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Observation of Microsecond wetting by microdroplets
微小液滴の超高速濡れ現象観察

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1. Introduction

Investigation of wetting behavior of liquids on solid substrates are becoming indispensable, as many of attempts to apply inkjet printing technique to industrial process (for example, printing process of manufacturing organic semiconductor circuit or OLED) is attracting more and more attension these days .

Interfacial dynamics between liquid and solid is so far investigated mainly on macroscopic and quasistatic system. Nevertheless, the dynamics of inkjet is microscopic system with extremely large shear rate over 10^5/s, which is hardly measureable by traditional macroscopic measurement technique.
In this paper, we observed the oscillation of droplet with partial contact on solid surface with different interfacial energy. The droplet is generated by our original inkjet equipment. To take the picture of micrometer-size droplet in micro-second time resolution, we used stroboscopic microscope.
To control the solid surface energy of solid substrate, we coated glass plate with silane coupling agents. The silane coupling agents react to the hydroxyl groups on the glass surface and chemically grafting onto the surface with their characteristic groups (alkyl or fluoroalkyl group for example).

2.Substrates

Microscope glass slides (Matsunami, frosted soda-lime glass) are chemically cleaned by methanol sonication to get rid of organic contamination. Then, silane coupling agents with alkyl and fluoroalkyl graft is deposited to the glass to control surface energy(**Fig.1**). The silane coupling agents consists of reactive parts and additional group. Reactive part is hydrolytic methoxy, ethoxy or chloro groups. They are hydrolized in water and become silanol. Silanol adheres to hydroxyl groups on the surface of media (e.g., glass) by hydrogen bond, and dehydrolizes to form siloxy bonds. The hydroxyl group on the surface is replaced by the additional group, for example, alkyl or fluoroalkyl group. The critical surface tension γ_c of the glass coated with octyltriethoxysilane (OTS) is 20-30mN/m, and that with 1H,1H,2H,2H-perfluorododecyltriethoxysilane (PFS) is 12mN/m, much smaller than the value of uncoated glass of 100mN/m. Macroscopic behavior of wetting of pure water on the coated glass and uncoated glass is shown in **Fig. 2**. We can control surface energy by changing reaction condition and surface density of silanes bonded.

3. Equipment and Observation system

Our inkjet nozzle consists of piezoquartz and glass capillary. The inner radius of capillary is 30μm, and droplet radius is 15-20μm. This inkjet is chemically tough enough to handle strong acid to alkali, viscous fluid whose viscosity is smaller than 50mPa s. **Figure 3** shows the schematic view of the experimental setup.

We use strobe method to take picture at high frame rate. Stroboscopic light that illuminates about 100ns enables time resolution less than microsecond. The trigger of stroboscopic light is delayed sequentially to the pulse that drives piezo actuator. For the behavior of droplet is stable to repetition, pictures of droplet show continuous motion.

4. Result and Discussion

The contact angle is obtained from the microscope photograph of microdroplet, which was found to be same with the value obtained for 1mm particle. The contact angle θ_c on the PFS coated glass, OTS coated glass, and silicon wafer is θ_c=115°, 85° and 60°, respectively.

The droplet has radius 20-30μm and it collides to the substrate with the velocity of 1-2m/s. The droplet oscillates after collision due to surface tension at frequency around 100kHz (**Fig. 4**).
The oscillation is damped within 200μs because of the viscosity. We compared the frequency with the Rayleigh's modes of isolated (in other words, levitated) drop oscillation induced by surface tension,

$$\omega_l = \sqrt{\frac{l(l-1)(l+2)\sigma}{\rho R^3}} \tag{1}$$

(σ: surface tension, ρ: density of liquid, R : radius of droplet, l : mode of oscillation) For a partially contact drop, we used radius of curvature as R.

The frequency of droplet on PFS coated glass is close to the l=2 mode, while on silicon wafer it is close to l=3 mode. OTS coated glass has the intermediate value.

The dominant mode of oscillation is likely to be determined by pinning on the liquid-solid interface and contact Strani and Sabetta[3] calculated the frequency of captured drop (suppose the drop on the top of needle), which is larger than isolated one, and l=1 mode (which is transitional motion in isolated drop) exists with finite frequency.

Our experiment is a sessile drop and not a captured drop. Contact angle of vibrating drop is movable but restricted around static one. The vibration of drop is largely influenced by liquid-solid interface friction. The damping rate of sessile drop suggests that viscous friction on the liquid-solid interface increases when the contact angle is smaller.

References

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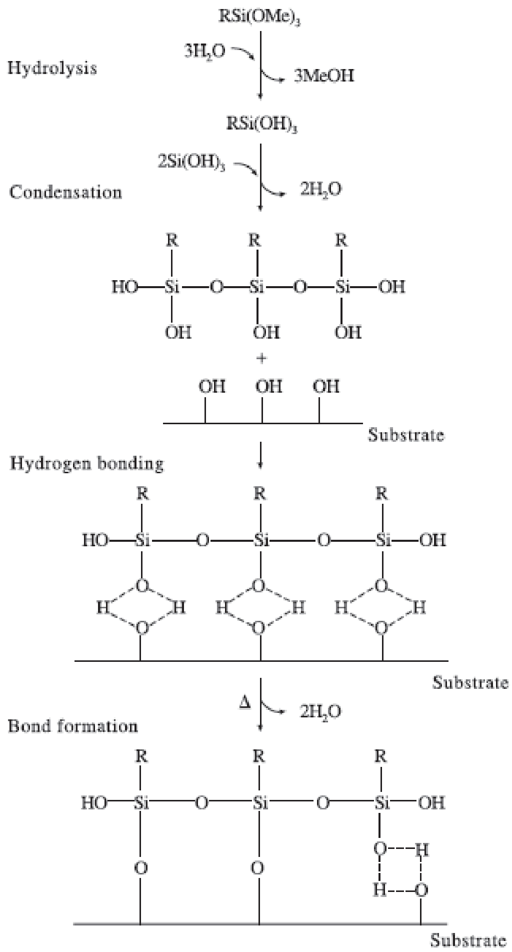

Fig. 1 The deposition of silane coupling agents[4]. Reactive parts (in this figure, methoxy groups) are hydrolyzed and become silanols. It bonds to hydroxyl group on the surface of substrate and forms covalent linkage with loss of water. Surface hydroxyl group is replaced with R, the additional group.

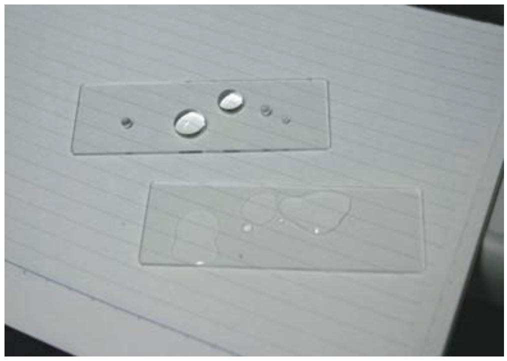

Fig. 2 Wettability of PFS coated glass (above) and uncoated clean glass (below).

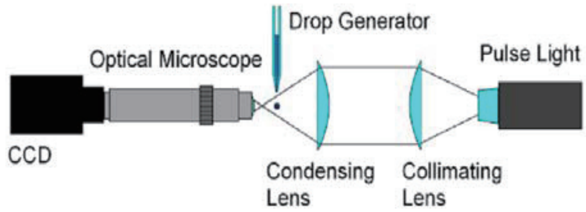

Fig. 3 Stroboscopic microscope observation system.

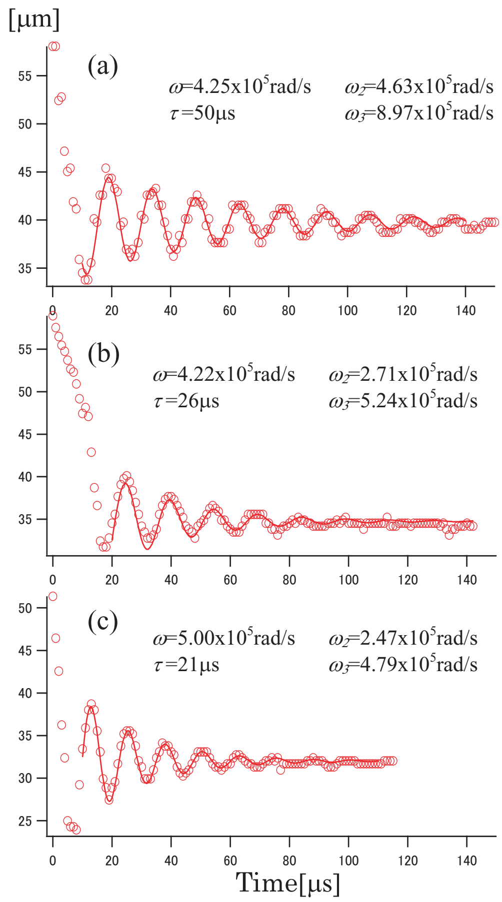

Fig. 4 Oscillation of a droplet on solid surface of different wettability. (a) PFS coated glass. θ_c=115° . (b) OTS coated glass. θ_c=85° . (c) silicon wafer surface. θ_c=60° . ω and τ are experimental value of frequency and damping rate. ω_2 and ω_3 are calculated from eq.(1).