

Fluidity of an oleophilic monomer in nano-gap between reactive adhesive monolayers for UV nanoimprinting

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UV nanoimprint lithography is one of promising technologies for the fabrication of fine patterns of sub-15 nm and following single-digit-nanometer size especially in the field of semiconductor devices. We think that fluidity of UV-curable resins between surfaces should be investigated because the increase in viscosity of liquid under confinement is known recently in the field of surface science. We previously reported that, for 1,10-decanediol diacrylate (AC10, Figure 1a) with a bulk viscosity of 10 mPa·s, the viscosity of AC10 began to increase at surface-surface distances less than 6 nm between hydrophilic unmodified silica surfaces.¹ The increase in the viscosity between mold and substrate surfaces would make alignment process difficult in UV nanoimprinting. In this study, in order to understand fundamental effect of the adhesion layer on the monomer viscosity, we investigated nanometer-resolved fluidity of AC10 between silica surfaces modified with a reactive adhesive monolayer by surface forces and resonance shear measurements.

We selected 3-(acryloyloxy)propyltrimethoxysilane (ACL) as a surface modifier to prepare the reactive adhesive layer (Figure 1b). Molecularly smooth silica surfaces were prepared and glued onto cylindrical lenses according to our previous report.¹ The silica surfaces were modified with ACL by chemical vapor surface modification method. Resonance shear measurement was performed for AC10 monomer between the ACL-modified silica surfaces with the decreasing surface-surface distances D in 0.1 nm resolution (Figure 2).

Figure 3 shows the resonance curves for AC10 with the decreasing D . The decrease of the resonance peak intensity represents the increase in the viscosity of confined liquid due to liquid structuring, which damped the movement of the upper surface. The peak intensity did not change at $D > 15$ nm, and began to decrease at $D = 12$ nm (Figure 3). This result indicated that the viscosity of AC10 between the ACL-modified silica surfaces increased at $D < \text{ca. } 15$ nm, which was a longer D than that of AC10 between unmodified surfaces (≤ 6 nm)¹. The difference of the viscosity behaviors in the case of ACL-modified and unmodified surfaces should be due to larger molecular interaction between the ACL and the monomer. This study suggested that the reactive adhesive layer increased viscosity at residual layer thickness of sub-15 nm during UV nanoimprinting, which would make alignment process difficult.

¹S. Ito et al., *ACS Appl. Mater. Interfaces* **9**, 6591–6598 (2017).

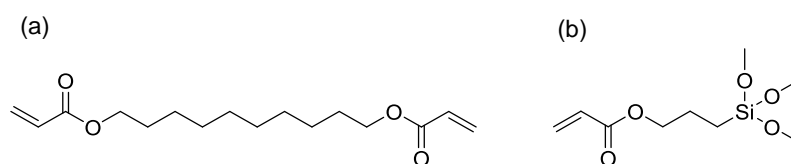


Figure 1: Chemical structures of (a) 1,10-decanediol diacrylate (AC10) and (b) 3-(acryloyloxy)propyltrimethoxysilane (ACL).

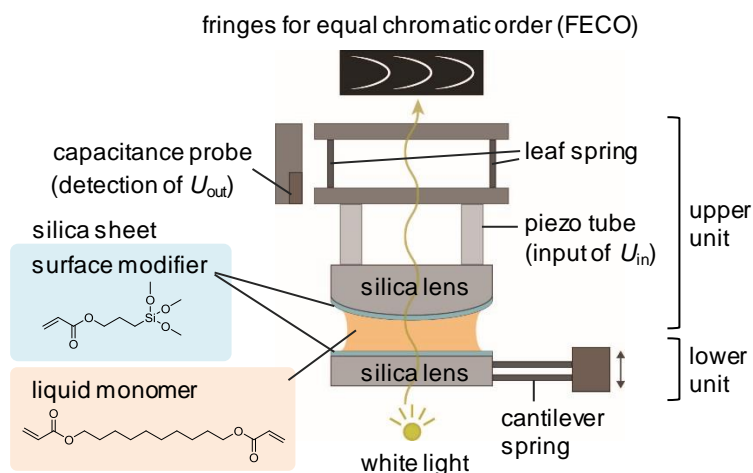


Figure 2: Schematic illustration of the experimental setup used for surface forces and resonance shear measurements.

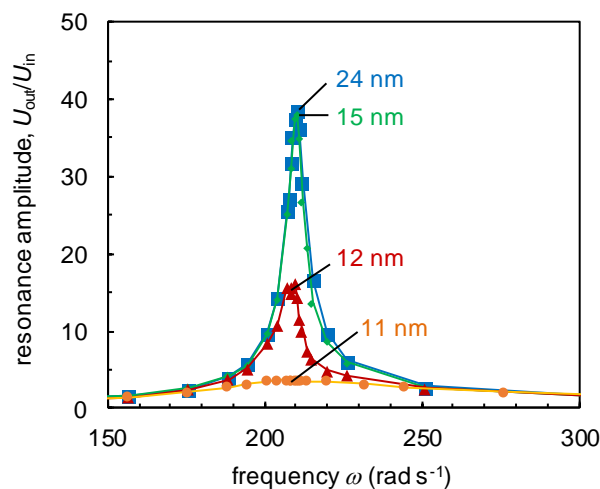


Figure 3: Resonance curves as a function of surface-surface distance D determined for AC10 monomer by resonance shear measurements upon stepwise decreases of the D between identical surfaces of ACL-modified silica.