Reproducible surface forces between VUV-exposed silica surfaces in a moisture-sensitive oleophilic diacrylate monomer liquid

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UV nanoimprint lithography is one of promising candidates as "More Moore Technology" for the fabrication of forefront semiconductor devices. In UV nanoimprinting, several demonstrations have been reported for sub-15 nm resist patterning.[1-3] However, suitable antisticking molecular surfaces and monomers for sub-15 nm UV nanoimprinting are still scientifically unclear because the reports were demonstrated by empirical knowledges. We think that impurities in UV curable resins such as water would cause pattern defects in sub-15 nm patterning by UV nanoimprinting. In this work, we investigated surface forces between silica surfaces, exhibiting different hydrophilicity, mediated with an oleophilic diacrylate monomer containing water at different concentrations.

Silica sheets with a molecularly smooth surface were prepared from flaming silica tubes and glued on cylindrical silica lens. The couple of the lenses were mounted on the setup for surface forces measurements (Fig. 1). An oleophilic diacrylate monomer of 1,10-decanediol diacrylate (AC10) with a viscosity of 10 mPa·s was inserted between the surfaces. The amount of water in AC10 affected by ambient humidity was determined by a Karl Fischer moisture meter. Figure 2 shows force curves working between flamed and cooled silica surfaces of a contact angle of 52.6 ± 1.7° for water. Reproducible surface forces were hardly measured in different scans in the case of even using identical silica surfaces in the same monomer medium. The amount of water in the monomer medium could be increased from 56 – 70 ppm to 420 – 429 ppm by keeping the monomer medium under a high humidity of 90 %. As shown in Fig. 2b, repulsion appeared at a longer distance than the case of (a), with the increasing water content in the monomer medium. Measured surface forces were also not reproducible. In contrast, reproducible surface forces could be measured in the case of VUV-exposed silica surfaces with a water contact angle of < 5° (Fig. 3). These results may have indicated that flamed and cooled silica surfaces with a high water contact angle adsorb clusters of water because the outermost silica surface is mainly composed of condensed Si-O-Si bonds, while the hydrophilic silica surface adsorbs water molecules uniformly. It was reported that water behaves differently depending on the hydrophilicity of silica.[4] Stable, hydrogen-bonded water is formed on water-vapor plasma treated, hydrophilic silica surface. We think that cleaning methods of silica mold surfaces to generate stable water layers in UV-curable resins are important in defect-free sub-15 nm UV nanoimprinting.

[1]F. Hua, et al., *Nano Lett.* **4**, 2467 (2004). [2]W. D. Li, et al., *J. Vac. Sci. Technol. B* **30**, 06F304 (2012). [3]S. Dhuey, et al., *Nanotechnol.* **24**, 105303 (2013). [4]M. Kasuya, et al., *J. Phys. Chem. C* **117**, 20738 (2013).

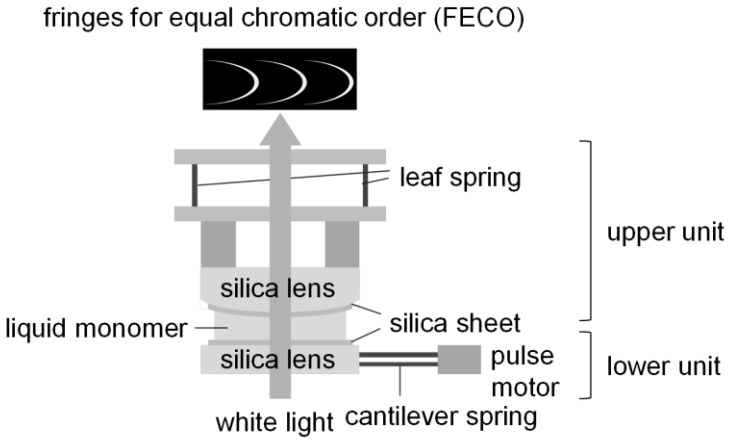

Figure 1: Schematic illustration of the experimental setup for surface forces measurements.

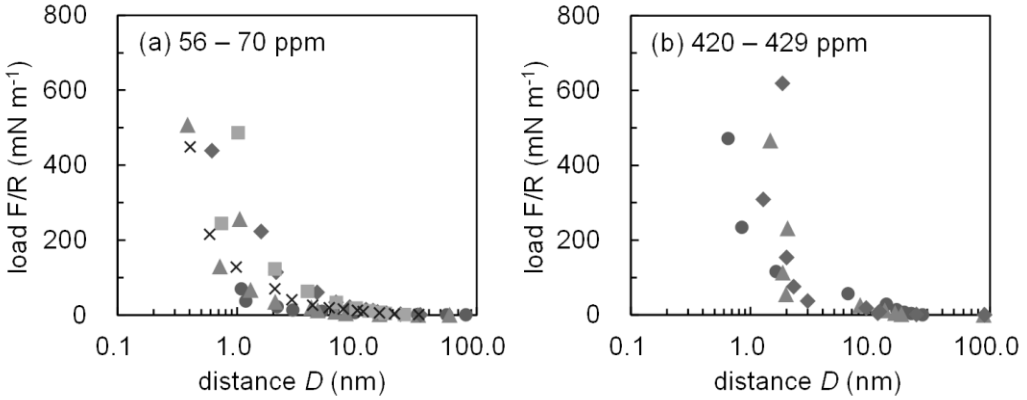

Figure 2: Force curves working between bare silica surfaces showing a contact angle of 52.6 ± 1.7° for water detected by surface forces measurements. AC10 liquids containing water of (a) 56 – 70 ppm and (b) 420 – 429 ppm were used. Marks with different shapes indicate different scans using identical samples.

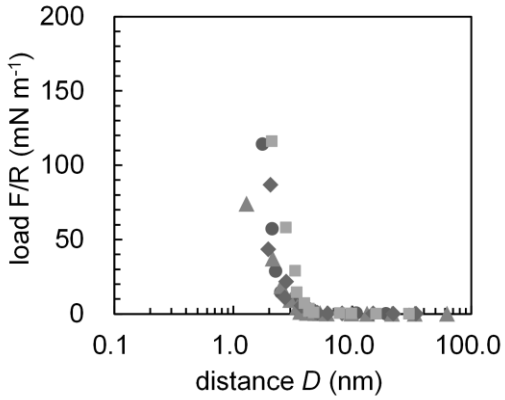

Figure 3: Force curves working between VUV-cleaned silica surfaces showing a contact angle of < 5° for water detected by surface forces measurements. Marks with different shapes indicate different scans using identical samples.