Similarity effect of polymerizable functional groups of monomers and adhesive agents on liquid advancement in UV nanoimprinting

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UV nanoimprint lithography (UV-NIL) is known as a nanofabrication method via resist process on the tens to single-digit nanometer scale. In the UV-NIL alignment process, it has been reported that shear stress begins to increase when a nanogap, the distance between the mold and substrate, becomes less than 30 nm, and the substrate hardly moves at nanogaps below 10 nm.¹ To understand this phenomenon, we have studied liquid advancement of isolated droplets of UV-curable liquid on substrate surfaces by pressing them with a flat mold surface. Herein, we report that a similar acrylate-type surface modifier on a silicon surface can promote liquid advancement of methacrylate-containing monomers better than an identical methacrylate-type surface modifier.

Dye-containing UV-curable droplets with average diameter (*d*) of 20 μ m and height (*h*) of 1.5 μ m were screen-printed and placed on a Si substrate surface treated with 3-(trimethoxysilyl)propyl acrylate (ACL) or 3-(trimethoxysilyl)propyl methacrylate (MCL) as an adhesive surface modifier. Thin isolated films (*d*, 0.2 mm; *h*, 0.01 μ m) were obtained by UV nanoimprinting with a flat modified surface (area, 100 mm²) of a synthetic quartz mold (Fig. 1).² Applied force was varied from 60 to 90 N. After demolding, spreading areas of transformed droplets were measured by fluorescence microscopy (Fig. 2a), and their heights were measured by surface profiling (Fig. 2b). Twenty-five transformed droplets were measured for respective samples prepared under different surface modifiers and applied forces.

Figure 3a shows spreading areas of thin films transformed under different applied forces. The spreading areas on ACL-modified surfaces increased with increasing applied force, whereas those on MCL-modified surfaces were almost maintained. This suggests that the adhesive surface modifier of acrylate-type ACL had a similarity effect of polymerizable functional groups on liquid advancement of methacrylate-type UV-curable liquid in UV nanoimprinting. As indicated in Figure 3b, the ACL-modified surface caused lower heights of thin transformed-droplet films than the MCL-modified surface. This also suggested that the homology of polymerizable groups between the adhesive surface modifier and monomer resulted in confinement at nanogaps. Such a similarity effect was identical to the report that a diacrylate monomer was confined at a nanogap between silica surfaces modified with ACL or MCL surface modifiers by resonance shear measurements.³

¹S. Kobayashi, et al. *Proc. SPIE*, **2016**, 9777, 977708.

²M. Nakagawa, et al. Jpn. J. Appl. Phys., **2023**, 62, SG1010.

³S. Ito et al. *Chem. Lett.*, **2019**, *48*, 943.

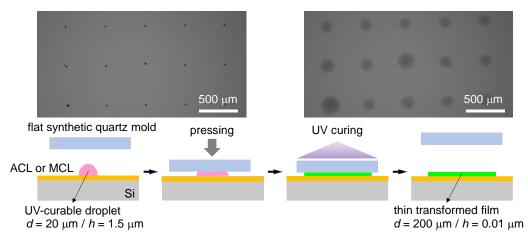


Figure 1: Schematic illustration of procedures to fabricate thin transformed-droplet films (right) by UV nanoimprinting using isolated UV-curable droplets (left) which were placed via laser-drilled screen-printing on a modified silicon surface.

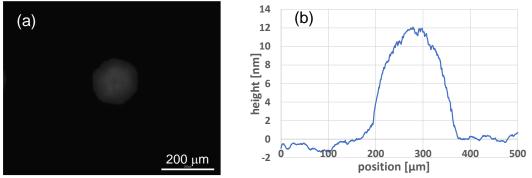


Figure 2: (a) Fluorescence microscope image and (b) height profile of a transformed-droplet film on an ACL-modified silicon surface.

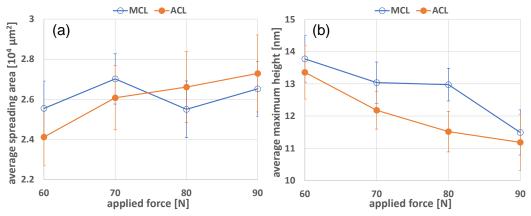


Figure 3: Relationships of applied force with (a) average spreading area and (b) average height of thin transformed-droplet films on silicon surfaces modified with adhesive surface modifiers of MCL (open cercle) and ACL (filled cercle).