

How far does a droplet of UV-curable liquid spread between the mold and silicon surfaces in nanoimprinting?

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Ultraviolet nanoimprint lithography (UV-NIL) is a candidate for next-generation lithography technology of single digit nanofabrication and is attracting attention for its low energy consumption. The amount of UV-curable liquid placed on the substrate surface is determined based on the local volumes of concave-pattern voids on the mold surface. Inkjet printing [1] or laser drilled screen printing [2] enables the fixed quantity layout of UV-curable liquid and achieve the uniformity of the residual layer for UV-cured resist patterns on the substrate surface. On the other hand, it has been pointed that, in some cases, applied force for alignment increased at nano-gaps between synthetic quartz mold and silicon substrate surfaces during the alignment process moving the substrate to the mold.[3] Although large alignment force is caused by the thinning of the residual layer, the reason is not well understood from scientific viewpoints. A residual layer thickness of less than 10 nm is desirable in accurate single digit nanofabrication involving the formation of resist masks and the dry etching of substrate surfaces. Such an ultrathin residual layer should maintain the fluidity to allow alignment.

The purpose of this study is to gain fundamental knowledge of how far the residual layer can be thinned. Sub-picoliter volume droplets of a UV-curable liquid were printed and placed on a silicon substrate and then pressed using a flat synthetic quartz mold. We investigated the dependence of the retention time after reaching a certain allied force, the applied force, and the thickness of the surface oxide layer of the silicon substrates on liquid advancing at nanogaps.

A UV-curable liquid (viscosity, 11 Pa · s) [2] causing methacrylate radical photopolymerization (Fig. 1) was used. A polyimide stencil mask with 10 μm-diameter through holes was used to place droplets on modified p-type silicon wafers. The surface modification of Si was performed with an adhesive agent of 3-(acryloyloxy)propyltrimethoxysilane. A flat synthetic quartz mold surface of 10 mm square was modified with a release agent of chlorodimethyl(3,3,3-trifluoropropyl)silane. As illustrated in Figure 2, the droplets were pressed with the flat mold at applied forces, maintained for certain retention time, cured by UV light exposure, and demolded. The shapes of the droplets spreading at nanogaps were measured by FE-SEM.

The spreading shapes of the droplets after pressing and curing were measured by approximating the circumference. The diameters of the circumference pressed at an applied force of 100 N were compared in the retention time between 1 min and 60 min. The diameters were 378 μm for 1 min and 396 μm for 60 min, whereas the diameters of droplets before pressing were 22 μm. No clear difference in the spreading behavior at nanogaps was observed in the controlled range of 30 - 100 N in applied force for a retention time of 1 min.

In contrast, thickness dependence of a silicon oxide layer on a Si substrate surface was observed for the spreading shapes of droplets after pressing at 30 N for 1 min. The diameter of the transformed droplets was 180 μm on a native oxide layer of 2 nm, whereas those were approximately 250 μm on thermal oxide layers of 10 nm or thicker (Figure 3). This study clearly suggests that the thickness of the surface silicon oxide layer is one of the dominant factors that inhibit liquid spreading at nanogaps. The UV-curable liquid contains a dimethacrylate monomer with two hydroxy groups. The monomers can form intermolecular

hydrogen bonds to increase viscosity. Van der Waals interactions arising from the Si/SiO₂ interface may have been strong and suppressed the spreading behavior of the hydrogen-bonded UV-curable liquid.

Reference

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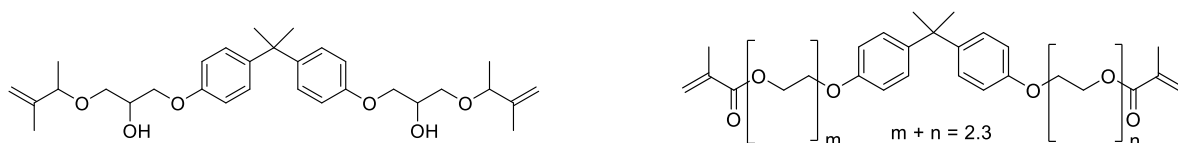


Figure 1. Chemical structures of two dimethacrylate monomers comprising UV-curable liquid (viscosity, 11 Pa·s) used in this study.

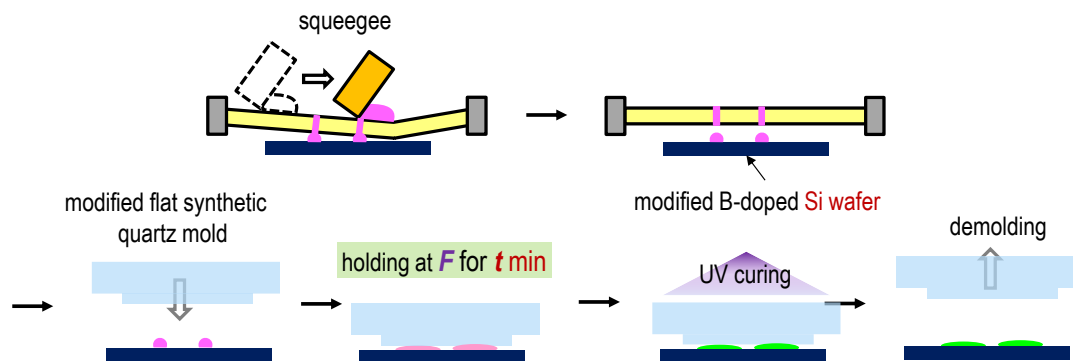


Figure 2. Schematic illustration of printing UV-curable liquid on a modified silicon wafer, pressing and transforming a droplet of UV-curable liquid with a modified flat synthetic mold.

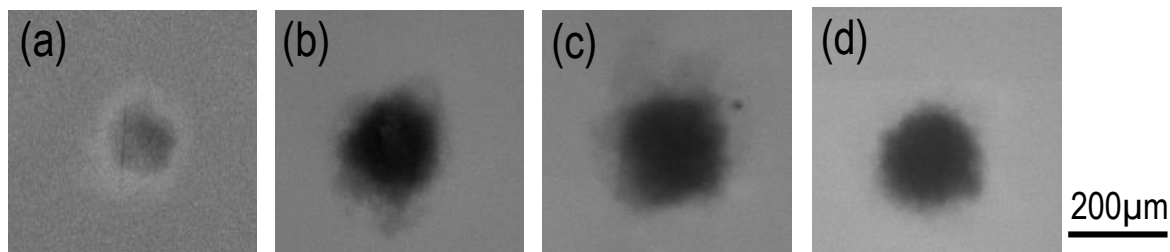


Figure 3. Surface FE-SEM images of transformed droplets at nanogaps between the mold and substrate surfaces. Printed droplets were transformed on modified Si wafer with different thicknesses of a silicon oxide layer. The thicknesses of the silicon oxide layer were (a) 2 nm, (b) 10 nm, (c) 20 nm, and (c) 30 nm.