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Thermal nanoimprint lithography using fluoropolymer mold

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ABSTRACT

We studied the properties of a fluoropolymer based on perfluoropolyether (PFPE) as the mold material for thermal nanoimprint lithography. The PFPE mold was duplicated from a hard master mold by casting and thermal-curing of the PFPE pre-polymer mixture. The PFPE mold was able to pattern 100 nm half-pitch grating into a resist, with the very fine line edge roughness of the master mold faithfully duplicated into the resist. This implies PFPE is capable of a resolution far beyond 100 nm, which is consistent with its high elastic modulus (two orders higher than PDMS) extracted from nanoindentation experiment. It was found that the elastic modulus is much higher near the film surface than deep inside the film. This is a very desirable property for an imprint mold, as the relatively stiff top surface offers high resolution, whereas the more flexible bulk is important for a conformal contact with the substrate and easy demolding.

1. Introduction

Nanoimprint lithography (NIL) is a cost-effective and high throughput patterning technique with sub-10 nm resolution. NIL can be divided into two categories: thermal NIL (or hot embossing lithography) and UV-curing NIL based on photo-polymerization of pre-polymer mixtures. Whereas UV-NIL has advantages including absence of thermal expansion that impedes precise alignment, low imprint pressure and low viscosity of the uncured resist, thermal NIL is still more widely employed for nano- and micro-patterning, largely because it is more straightforward and works with a broad range of polymer materials. Moreover, the mold release agent used for anti-sticking during demolding is not degraded by thermal NIL as it is by UV-curing NIL [1,2]. In NIL, one key element is the mold that is typically fabricated in silicon or quartz wafers. However, they are brittle and susceptible to damage, which is a serious problem for NIL because the molds are usually fabricated by very costly electron beam or focused ion beam lithography. In addition, they are rigid and thus unsuitable for imprint on non-flat surfaces and automatic demolding necessary for high-throughput prototyping [3].

To overcome this limit, various polymeric materials have been investigated for use as NIL mold material. Simple thermoplastic polymers such as PMMA and polystyrene can be used for UV-NIL that is carried out at room temperature. However, they are rigid and brittle like silicon, and incompatible with mold release layer treatment using silane surfactant. The former issue can be overcome by coating the polymer on a soft elastomeric xpolydimethylsiloxane (PDMS) support [4]; and the latter by using a polymeric material containing silicon, whose surface can be converted into silica upon oxygen plasma treatment [5–7]. Up to now, PDMS is undoubtedly the most widely used polymer mold material since it has flexible backbone structure, high degree of toughness and large elongation. More importantly, PDMS mold can be fabricated easily by cast-molding from a rigid mater template. However, it is not suitable for high resolution and high aspect ratio patterning due to its low elastic modulus (1.5 MPa). Moreover, its surface energy (25 mN/m) is still not low enough for non-destructive demolding.

Polytetrafluoroethylene (PTFE, Teflon) is an excellent mold material for thermal and UV-NIL owning to its very low surface energy, ideal elastic modulus (0.5 GPa, between the too soft PDMS and the too brittle PMMA), stability at elevated temperature, and resistance to most chemicals. Unfortunately, it is difficult to duplicate PTFE mold from a master by hot embossing because of its very high melting temperature of 327 °C. Ethylene tetrafluoroethylene (ETFE, DuPont "Tefzel") has favorable properties close to PTFE and it can be molded at 250 °C [8,9], which is within the limit of some thermal NIL tools. It is apparently desirable to have a PTFE-like material that can be molded at room or moderate temperatures. This was first realized using a fluoropolymer material Teflon AF 2400, which is a powder and can be dissolved in a perfluorinated solvent for cast-molding from a master [10]. However, it demonstrated a resolution of only 150 nm.

Recently perfluoropolyether (PFPE) and its derivatives have gained popularity as soft mold materials [11–14]. The pre-polymer mixture is a liquid at room temperature, and can be cross-linked under UV exposure or thermal annealing. With a very low surface energy of 12 mN/m [15,16], mold release agent is no longer needed, thus the mold can be used repeatedly with less severe

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(yet noticeable) degradation by UV-curing NIL [2]. Like PTFE, it is chemically and thermally stable and swells much less than PDMS when exposed to most organic compounds. Moreover, particles can be easily removed from the mold surface [16]. Previous studies using PFPE-based mold material only focused on UV-curing NIL carried out at room temperature, with the PFPE mold duplicated by UV-curing from a master. In this work we studied its performance for thermal-NIL to fully take advantage of its high temperature (up to 288 °C) stability, with the mold duplicated by thermal-curing from a master. We also studied the mechanical properties of PFPE thick film using nanoindentation technique.

2. Experiment

To eliminate thermal expansion mismatch when imprinting onto a resist-coated silicon substrate, we used a silicon wafer as a support for the fluoropolymer layer. Since silicon is opaque to UV, the PFPE-based fluoropolymer mold was duplicated by thermal annealing (Fig. 1a). We first dissolved a thermal free radical initiator 1,1′-azobis(cyclohexanecarbonitrile) (ABCN, Sigma Aldrich) in ethanol to a concentration of 0.1 M, and then added 1 ml of this mixture into 50 ml of bi-functional urethane methacrylate perfluoropolyether (Fluorolink MD 700, Cornerstone Technology Inc.). The ethanol was subsequently removed by vacuum. The Si master mold has 200 nm period grating pattern with 120 nm depth, and was fabricated by interference lithography. Next, a few drops of the pre-polymer mixture was applied on the master mold and covered by another flat silicon wafer as support. In order to facilitate demolding from the master mold, the master mold was coated with a mold release agent 1H,1H,2H,2H-perfluorooctyltrichlorosilane. Finally, thermal curing of the pre-polymer mixture was carried out at 90–120 °C for 1–3 h in a nitrogen environment. One critical issue is the adhesion of the fluoropolymer to the silicon support, which is very poor due to the low surface energy of the fluoropolymer. We believe that the poor adhesion is also an issue for UV-curing NIL, though to a less degree than thermal NIL that involves high pressure. To improve the adhesion, we treated the silicon support with (3-acryloxypropyl) trichlorosilane (SIA0199.0, Gelest) in vapor phase.

For thermal NIL using the PFPE mold (Fig. 1b), we chose poly (vinyl phenyl ketone) (PVPK) as resist, which is 3× more resistant to plasma etching than PMMA. Additionally, PVPK has lower glass transition temperature (58 °C vs. ~105 °C for PMMA) and surface energy (water contact angle 75°, vs. 68° for PMMA) for easier demolding. It was dissolved in toluene with concentration of 4 wt/vol.% and spin-coated on a silicon wafer, followed by baking at 120 °C for 2 min. Thermal NIL was carried out at 90 °C and 7 bars for 10 min using a house-built parallel plate imprint tool. The imprint results were characterized using a LEO 1530 field emission scanning electron microscope (SEM).

The mechanical properties of PFPE films with thickness greater than 250 μm were characterized by using the nanoindentation technique, according to the Oliver and Pharr method [17]. These experiments were carried out using an in situ nanoindenter (Nanomechanics Inc., Knoxville, TN) equipped with a sharp Berkovich diamond tip. Fused silica was used to calibrate the area function of the indenter tip, and at least nine indentations were performed on each specimen. The indentation experiments were performed by using the load controlled technique with peak loads of ~1, 0.5, 0.25, 0.13 and 0.06 mN. These maximum loads were achieved in 20 s with the corresponding loading rates of ~0.05, 0.025, 0.013, 0.006 and 0.003 mN/s, respectively. At each maximum load, the force applied was held for 10 s. The elastic modulus (*E*) and the hardness (*H*) values were extracted using a Poisson's ratio of 0.18 based on the unloading data obtained from 5 cycles of loading and unloading.

3. Results and discussion

Fig. 2 shows the top view and cross-section of 200 nm period grating imprinted into PVPK using the PFPE mold with 20–30 μm thickness on a silicon support wafer. The height of the grating lines is about 120 nm. As shown in Fig. 2b, the fine details of the line-edge roughness of the master mold were faithfully duplicated into the resist, implying the fluoropolymer mold is capable of resolution far better than 100 nm. This is expected, given that our PFPE has an elastic modulus (E) two orders higher (see below) than PDMS that can typically achieve a resolution of several 100s nm, and that theoretically the resolution of the mold material can be approximated by γ/E with γ being the surface tension [18]. In fact, high resolution of sub-20 nm has been demonstrated previously using PFPE mold and UV-curing NIL [18]. To study the thermal stability of the PFPE mold, as our home-built imprint tool cannot achieve high temperatures, we annealed a mold having 200 nm

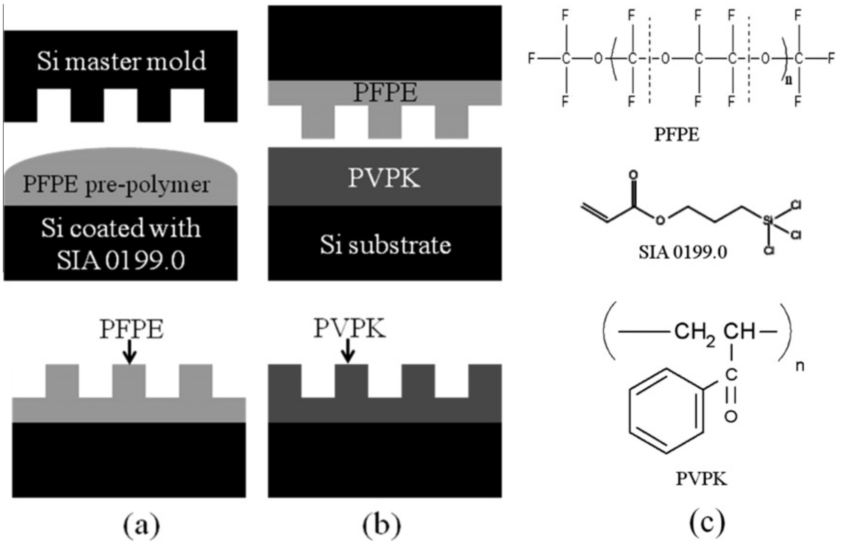

Fig. 1. (a) Schematics of the fabrication of the PFPE mold from a hard master mold; (b) thermal nanoimprint into PVPK using the PFPE mold; (c) chemical structure of PFPE, SIA 0199.0 surfactant, and PVPK resist.