Control of Sub-50 nm Thickness of UV-Cured Thin Films by Print-and-Imprint Method

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Introduction: The process of ultraviolet nanoimprint lithography (UV-NIL) involving several dry etching procedures has one of crucial issues. The issue is to level a whole residual layer thickness of an imprinted resist layer as thin as possible. Some displacement technique of UV-curable liquid droplets is necessary for achieving the leveling of residual layer thicknesses independently of differences in area density of pattern recesses on a mold surface. For the purpose, ink-jet printing to dispense low-viscosity UV-curable liquid is adopted in jet and flash imprint lithography (J-FIL). Alternatively, we have proposed laser-drilled screen printing [1] and study its applicability to high-viscosity UV-curable liquids. The residual layer thickness would be determined simply by a total volume of UV-curable liquid displaced on a substrate surface, under the condition that an imprinted area is constant in UV nanoimprinting. However, an undefined imprinted area is generally formed after imprint in the case that the external dimension of the mold is larger than the area of displaced liquid droplets (Figure 1). Even if the mold with a mesa structure is used, the liquid exudes out of the mesa region. The undefined imprinted area and the liquid exudation cause difficulty to control residual layer thickness. In this study, we selectively modified mold and substrate surfaces with an oleophobic fluorinated self-assembled monolayer (*F*-SAM) to investigate whether the presence of *F*-SAM enabled to prepare a certain area of UV-cured thin films and to control the residual layer thickness lower than 50 nm by tuning total volumes of UV-curable liquid.

Experimental: Surfaces of fused silica superstrates with a 10×10 mm^2 mesa structure and silicon wafer substrates were wholly modified with tridecafluoro-1,1,2,2-tetrahydrooctyltrimethoxyilane (FAS13) [2]. Each 8.4×8.4 mm^2 area of the superstrate mesa region and the substrate were cleaned by UV/O_3 mask exposure. The selectively cleaned surface was modified with an adhesive layer of 3-(acryloxyoxy)propyltrimethoxysilane (ACL) for the substrate and with a release layer of chlorodimethyl(3,3,3-trifluoropropyl)silane (FAS3-Cl) for the superstrate. Polyimide (PI) laser-drilled screen masks [3] with 10-μm-diameter through holes of certain pitches were used. Print-and-imprint method with fluorescent UV-curable liquid (NL-SU1FL) [4] was carried out as illustrated in Figure 2.

Results and Discussion: PI masks with three types of pitches of 80, 125, and 175 mm were prepared. The three-type pitches corresponded to total numbers of 11,025, 4,489, and 2,304 liquid droplets, which were designed for the residual layer thickness of 50, 20, and 10 nm. The superstrate with a mesa modified with FAS13 and FAS3 was contacted with the substrate as shown in Figure 2 under an applied force of lower than 30 N. Figure 3 shows reflection-mode optical microscope images of cured resin films with designed thicknesses of 50 nm [Fig. 3(a)], 20 nm [Fig. 3(b)], and 10 nm [Fig. 3(c)]. The shapes of cured thin films were almost consistent with those of chemical registration which were performed for the superstrate and substrates. The chemical registration had a suppressive effect on unintended spread of the UV-curable resin between the superstrate and substrates. The actual average thicknesses determined by surface profiling were 41.6, 20.4, and 7.5 nm.

Reference: [1] WO.2016031237.A1. [2] *ACS Appl. Mater. Interfaces* **9**, 6591 (2017). [3] *J. Vac. Sci. Technol. B* **35**, 06G301 (2017). [4] *Bull. Chem. Soc. Jpn.* **91**, 178 (2018).

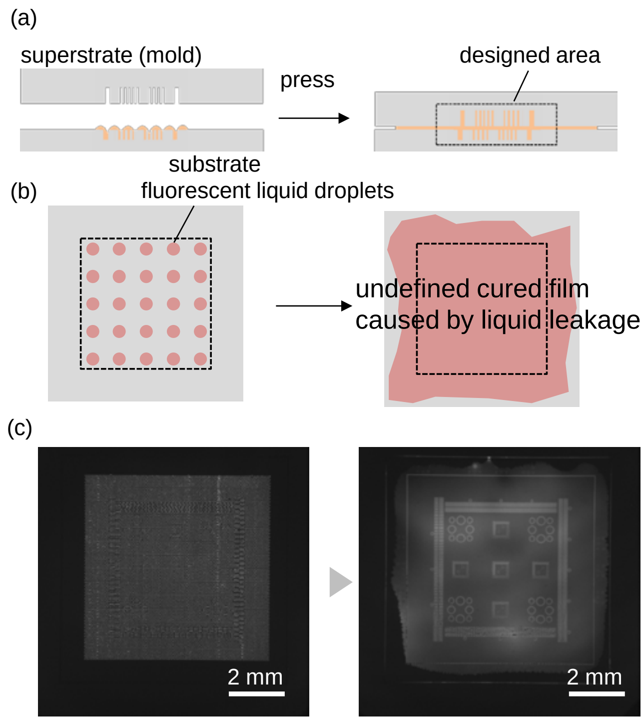

Figure 1. (a, b) Schematic illustrations of (a) cross-sectional view and (b) top-view of liquid spreading on contact of a (mold) superstrate with a substrate on which droplets of UV-curable liquid were screen-printed with a polyimide laser-drilled mask. (c) Actual fluorescence microscope images of fluorescent liquid droplets on a substrate and fluorescent UV-curable liquid placed between a mold and substrate.

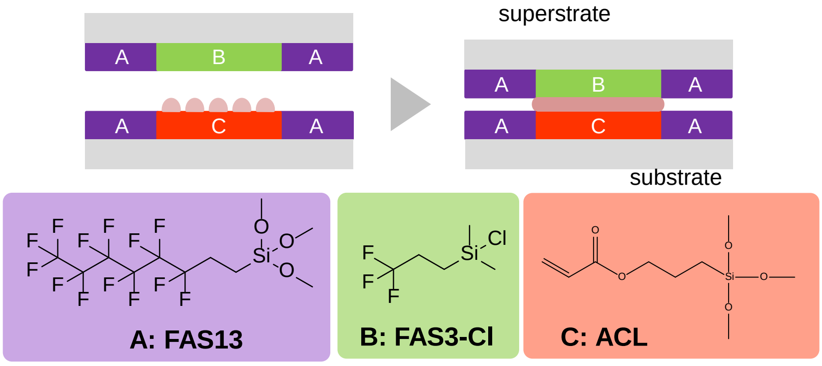

Figure 2. Concept of chemical registration to suppress liquid leakage on contact of a superstrate with a substrate. The superstrate surface has an external region of FAS13 and an internal region of FAS3-Cl, while the substrate had an external region of FAS13 and an internal region of ACL.

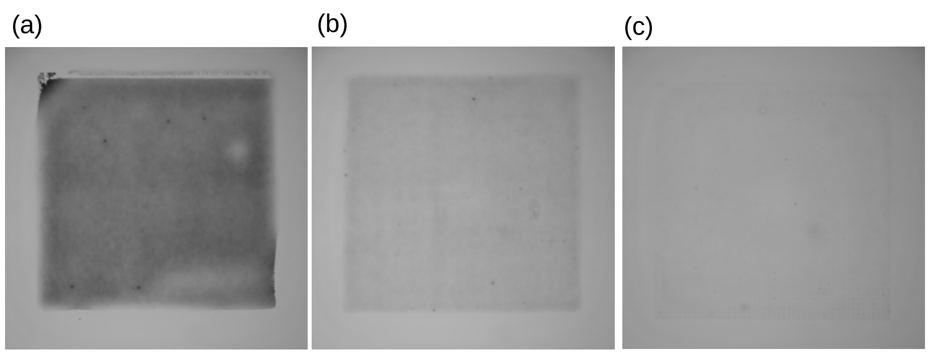

Figure 3. Reflection-mode optical microscope images of UV-cured thin films with a thickness of (a) 42, (b) 20, and (c) 8 nm which were prepared by tuning the total number of liquid droplets screen-printed onto substrates in print-and-imprint.