

Crystallization of thin water films on graphite: Effects of *n*-hexane, formaldehyde, acetone, and methanol additives



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ABSTRACT

Interactions of molecular additives with amorphous solid water have been investigated using time-of-flight secondary ion mass spectrometry and temperature programmed desorption. The crystallization temperature of water on a clean graphite substrate decreases from the bulk value of 160 K to 150 K when water deposition temperature increases from 20 K to 100 K. This phenomenon is induced by the formation of a specifically oriented water layer at the interface, as evidenced by that a submonolayer of *n*-hexane adspecies on graphite quenches this behavior. Thermal desorption spectra of additives reflect their hydration forms. The *n*-hexane molecules are trapped in the interior of a porous water film via hydrophobic hydration and released explosively during crystallization. The thermal desorption spectra of methanol resemble those of water from multilayer films because methanol can enter the hydrogen-bond network of water via hydrophilic hydration. The hydration of formaldehyde is hydrophobic in nature despite the presence of the polar carbonyl group. Features of both hydrophilic and hydrophobic hydrations are identifiable in acetone–water interactions; the branching ratio depends on the water preparation method and substrate.

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1. Introduction

Water in nanoconfined geometry is ubiquitous in nature, and understanding of its properties is important in many research fields. Unique physical and chemical properties of water in the bulk originate from a highly polar hydrogen bond, and they are modified significantly upon nanoconfinement because of the interplay between the intermolecular hydrogen bond and the water–substrate bond [1–10]. On the other hand, additives in water induce structural transformation in nanoscale regions via the formation of solvation shells [11–15]. The solvation force competes with forces of surface segregation and adhesion to the substrate in the nanoconfined geometry.

Thin films of amorphous solid water (ASW) can be formed by deposition of water molecules onto cold substrates. The structure of ASW deposited at temperatures well below the glass-transition temperature, T_g , is characterized by a microporous structure, as evidenced by the ability to incorporate a large amount of adspecies in thin film interior [16,17]. The occurrence of liquidlike mobility in nanoconfined ASW films has been investigated using time-of-flight secondary ion mass spectrometry (TOF-SIMS) as a function of temperature [18–21]. The molecules become mobile at around bulk T_g

of water (136 K) when thin films are deposited onto a Ni(1 1 1) substrate [18]. However, a water monolayer tends to form droplets in the sub- T_g region (~ 110 – 120 K) on hydrophobic substrates [19,20]. The dewetting temperature of ASW depends on film thickness on highly oriented pyrolytic graphite (HOPG) although it is fixed at around 160 K on Ni(1 1 1) [21].

The crystallization kinetics of thin ASW films has been discussed based on isothermal desorption [22–25], temperature-programmed desorption (TPD) [25–31], and reflection absorption infrared spectroscopy (RAIRS) [32–35]. The crystallization process is also substrate dependent at specific film thickness [22,23], although the contrary is also suggested that crystallization is initiated from the free surface [33]. The crystallization temperature, T_c , of ASW is around 160 K on hydrophilic metal substrates [26]. However, the nucleation kinetics can be controlled by increasing the deposition temperature of water molecules on CCl_4 multilayer films because mobility of the adsorbing water molecules is high on hydrophobic surfaces [31], suggesting that the morphology of initial ASW films is related to the crystallization kinetics.

The desorption kinetics of water also depends on hydrophilicity and hydrophobicity of substrates [30,36,37]. The water TPD spectra from a hydrophobic graphite substrate are complicated in coverage dependence [28,37]. It is proposed that water on monolayer graphite form a new ice polymorph that consists of two flat hexagonal sheets of water molecules [10]. It is also suggested that

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orientation of the water molecules in the first monolayer on HOPG can be changed with increasing temperature [37]. Consequently, nanoconfinement effects appear more evidently on hydrophobic substrates because of weak substrate–water interactions.

In this paper, interactions of simple molecular additives with water and their effects on the phase transition of thin ASW films on the HOPG substrate are investigated. The crystallization kinetics is discussed based on TPD spectra of water and molecular additives from ASW films [31], as well as the occurrence of film dewetting using TOF-SIMS [35]. Regarding additives, nonpolar molecules are believed to have no effects on water crystallization kinetics although methanol changes the properties of ASW films significantly [38,39]. However, no systematic studies have been performed concerning the effects of other molecular additives on nanoconfined water. To this end, interactions of water with nonpolar aprotic (*n*-hexane), polar aprotic (formaldehyde, acetone), and polar protic (methanol) molecules are explored to gain insights not only into the phase transition of nanoconfined water but also into hydration of these additives.

2. Experiment

Experiments were performed in an ultrahigh vacuum (UHV) chamber with a base pressure of $<1 \times 10^{-10}$ Torr. The HOPG substrate was purchased from Panasonic Inc. (PGC grade). It was attached to a Ta holder using Ta strips after cleavage by the Scotch Tape method. The sample holder was mounted on the end of a Cu cold finger extended from a closed-cycle helium refrigerator. Temperature was controlled using a digital temperature controller by monitoring temperature of the cold finger close to the sample position using Au(Fe)-chromel thermocouples. For cleaning, the sample was heated several times in UHV to approx. 1300 K by electron bombardment from behind. Sample cleanliness was confirmed by the absence of any impurity peaks in TOF-SIMS. Water, *n*-hexane (96%), acetone (99.5%), and methanol (99.8%) were degassed by several freeze-pump-thaw cycles. Gaseous formaldehyde was obtained by heating a solid paraformaldehyde sample that was outgassed thoroughly before use. Thin films were deposited onto a cold HOPG substrate by back-filling the chamber with the gases admitted through high precision leak valves.

TPD spectra were recorded using a quadrupole mass spectrometer (HIDEN, IDP 300S) placed in a differentially pumped housing; a retractable orifice at the end of the housing was placed ~ 3 mm apart from the sample surface. For TOF-SIMS measurements, a primary beam of 2 keV He^+ ions was generated in an electron-impact-type ion gun (Specs, IQE 12/38) and was chopped into pulses using electrostatic deflectors. Negatively charged secondary ions ejected perpendicularly to the sample surface were detected using a microchannel plate after passing through a field-free TOF tube. To extract low-energy secondary ions efficiently, a bias voltage (-500 V) was applied to the sample. The temperature was ramped at a rate of 5 K min^{-1} for both TPD and TOF-SIMS measurements. The fluence of He^+ in TOF-SIMS measurements was restricted below $1 \times 10^{12} \text{ ions cm}^{-2}$ to minimize surface decomposition.

3. Experimental results

3.1. *n*-Hexane

The morphology of initially flat ASW films changes during the glass-liquid transition and crystallization. TOF-SIMS reveals the droplet formation straightforwardly by monitoring ion yields from the substrate as a function of temperature [18]. In the present study, TOF-SIMS spectra of negative ions are focused because no

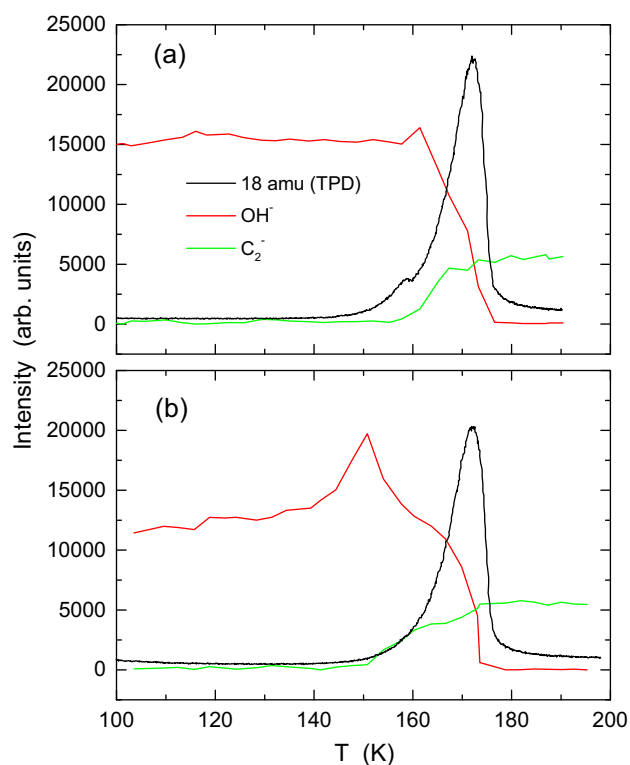


Fig. 1. Temperature-programmed TOF-SIMS intensities of anions (OH^- and C_2^-) and TPD spectra of water (18 amu) from ASW films formed by exposure of 20 L H_2O to a clean HOPG substrate at (a) 20 K and (b) 100 K.

positive ions are sputtered from the clean HOPG surface [21]. Temperature-programmed TOF-SIMS intensities of OH^- and C_2^- ions are plotted in Fig. 1, together with TPD spectra of water (18 amu). The ASW films were formed by deposition of 20 L (Langmuir; $1 \text{ L} = 1 \times 10^{-6} \text{ Torr s}$) of H_2O onto the clean HOPG substrate at (a) 20 K and (b) 100 K. It has been determined that 1 monolayer of water is attained at exposure of ca. 2.5 L H_2O for HOPG based on the saturation point of ion evolution curves [21]. In general, the monolayer thus determined by TOF-SIMS differs from that by TPD because the former (latter) corresponds to a crowded (scattered) monolayer interacting mainly with adspecies (substrate). In this study, effects of adspecies at typical exposure of 1 L are investigated. The coverage of adspecies is estimated based on the TPD spectra.

In Fig. 1, the film morphology change is identified as an increase of the C_2^- intensity. This occurs at ca. 160 and 150 K, respectively, for the ASW films deposited at 20 and 100 K. A characteristic peak is also observed in the OH^- intensity during film dewetting. The TPD spectrum of water in Fig. 1(a) exhibits a bump at 158 K. The decrease in the water TPD signal at this temperature is due to crystallization of the film: Crystalline ice is more stable and thus has a lower vapor pressure than ASW, leading to the decreased signal. The crystallization and dewetting are coupled because nucleation occurs in a liquidlike phase [18]. Thus, when the film crystallizes it also dewets. However, the bump in Fig. 1(b) is not clearly recognizable. Probably, this is because the desorption yield of water is small during crystallization at around 150 K. Consequently, the results in Fig. 1 indicate that T_c is controlled by the deposition temperature of the water molecules on HOPG. No such a behavior is observed using metal substrates like Ni(1 1 1) [21].

Fig. 2 displays logarithmic plots of TPD spectra of *n*-hexane adsorbed on HOPG and two differently tailored ASW films. Here, a porous ASW film (20 L) that is deposited directly onto HOPG at

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