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Residual-layer-free 3D nanoimprint using hybrid soft templates

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ABSTRACT

Specially designed hybrid soft templates are fabricated, evaluated and characterized for the application in UV-Substrate Conformal Imprint Lithography (SCIL), to enable residual layer free 3D patterning. The flexibility of soft templates allows imprinting over uneven substrates but today they suffer from laterally varying residual layer thickness in-between the imprinted structures, which cannot be removed by conventional processes. The hybrid template is a combination of UV-transparent Polydimethylsiloxane (PDMS) material and an UV-blocking metal layer over the top of the template protrusions. These templates aggregate the advantages of the photomasks in photolithography and conformal imprinting of the soft templates in SCIL process. Thereby, the hybrid template enables individual patterning by selective curing of the UV-curable imprint material during the imprint process and complete removal of the uncured residual layer areas in a single step. We investigated and characterized the surface properties of the PDMS material and its metallization techniques. The geometric design of the template, and corresponding process parameters are developed. We achieved residual-layer-free 3D imprinting irrespective of the initial residual thickness and enabling fabrication cost.

1. Introduction

UV-Nanoimprint lithography (NIL) is a technique of patterning nano and micro scale structures on UV-curable resist materials, using either rigid or flexible template materials [1,2]. NIL has potential applications in many research fields and it has been approved as next generation lithography in International Technology Road Map for Semiconductors (ITRS). SCIL is an enhancement to soft-UV-NIL, developed by Philips research and SÜSS MicroTech. This technique enables conformal imprinting over flexible/non-flexible substrates, while maintaining minimal pattern deformation [3,4]. However, despite of the imprint technique being used, removal and minimization of the residual layer in-between the imprinted structures are challenging. UV-NIL and SCIL templates with consistent structures leave a uniform and thin residual layer on the imprinted substrate and this can be removed by a reactive ion etching (RIE) process step, at a cost of lateral structure deformation due to anisotropic etching. Templates with distinctive 3D features result in a laterally varying residual layer between the imprinted structures. This non-uniformity is caused due to the filling of resist material into template cavities by capillary forces and the very low (~0.02 mbar) contact force during imprinting. Due to this capillary effect, larger cavities are filled with more amounts of resist and leaving behind a thin residual layer. While other small cavities are filled with smaller amount of resist leaving a thicker residual layer around them. Thus in 3D SCIL process, the thickness of the residual layer depends upon the volume of the structures present on the template. A 3D soft template fabricated with a UV-transparent PDMS material, attached to a flexible carrier, is shown in Fig. 1(a). A Schematic representation of the non-uniform residual layer in-between the imprinted structure is shown in Fig. 1(b). Wang et al. are minimizing the residual layer by complementary patterns but complete removal of residual layer in-between the imprinted structures is still not possible [5]. Etching of the 3D residual layer results in over etching of thin residual areas and incomplete etching of thick residual areas, making it impossible to keep the imprinted structures disconnected over the entire sample. The effect of non-uniform etching of the residual layer is shown in Fig. 1(c). Although various UV-NIL techniques like Combined Nanoimprint Lithography [6] and Reverse-Contact Nanoimprint lithography [7] are promising for complete removal of the residual layer, but they are limited by the template material (non-flexible) and are not yet been used for soft-conformal lithography. Methodologies like template filling, reducing initial resist thickness and micro-contact imprinting were also proposed to minimize the residual layer using flexible template materials [8,9,10]. But these techniques suffer from incomplete filling of the template cavities for 3D templates and limited aspect ratio. They are also limited by the surface energy mismatch between the template and the substrate materials during the transfer process. Cheng et al. have demonstrated the hybrid selective curing technique on fused silica templates for residual layer removal in UV-NIL [6]. But to achieve a complete removal of residual layer with 3D soft templates, with minimal template and structure deformation is a challenging task. In order to solve this problem, we

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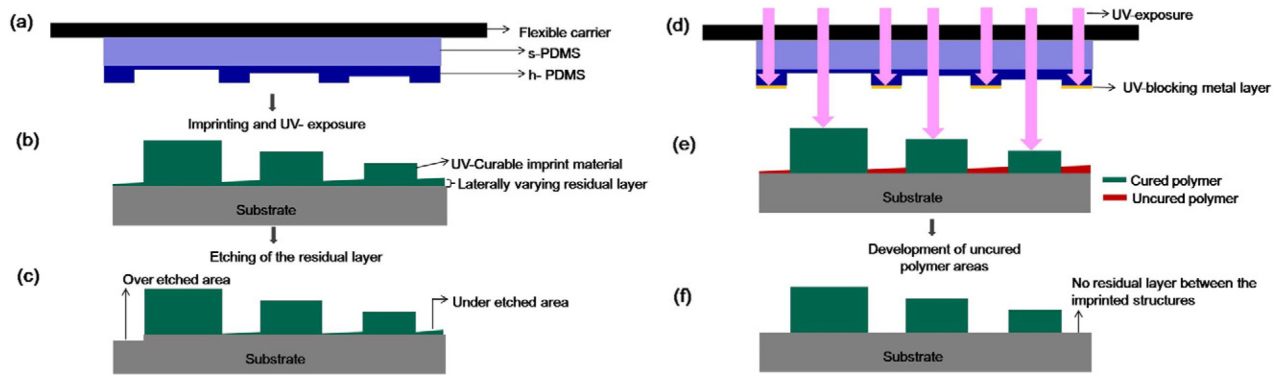

Fig. 1. (a) Standard soft template for SCIL, (b) non-uniform residual layer after imprint on an UV-curable resist material, (c) over and under etched areas of the residual layer between the structures, (d) hybrid soft template with UV-blocking metal on its structure protrusions, (e) imprinted structures separated into cured and uncured polymer areas and (f) imprinted structures revealing no residual layer after the development process.

introduce a hybrid soft template consisting of the PDMS material adjoined with a metal layer structured over its heights and thereby enabling selective UV-curing of the imprint material. Therefore, the uncured residual areas between the template protrusions are removed completely by the development process, despite their non-uniformity.

This paper is organized as follows: In the second section, the principle of proposed methodology and its functioning are presented. In the third paragraph, physical and chemical properties of the PDMS material and different surface modification techniques are considered. Finally in the fourth paragraph, the results and discussions about the fabrication of hybrid template and residual-layer-free imprinting are characterized and explained.

2. Methodology and design

In the proposed technique, a hybrid PDMS template is fabricated as such its microstructure protrusions are covered with an UV-blocking metal layer and the rest of the template is left UV transparent. Thereby the hybrid template is embedded with the selective UV blocking properties of a photomask in photolithography and conformal imprinting advantages of the soft template in SCIL process. Fig. 1(d) represents a schematic of hybrid SCIL with the structured metal layer on top of its protrusions. The 3D soft template fabricated with soft PDMS material, attached to a flexible carrier allows conformal imprinting over large areas. The hard PDMS, which has higher Young's Modulus than the soft PDMS, avoids lateral deformation of the template and maintains high resolution [11]. When the template is imprinted over the UV-curable resist material, the metal layer blocks the UV light and the rest of the template is transparent, allowing the light to pass through it, as shown in Fig. 1(e). So that the polymer underneath the template protrusion is left uncured, this will remain as the residual layer after the imprint process. The rest of the imprinted structure areas are cured by the UV light. Fig. 1(e) represents the cured and uncured polymer parts of the resist material after the imprint process. The imprinted samples are developed and this enables complete removal of uncured polymer underneath the metal areas by the developer solution. Thus irrespective of its thickness, the residual layer is removed in a single step, as shown in Fig. 1(f). The expensive and time consuming steps like reactive ion etching and plasma etching are not necessary. The fabrication of the hybrid template and detailed explanation about PDMS and its modifications are discussed in the following sections.

3. PDMS and its surface modification methodologies

PDMS is a polymeric organosilicon elastomeric compound. Its medium-high elastic modulus, low shrinkage during the curing process and its hydrophobic nature makes it an excellent material for standard NIL templates [12,13]. However the metallization and selective pattering of the PDMS surface are extremely difficult due to its hydrophobic nature and low surface energy. Deposition of different metal on untreated PDMS surface results in random buckling. This is due to the mismatch of thermal expansion coefficients between the deposited metal and the PDMS. Hence, the adhesion of metal to PDMS is very poor and slight mechanical stress results in delaminating of the deposited metal [14, 15]. Different surface modification techniques for PDMS surface like wet chemical methods, thermal aging, chemical vapor depositions and many other dynamic surface modifications have been reported and used in micro fluid device applications over the years [16]. Research on bonding strength of various metals and their structuring on the treated PDMS surface has been of research interest for flexible electronics in recent years [17,18]. In this paper, a combination of oxygen-plasma and UV surface modification methodologies are implemented to stabilize the surface properties of the PDMS and thereby making the template suitable for flexible metallization and conformal imprinting.

3.1. O_2 plasma surface treatment

The hydrophobic behavior of PDMS is from the non-polar Si–CH_3 (methyl) groups on its surface, consequently making the adhesion of any polar material on the surface impossible. This weak boundary surface layer with short hydrocarbon chains can be modified with O_2 plasma oxidation treatment [19]. The partially ionized oxygen molecules inside the plasma react with the methyl groups and form polar Si–OH (silanol) groups. The hydrophilic nature and polar components over the surface are improved and there by resulting in permanent bonding between the deposited materials on the PDMS surface [16]. In general, goniometric contact angle measurement setups are used to determine the improvements in hydrophilic property of PDMS [20,21]. The surface energies of treated PDMS surface are calculated using the Owens & Wendt method, using Eq. (1).

$$\frac{\sigma_L(1+\mathrm{COS}\theta)}{2(\sigma_L{}^D)^{1/2}} = \left(\sigma_S{}^P\right)^{1/2} + \left(\sigma_S{}^D\right)^{1/2} \quad (1)$$

where σ_L is overall surface tension of the wetting liquid, $\sigma_L{}^D$ is the dispersive component of surface tension of the wetting liquid, $\sigma_L{}^P$ is the polar component of surface tension of the wetting liquid, σ_S is the overall surface energy of the solid, $\sigma_S{}^D$ is the dispersive component of surface energy of solid, $\sigma_S{}^P$ is the polar component of surface energy of solid and θ is the contact angle.

3.2. UV treatment on pre-strained of PDMS surface

UV treatment is a photo-sensitized process of oxidizing the PDMS surface, during which the weak boundary methyl groups are destroyed