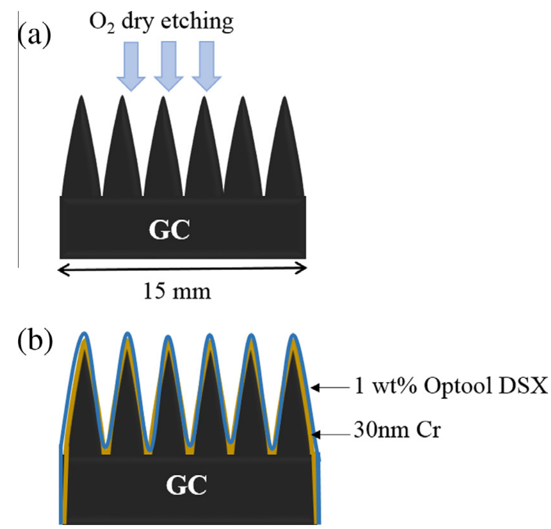

Fig. 2. (a) Fabrication of ARS on top of GC by etching process. (b) Fluorine coating to construct a robust ARS mold.

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 μm; Toyobo Cosmoshine 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/cm^2 UV dose, and a 5-s irradiation time; the

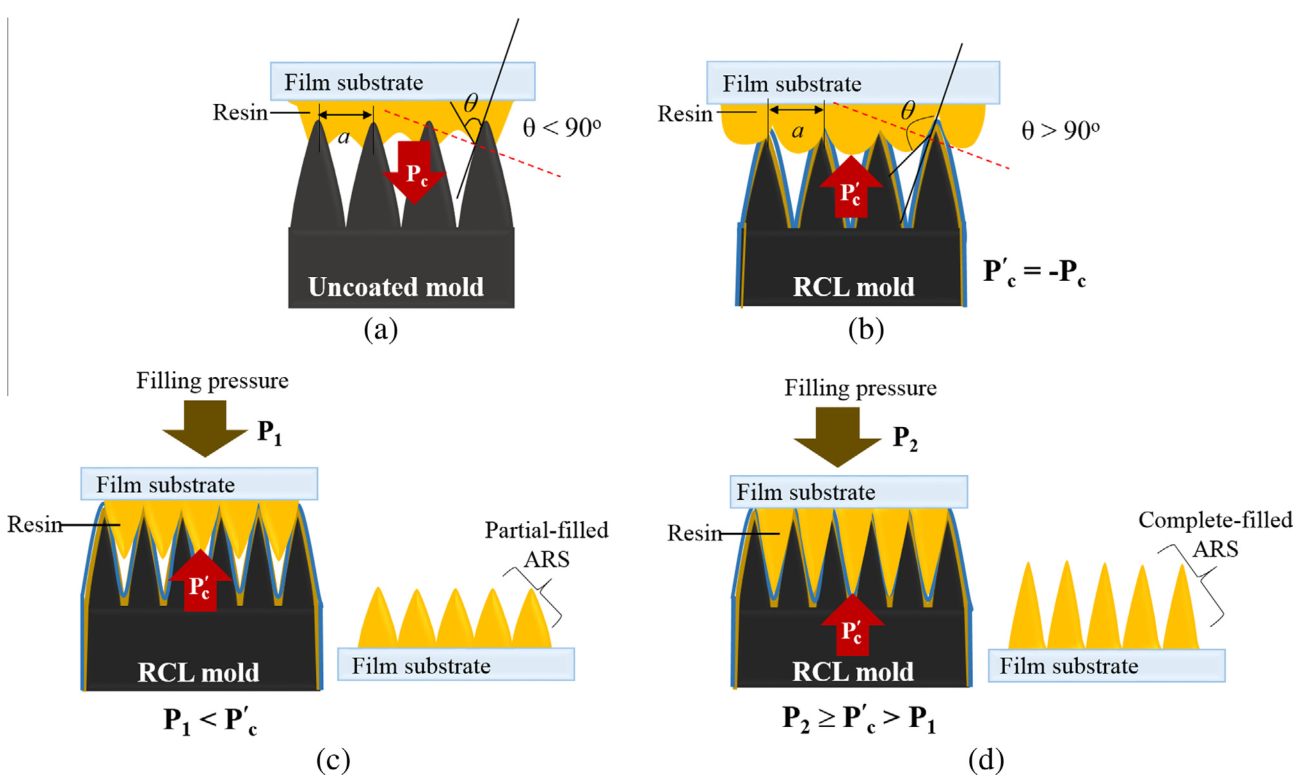

Fig. 1. Phenomenon of resin filling behaviors in UV-NIL: (a) positive value of capillary force that attracts resin filling in hydrophilic ARS mold denotes as P_c; (b) negative value of P_c that against the resin filling in hydrophobic ARS mold denotes as P'_c. (c) Partial filling with filling pressure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