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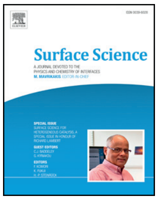

Surface and bulk crystallization of amorphous solid water films: Confirmation of “top-down” crystallization

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ABSTRACT

The crystallization kinetics of nanoscale amorphous solid water (ASW) films are investigated using temperature-programmed desorption (TPD) and reflection absorption infrared spectroscopy (RAIRS). TPD measurements are used to probe surface crystallization and RAIRS measurements are used to probe bulk crystallization. Isothermal TPD results show that surface crystallization is independent of the film thickness (from 100 to 1000 ML). Conversely, the RAIRS measurements show that the bulk crystallization time increases linearly with increasing film thickness. These results suggest that nucleation and crystallization begin at the ASW/vacuum interface and then the crystallization growth front propagates linearly into the bulk. This mechanism was confirmed by selective placement of an isotopic layer (5% D_2O in H_2O) at various positions in an ASW (H_2O) film. In this case, the closer the isotopic layer was to the vacuum interface, the earlier the isotopic layer crystallized. These experiments provide direct evidence to confirm that ASW crystallization in vacuum proceeds by a “top-down” crystallization mechanism.

1. Introduction

Amorphous solid water (ASW) is a metastable glassy phase form of water that can be created in the laboratory by vapor deposition onto a cold substrate ($T < 130$ K). The properties of ASW are of interest for a variety of reasons including its use as a model for liquid and supercooled liquid water [1–5], its use as a model for studying the properties of amorphous solids, and because it is believed to be the predominant form of water in astrophysical and planetary environments [6–8]. The crystallization of ASW films has been studied using a variety of methods including temperature-programmed desorption (TPD) [9–15], adsorbate physisorption [16–20], electron diffraction [21,22], and infrared techniques [14,15,20,23–25]. Most of these studies either report or assume that ASW crystallization proceeds via a random bulk nucleation and growth mechanism. However, one study reports that crystallization may start at the vacuum interface, although detailed kinetic modeling was required to separate the surface and bulk crystallization rates in the relatively thin film (45 ML) [20,26].

It has been shown previously that inert adsorbates trapped underneath or within ASW films desorb in an episodic release that occurs in concert with ASW crystallization, a phenomenon called the “molecular volcano” [27,28]. The abrupt desorption of gases is due to cracks that form during crystallization of the ASW overlayer. Some more recent work studying the crack formation that accompanies ASW crystallization in thicker films showed that crack formation begins at the ASW/vacuum interface [29–31]. In that work, selective placement of the inert gas layer in the ASW film showed that cracks form near the top of the film and propagate downward into the film. Given the link between crystallization and crack formation, these results suggested that ASW crystallization may also begin at the ASW/vacuum interface and proceed into the bulk.

In the present paper, we provide direct evidence that ASW crystallization proceeds via a “top-down” mechanism. This is accomplished by simultaneously monitoring crystallization on the surface and in the bulk as a function of ASW film thickness (100 to 1000 ML). Temperature-programmed desorption (TPD) measurements are used to probe surface crystallization and RAIRS measurements are used to probe bulk crystallization. Our experimental observations are consistent with a two-step model in which nucleation and crystallization begin at the vacuum-ASW and then the crystallization front propagates into the film bulk.

2. Material and methods

The experiments were performed in an ultra-high vacuum system (UHV) with a base pressure of $<10^{-10}$ Torr that has been described in detail previously [14,32]. Briefly, a 1 cm diameter Pt(111) substrate, cooled by a closed cycle helium cryostat capable of achieving a base temperature of ~25 K, was used as a substrate. The substrate was resistively heated and the temperature was measured by a K-type thermocouple spot-welded to the back. The temperature was measured

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with a precision of better than ±0.01 K. The absolute temperature was calibrated using the desorption of multilayer H_2O TPD and estimated to have an accuracy of ±2 K. The Pt substrate was cleaned by Ne^+ ion sputtering at 1.5 kV and then annealed at 1100 K in UHV. The Pt substrate was then heated to 1100 K in the presence of decane to form a single layer of graphene on its surface [33]. The ASW films in this experiment were deposited on top of 50 ML of decane to eliminate (or at least minimize) the potential effects of substrate-induced nucleation. We hypothesize that the long chain hydrocarbon deposited at low temperature will not form an extended ordered surface that could act as a crystallization template. Graphene is inert to hydrocarbon decomposition (Pt is not) and this provided a clean reproducible surface for growing the ASW/decane films.

Water and decane were deposited using a quasi-effusive molecular beam at normal incidence and at ~30 K. Surface crystallization was measured by monitoring the desorption rates of H_2O ($m/z = 18$) utilizing an Extrel quadrapole mass spectrometer in a line-of-sight configuration. Simultaneous with the desorption measurements, the RAIRS spectra were recorded with a Bruker Vertex 70 Fourier transform infrared spectrometer where the infrared beam was incident on the sample at an angle of 82 ± 1°. The infrared spectra were acquired with a resolution of 8 cm^{-1}. During a typical isothermal crystallization experiment, 100 infrared spectra were acquired in 900 s, and each spectrum was averaged for 64 scans. To clearly measure the ASW crystallization kinetics by infrared spectroscopy, a 5% D_2O in H_2O liquid solution was used to create the ASW films. In solution, H-D exchange results in the solution being ~10% HOD. The deposited ASW films have an O-D stretching peak near 2450 cm^{-1} which transforms into a sharp peak at ~2426 cm^{-1} when crystallized. These peaks (compared to the OH stretch in pure H_2O) are sharper because the O-D stretch of HOD is decoupled from interactions with neighboring OH bonds [34]. The use of the 5% D_2O in H_2O solution facilitated the analysis of the infrared spectra and also allowed for the isotope layer experiments described in Section 3.4.

3. Results and discussion

3.1. Surface crystallization of ASW films

The surface crystallization of ASW films in vacuum was determined using isothermal desorption measurements. All ASW films were deposited on top of 50 ML of decane. The composite ASW/decane films were deposited at normal incidence and at 30 K. After deposition the films were heated via a linear temperature ramp (1 K/s) to and then held at 150 K. Fig. 1(a) displays the isothermal TPD spectra for a series of ASW films with thicknesses of 100 (blue curve), 200 (red curve), 500 (black curve), and 1000 ML (green curve). The vertical dashed line ($t = 0$) marks the time when the temperature reaches 150 K. The desorption spectra for all four ASW thicknesses are nearly identical and have the same desorption rate versus time dependence that has been observed previously [11,15]. This desorption behavior is due to the metastable amorphous phase having a higher free energy than the more stable crystalline phase. The higher free energy means that the amorphous phase has a higher vapor pressure than the crystalline phase and thus a higher desorption rate. The isothermal spectra in Fig. 1(a) show that upon reaching 150 K, the desorption rate is at its maximum value. Subsequently, the rate decreases in time until about 200 s where the rate plateaus. This is because the initial desorption rate is from a film that is nearly all amorphous but as the surface begins to crystallize, the rate decreases until the film's surface is entirely crystalline.

The crystallization kinetics can be obtained by analyzing the time dependence of the isothermal desorption rate. In the analysis, the initial desorption rate (~0 s in Fig. 1(a)) is taken to be the desorption rate from a surface that is 100% amorphous, $\mathrm{Rate}_{\mathrm{ASW}}$, and the desorption rate in the plateau region (~200 s) is taken to be desorption rate from a surface that is 100% crystalline, $\mathrm{Rate}_{\mathrm{CI}}$. The desorption rate in the intermediate region is linear combination of the two desorption rates,

$$\mathrm{Rate} = \mathrm{Rate}_{\mathrm{ASW}} \cdot (1 - x(t)) + \mathrm{Rate}_{\mathrm{CI}} \cdot x(t) \tag{1}$$

where $x(t)$ is the fraction crystallized at the surface. The fraction crystallized versus time, $x(t)$, is determined using the lever-rule type construction in the equation:

$$x(t) = 1 - \frac{\mathrm{Rate}(t) - \mathrm{Rate}_{\mathrm{CI}}}{\mathrm{Rate}_{\mathrm{ASW}} - \mathrm{Rate}_{\mathrm{CI}}} \tag{2}$$

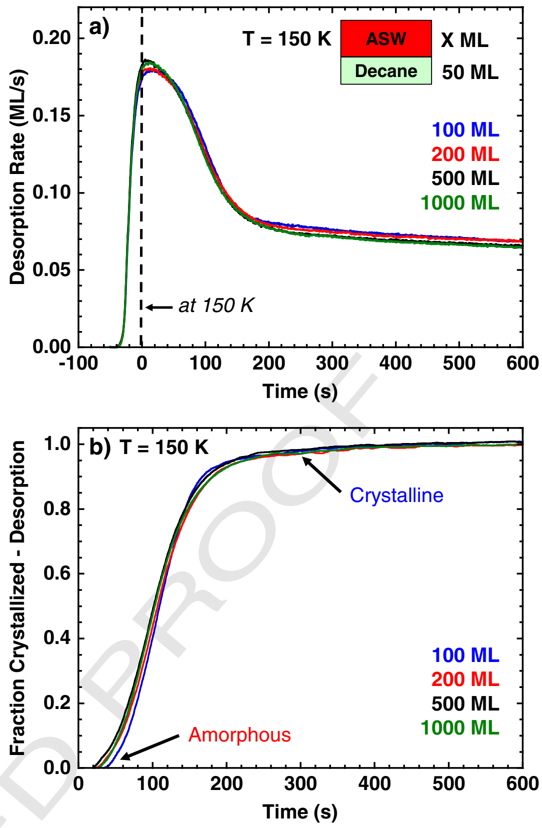

Fig. 1. (a) Isothermal TPD spectra for a series of films with ASW thicknesses of 100 (blue curve), 200 (red curve), 500 (black curve), and 1000 ML (green curve). The ASW films (5% D_2O in H_2O solution) were deposited on top of 50 ML of decane. The composite ASW/decane films were deposited at normal incidence and at 30 K. After deposition the films were heated to and held at 150 K. Time zero (vertical dashed line) marks the time the isothermal temperature is reached. (b) The fraction crystallized versus time, $x(t)$, obtained from the isothermal TPD spectra in (a).

Fig. 1(b) displays the $x(t)$ curves obtained from the isothermal TPD spectra in Fig. 1(a) for ASW thicknesses of 100 (blue curve), 200 (red curve), 500 (black curve), and 1000 ML (green curve). The curves for all thicknesses are similar in shape and nearly aligned as is expected since the desorption spectra are nearly identical. The results in Fig. 1 confirm that the surface crystallization kinetics of ASW films in vacuum are thickness independent from 100 to 1000 ML.

The observed thickness-independent surface crystallization kinetics could be explained by two possible mechanisms. The first mechanism is one where there are random nucleation sites evenly distributed throughout the film. In this case, no matter the film thickness, the surface would crystallize at the same rate given that there is an equal probability of a nearby nucleation site. In this mechanism the bulk crystallization kinetics would also be independent of thickness. The second mechanism is one where there is a preference for nucleation at the ASW surface/vacuum interface. In this case, if the surface is the

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