

Probing Surface Properties and Glass–Liquid Transition of Amorphous Solid Water: Temperature-Programmed TOF-SIMS and TPD Studies of Adsorption/Desorption of Hexane

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The interaction of hexane with amorphous solid water has been investigated in terms of the surface diffusion, hydrogen bond imperfections, hydrophobic hydration, crystallization, and glass–liquid transition. The hexane exhibits two main peaks in temperature-programmed desorption: one is ascribed to a complex formed at the surface or subsurface sites (135 K) and the other is caused by a bulk complex (165 K). The latter is associated with the presence of frozen-in imperfections in hydrogen bonds and formed provided that the annealing temperature of the film is below 130 K, whereas the former is created even when the film is annealed up to 150 K. Thus, the hexane–water interaction is hardly characterized by simple physisorption. The hexane is incorporated in the bulk during reorganization of hydrogen bonds due to rotational and translational diffusions of water molecules above 120–140 K, whereas the surface complex is formed even below 120 K due to the surface diffusion of molecules. The film undergoes abrupt dewetting at 165 K as a consequence of the glass–liquid transition. The slow evolution of the fluidity in the supercooled liquid phase may be responsible for the delay of the structural relaxation (165 K) relative to the onset of the translational molecular diffusion (135–140 K).

1. Introduction

The hydrophobic hydration is of great importance in such biological phenomena as membrane dynamics, drug adsorption, and conformation of proteins and DNA in aqueous solution. The hydration of small nonpolar molecules takes place by the spontaneous formation of a cavity and a highly ordered cage of water molecules as a consequence of modification of the stable tetrahedral network of hydrogen bonds.¹ The bottleneck of investigating hydrophobic hydration arises due to the immiscibility of nonpolar molecules with liquid water. On the other hand, amorphous solid water (ASW) that is formed by slow deposition of water vapor at temperatures below 80 K is characterized by a microporous structure, so that large volumes of adsorbed gases can be incorporated in the bulk at low temperatures.^{2,3} The ASW can be converted into the viscous-liquid or crystalline phase above the glass transition temperature ($T_g = 136$ K).⁴ The crystallization of ASW has been discussed extensively from measurements of the isothermal desorption rate of water molecules,^{5–8} as well as the temperature-programmed desorption (TPD) of physisorbed molecules:^{9–12} it is assumed that water desorbs from the amorphous domain much easier than from the crystal domain and that the presence of the crystalline and amorphous domains results in the bimodal TPD spectra of physisorbed molecules. In reality, however, these assumptions are not fully established because the other possibilities, such as the evolution of the viscous liquid phase and the morphological change of the film,^{13–15} are ignored completely. Apparently, more systematic studies on the interaction of nonpolar molecules with the ASW film are necessary to gain insight into the hydrophobic hydration, crystallization, and glass–liquid transition of water.

So far, T_g has been determined calorimetrically from the jump in heat capacity.⁴ However, precise assignment of the calorimetric glass transition temperature of water is quite complicated, as typically seen in the current controversies.^{16–21} On the other hand, the glass–liquid transition can be explored if the translational diffusion of molecules and fluidity of a macroscopic film can be monitored experimentally because they are related to each other via the Stokes–Einstein relation. In this respect, a new experimental approach to the glass–liquid transition has been developed recently by using temperature-programmed time-of-flight secondary ion mass spectrometry (TP-TOF-SIMS):^{13–15} so far, self-diffusion of water molecules, intermixing of physisorbed molecules with water, and dewetting of the fluidized water films have been investigated. On the other hand, TPD can distinguish between the hydration/dehydration and adsorption/desorption of physisorbed molecules unambiguously if combined with surface-sensitive techniques such as TP-TOF-SIMS. In this paper, the hydrogen bond reorganization and glass–liquid transition of the ASW film are explored on the basis of the interaction with hexane. The kinetics of the glass–liquid transition is also discussed from the comparison between the isothermal and temperature-programmed TOF-SIMS experiments.

2. Experimental Section

Experiments were conducted in a stainless steel ultrahigh-vacuum chamber of base pressure below 1×10^{-8} Pa. The vacuum system was equipped with an electron-impact-type ion source, a linear-TOF tube, and a differentially pumped quadrupole mass spectrometer for TPD. To minimize charging and damage of a surface, a pulsed He^+ beam (1.5 keV) with a low incident flux (0.1 nA/cm^2) was used. In each TP-TOF-SIMS

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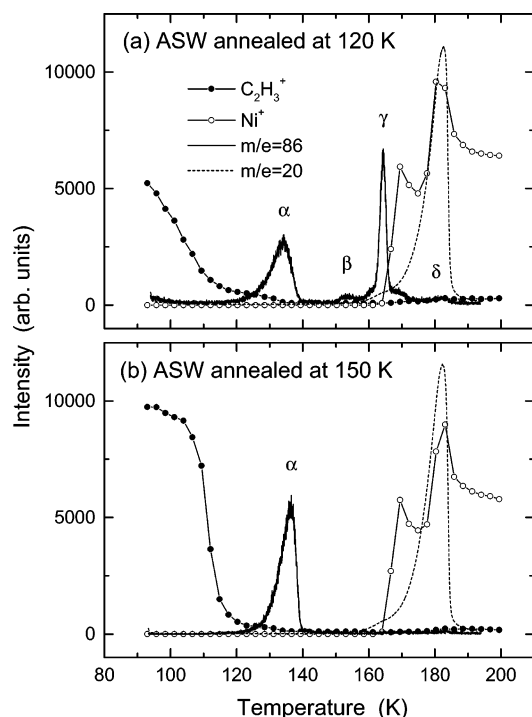


Figure 1. TP-TOF-SIMS intensities of $C_2H_3^+$ and Ni^+ ions and TPD spectra of C_6H_{14} (m/e 87) and D_2O (20) from the hexane-adsorbed nonporous heavy-water film. The results for the D_2O films (thickness of 50 ML deposited at 90 K) annealed up to (a) 120 and (b) 150 K are compared to each other. The 1 ML of hexane was adsorbed on these films after cooling to 90 K. The temperature was ramped at a rate of 6 K/min for both TP-TOF-SIMS and TPD measurements.

measurement, a spectrum was taken continuously at a time interval of 30 s and the temperature was ramped at a rate of 6 K/min. The ion-induced damage of the surface, as estimated from the isotope scrambling between the adsorbed H_2O molecules and the D_2O layer, was recognized if the ion dose exceeded 2×10^{14} ions/cm² [ref 22]. The TP-TOF-SIMS experiment was completed within a dosage of 6×10^{12} ions/cm², so that no appreciable sample damage should be induced. The Ni(111) substrate was mounted on a sample holder cooled to 15 K by means of a closed-cycle He refrigerator. The surface was cleaned by annealing at around 1200 K. The molecules were deposited on the surface by backfilling the vacuum chamber. One-monolayer (1 ML) coverage of the adsorbed molecules was determined from the decay curve of the sputtered ion intensities as a function of exposure, and the film thickness was estimated by using this value. The TPD spectra were taken separately at the same ramping speed as in TP-TOF-SIMS.

3. Results

The possibility for the uptake of physisorbed hexane in the ASW film has been studied as a function of temperature. Figure 1 shows typical experimental results of the TP-TOF-SIMS intensities of $C_2H_3^+$ and Ni^+ ions and the TPD spectra of C_6H_{14} (m/e 86) and D_2O (m/e 20) molecules. To exclude the effects of pores on molecular uptake,³ the D_2O film (50 ML) was deposited at 90 K. The nonporous ASW films thus deposited were heated to (a) 120 and (b) 150 K, and then 1 ML of C_6H_{14} molecules was adsorbed on them after cooling to 90 K. On both films, the $C_2H_3^+$ intensity in TP-TOF-SIMS decays prior to the evolution of the hexane TPD peaks, indicating that the hexane tends to dissolve in the nonporous ASW film. The incorporated hexane desorbs above 120 K, and the TPD spectra exhibit at least four structures, α – δ . Peak α should be assigned to C_6H_{14}

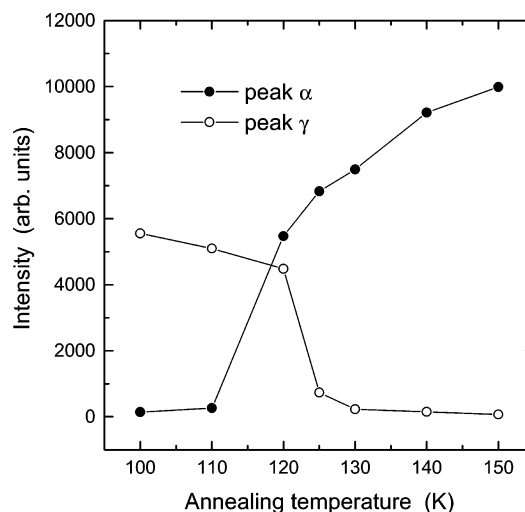


Figure 2. The intensities of peaks α and γ in the hexane TPD spectra as a function of the annealing temperature of the D_2O films. The 50 ML D_2O films deposited at 90 K were heated to temperatures between 100 and 150 K and then 1 ML of hexane was deposited on them after cooling to 90 K.

molecules physisorbed on the surface or incorporated in the subsurface sites, whereas peaks β – δ arise from those incorporated in the bulk. The $C_2H_3^+$ intensity in Figure 1a is considerably small relative to that in Figure 1b, indicating that the uptake of hexane occurs even at 90 K on the 120 K annealed film. No bulk complexes are created in the 150-K annealed film, but hexane is incorporated in the subsurface site or covered by water molecules above 110 K. The Ni^+ intensity evolves at 164 K, where peak γ appears simultaneously as seen in Figure 1a. Moreover, the slope of the D_2O TPD spectrum changes at the decay edge of peak γ (167 K) and the Ni^+ intensity exhibits a hump at this temperature. This behavior has been ascribed to dewetting of the ASW film due to the formation of microscopic water droplets.^{13,14} The dewetting behavior of the film is not affected by the presence or absence of hexane. It is thus found that the adsorption/desorption kinetics of hexane is intimately related to the surface and bulk properties of the ASW film and that hexane should never undergo simple physisorption on the nonporous ASW film.

Figure 2 shows the intensities of two dominant peaks, α and γ , in the hexane TPD spectra as a function of the annealing temperature (100–150 K) of the nonporous ASW film (50 ML deposited at 90 K). The intensity of peak α (peak γ) tends to increase (decrease) with increasing the annealing temperature of the film. The fact that the intensity of peak α is considerably small for the films annealed below 110 K indicates that most of the hexane molecules dissolve in the bulk. The annealing of the ASW film above 130 K is required to quench the bulk complex formation completely. Thus, the bulk properties of the ASW film change drastically at around 120–130 K as far as the uptake of hexane is concerned.

The dewetting of the ASW films, though independent of the incorporated hexane, is largely influenced by the presence of a monolayer of methanol at the surface.¹³ From these facts, it is suggested that dewetting is induced by the surface tension of the liquidlike water film. To gain more insight into the kinetics of the glass–liquid transition, dewetting of a pure ASW film has been investigated under the isothermal condition. In Figure 3 is shown the TOF-SIMS intensities of Ni^+ from the 50 ML $H_2O/Ni(111)$ surface as a function of time at fixed temperatures: the sample was prepared by adsorption of H_2O molecules at 100 K and then heated at a rate of 8 K/min to temperatures

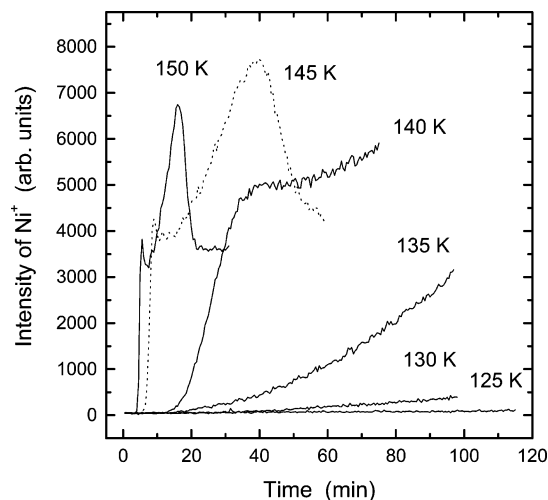


Figure 3. Time evolutions of the TOF-SIMS Ni^+ intensities at fixed temperatures. The H_2O films with a thickness of 50 ML were grown on the Ni(111) substrate at 100 K and then heated at a rate of 8 K/min to temperatures for the isothermal TOF-SIMS measurements.

for each measurement. The dewetting is not observed below 130 K in the time scale of an hour and commences at around the conventional T_g (136 K) within 15 min. At higher temperatures, dewetting takes place abruptly within 1 min after some “aging time”. The aging time is shortened progressively with increasing temperature. The film is thinning during measurements above 140–145 K due to desorption of water molecules, but the abrupt dewetting cannot be explained by the continuous desorption of water molecules or recondensation of the gas-phase molecules. The Ni^+ intensities increase just before the water multilayer disappears. This is because the Ni^+ ion is formed during collisions between sputtered Ni atoms and water molecules and its intensity has a maximum at around 1 ML coverage of water molecules.¹⁵ A quite similar behavior is observed in the TP-TOF-SIMS experiments as seen in Figure 1. The present results clearly show that the ASW film inevitably dewets the Ni(111) surface in both isothermal and temperature-programmed experiments before the film evaporates and that the dewetting temperature observed in TP-TOF-SIMS (typically 165 K) should be dependent on the ramping speed of the experiment, indicating that dewetting is a highly kinetic event.

4. Discussion

The mechanism of hydrophobic hydration has been discussed extensively for the liquid water in terms of solute size, shape, and temperature effects.^{23–29} The immiscibility of nonpolar solutes with water has been explained by a large cavitation energy to modify the stable hydrogen bond network. It is believed that nonpolar solutes increase the hydrogen bonding structure of water molecules in the first hydration shell, but recent experiments revealed that the hydration cage in liquid water is rather loosely defined compared to that in clathrate hydrates.^{27–29} In any case, the cavity formation is the important first step in solvating any nonpolar molecules in water, where a poor solubility of nonpolar molecules in liquid water is attributed to the excluded volume effect, which is amplified by the small size of water molecules themselves. The situation for the gas-deposited ASW films discussed here is considerably different from that of the liquid water because the ASW film has a large number of frozen-in imperfections in the hydrogen bonds. The uptake of nonpolar molecules should be promoted by the presence of no-bonded or “dangling” O–H groups. For the ASW films deposited below 80 K, the pores play an

important role in incorporation of simple molecules, such as N_2 , CO , and CH_4 .^{30,31} They are trapped in the bulk during the pore collapse upon heating. In contrast, it was revealed that the porosity of the ASW film has much less influence on the uptake of larger molecules such as hexane.¹⁴ They are incorporated even in the *nonporous* ASW films as clearly demonstrated in the present paper. Probably, the size of the pore is not sufficient for diffusion of larger molecules. These experimental findings indicate that permeation through pores is not the unique mechanism for the bulk hydrate formation and that the hydrogen bond defects of the *nonporous* ASW film should play an important role in the uptake of heavier molecules. The dangling bonds of the ASW films do not directly interact with hexane, but their reorganization, associated with the diffusion of hexane, may result in the incorporation of molecules in the bulk. The uptake of hexane should be caused by the rotational and translational diffusions of water molecules, which are closely related to the glass–liquid transition. The rotational relaxation of localized hydrogen bond defects is expected to occur above 120–125 K,³² and it may lead to the uptake of hexane in the subsurface site. The translational diffusion of water molecules above 135–140 K^{13–15} should induce the transportation of (hydrated) hexane into the bulk. This mechanism works only for the adsorbates that can stay on the film surface at higher temperatures comparable to T_g of water, so that the heavier molecules tend to dissolve in the bulk of the nonporous ASW film. The lighter molecules desorb from the surface at temperatures below the onsets of such relaxations, thereby resulting in very little uptake. The frozen-in imperfections of the water’s hydrogen bonds are annealed almost completely at temperatures above 135–140 K, so that the incorporation of hexane in the bulk of the annealed ASW film is quenched. Even on such an annealed ASW film, however, the surface complex is formed between water and hexane, as evidenced by the emergence of peak α after almost complete absence of hexane at the topmost surface [see Figure 1b]. This phenomenon may be better explained by the aggregation of water molecules around hexane rather than the penetration of hexane into the bulk or subsurface sites. Thus, the adsorption/desorption behaviors of hexane not only provide us information of the hydrogen bond imperfections in the bulk but also reveal the presence of mobile water molecules on the surface even at such a low temperature below 120 K.

Regarding the origin of peak γ , two related studies have been performed under a different experimental condition. Asscher et al. found that the N_2 and CD_3Cl molecules embedded under the H_2O layer desorb explosively at 165–167 K.^{33,34} They discussed the possibility of strong intermolecular interactions, such as the compression and conging of the molecules by the H_2O overlayer. On the other hand, Kay and co-workers reported a similar result in the CCl_4 desorption when it is embedded in the thick ASW films.³⁵ The result has been explained in terms of the abrupt transformation of ASW into crystalline ice: the CCl_4 molecules diffuse through cracks of crystal grains without incorporation in water ice. The present result indicates that the interaction between nonpolar molecules and ASW is not characterized by simple physisorption, so that some complexes should be formed during diffusion of the embedded molecules into the ASW film.

The fact that peak γ occurs simultaneously with dewetting of the ASW film indicates that the bulk hydrates of hexane collapse due to the glass–liquid transition of water and that hexane becomes immiscible with the resulting liquidlike water. As far as the short-range structures are concerned, there exist

significant similarities between ASW and crystalline ice,²⁹ so that the clathrate-like hydration shell can be formed easily in ASW. Probably, this is responsible for the preferential incorporation of hexane in the bulk of the ASW film at cryogenic temperatures. On the other hand, the imperfect hydration shell of liquid water^{27–29} would be related to a poorer solubility of nonpolar molecules, which may explain the abrupt dehydration of hexane before the emergence of the liquidlike phase at 165 K. In any case, the dewetting temperature (165 K) is much higher than the conventional T_g (136 K). The origin of this discrepancy is discussed in the last part of this paper.

The ASW film heated above 150 K might be regarded as crystalline ice. Indeed, the calorimetric study exhibits a large crystallization exotherm above 150 K.⁴ However, there exist significant controversies regarding what percent of the molecules is transformed from the amorphous to crystalline phase. Fisher and Devlin³² assumed that ASW freezes directly to crystalline ice near 150 K without passing through the liquid phase, whereas Jenniskens et al.³⁶ suggested that viscous liquid water may coexist with the crystalline ice in the temperature range 140–210 K. As demonstrated in the present paper, it is apparent that the ASW film heated to 150 K [see Figure 1b] is not a thermodynamically stable *crystalline ice* since this film undergoes structural relaxation at 165 K. This is because the annealing time of the sample was much shorter than the aging time required for dewetting at 150 K [4 min, see Figure 3]. The crystallization is also a kinetic event, so that the heating rate or the annealing time is an important factor determining the crystal-to-amorphous ratio in the film. It is reported by FTIR spectroscopy that the glassy water crystallizes gradually in the time scale of hours when kept isothermally at 140–150 K.³⁷

So far, the crystallization of the ASW film has been discussed extensively in the isothermal and temperature-programmed desorption studies.^{5–12} It was claimed that the crystallization of the ASW film occurs abruptly within 10 min in the temperature range of 140–150 K⁷ and that the crystallization time of water deposited on the crystalline ice is 1000 times shorter than that deposited on the ASW film at 128 K.⁹ The bump observed in the water TPD spectra at around 160 K is also attributed to the crystallization of the ASW film.^{8,35} On the other hand, the TPD spectra of N₂, CHF₂Cl, and CHCl₃ molecules physisorbed on the ASW film annealed at 140–150 K are bimodal and the peak at higher (lower) temperature has been assigned to the molecules that desorbed from the crystal (amorphous) domains.^{10–12} In these studies, nothing has been considered about the morphological change of the film, but all of these observations can be explained by the film dewetting. For example, the reported “crystallization time”⁷ agrees well with the aging time required for dewetting as seen in Figure 3, so that this phenomenon can be simply explained by the change in the desorption rate associated with the abrupt droplet formation. Moreover, it is very likely that the bimodal TPD spectra result from the desorption of physisorbed molecules from the holes (or dried area) and droplets of the dewetted water films. The possibilities for some complex formations should also be considered, as revealed in the present study. Thus the previous studies on isothermal and temperature-programmed desorption never provide any evidence for crystallization of water. It is apparent that the long-range order like crystallization is hardly concluded without reliable diffraction data. The electron diffraction analysis suggested that at most 30% of the film is converted into crystalline ice.³⁶ Thus, we can conclude that dewetting should be related to the glass–liquid transition of the ASW film rather than crystallization.

Very little is known about the properties of supercooled liquid water, and the precise assignment of the glass-transition temperature of water is under significant debate. T_g has been determined as 136 K in the calorimetric study,⁴ but the related endothermic effect is exceptionally small. From the comparison of the T_g -scaled heat capacity between water and other inorganic glasses, T_g has been reassigned to 165 ± 5 K,^{16,19–21} though it is believed that such a transition is not observable experimentally due to the preceding crystallization at around 150 K. On the other hand, we have discussed the glass–liquid transition on the basis of the self-diffusion of water molecules and the resulting fluidity in the macroscopic film. In the previous studies, the onset of translational molecular diffusion has been determined as 135–140 K from the measurements of the intermixing^{13–15} and H/D exchange^{38,39} of water molecules. It should be noticed that the dewetting temperature observed in the temperature-programmed TOF-SIMS measurements coincides with the reassigned T_g (165 K) whereas dewetting occurs at the conventional T_g (136 K) in the isothermal TOF-SIMS experiment after a considerably long aging time. These experimental results indicate that some “incubation stage” is necessary for the fluidity to evolve in the macroscopic film after the onset of the microscopic molecular diffusion. Thus, the glass transition of water is a highly kinetic event due to the presence of a considerably long relaxation time for the molecular rearrangement relative to the experimental time scale. This is the origin of the controversies in the assignment of the calorimetric glass-transition temperature.^{16–21} The dewetting temperature observed in the TP-TOF-SIMS experiments (165 K), as well as the reassigned T_g (165 ± 5 K), has no physical background. The crystallization also takes place in this temperature range as a consequence of translational molecular diffusion, but it should have only a minor contribution as inferred from the very liquidlike nature of the film.

The delay in the structural relaxation relative to the onset of the molecular diffusion may be related to the well-known properties of supercooled liquid, i.e., the decoupling of self-diffusion and viscosity.⁴⁰ Below approximately $1.2 T_g$ ($T < 163$ K for water), the diffusivity of molecules is enhanced by as much as 2 orders of magnitude relative to the value expected from the viscosity via the Stokes–Einstein relation. This phenomenon has been explained in terms of the spatial heterogeneity, i.e., the fluidized domains are dispersed throughout an essentially solid matrix in the supercooled liquid phase. These two domains are expected to vary in size and shape.⁴¹ All of the mobile molecules emerging above 136 K may not contribute to the structural relaxation immediately since the fluidity arises only from a correlated, nonlocal motion of the molecules. Probably, the slow evolution of the cooperatively rearranging molecules in the fluidized domains is responsible for the delay of the structural relaxation relative to the onset of the translational diffusion.

5. Conclusion

The interaction of hexane with the ASW film has been investigated in terms of the surface diffusion, hydrogen bond imperfections, hydrophobic hydration, crystallization, and glass–liquid transition. The hexane physisorbed on the nonporous ASW film forms surface and bulk complexes. The bulk complex leads to a TPD peak at 165 K where the dewetting of the film takes place concomitantly. The formation of the bulk complex is quenched in the ASW film that is preannealed above 130 K, but hexane forms the surface complex even on the 150 K annealed ASW film due to the presence of mobile water

molecules on the surface. The reorganization of the hydrogen bonds associated with the rotational and translational diffusions of water molecules should lead to the incorporation of hexane in the bulk. The temperature at which the structural relaxation takes place has been determined experimentally from the occurrence of dewetting of the fluidized films. It is found that the structural relaxation commences at the conventional glass-transition temperature (136 K) but it requires considerably long aging time (4–20 min for 150 K > T > 135 K). This behavior causes the controversies in precise determination of the glass-transition temperature of water.

References and Notes

- (1) Frank, H. S.; Evans, M. W. *J. Chem. Phys.* **1945**, *13*, 507.
- (2) Mayer, E.; Plezer, R. *Nature* **1986**, *319*, 298.
- (3) Kimmel, G. A.; Stevenson, K. P.; Dohnalek, Z.; Smith, R. S.; Kay, B. D. *J. Chem. Phys.* **2001**, *114*, 5284.
- (4) Johari, G. P.; Hallbrucker, A.; Mayer, E. *Nature* **1987**, *330*, 552.
- (5) Kouchi, A. *Nature* **1987**, *330*, 550.
- (6) Smith, R. S.; Huang, C.; Wong, E. K. L.; Kay, B. D. *Surf. Sci.* **1996**, *367*, L13.
- (7) Lofgren, P.; Ahlstrom, P.; Ghakarov, D. V.; Lausmaa, J.; Kasemo, B. *Surf. Sci.* **1996**, *367*, L19.
- (8) Smith, R. S.; Kay, B. D. *Nature* **1999**, *398*, 788.
- (9) Dohnalek, Z.; Ciolli, R. L.; Kimmel, G. A.; Stevenson, K. P.; Smith, R. S.; Kay, B. D. *J. Chem. Phys.* **1999**, *110*, 5489.
- (10) Dohnalek, Z.; Kimmel, G. A.; Ciolli, R. L.; Stevenson, K. P.; Smith, R. S.; Kay, B. D. *J. Chem. Phys.* **2000**, *112*, 5932.
- (11) Safarik, D. J.; Meyer, R. J.; Mullins, C. B. *J. Chem. Phys.* **2003**, *118*, 4660.
- (12) Backus, E. H. G.; Grecea, M. L.; Kleyn, A. W.; Bonn, M. *Phys. Rev. Lett.* **2004**, *92*, 236101.
- (13) Souda, R. *Phys. Rev. Lett.* **2004**, *93*, 235502.
- (14) Souda, R. *J. Chem. Phys.* **2004**, *121*, 8676.
- (15) Souda, R. *Phys. Rev. B* **2004**, *70*, 165412.
- (16) Velikov, V.; Borick, S.; Angell, C. A. *Science* **2001**, *294*, 2335.
- (17) Johari, G. P. *J. Chem. Phys.* **2002**, *116*, 8067.
- (18) Johari, G. P. *J. Chem. Phys.* **2003**, *119*, 2935.
- (19) Yue, Y.; Angell, C. A. *Nature* **2004**, *427*, 717.
- (20) Giovambattista, N.; Angell, C. A.; Sciortino, F.; Stanley, H. E. *Phys. Rev. Lett.* **2004**, *93*, 047801.
- (21) Minoguchi, A.; Richert, R.; Angell, C. A. *Phys. Rev. Lett.* **2004**, *93*, 215703.
- (22) Kondo, M.; Shibata, T.; Kawanowa, H.; Gotoh, Y.; Souda, R. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2005**, *232*, 140.
- (23) Southall, N. T.; Dill, K. A.; Haymet, A. D. J. *J. Phys. Chem. B* **2002**, *106*, 521.
- (24) Cui, Q.; Smith, V. H., Jr. *J. Phys. Chem. B* **2002**, *106*, 6554.
- (25) Patel, H. A.; Nauman, E. B.; Garde, S. *J. Chem. Phys.* **2003**, *119*, 9199.
- (26) Scatena, L. F.; Brown, M. G.; Richmond, G. L. *Science* **2001**, *292*, 908.
- (27) Bowron, D. T.; Filippini, A.; Roberts, M. A.; Finney, J. L. *Phys. Rev. Lett.* **1998**, *81*, 4164.
- (28) Filippini, A.; Bowron, D. T.; Lobban, C.; Finney, J. L. *Phys. Rev. Lett.* **1997**, *79*, 1293.
- (29) Finney, J. L.; Hallbrucker, A.; Kohl, I.; Soper, A. K.; Bowron, D. T. *Phys. Rev. Lett.* **2002**, *88*, 225503.
- (30) Souda, R. *Surf. Sci.* **2004**, *551*, 171.
- (31) Kawanowa, H.; Kondo, M.; Gotoh, Y.; Souda, R. *Surf. Sci.* **2004**, *566*, 1087.
- (32) Fisher, M.; Devlin, J. P. *J. Phys. Chem.* **1995**, *99*, 11584.
- (33) Livneh, T.; Romm, L.; Asscher, M. *Surf. Sci.* **1996**, *351*, 250.
- (34) Lilach, Y.; Asscher, M. *J. Chem. Phys.* **2002**, *117*, 6730.
- (35) Smith, R. S.; Huang, C.; Wong, E. K. L.; Kay, B. D. *Phys. Rev. Lett.* **1997**, *79*, 909.
- (36) Jenniskens, P.; Banham, S. F.; Blake, D. F.; McCoustra, M. R. S. *J. Chem. Phys.* **1997**, *107*, 1232.
- (37) Hage, W.; Hallbrucker, A.; Mayer, E.; Johari, G. P. *J. Chem. Phys.* **1995**, *103*, 545.
- (38) Souda, R.; Kawanowa, H.; Kondo, M.; Gotoh, Y. *J. Chem. Phys.* **2003**, *119*, 6194.
- (39) Souda, R. *J. Chem. Phys.* **2003**, *119*, 2774.
- (40) Debenedetti, P. G.; Stillinger, F. H. *Nature* **2001**, *410*, 259 and references therein.
- (41) Donati, C.; Glotzer, S. C.; Poole, P. H.; Kob, W.; Plimpton, S. J. *Phys. Rev. E* **1999**, *60*, 3107.