Effect of Electrification Conditions on the Freezing of Supercooled Water Droplets on a Hydrophobic Coating

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The effects of electrification processes on ice nucleation on an octadecanethiol (ODT) coating were investigated under two different conditions. Electrification provides the driving force of the movement to the three-phase contact line. This change promotes ice nucleation on the supercooled water droplet. In contrast, electrification before cooling inhibits freezing, probably because of the limitation of orientational freedom by the interaction between the surface charge and the dipole moment of water molecules.

Hydrophobic coatings suppress chemical interaction between a solid surface and water. Such coatings have been applied to various industrial items for anti-ice and antisnow adhesion.[1]

Water is readily supercooled if vibration and contamination, such as that of adherent dust, are suppressed during cooling. Maximum supercooling is expected to be about −45 °C at almost zero-gravity.[2] This temperature is assumed as the freezing temperature of supercooled water by homogeneous ice nucleation. Generally, ice nucleation of a supercooled water droplet on a solid surface occurs from a solid–liquid interface by a heterogeneous nucleation mechanism. Observations using a high-speed camera system revealed that the nucleation site is commonly at the three-phase (solid–liquid–air) contact line.[3]

However, various external fields affect the solid surface's wettability. Electrowetting, an effect of an electric field, has been particularly well investigated.[4] Moreover, electric fields affect water's freezing behavior. So-called electrofreezing promotes ice nucleation in supercooled water.[5] Most such studies of electric fields have used a face-type electrode; few studies have examined electrification of solid surfaces.

Contact angles of water on ceramics and polymers are decreased by providing a charge to the solid surface,[6] meaning that the three-phase contact line between a water droplet and a solid surface is moved by electrification. Consequently, for supercooled water droplets, ice nucleation is expected to be promoted. However, the solid surface charge reduces the entropy of the dipole moment of water molecules at the interface because of the interaction and consequent limitation of orientational freedom. Therefore, electrification inhibits ice nucleation if the interaction is strong. For this study, we changed the voltage application timing and examined electrification effects on ice nucleation of supercooled water droplets on a hydrophobic coating under two conditions.

We chose octadecanethiol (ODT, $CH_3(CH_2)_{17}SH$) as a hydrophobic agent because it reacts with Au; furthermore, application of the DC voltage affects the Au coating more directly. A Si(100) wafer was cut into plates ($15 \times 15\,mm^2$). Then Cr and Au coated sequentially the wafer using physical vapor deposition (VPC-200; Ulvac Co.) under 10^{-5} Torr (coating thickness: Cr, 50 nm; Au, 200 nm). Then, ODT (Wako Pure Chemical Industries Ltd., 26 mg) was dissolved into ethanol (Wako Pure Chemical Industries Ltd., 50 mL). The wafer was soaked in the solution for 3 h. After washing and drying, an ODT coating was obtained. Surface roughness (*R*a) was evaluated in a 500-nm-square area using atomic force microscopy (AFM, NanoScope RIII; Digital Instruments Co.) with a Si cantilever. Contact angles of 3-μL water droplets were measured using sessile drop method with a contact angle meter (Dropmaster 500; Kyowa Interface Science Co., Ltd.). The surface was blown with ionized air before normal contact angle measurements to eliminate any electrostatic charge. The coating was laid down horizontally and the Au-coating area without ODT coating was connected to a DC power supply (HVS448; LabSmith). Another electrode was connected to ground. The contact angle change was evaluated under 0 ± 2000 V.

We prepared an original cell unit[7] to observe freezing behavior. Figure 1 shows a schematic illustration of the cell, which was blocked from ambient air by double walls of transparent acrylic polymer plate. A sample wafer was attached to the bottom copper stage with a thermocouple using heat-conductive grease. The same copper stage was set on the opposite side (top) of the sample; cooling medium (ethanol) was circulated

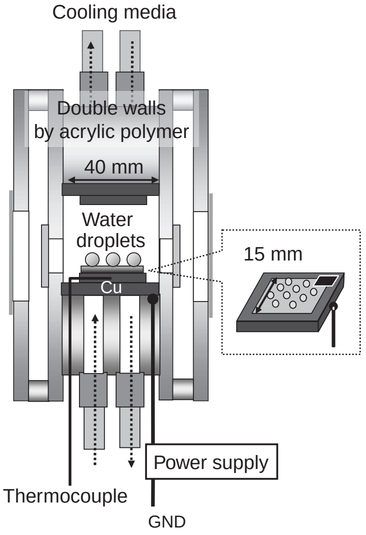

Figure 1. Schematic illustration of the experimental cell.

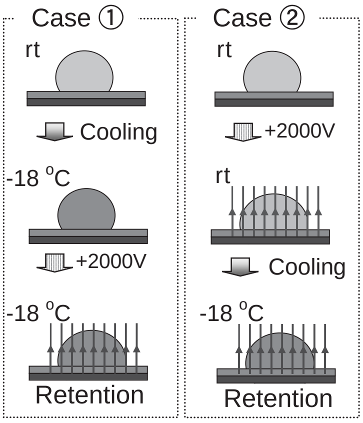

Figure 2. Schematic illustration of the experimental condition.

to both copper stages. The upper stage temperature was set 1 °C lower than that of the bottom stage to inhibit frost formation on the sample stage. Temperature fluctuation in the bottom sample wafer was confirmed within 0.1 °C. The sample surface's Au coating was connected to the DC power supply; another electrode was connected to ground.

First, we evaluated the freezing behavior's voltage dependence. Ten water droplets of 1.5 μL each were placed gently on the sample surface. Samples were then cooled from room temperature (rt) at 0.5 °C/min under 0, +1000, or +2000 V. Each droplet's freezing temperature was recorded by direct observation.

The effect of voltage application timing on ice nucleation was evaluated under two different situations. Ten water droplets of 1.5 μL each were placed gently on the sample surface. Then, (1) samples were cooled from rt to −18 °C at 0.5 °C/min. Once the sample temperature reached −18 °C, DC +2000 V was applied to the sample; we then counted the droplets that had frozen during 1800 s while maintaining this temperature; and (2) DC +2000 V was applied to the sample at rt before cooling, then the sample was cooled from rt to −18 °C at 0.5 °C/min. Once the sample temperature reached −18 °C, we counted the droplets that had frozen during 1800 s while maintaining this temperature. Figure 2 shows these two cases.

Water contact angle and surface roughness values of the sample obtained at rt under no voltage were 106.5 ± 0.3° and 1.6 nm, respectively. Applying voltage to the surface decreased the contact angle to 102.7 ± 0.9° under +1000 V, and 101.7 ± 0.6° under +2000 V. A similar contact angle change was observed, even under negative voltage. Therefore, this change was attributed to the increase of contact voltage (ζ–potential) between the solid and water, thereby improving solid wettability. Freezing temperatures were −22.5 ± 0.5 °C (without voltage), −23.5 ± 0.3 °C (under +1000 V), and −23.3 ± 0.3 °C (under +2000 V). Although the voltage dependence was small, freezing temperatures were decreased slightly by applying voltage, which suggests that water molecules at the ODT–water interface are lost their mobility for ice nucleation by electrification.

Figure 3 shows the effect on ice nucleation of the voltage application timing. In cases (1) and (2), no droplet froze when the temperature reached −18 °C. Case (1) exhibited more frozen droplets than case (2). Although nucleation is a statistical process, we confirmed the reproducibility of this result. The numbers of frozen droplets differed greatly in the early stage, probably because the voltage application drives the movement of the three-phase contact line between a supercooled water droplet and the ODT coating in case (1); this motion would promote ice nucleation. In contrast, water molecules were pinned at the ODT–water interface in case (2), and ice nucleation occurred with greater difficulty than in case (1). Although electrification might affect the water molecules' orientation at the water–air interface, we think the effect on this result is negligible because freezing was confirmed to initiate at the solid–liquid interface by direct observation using high-speed camera.

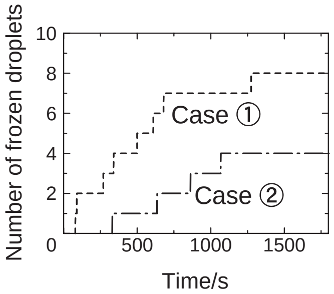

Figure 3. Dependence of the number of frozen droplets during 30 min on voltage application conditions.

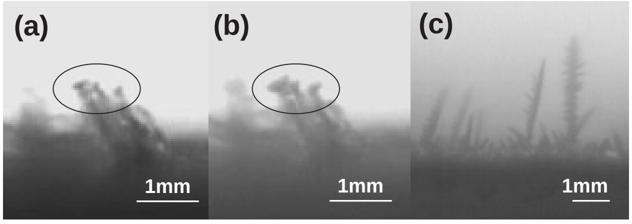

Figure 4. Morphology of frost: (a) and (b) under electrification by 2000 V, (c) no electrification.

Frost formation was observed on the sample stage by vapor transport from water droplets when the upper stage was set at the same temperature as the sample stage in the cell unit. Under electrification at 2000 V, frost initially grows perpendicularly to the solid surface. Once its height reaches around 1 mm (Figure 4a), it spreads to form an umbrella shape (Figure 4b, circled part). Dendritic frost grows by higher population when DC is not applied (Figure 4c). These behavioral differences imply that electrification affects freezing behavior of water molecules. Freezing kinetics and the behavior of supercooled water droplets on the hydrophobic surface are governed by voltage application conditions.

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

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