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Three-dimensional thermal nanoimprinting by using lift-off patterns made of polymer resin

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ABSTRACT

Thermal nanoimprinting is expected to be a major breakthrough in the high-throughput fabrication of nanoscale structures made of polymers. However, it is generally recognized that residual layers generated in the nanoimprinting process are troublesome because they affect subsequent processes, such as etching or lift-off. Such residual layers are also undesirable when the imprinted patterns are used directly, especially in optical applications. We examined the fabrication of nanoscale steps of various heights on glass substrates by thermal nanoimprinting. We used a three-dimensional (3D) mold to produce multiheight structures made of polymer resin and, without using an etching process, we succeeded in fabricating 3D structures made of polymer resin in which no region carried a residual layer. We used such a structure, fabricated on a glass plate, to perform a calibration of layer-total internal reflection fluorescence microscopy in water.

1. Introduction

To fabricate effective fluidic devices, such as lab-on-chip devices or micro total-analysis systems, it is necessary to understand the three-dimensional (3D) fluid flow in micro- and nanoscale channels. The flow speed depends on the nature of the particular application; for example, for microreactors, single-phase laminar flow at a speed of 0.5–6 mm/s is required [1]. Total internal reflection fluorescence microscopy (TIRFM) [2] is a promising method for measuring two-dimensional (2D) fluid flow near a substrate at a submicron resolution by using fluorescent particles and evanescent light. The evanescent light is generated on the surface of a glass slide by total internal reflection of a laser beam, and it exists only very near the glass slide. Consequently, the background noise of an image captured by using evanescent light is lower than that obtained with vertical illumination. In addition, 3D fluid flows can be measured by the layer-TIRFM method [3,4]. In the case of layer-TIRFM, the z-position of the fluorescent particle can be calculated from the intensity of fluorescence $I(z)$, because it is known that this decays exponentially with the distance z normal to the surface of the glass slide, as expressed by Eq. (1) [3]:

$$I(z) = I_0 \exp\left\{-\frac{z}{z_p}\right\}. \tag{1}$$

Here, I_0 is the intensity of fluorescence at the interface; the penetration depth z_p is given by Eq. (2) [3]:

$$Z_p = \frac{\lambda}{4\pi n_2}\left[\sin^2\theta - \left(\frac{n_1}{n_2}\right)^2\right]^{-\frac{1}{2}}. \tag{2}$$

Here, λ is the wavelength of the laser beam (532 nm), and n_1 and n_2 are the refractive indices of water (1.333) and the glass slide (1.525), respectively. θ is the angle of incidence of the laser beam. Because the laser beam passes through an objective lens, and because the experimental set-up of our TIRFM equipment is complicated, we do not know the angle of incidence exactly; consequently, calibrations in z-direction of the fluorescence intensity are required before each measurement. It is therefore necessary to calibrate I_0 and θ by using an index-matching technique before performing layer-TIRFM measurements [3]. To achieve this, it is necessary to produce calibration plates with nanoscale steps of various heights. Furthermore, the refractive index of the nanoscale steps on the calibration plate must be identical to that of the working fluid; otherwise, the angle of the total internal reflection will be changed. MEXFLON is a polymer resin whose refractive index (1.33) is close to that of water. Someya et al. [5] have reported that MEXFLON can be used in an index-matching method with water. When the refractive index of an obstacle closely matches that of the fluid in which it is immersed, the obstacle will become invisible, and there will be no optical distortion. As a result, it is possible to measure the flow of the fluid around the obstacle.

We previously succeeded in fabricating a calibration plate for the layer-TIRFM method that had nanoscale steps made of MEXFLON [6].

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Our previous study showed that calibrations for layer-TIRFM can be performed by using these nanoscale MEXFLON steps. However, each fabricated plate used in our previous study had steps of a uniform height because the lift-off process that we used to fabricate the plates is a 2D patterning method. Because each of these calibration plates gave only a single data plot, we had to prepare a number of plates to permit curve-fitting of Eq. (1); this increased the number of experimental runs that were required and raised concerns about the parallelism and differences in thicknesses of the glass plates. We believed that the use of a single calibration plate with nanoscale steps of various heights might provide more-accurate conditions for calibration of layer-TIRFM.

Because the conventional lift-off process is a 2D patterning technique, it cannot be used to fabricate a multiheight calibration plate in one shot, and it was necessary to repeat both the deposition process and the lithography process to obtain multiheight plates. Since the evacuation time for vacuum deposition tends to be long, it is desirable to avoid repeating this process. Moreover, it is awkward to repeat the lithography process while overlaying. Consequently, a need existed for a fabrication technique that would be capable of producing a multiheight calibration plate in one shot.

We therefore used a thermal nanoimprinting technique [7] to fabricate nanoscale steps of several different heights on a single glass substrate. Thermal nanoimprinting is typically used to process a thermoplastic film, and it permits the fabrication of nanoscale steps with several different heights in one shot by using a 3D master mold. However, the generation of a residual layer beneath the fabricated nanosteps is unavoidable in the thermal nanoimprinting process, and the presence of this residual layer making it impossible to calibrate the base intensity of fluorescence on a glass substrate. Without specific precautions, it is hard to obtain an imprint with zero residual-layer thickness. Although the residual layer can be removed by reactive-ion etching, the plasma treatment results in roughening of the surface and edges of the polymer pattern, impeding precise calibration. Consequently, there is an urgent need for a 3D patterning technique based on thermal nanoimprinting that does not generate a residual layer. In this study, we performed nanoimprinting by using lift-off patterns made of MEXFLON. As a result, we succeeded in fabricating a multiheight calibration plate without using an etching process to remove any residual layer. The resulting MEXFLON pattern was shown to be suitable for use in the layer-TIRFM method.

2. Experimental

2.1. Preparation of multiheight calibration plates

Fig. 1 shows our process for 3D thermal nanoimprinting with zero residual-layer thickness. The process uses a lift-off pattern fabricated in poly(vinyl alcohol) (PVA) by using a metal mask [6]. First, a glass slide (Micro cover glass No. 1; Matsunami Glass Ind., Ltd., Osaka) was cleaned ultrasonically in a bath of acetone and deionized water for 15 min. The substrate was dried and spin-coated at 5000 rpm by using a solution of PVA (PVA-205; Kuraray Co., Okayama) diluted to 11% with deionized water. The PVA was then baked at 120 °C for 10 min to give a film approximately 500 nm thick [Fig. 1(a)]. Nano transfer printing (nTP) was carried out to form a metal mask on the PVA film [8]. A replica stamp for nTP, made from PAK-01-CL (Toyo Gosei Co., Tokyo) was previously prepared by UV nanoimprinting (UV-NIL). The stamp had a 40-μm-wide line/space pattern with a height of 2.2 μm. To improve its release properties, the nTP stamp was coated with a layer of chromium oxide (Cr_2O_3) [8,9]. A chromium layer approximately 30 nm thick was deposited by physical vapor deposition with a resistance-heating type vacuum vapor-deposition system (VPC-260F; Ulvac Kiko Inc., Saito City), and the vacuum evaporation system was subsequently ventilated to oxidize the surface of the chromium to Cr_2O_3. Subsequently, a 40-nm-thick layer of gold was deposited onto the nTP stamp by using the same equipment. The metal-coated nTP stamp was then used to imprint the PVA film at 120 °C for 5 min, giving a gold line/space pattern on the PVA film [Fig. 1(b)]. With the gold line/space pattern as a mask, the PVA film was selectively dry etched with oxygen by using inductively coupled plasma equipment (EIS-700; Elionix Co., Tokyo) [Fig. 1(c)]. The sample bias was 50 W, and the radio-frequency (RF) power was 300 W. The rate of oxygen gas flow was 50 SCCM and the etching time was 60 s. After etching, a layer of MEXFLON (E-PDx; Unimatec Co. Ltd., Ibaraki) was deposited onto the glass slide by using the etched pattern and the same vacuum-deposition equipment [Fig. 1(d)]. The PVA film was then removed by washing with deionized water [Fig. 1(e)] to leave a line/space pattern of MEXFLON on the glass slide. This pattern was equivalent to the calibration plate with nanoscale steps of a single height that we fabricated in our previous work [6].

Next, we performed thermal nanoimprinting of the resulting MEXFLON pattern by using a 3D mold [Fig. 1(f)]. The 3D master mold

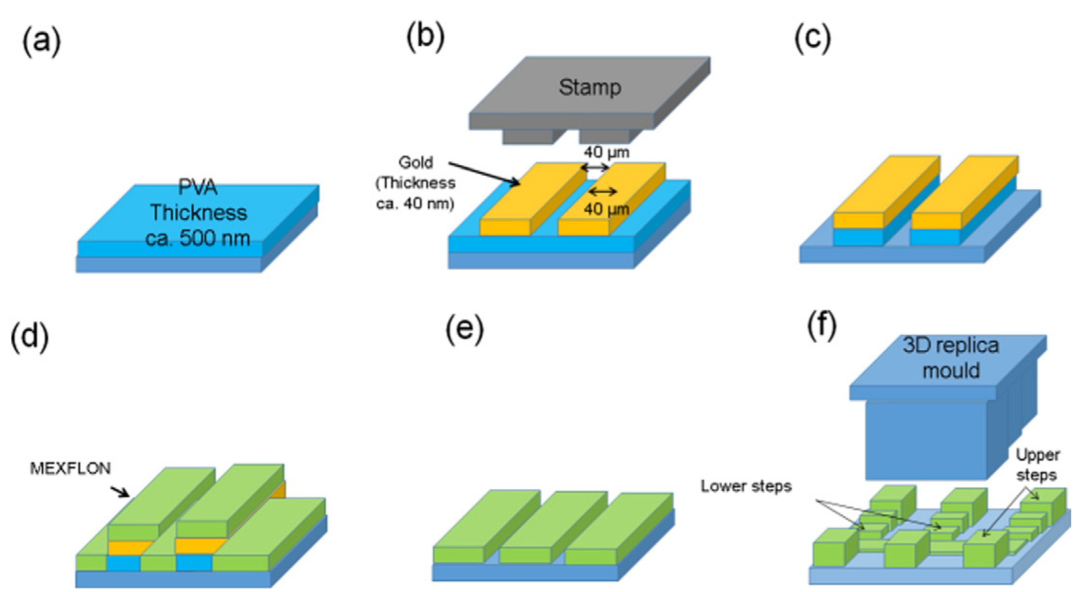

Fig. 1. Idealized sketch of preparation and use of multi-height calibration plate. (a) ultrasonic cleaning and spin-coating with PVA, (b) nanotransfer printing, (c) O_2 plasma etching, (d) vacuum deposition of MEXFLON, (e) lift-off with water, and (f) thermal nanoimprinting using the 3D replica mold.