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Substrate induced crystallization of amorphous solid water at low temperatures

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We show that N_2 monolayer desorption from ice surfaces is a quantitative, highly sensitive method for following the surface crystallization kinetics at low temperatures. Vapor deposited water films on a crystalline ice substrate exhibit amorphous growth at temperatures below ~ 110 K. The rate of crystallization for these amorphous films is dramatically accelerated compared to the rate of crystallization observed for the amorphous films deposited directly on Pt(111). We find that the crystalline ice substrate acts as a two-dimensional nucleus for the growth of the crystalline phase, thereby accelerating the crystallization kinetics. © 1999 American Institute of Physics. [S0021-9606(99)70212-6]

Amorphous solid water (ASW) is an important constituent of astrophysical environments^{1,2} and its properties have been widely investigated.^{3–7} The crystallization of ASW, which is an important process in the thermal aging⁸ and outgassing⁹ of icy bodies in outer space, has been studied previously.^{2,10–14} These studies indicate that the crystallization of ASW on heterogeneous substrates occurs via bulk nucleation and growth.^{2,10–13} Therefore, these substrates do not act as nucleation sites for crystallization during deposition or during the annealing of the ice film. However the role of crystalline ice (CI) as a substrate in promoting the ASW crystallization is unclear. Löfgren *et al.*¹⁴ proposed that water deposited at 100 K on CI grows crystalline, based on measurement of the water desorption rate at 148 K. However, as we demonstrate below, their experiments do not rule out the possibility that CI acts as a nucleus for the crystallization of ASW during subsequent annealing of the film.

In this paper we show that water deposited at low temperatures (<110 K) and slow deposition rates (<0.1 bilayer/s) on CI is amorphous and the CI substrate acts as a nucleation site for the subsequent crystallization of the amorphous phase upon heating. We find that at 128 K the crystallization time for 10 bilayers (BL) of ASW deposited on CI is ~ 1000 times shorter than the crystallization time for ASW deposited on Pt(111). These changes of the ASW surface crystallinity occur at temperatures below those where any appreciable water desorption occurs and were monitored using a new surface sensitive N_2 desorption “spectroscopy,” which is described below.

The experiments were conducted in a ultrahigh vacuum (UHV) chamber with a base pressure of $\sim 1 \times 10^{-10}$ Torr. The Pt(111) substrate was prepared using standard cleaning procedures¹⁵ and the surface purity and order were checked using Auger electron spectroscopy (AES) and low energy electron diffraction (LEED), respectively. An effusive mo-

lecular beam of H_2O directed normal to the surface was used to deposit thin films of crystalline and amorphous water ice on a Pt(111) crystal. As shown in a previous study, this leads to the formation of relatively dense, smooth, and nonporous ASW films.¹⁶ A N_2 monolayer deposited on the ice with a supersonic molecular beam was used to study the crystallization of the ice films. The temperature of the Pt(111) substrate during the N_2 deposition was fixed at 26.5 ± 0.5 K to avoid the formation of N_2 multilayers on the H_2O surfaces. The N_2 uptake kinetics and saturation coverage were monitored using temperature programmed desorption (TPD) and the beam reflection technique of King and Wells.¹⁷ The TPD of the N_2 and H_2O films was monitored using a quadrupole mass spectrometer in an angle integrated manner⁴ with a linear ramp rate of 0.6 K/s. The H_2O and N_2 coverages were normalized with respect to the desorption peak from the first H_2O bilayer (BL) on Pt(111) and from the first N_2 monolayer (ML) on CI, respectively.

The H_2O TPD spectra from 25 BL of H_2O deposited on Pt(111) at different substrate temperatures are shown in Fig. 1. The spectrum in Fig. 1(a) represents the TPD from the film deposited at 22 K. Low-temperature growth results in the formation of ASW as shown in previous studies.^{2,12,13,18} The characteristic feature of the amorphous phase in the desorption spectrum is the presence of a shoulder at ~ 158 K due to the higher desorption rate of ASW as compared to CI phase [Fig. 1(b)].^{4,13,18} The difference between the ASW and CI desorption rates is more easily seen in the inset of Fig. 1. As the crystallization of the ASW film occurs (157–160 K), the H_2O desorption rate decreases to the desorption rate of CI and follows the zero-order desorption dependence for higher temperatures.¹⁴

Since the H_2O TPD clearly distinguishes between ASW and CI, we have used it to investigate the affect of a CI substrate on the subsequent growth of low temperature vapor deposited ice. Figure 1(c) shows the H_2O desorption spectrum from a thin film prepared by the initial deposition of 15

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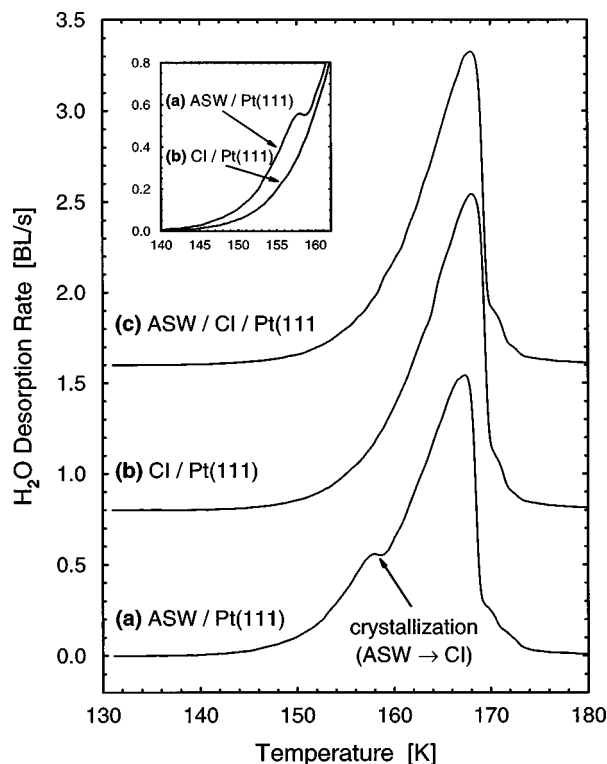


FIG. 1. H_2O TPD spectra from the H_2O films deposited on a Pt(111) substrate at different temperatures. (a) 25 BL deposited at 22 K (ASW), (b) 25 BL deposited at 140 K (CI), (c) 15 BL deposited at 140 K (CI) followed by 10 BL deposited at 22 K (ASW). The spectra are offset for clarity. The inset shows a superposition of spectra (a) and (b) to indicate the higher desorption rate of ASW compared to CI.

BL of H_2O at 140 K to form a CI base followed by the deposition of 10 additional bilayers of H_2O at 22 K. Despite the fact that the H_2O deposition at 22 K is expected to result in the formation of an ASW film, the low desorption rate in the H_2O TPD shows only the presence of CI phase analogous to the spectrum of CI film in Fig. 1(b). As mentioned earlier, two explanations are possible: (1) The CI substrate acts as a template for the subsequent growth of crystalline ice during low temperature deposition,¹⁴ or (2) the low-temperature vapor deposited ice overlayer is amorphous, but the CI substrate acts as a nucleation site thereby accelerating the crystallization of ASW overlayer. The limitation of H_2O TPD for investigating the crystallization in this case is that prior to the temperatures where desorption becomes appreciable (>140 K), significant crystallization may have occurred. To avoid the high temperature annealing of the ASW layer we utilize a surface sensitive method that is based on the low temperature desorption of N_2 monolayers physisorbed on H_2O surfaces.

The N_2 TPD spectra from the surfaces of the H_2O films described in Fig. 1 are shown in Fig. 2. After the deposition of the ice films, the sample temperature was set to 26.5 K and the ice films were exposed to the N_2 beam until a saturation (monolayer) coverage was achieved. The N_2 desorption spectra from ASW [Fig. 2(a)] and CI [Fig. 2(b)] are readily distinguished. Two significant differences are observed: (1) The maximum of the desorption peak shifts from 31.5 K for ASW to 35.5 K for CI, and (2) the integrated N_2

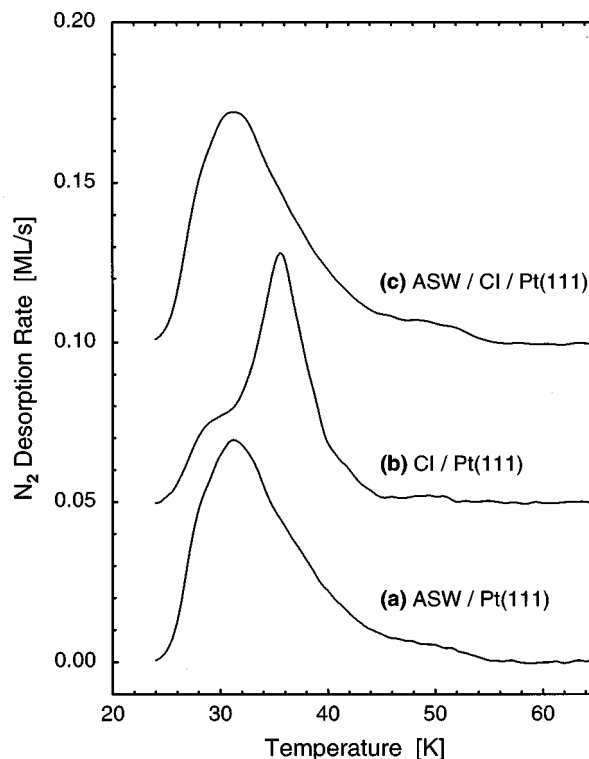


FIG. 2. N_2 TPD spectra from 1 ML of N_2 physisorbed on 25 BL of H_2O adsorbed at different temperatures as described in Fig. 1. (a) 25 BL deposited at 22 K (ASW), (b) 25 BL deposited at 140 K (CI), (c) 15 BL deposited at 140 K (CI) followed by 10 BL deposited at 22 K (ASW). The spectra are offset for clarity.

TPD area from the CI surface decreases by $\sim 30\%$ compared to that of ASW. The shift in the peak desorption temperature suggests that the physisorbed N_2 has a slightly higher binding energy on the CI surface as compared to the ASW surface. The higher surface area of the ASW film may be attributed to the formation of slightly rougher surfaces due to significantly slower H_2O surface diffusion at low temperatures.

As shown in Fig. 2(c), the N_2 desorption from a 10 BL H_2O film grown at 22 K on a 15 BL CI substrate yields a desorption spectrum that is identical to the spectrum from the ASW film grown at 22 K on Pt(111) [Fig. 2(a)]. This is in contrast with the result presented in Fig. 1(c), which shows the H_2O desorption rate corresponding to that of the CI phase. Based on the similarity of Fig. 2(c) and Fig. 2(a), we conclude that the H_2O film deposited on the CI substrate at 22 K is amorphous. We have also investigated the growth of H_2O overlayers at higher temperatures. The N_2 desorption spectra indicate that for temperatures less than ~ 110 K the films deposited on CI are amorphous as well. The subsequent crystallization of the ASW is accelerated by the presence of the CI substrate and occurs at a temperature below the onset of any appreciable H_2O desorption ($T < 140$ K) as confirmed by Fig. 1(c).

As illustrated in Fig. 3 the N_2 TPD line shape can be used to determine the crystallinity of the ASW surface as a function of annealing time. For this data, a 10 BL ASW film was deposited on 15 BL of CI and subsequently annealed at 128 K for a period of time, after which it was cooled to 26.5

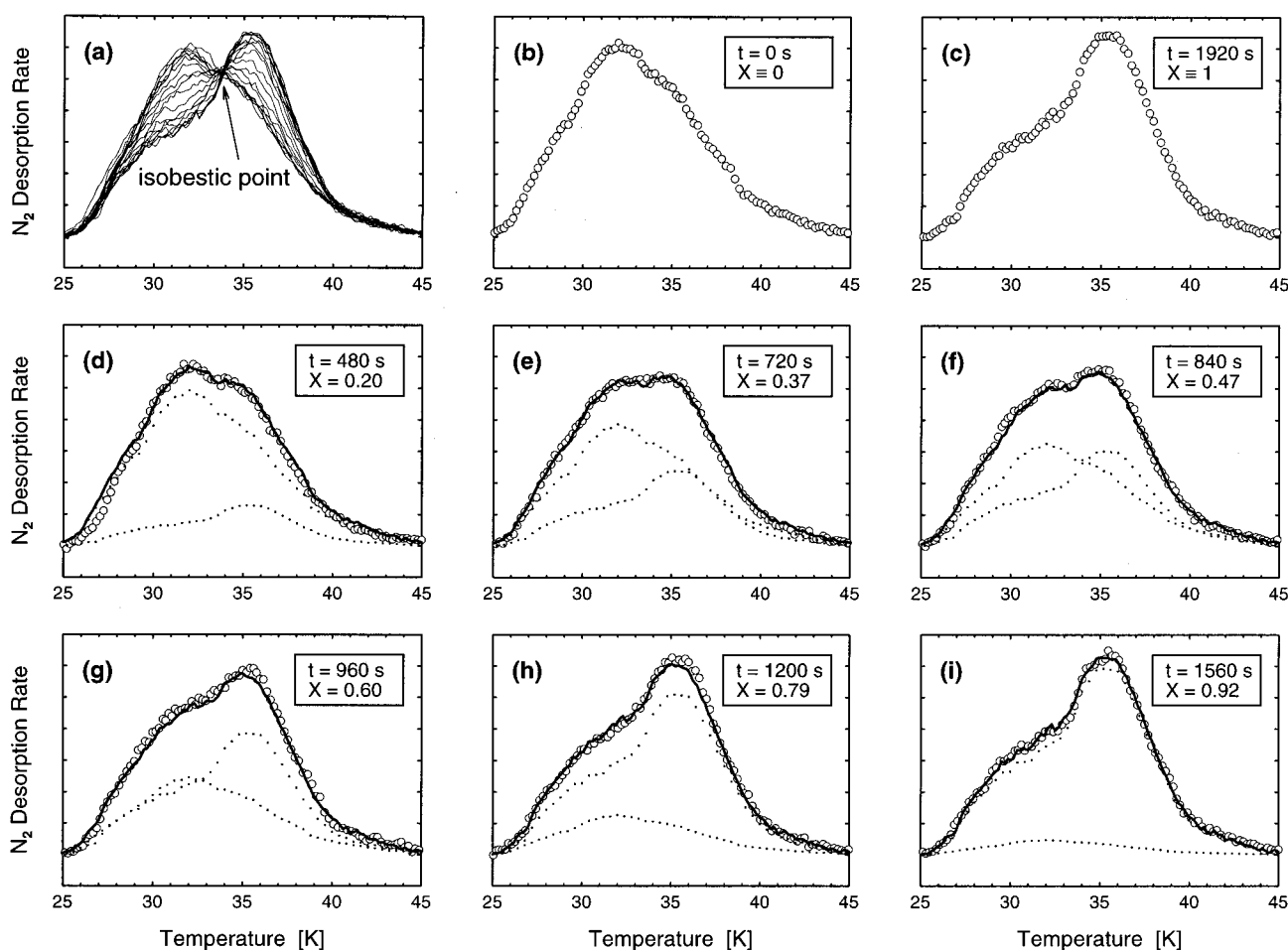


FIG. 3. N_2 TPD from 1 ML of N_2 adsorbed at 26.5 ± 0.5 K on the H_2O film prepared as described in Fig. 1(c) [10 BL of ASW/15 BL of CI/Pt(111)] as a function of annealing time at 128 K. A temperature of 128 K was chosen to observe the crystallization on a feasible experimental time scale. (a) shows the set of N_2 TPD spectra vs annealing time exhibiting an isobestic point at ~ 33.5 K. In (b)–(i), the empty circles represent the experimental points, solid lines represent the fit of spectra by a linear combination of the initial [(b)] and final [(c)] spectra with their partial fractions shown as dotted lines.

K, dosed with a monolayer of N_2 and then heated to obtain the N_2 TPD spectrum. The same film was then further annealed at 128 K and the process was repeated. In this way, a series of N_2 TPD spectra was obtained for partially crystallized surfaces. The complete set of spectra in Fig. 3(a) demonstrate a decrease in the intensity of ASW peak (~ 31.5 K) and an increase in the intensity of CI peak (~ 35.5 K) with increasing annealing time, showing the gradual crystallization of the surface. All the spectra intersect at a single isobestic point (~ 33.5 K) that is generally associated with the existence of two interconvertible species which have overlapping spectra. Therefore, the N_2 TPD spectra of partially crystallized surfaces can be expressed as a linear combination of the ASW and crystallized ice spectra weighted by their corresponding fractions

$$s(T, X) = (1 - X) \times s_{\text{ASW}}(T) + X \times s_{\text{Cryst}}(T). \quad (1)$$

Here $s_{\text{ASW}}(T)$ and $s_{\text{Cryst}}(T)$ represent the temperature dependent spectra of the ASW [Fig. 3(b)]¹⁹ and crystallized ice [Fig. 3(c)] surfaces, respectively, and X is the fractional area of the surface corresponding to the crystallized ice spectrum in Fig. 3(c). Figures 3(d)–(i) show the fits (solid lines) to the experimental data (empty circles) as well as the partial

fractions (dotted lines) of the crystalline and amorphous spectra for a representative subset of measurements. Excellent agreement is found between the fits and the data, demonstrating that N_2 TPD provides a sensitive method to quantitatively study the crystallization of ASW surfaces.

The comparison of the N_2 TPD spectra of the film crystallized at 128 K [Fig. 3(c)] and the CI film grown at 140 K [Fig. 2(b)] shows $\sim 25\%$ decrease in the intensity of the low-temperature shoulder (~ 30 K) for the ice grown at 140 K. The differences in the spectra suggest that the structures of these films are not identical. Increased surface roughness, higher concentration of grain boundaries, and a residual amorphous component are possible factors that could lead to the observed differences.

The converted surface fraction, $X(t)$, of ASW films (10 BL) on CI (open circles) and Pt(111) (filled circles) substrates as a function of annealing time at 128 K is shown in Fig. 4. The crystallization of the ASW film on a CI substrate shows a dramatic acceleration compared to the crystallization of ASW on the Pt(111) substrate. Only small changes in the converted fraction (< 0.10) of the ASW film on Pt(111) are observed within the time that leads to complete crystallization of the ASW film on the CI substrate. We estimate

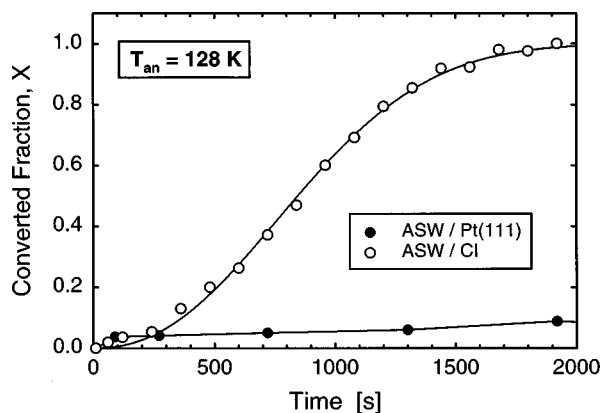


FIG. 4. The isothermal crystallization of the surface of 10 BL thick ASW film on CI (open circles) and Pt(111) (filled circles) substrates at 128 K. Solid lines are provided to guide the eye.

that the crystallization of 10 BL of ASW on Pt(111) at 128 K would take ~ 1000 times longer compared to the crystallization of the same film on a CI substrate.²⁰

In general, during the crystallization two processes occur: (1) Formation of the nucleation embryos, and (2) their subsequent growth. Each step is associated with a kinetic barrier towards the formation of the thermodynamically favored crystalline phase. The increase of the crystallization rate observed on the CI substrate is attributed to the fact that the CI substrate acts as a two-dimensional nucleation center. Hence, the crystallization rate is determined by the rate of propagation of the ASW–CI interface (i.e., the growth of the crystalline phase).

The converted fraction as a function of time, $X(t)$, (Fig. 4) gives us valuable information about the crystallization process. If the ASW–CI interface propagated layer by layer through the film, then $X(t)$ would be a step function. Instead, $X(t)$ is significantly broadened suggesting that the ASW–CI interface is rough. Some of the width of $X(t)$ may be due to initial roughness of the CI substrate and/or the ASW overlayer. However, the width of $X(t)$ probably also has contributions from stochastic roughening of the interface as the crystallization proceeds.

In summary, we have used N_2 TPD (22–65 K) from a monolayer of N_2 physisorbed on H_2O surfaces to investigate the crystallization of amorphous solid water (ASW) at low temperatures. The changes in the N_2 desorption spectra are directly proportional to the changes in the crystallized fraction of the ASW surface. The H_2O films deposited on crys-

talline ice (CI) substrates at temperatures below ~ 110 K are amorphous. Upon annealing, the CI substrate acts as a two-dimensional nucleus for ASW crystallization and hence the crystallization is not limited by the kinetic barrier associated with the formation of bulk nucleation embryos as on heterogeneous substrates.^{2,10–14} Instead the crystallization rate is limited only by the barrier associated with the propagation of the ASW–CI interface. This results in a dramatic increase of the crystallization rate (~ 1000 times at 128 K) of ultrathin (10 BL) ASW films deposited on CI compared to the rate of bulk crystallization observed for films deposited directly on a Pt(111) substrate.

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¹⁹The slight differences between spectra in Fig. 3(b) and Fig. 2(c) are the result of annealing processes that occur during the first ramp to 128 K. These processes are unrelated to the ASW crystallization.

²⁰The estimate is based on the extrapolation of the crystallization time for ASW on Pt(111) at higher temperatures (140–146 K, data not shown).