



ELSEVIER

Surface Science 367 (1996) L13–L18

surface science

Surface Science Letters

# Desorption and crystallization kinetics in nanoscale thin films of amorphous water ice

R. Scott Smith, C. Huang, E.K.L. Wong, Bruce D. Kay \*

*Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, P.O. Box 999, MSN K2-14, Richland, WA 99352, USA*

Received 20 May 1996; accepted for publication 27 June 1996

## Abstract

The amorphous to crystalline ice phase transition is studied by measuring the water desorption rate from nanoscale thin films of water vapor deposited on Au(111) and Ru(001) single crystal metallic substrates. The desorption kinetics are substrate dependent and suggest strongly that the film morphology is governed by the hydrophilicity of the substrate. The crystallization kinetics are independent of substrate but depend strongly on both temperature and film thickness and are consistent with a spatially random nucleation and isotropic growth model.

*Keywords:* Amorphous thin films; Crystallization; Evaporation and sublimation; Thermal desorption; Water

## 1. Introduction

Amorphous and glassy materials have important applications in many areas of physical, biological and materials science and extensive reviews have appeared recently [1,2]. In particular, amorphous water ice has been the focus of considerable diverse and interdisciplinary research. The reasons include its applicability as a model for liquid water [3–8], its existence as a major component in cometary and interstellar ice [9–12], and the current debate over its physical and thermodynamic properties [13–25]. The experiments described here, although germane to all of these areas, were designed to help understand the structure and molecular level interactions of nanoscale thin films of water ice with the underlying substrate.

There is a wealth of literature on water adsorption on surfaces (see Ref. [26] for a review), but despite its importance the microscopic details of the structure and energetics are not fully understood. The prevailing interpretation is that water deposited on surfaces forms a smooth ice-like bilayer structure and evaporates with zero-order kinetics suggestive of layer-by-layer desorption [26]. Zero-order kinetics are expected if sublimation occurs from a smooth film of constant exposed surface area. Surprisingly, we find that the desorption kinetics are not consistent with zero-order evaporation, and are strongly dependent on the hydrophilicity of the substrate. The kinetics for the amorphous to crystalline ice phase transformation are also studied. These experimental results are completely accounted for by a quantitative kinetic model. The results provide information about water–substrate interactions and fundamental data

\* Corresponding author. Fax: +1 509 375 6442;  
e-mail: bd\_kay@pnl.gov

about phase transformation mechanisms in glasses and amorphous materials.

Water vapor deposited on cold substrates ( $< 145$  K) is known to form a metastable amorphous phase [3,10,13,14,16,17,20,22,23,27–31]. The metastable amorphous ice has a higher free energy than the crystalline ice, and as a result, the water desorption rate from the amorphous ice is higher. This has been observed previously [28,30]. Hinch and Dubois have observed metastable water growth for films less than ten layers thick on Cu(111) [32,33]. The enthalpy difference between the amorphous and crystalline phases is about  $1.3 \text{ kJ mol}^{-1}$  [29], but a direct measure of the free energy difference has been difficult. Recently, we have used the difference in the desorption rates to determine the relative free energy of the two phases [24,25]. In this Letter we use the time dependent desorption rate to quantitatively follow the kinetics of crystallization. Related and independent studies are reported by Löfgren et al. in the following Letter.

## 2. Experimental

The experimental technique and apparatus have been described elsewhere and are only summarized here [34,35]. An effusive molecular beam having a flux of  $0.06 \text{ ML s}^{-1}$  ( $1 \text{ layer} \cong 10^{15} \text{ molecules cm}^{-2}$ ) was used to grow precise thicknesses of the ice films on both Ru(001) and Au(111) single crystal substrates at 85 K. After ice film growth, the substrates were resistively heated at a linear ramp rate of  $0.6 \text{ K s}^{-1}$  from 85 K to the desired desorption temperature, after which the temperature was held constant. A quadrupole mass spectrometer was used to measure the angle-integrated desorption rate as a function of time.

## 3. Results and discussion

Isothermal desorption spectra for  $\text{D}_2\text{O}$  ice thin films grown on Ru(001) and Au(111) are shown in Fig. 1. The dose on both substrates was 56 layers. Similar experiments with  $\text{H}_2\text{O}$  gave analogous results. The desorption rate exhibits an

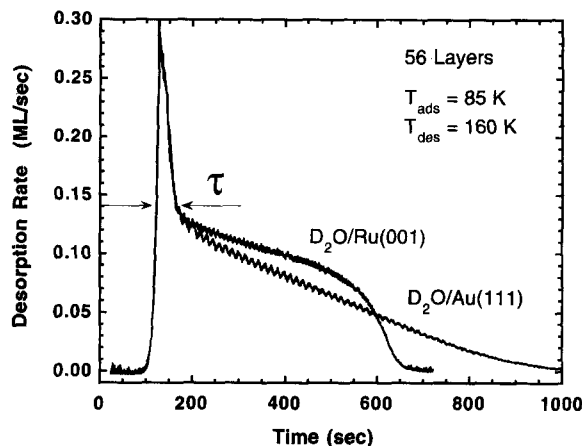


Fig. 1. Isothermal desorption spectra for amorphous  $\text{D}_2\text{O}$  ice grown at 85 K on Ru(001) and Au(111). The initial time dependence of the desorption rate is the result of the conversion from amorphous to crystalline ice. The late-time difference in the desorption kinetics is believed to reflect the morphologies of the ice films on the two substrates.

initial rapid increase due to ramping the temperature from 85 to 160 K. At 160 K, the desorption rate decreases rapidly to a value approximately half the initial rate, followed by a much slower decrease. The small oscillations in the experimental spectra are due to small fluctuations ( $\pm 0.05$  K) in the isothermal temperature control.

Initially, desorption is from ice that is predominately amorphous, but as the phase transition proceeds, there is a rapid decrease in the desorption rate because the amorphous ice is being converted to the more stable crystalline phase. After the phase transition is complete, the decrease in the desorption rate slows. The time it takes to complete the phase transition is labeled as  $\tau$ . Although  $\tau$  is the same for both the Ru(001) and Au(111) substrates, there are clear differences in the slopes of the desorption rate after the phase transition. The non-zero slopes indicate that the desorption kinetics are non-zero order and suggest that the morphologies of films grown on the two substrates are different. These differences in the slopes persist for film thicknesses up to 150 layers ( $\sim 500 \text{ \AA}$ ). Above 150 layers, the Au(111) spectra begin to appear more like that of Ru(001).

The observed differences between Ru(001) and Au(111) can be understood by considering the

strength of the water-substrate interaction. Water is known to wet the hydrophilic Ru(001) surface and form an ice-like bilayer structure [26]. The water-Au(111) interaction is weaker than the water-water interaction and leads to hydrophobic non-wetting [34]. As a consequence, ice films grown on Ru(001) are expected to be smooth and extended, exhibiting desorption kinetics close to zero-order, whereas ice films grown on Au(111) may tend to form sphere-like, three-dimensional nanoclusters, and the desorption kinetics will be markedly non-zero order. Analysis of the isothermal desorption spectra yield apparent orders of  $\sim 0.2$  and  $\sim 0.6$  for the Ru(001) and Au(111) substrates, respectively.

Isothermal desorption spectra for various initial thicknesses of  $D_2O$  on Au(111) are displayed in Fig. 2 and clearly indicate that the crystallization kinetics are thickness dependent. Similar behavior is observed for films grown on Ru(001). Fig. 3A displays the observed crystallization time  $\tau$  as a function of film thickness for both Ru(001) and Au(111). The data show that  $\tau$  increases with thickness to a saturation value independent of the substrate. Fig. 3B displays the observed crystallization time  $\tau$  as a function of substrate temperature for both Ru(001) and Au(111). The observed temperature dependence shows Arrhenius-like

behavior with a substrate independent apparent activation energy of  $84 \text{ kJ mol}^{-1}$ .

The substrate independent, nonlinear, saturable thickness dependence of  $\tau$  argues against substrate catalyzed crystallization. If the crystallization were catalyzed at the substrate/ice interface, then  $\tau$  would increase linearly with film thickness and be expected to be substrate dependent. Our data can be described by the equation  $\tau = \tau_\infty(1 - \exp(-L/L^*))$  where  $\tau_\infty$  and  $L^*$  are fit parameters and  $L$  is the film thickness in layers. The  $L^*$  parameter is related to the spatial distribution of nucleation embryos and can be interpreted as the average distance between embryos in the amorphous ice material. When the thickness of the film is small compared to  $L^*$ ,  $\tau$  will increase linearly with thickness because the volume of material a given nucleation embryo must crystallize increases linearly with thickness. When the films are thick compared to  $L^*$ , then the volume of material a given nucleation embryo must crystallize is constant, and as such,  $\tau$  becomes independent of thickness. The thickness dependence data from both substrates give a similar value for  $L^*$ . Our interpretation that  $L^*$  is a measure of the spacing between nucleation embryos is consistent with these embryos being located within the ice and independent of substrate.

The desorption time dependence can be simulated by a kinetic model that assumes that the total desorption rate is the sum of the amorphous and crystalline desorption rates weighted by their respective volume mole fractions. Because desorption occurs from the surface, this assumption means that the surface mole fraction must equal the volume mole fraction. Such a situation can arise if the amorphous phase exhibits mobility on a length scale exceeding  $L^*$  during crystallization. Experimental evidence for such mobility will be presented in a future publication. The crystallization kinetics are contained in the time dependence of the crystalline mole fraction. This time dependence is best described using a classical nucleation and growth kinetic model [36-38]. The isothermal time dependence of the crystalline mole fraction is given by the Avrami equation,  $\chi(t) = (1 - \exp(-(kt)^n))$ , where  $\chi$  is the mole fraction,  $k$  is a phenomenological rate constant, and  $n$

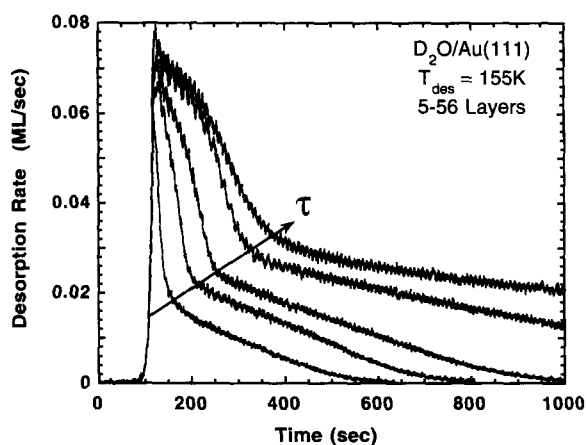


Fig. 2. Isothermal desorption spectra for various thickness  $D_2O$  ice films deposited on Au(111). The crystallization time  $\tau$  increases with increasing film thickness. The initial film thicknesses are 5, 10, 15, 30 and 56 ML.

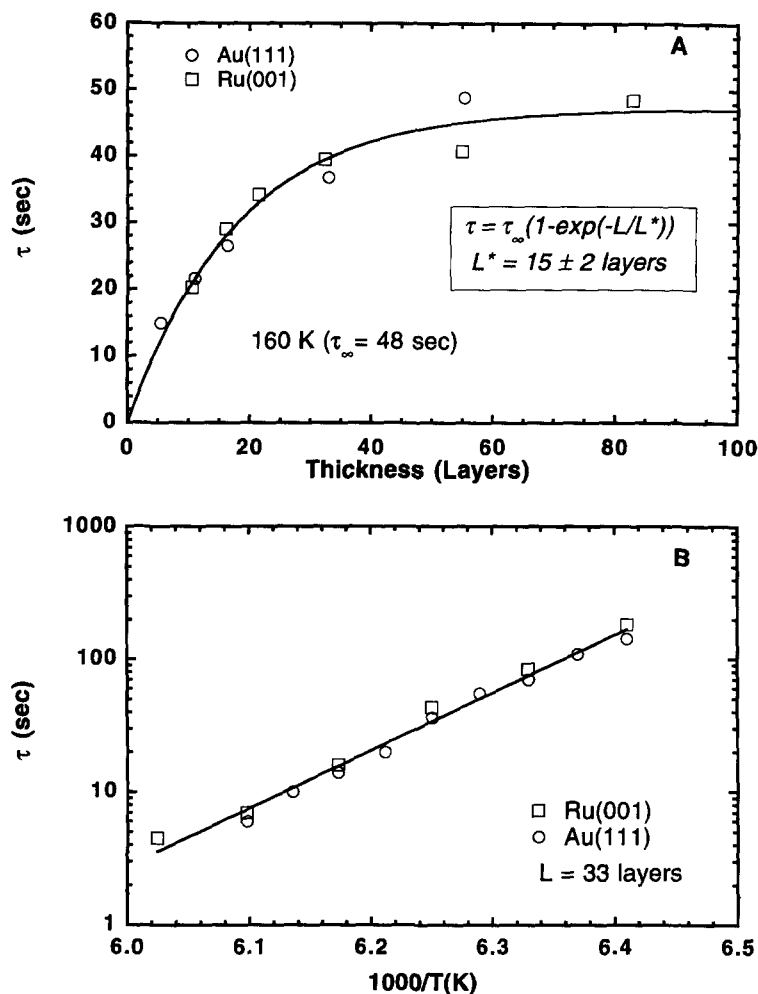


Fig. 3. (A) The dependence of the crystallization time  $\tau$  upon initial ice film thickness for  $D_2O$  films deposited on both Ru(001) (squares) and Au(111) (circles) substrates. The solid line is a fit to the equation  $\tau = \tau_{\infty}(1 - \exp(-L/L^*))$ , where  $\tau_{\infty}$  and  $L^*$  are fit parameters and  $L$  is the thickness in molecular layers. The same parameters describe the  $\tau$  versus thickness dependence for films grown on both Ru(001) and Au(111) substrates. The  $L^*$  parameter is related to the average distance between nucleation embryos and corresponds to a distance of about 15 molecular layers ( $\sim 50 \text{ \AA}$ ). (B) Arrhenius plot of  $\tau$  versus substrate desorption temperature for 33-layer-thick films grown on Ru(001) (squares) and Au(111) (circles) substrates. The observed temperature dependence shows Arrhenius-like behavior with a substrate independent apparent activation energy of  $84 \text{ kJ mol}^{-1}$ .

is a parameter dependent on the nucleation and growth mechanism of the crystalline phase. The best fit to the experimental data yields  $n=4$ , which corresponds to a spatially random constant nucleation rate and spatially isotropic three-dimensional growth [37,38]. The kinetic parameters are all obtained directly from the experimental data. The model treats the coupled crystallization/desorption kinetics assuming an apparent desorption order of

$\sim 0.2$  and  $\sim 0.6$  for the Ru(001) and Au(111) substrates, respectively. The mathematical details of the kinetic model and the origin of the observed non-zero order desorption will be discussed in a future publication.

Fig. 4 shows a comparison of the experimental results and the kinetic model for three different desorption temperatures. The total desorption rate and the component desorption rates from the

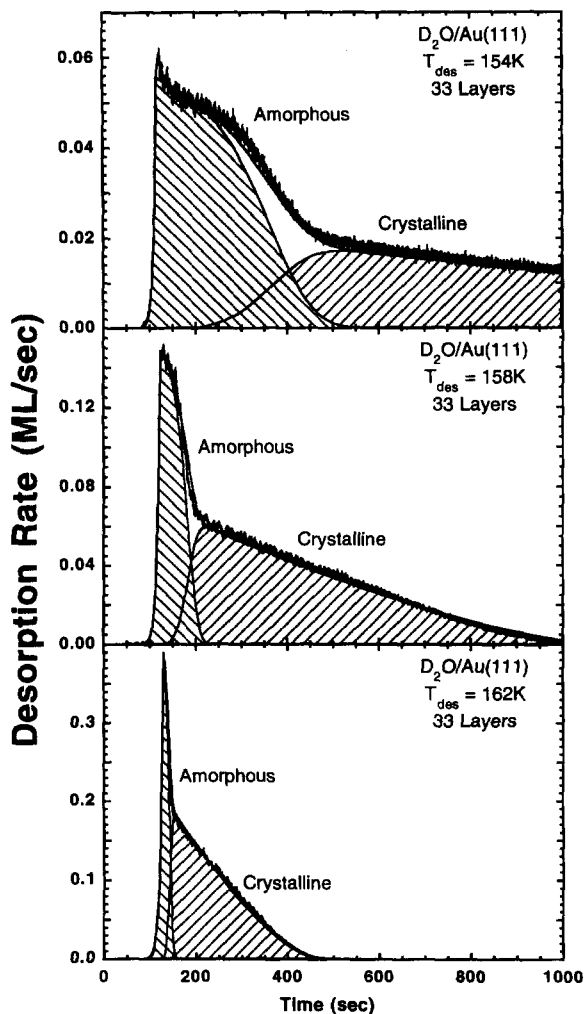


Fig. 4. Comparison of the experimental isothermal desorption spectra with model simulations for various temperatures. The smooth line through the experimental data is the simulated total desorption rate. The contributions to the total rate from amorphous ice is shaded \\\ and from crystalline ice is shaded ///. The decomposition of the total desorption rate into the amorphous and crystalline contributions clearly indicates the autocatalytic nature of the crystallization kinetics.

amorphous and crystalline phases are displayed. The results indicate that the model accurately describes the time and temperature dependence of the crystallization and desorption kinetics. The simulation provides a clear explanation for the overall time dependence of the desorption rate. The initial rapid decay in the desorption rate is the result of the transformation of the amorphous

phase into the crystalline phase. The autocatalytic crystallization kinetics are clearly evident from the time evolution of the crystalline component and reflect the increasing crystalline grain surface area as a function of time [37,38]. Fitting the experimental data to the kinetic model yields 67 kJ mol<sup>-1</sup> for the apparent crystallization activation energy, which is consistent with a prior spectroscopic study on hyperquenched glassy water [31]. The simulations show that the higher value of 84 kJ mol<sup>-1</sup> obtained from Fig. 3B arises from partial crystallization that occurs during the temperature ramp up to the isothermal desorption temperature.

The crystallization kinetics are substrate independent and consistent with a random nucleation and isotropic growth model in which the mean distance between nucleation embryos,  $L^*$ , is about 50 Å. The substrate dependence of the desorption kinetics can be understood by considering the hydrophilic (Ru(001)) versus hydrophobic (Au(111)) nature of the substrate. The hydrophilic substrate yields smoother extended films, while the hydrophobic substrate yields three-dimensional sphere-like nanoclusters. Desorption from an ensemble of identical spherical droplets would exhibit a desorption order of 2/3, in accord with the apparent order of  $\sim 0.6$  for Au(111) observed experimentally. The substrate independence of the crystallization kinetics suggests that the morphological differences responsible for the substrate dependent desorption occur on length scales exceeding  $L^*$ , the mean distance between nucleation embryos.

The present work and the following Letter by Löfgren et al. reveal that the interfacial ice-substrate interaction plays a critical role in determining the nanoscale morphology and macroscopic evaporation kinetics of ice films. These findings should have important applications in the diverse areas of astrophysics, atmospheric science, materials science, wetting phenomena, and the physics and chemistry of liquids.

#### Acknowledgements

The authors gratefully acknowledge helpful discussions with Dr. S.A. Joyce and Dr. G.A. Kimmel.

This work was supported by the Chemical Physics Program of the Chemical Sciences Division of the US Department of Energy Office of Basic Energy Science. Pacific Northwest National Laboratory is operated for the US Department of Energy by Battelle under contract DE-AC06-76RLO 1830.

## References

- [1] C.A. Angell, *Science* 267 (1995) 1924.
- [2] F.H. Stillinger, *Science* 267 (1995) 1935.
- [3] C.A. Angell, *Ann. Rev. Phys. Chem.* 34 (1983) 593.
- [4] C.A. Angell, *Nature* 331 (1988) 206.
- [5] P.H. Poole, F. Sciortino, U. Essman and H.E. Stanley, *Nature* 360 (1992) 324.
- [6] C.M. Sorensen, *Nature* 360 (1992) 303.
- [7] F.X. Prielmeier, E.W. Lang, R.J. Speedy and H.-D. Ludemann, *Phys. Rev. Lett.* 59 (1987) 1128.
- [8] P.H. Poole, F. Sciortino, T. Grande, H.E. Stanley and C.A. Angell, *Phys. Rev. Lett.* 73 (1994) 1632.
- [9] D. Blake, L. Allamandola, S. Sanford, D. Hudgins and F. Freund, *Science* 254 (1991) 548.
- [10] E. Mayer and R. Pletzer, *Nature* 319 (1986) 298.
- [11] S.A. Sanford and L.J. Allamandola, *Icarus* 76 (1988) 201.
- [12] M.S. Westly, R.A. Baragiola, R.E. Johnson and G.A. Baratta, *Nature* 373 (1995) 405.
- [13] J.A. McMillan and S.C. Los, *Nature* 206 (1965) 806.
- [14] J.A. Ghormley and C.J. Hochenadel, *Science* 171 (1971) 62.
- [15] G.P. Johari, *Nature* 260 (1976) 421.
- [16] A. Hallbrucker and E. Mayer, *J. Phys. Chem.* 91 (1987) 503.
- [17] G.P. Johari, A. Hallbrucker and E. Mayer, *Nature* 330 (1987) 552.
- [18] J. Maddox, *Nature* 326 (1987) 823.
- [19] R.J. Hemley, L.C. Chen and H.K. Mao, *Nature* 338 (1989) 638.
- [20] E. Whalley, D.D. Klug and Y.P. Handa, *Nature* 342 (1989) 782.
- [21] R.J. Speedy, *J. Phys. Chem.* 96 (1992) 2322.
- [22] G.P. Johari, G. Fleissner, A. Hallbrucker and E. Mayer, *J. Phys. Chem.* 98 (1994) 4719.
- [23] P. Jenniskens and D.F. Blake, *Science* 265 (1994) 753.
- [24] R.J. Speedy, P.G. Debenedetti, C. Huang, R.S. Smith and B.D. Kay, in *Physical Chemistry of Aqueous Systems: Meeting the Needs of Industry*, Eds. J.H.J. White, J.V. Sengers, D.B. Neumann and J.C. Bellows (Begell House, New York, 1995) p. 347.
- [25] R.J. Speedy, P.G. Debenedetti, R.S. Smith, C. Huang and B.D. Kay, *J. Chem. Phys.* (1996), to be published.
- [26] P.A. Thiel and T.E. Madey, *Surf. Sci. Rep.* 7 (1987) 211.
- [27] M.G. Sceats and S.A. Rice, in: *Water, a Comprehensive Treatise*, Vol. 7, 1st ed., Ed. F. Franks (Plenum, New York, 1982) p. 83.
- [28] A. Kouchi, *Nature* 330 (1987) 550.
- [29] G.P. Johari, A. Hallbrucker and E. Mayer, *J. Chem. Phys.* 92 (1990) 6742.
- [30] N.J. Sack and R.A. Baragiola, *Phys. Rev. B* 48 (1993) 9973.
- [31] W. Hage, A. Hallbrucker and E. Mayer, *J. Chem. Phys.* 100 (1994) 2743.
- [32] B.J. Hinch and L.H. Dubois, *Chem. Phys. Lett.* 181 (1991) 10.
- [33] B.J. Hinch and L.H. Dubois, *J. Chem. Phys.* 96 (1992) 3262.
- [34] B.D. Kay, K.R. Lykke, J.R. Creighton and S.J. Ward, *J. Chem. Phys.* 91 (1989) 5120.
- [35] D.E. Brown, S.M. George, C. Huang, E.K.L. Wong, K.B. Rider, R.S. Smith and B.D. Kay, *J. Phys. Chem.* 100 (1996) 4988.
- [36] M. Avrami, *J. Chem. Phys.* 9 (1941) 177.
- [37] C.N.R. Rao and K.J. Rao, *Phase Transitions in Solids* (McGraw-Hill, New York, 1978).
- [38] R.H. Doremus, *Rates of Phase Transformations* (Academic Press, New York, 1985).