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Wetting Mode Transition of Water Droplets by Electrowetting on Highly Hydrophobic Surfaces Coated with Two Different Silanes

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Highly hydrophobic surfaces with nanoscale roughness were prepared by coating two fluoroalkylsilanes (FAS17 and FAS3) respectively onto boehmite deposition layers. The droplet shape change on the surface was then observed with application of voltage between the droplet and the coating surfaces. The wetting mode transition on FAS3 coating advanced continuously once the applied voltage exceeded 120 V, whereas that on FAS17 coating at less than 200 V. The droplet shape changed with sustaining air phase at the solid–liquid interface.

Highly hydrophobic surfaces with a water contact angle of around 150° are obtained by combining surface roughness with lower surface energy.[1] Two mechanisms are well known to enhance hydrophobicity by surface roughness: increase of the practical solid surface area (Wenzel's mode),[2] and air intruding into the solid–liquid interface (Cassie's mode[3]). Although the practical contribution of these two modes depends on the size and shape of the surface roughness, Cassie's mode is commonly dominant for such a highly hydrophobic surface.[4]

These two modes do not always appear as the most stable state. When the Cassie mode is a metastable state compared with that of Wenzel, the wetting mode transition (WMT) from Cassie to Wenzel is induced once energy greater than the potential barrier between these two modes is applied. This WMT has been reported during evaporation and condensation, and under external fields such as vibration and pressure.[5]

When a certain voltage is applied between the solid surface and the deposited water droplet, electric charges are stored in the solid–liquid interface and solid wettability is altered. This phenomenon is called electrowetting (EW).[6] Various studies of EW have been conducted from the viewpoint of controlling deformation or transportation of a liquid droplet on a solid surface.[5] The WMT from Cassie to Wenzel by EW has been reported on a highly hydrophobic surface.[7–9] However, almost all of these studies have been conducted using a surface with regular rod-like or random fiber-like structures. Few investigations have examined this phenomenon using a surface with different roughness topography, such as particulate deposition. Additionally, no time-dependent change of the droplet shape has been investigated precisely during and after voltage application. Moreover, effects of silane coupling agents used for the hydrophobic treatment of random roughness structure on the WMT by EW have not been investigated to date.

For this study, we used the deposition of boehmite particles[10] and the subsequent coating of two different silanes to prepare two highly hydrophobic surfaces with random nanoscale roughness. Then, the time-dependence of droplet shape change by EW was investigated during and after voltage application.

Boehmite powder (AlOOH, 50 mg) and acetylacetonate (0.915 g, $Al(C_5H_7O_2)_3$) were mixed with ethanol (25 g). Then the suspension was sonicated for 40 min. The suspension was coated onto indium tin oxide (ITO) coated glass plates (20 × 20 mm) by spin coating at 1000 rpm for 10 s. The coated wafer was dried at room temperature for 30 s; then it was heated at 460 °C for 20 s. These coating and heating procedures were repeated five times, yielding boehmite films with nanoscale roughness.

The boehmite-coated plates were cleaned using vacuum ultraviolet light irradiation (VUV, 172 nm wavelength) for 15 min in air at room temperature. These precleaned plates were then coated with fluoroalkylsilanes using chemical vapor deposition by heating together with 20 µL of either (trifluoropropyl)trimethoxysilane ($CF_3C_2H_4Si(OCH_3)_3$, FAS3) or (heptadecafluorodecyl)trimethoxysilane ($CF_3(CF_2)_7C_2H_4Si(OCH_3)_3$, FAS17) in a Petri dish at 150 °C for 60 min (FAS17) or 100 °C for 90 min (FAS3) with flowing N_2. The sample surfaces were rinsed using toluene, acetone, and distilled water. Then they were dried. Hereinafter, we designate these samples respectively as "FAS17 coating" and a "FAS3 coating."

The surface roughness (R_a) of each coating was calculated from the coordinate data obtained from a 281 × 211 μm^2 rectangle area (1024 × 768 pixel) using a 3D laser scanning microscope. The static contact angle of 3.0 µL water droplets was measured at five points using a contact angle meter with the sessile drop method. The sliding angle of a 30 µL water droplet was measured at three points using an automatic measurement system. These values are described as (average) ± (standard deviation) in the text.

Although a dielectric material layer is commonly inserted between a conductive layer and surface structure to enhance the contact angle change by EW, we deposited boehmite powder directly onto the ITO layer to confirm the air layer in the solid–liquid interface. Figure 1 portrays schematic images of the measurement system. If water penetrates into the surface structure and contacts ITO, then the percolation current is detectable. A 12 µL water droplet was placed on the coatings. Then a Cu electrode was inserted into the droplet. The distance between the electrode and sample surface was adjusted to 2.4 mm in all EW measurements. Part of the boehmite film was peeled off. Then Cu tape was fixed to the ITO surface as the counter electrode. Subsequently, voltage of 50–700 V was applied between the Cu electrode and the sample surface using a DC power supply (the Cu electrode was positive; the sample surface was negative). The contact radius (r) and the contact angle (θ) of the water droplet were observed for 0–90 s with

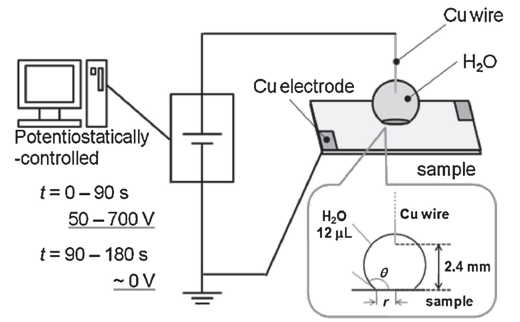

Figure 1. Schematic image of the measurement system for EW.

application of a constant voltage, and until 180 s after shutting off the voltage. To neutralize electrification charges, the circuit including the electrode was connected to ground. Detailed information related to the starting materials and evaluation facilities is described in Supporting Information (SI) I.[14]

The prepared samples possess nanoscale roughness at the surface (SI II[14]). The average surface roughness (R_a) was 23 nm on each surface. The static contact angles were, respectively, 162° ± 2° (FAS17) and 141° ± 1° (FAS3). Based on the contact angles without surface roughness (FAS3: 78° ± 1°,[11] FAS17: 104° ± 1°[11]), the static wetting modes of these surfaces were Cassie's mode and air phase should be included at the solid–liquid interfaces. The sliding angle for 10-μL water droplets on FAS17 coating was 12° ± 4°; that on FAS3 coating was greater than 80°.

Figures 2a and 2b present the contact radius change of FAS17 and FAS3 coatings during and after voltage application. The contact radius value at each time (r_t) is normalized to the initial value (r_0). On FAS17 coating, the contact radius did not increase unless the applied voltage exceeded 80 V. For the FAS3 coating, the increase of the contact radius commences from around 120–140 V. For inducing WMT, it is necessary to apply pressure greater than that supported by the surface structure against the liquid phase.[12] In this study, the threshold pressure was provided at 90 V on FAS17 coating, and around 120–140 V on FAS3 coating. This difference is expected to be attributable to the difference of the initial contact angle, and to the poor mobility of the three-phase contact line on FAS3 coating. The sliding angle result corresponds to that expectation.

The contact radius increased continuously during voltage application on the FAS3 coating. However, that on the FAS17 coating saturated within 30 s after applying voltage. When 250 V was applied on the FAS3 coating, the liquid phase conducted with the ITO surface around 60 s. As shown by the cross mark (×) in Figure 2b, the contact radius reached the same value as that of the case for 250 V ($r_t/r_0 \approx 1.33$) when 180 V was applied for more than 90 s on the FAS3 coating. This result implies that the WMT advances continuously on FAS3 coating once the applied voltage exceeds the threshold value. On the FAS17 coating, the contact radius increased with sustaining air phase at the solid–liquid interface. Very recently, a report described that the WMT advanced with increasing dew condensation on the FAS3 coating, but it did not advance over a certain level on the FAS17 coating.[11] Results of the present study correspond to that trend, and are attributable to the lower hydrophobicity of FAS3 than that of FAS17. The contact angle for each applied voltage on FAS17 and FAS3 coatings decreased correspondingly with the contact radius change (SI III[14]).

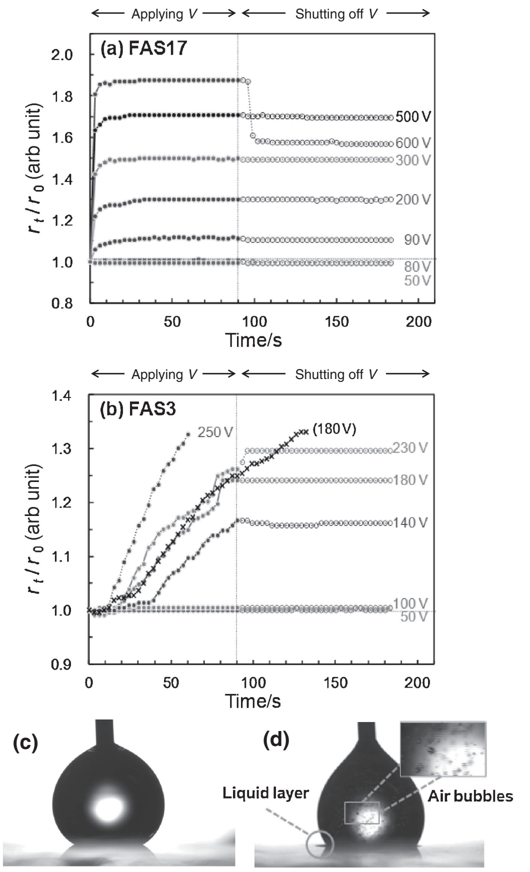

Figure 2. Normalized contact radius (r_t/r_0) changes during voltage application ($t = 0–90$ s), and after voltage application ($t = 90–180$ s): (a) FAS17 coating and (b) FAS3 coating. Inset: photographs of water droplet ($t = 60$ s) with applied 200 V on (c) FAS17 coating and on (d) FAS3 coating.

Figures 2c and 2d portray photographs of a water droplet ($t = 60$ s) when 200 V was applied on FAS17 and FAS3 coatings. For the FAS3 coating, the liquid film formed on the coating surface, and bubbles were generated from the solid–liquid interface. During this measurement, bubble generation was observed neither around the Cu electrode nor in the droplet at the beginning of voltage application. The authors infer that both the rapid displacement of air to water on the solid surface under water penetration with formation of the liquid film and the reduction of water on the ITO surface contribute to this phenomenon on the FAS3 coating. However, neither liquid film formation nor bubble generation was observed on the FAS17 coating, probably because of lower surface energy than that of the FAS3 coating (SI IV[14]).

The relation between the difference of contact angle before and after voltage application and the square of applied voltage (V^2) in EW is[13]

$$\Delta \cos\theta = \cos\theta(V) - \cos\theta(0) = \frac{\varepsilon}{2d\gamma_{\mathrm{LV}}} V^2 \qquad (1)$$

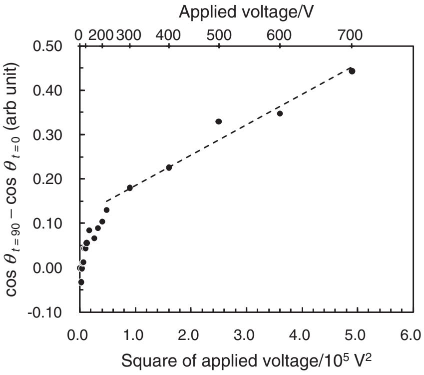

Figure 3. Contact angle difference ($\Delta\cos\theta$) in each square of applied voltage (V^2) on FAS17 coating.

where θ (V), and θ (0) represent the contact angles before and after voltage application, ε denotes the dielectric constant of insulation layer, d denotes the insulation layer thickness, and γ_{LV} signifies the interfacial free energy of liquid–gas interface. From eq 1, the relation between $\Delta\cos\theta$ and V^2 is linear when both ε and d are constant. Krupenkin et al. reported the remarkable increase of $\Delta\cos\theta$ at the certain voltage attributable to the WMT on a superhydrophobic surface with regular rod-like roughness structure, in addition to a linear relation between $\Delta\cos\theta$ and V^2 in other voltage ranges.[7] Because the contact angle change did not saturate on the FAS3 coating within the measurement time range, we show $\Delta\cos\theta$ ($\cos\theta_{t=90} - \cos\theta_{t=0}$) and V^2 only for FAS17 coating (Figure 3). The relation between $\Delta\cos\theta$ and V^2 over the 200 V range was nearly linear, suggesting that the thickness (d) and the dielectric constant (ε) of the insulation layer (the surface structure and the air phase contained into the solid–liquid interface) were almost constant. Results showed that the WMT occurred at less than 200 V because of the steep increase of $\Delta\cos\theta$ in this voltage range. The WMT on FAS17 coating is expected to advance stepwise because of its random roughness structure. Therefore, it does not occur rapidly at a certain voltage.

The contact radius on FAS17 coating for 600 V decreased after stopping voltage application ($t > 90$ s). Figure 4 presents schematic models of energy levels. When voltage is applied between the liquid and solid phase, the interfacial energy of the solid–liquid interface decreases. Thereby, a more stable state (Voltage ON state) is attained. The mode shift is feasible if the applied energy is greater than the potential barrier of WMT (ΔE_1, from Figure 2a, expected at around 90 V). When ceasing voltage application, the Voltage ON state shifts to an unstable state (Voltage OFF state) because of the recovery of the initial interfacial energy at the solid–liquid interface. If the Voltage OFF state includes excessive shape change of the droplet that is greater than the shape of the most stable state after WMT (Stable state), then the energy level is higher than that of the Stable state, and the Voltage OFF state becomes unstable. When energy from the excess shape change is greater than the potential barrier (ΔE_2), the mode shift occurs from the Voltage OFF state to the Stable state. In this measurement condition on FAS17 coating, the contact radius change did not occur below 500 V, probably because the energy by the excess shape change was less than ΔE_2. An additional explanation for these states is described in SI V.[14] Perfect recovery of the droplet shape after stopping voltage application has been reported for a superhydrophobic surface with a limited contact area between a solid and liquid, such as a rod- or fiber-like structure.[8,9] The boehmite film in this study provides surface roughness by the difference of the particle deposition ratio. Thereby, the solid–liquid contact area is not so small and a threshold value exists for the droplet shape recovery. This study demonstrated that the progress of the WMT on the highly hydrophobic solid surface with nanoscale roughness depends on the silanes used for hydrophobizing treatment. Detailed analysis of the effect of surface energy on EW requires preparation of smooth silane coatings on a highly insulating material. Such analyses will be conducted in future studies.

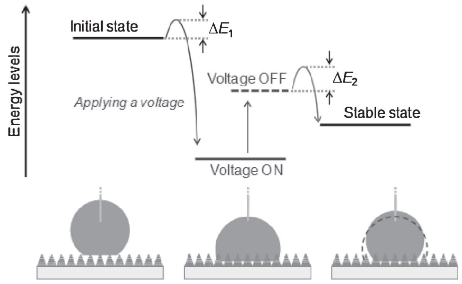

Figure 4. Schematic images of energy levels on a FAS17 coating under applied voltage (600 V) and after shutting off voltage.

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14 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.