Glass Transition and Intermixing of Amorphous Water and Methanol

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The diffusion of molecules in amorphous water and methanol films has been investigated on the basis of time-of-flight secondary ion mass spectrometry as a function of temperature. The glass-liquid transition of the amorphous water film occurs at 130–145 K as confirmed from the surface segregation of embedded methanol molecules. The morphology of the pure amorphous water film changes drastically at 160 K as a consequence of dewetting induced by the surface tension and the strongly decreased viscosity of the film. The morphology of the amorphous methanol film changes at 115 K following the self-diffusion onset at 80 K. The binary films of water and heavy methanol are intermixed completely at 136 K as evidenced by the occurrence of the H/D exchange.

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The glassy films can be formed by slow accumulation of gas-phase molecules onto cold substrates. The properties of such amorphous thin films depend on the growth conditions, and it is expected to have a glass-transition temperature at which the substance becomes a viscous liquid [1]. For water and methanol, however, precise assignment of the glass-transition temperatures and properties of the liquid phase are still uncertain. The isotope scrambling of amorphous solid water occurs up to the glass-transition temperature (136 K), but the possibility of translational diffusion of water molecules is denied [2]. It has been recently claimed that the glass transition of amorphous solid water should be assigned to a higher temperature (165 ± 5 K) [3], though such a transition would not be observable explicitly due to the preceding crystallization to ice I*c*. In reality, there exist significant controversies regarding the exact crystallization temperatures and how much percentage of the molecules is transferred from the amorphous to the crystalline phase [2–6]. In the case of amorphous methanol, the glass transition and crystallization temperatures, respectively, have been assigned to 103 and 120 K [7]. For both amorphous water and methanol, no direct experimental evidence for the glass- transition, such as the translational diffusion of molecules and the morphological change of the film, has so far been presented.

On the other hand, the methanol-water mixture in the liquid phase has been regarded as a simple model system for studying the hydrophobic effect. The increase in the entropy of water-methanol mixture is far less than that expected from the ideal solution. This phenomenon has been explained by the formation of clathratelike water structures around the hydrophobic entity (so-called "iceberg" model) [8]. However, a recent neutron diffraction study concluded that the smaller entropy increase is caused by the incomplete mixing [9]. A counterclaim suggests that the molecules in pure liquid methanol persist as hydrogen bonded chains and the water molecules bridge methanol chains to form rings [10]. Thus, a convincing description of the details of the water-methanol mixture is still lacking at the molecular level.

In this Letter, we discuss the behaviors of amorphous solid water and methanol films around the glass-transition temperature and the intermixing between them on the basis of the experiment of time-of-flight secondary ion mass spectrometry (TOF-SIMS) and temperature-programed desorption (TPD). TOF-SIMS can monitor the surface molecular species directly, so that it reveals the possible diffusion or intermixing of molecules as a function of temperature [11,12]. It is found that the glass-liquid transition characterized by the molecular diffusion takes place at 136 and 80 K, respectively, for water and methanol films, which is followed by the abrupt morphological change of the films (at 160 and 115 K) induced by the surface tension, as a consequence of the increased fluidity of the liquid state. The water and heavy-methanol layers intermix completely at the molecular level above 136 K.

The experiments were carried out in an ultrahigh-vacuum chamber (base pressure of 1×10^{-10} mbar) equipped with facilities for standard surface characterization. The details of the TOF-SIMS experiment have been described elsewhere [11,12]. Briefly, the surface was irradiated with pulsed He^+ ions (2 keV). The damage of the amorphous water film was recognized if the ion dose exceeded 2×10^{14} ions/cm^2. The temperature-programed TOF-SIMS measurements were completed within the dosage of 5×10^{12} ions/cm^2, so that no appreciable 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 water, methanol, and methane molecules were dosed from separate gas inlet systems to the substrate by backfilling the vacuum system. 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 on the basis of this value. The TPD spectra were taken by using a differentially pumped quadrupole mass spectrometer. The temperature was monitored by using Au-Fe7% Chromel thermocouples with an accuracy of ±1 K. The substrates were heated at a ramp rate of 0.1 K/s from 15 K to a temperature above which the water multilayer had completely desorbed. The TOF-SIMS spectra were accumulated continuously every 30 s.

Figure 1(a) shows temperature evolutions of the intensities of typical secondary ions sputtered from the CH_3OH molecules (25 ML) adsorbed on the Ni(111) substrate. The film was grown at 15 K and then the temperature was ramped. Not only the fragment ions (H^+, $CH_3{}^+$) but also the protonated molecular ions $[H^+(CH_3OH)_n]$ are emitted from the methanol film. With increasing temperatures, the H^+ and $CH_3{}^+$ ions increase in intensity above 80 K and then decay abruptly above 115 K. At this temperature, the Ni^+ ions are sputtered from the Ni(111) substrate. The multilayer of methanol evaporates at 150 K where all of the ion intensities exhibit a pronounced peak. It should be noted that the property of the methanol layer changes drastically at around 115 K. The emergence of the hump in the Ni^+ intensity cannot be ascribed to the desorption of the methanol film, since it is quenched up to 120 K as confirmed from the TPD measurement. Thus, the amorphous methanol film undergoes an abrupt morphological change at this temperature.

In Fig. 1(b) is shown the TOF-SIMS intensities from the amorphous methanol film prepared by deposition of 25-ML CD_3OD on 25-ML CH_3OH at 15 K. Note that a complete molecular mixing is induced abruptly at around 110 K within quite narrow temperature (<5 K) and time (<1 min) scales. Such a transition should be related to the morphological change of the film. At this temperature, the H/D exchange is induced as a consequence of the hydrogen-bond formation between the CD_3OD and CH_3OH molecules as confirmed from the emission of $D^+(CH_3OD)$ and $H^+(CD_3OH)$ ions in TOF-SIMS and the desorption of CD_3OH comparable to that of CD_3OD in TPD (for $T > 120$ K), indicating the occurrence of almost complete mixing at the molecular level. The emergence of the liquidlike phase should be responsible for the morphological change or long-range intermixing of the methanol film. The transition temperature observed here (115 ± 5 K) is in good agreement with the reported glass-transition temperature of methanol (103 K). The amorphous methanol film is known to crystallize at 116 K in the time scale of 10–20 min [7], suggesting that the crystalline methanol may coexist with the liquid phase after the morphological change above 115 K.

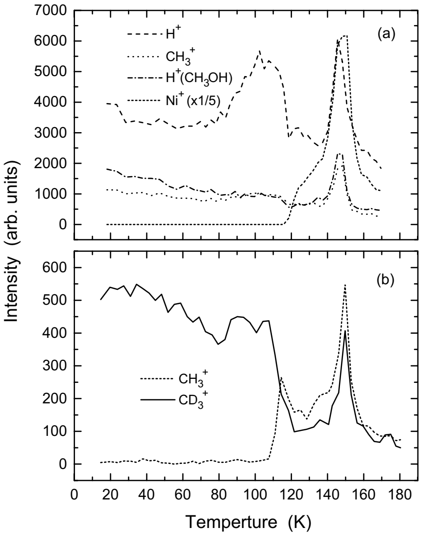

FIG. 1. The temperature-programed TOF-SIMS intensities for the amorphous methanol films. (a) The CH_3OH molecules with a thickness of 25 ML were deposited on the Ni(111) substrate at 15 K. The temperature was linearly ramped at a rate of 0.1 $K\,s^{-1}$. The ions sputtered from the CH_3OH film [the Ni(111) substrate] decrease (increase) at 115 K due to the morphological change of the film. (b) The amorphous methanol film prepared by deposition of 25-ML CD_3OD on top of 25-ML CH_3OH at 15 K. The intermixing of the layers occurs abruptly at 110–115 K.

The long-range translational diffusion of molecules is associated with the abrupt morphological change so that it is independent of the molecular diffusion at the well-defined interface. In order to shed more light on this point, the TOF-SIMS experiments were performed for the 1-ML CD_3OD molecule adsorbed on the CH_3OH films (50 ML). In Fig. 2(a), the evolution of the $CD_3{}^+$ ion sputtered from the CD_3OD molecule is plotted as a function of temperature. The results for four CH_3OH films prepared by different procedures were compared to each other: The amorphous methanol film deposited at 15 K should have bulk pores since nonpolar molecules such as CH_4 are incorporated in the bulk considerably [13] (referred to as "porous-amorphous film"). The inner pores disappear completely by heating the as-deposited film up to 100 K ("amorphous film"). The film heated up to 120 K and then immediately quenched is referred to as "dewetting film" and that kept at 120 K for 30 min as "crystalline film." The CD_3OD molecule was deposited on these films after cooling down to 15 K and then the temperature was ramped. The $CD_3{}^+$ intensity decreases gradually with increasing temperature for all films, but the temperature at which the complete uptake of CD_3OD occurs depends on the quality of the films. The highest uptake of the CD_3OD molecule at the porous-amorphous film would be caused by the reorganization of molecules during the collapse of the inner pores. The porous-amorphous and amorphous films undergo the morphological change so that the adsorbed CD_3OD molecule disappears from the surface completely up to 110 K. For these surfaces, the diffusivity of the molecules is apparently enhanced above 80 K as evidenced by the increased inclination of the decay curves. In this temperature regime, broad peaks evolve in the H^+ and $CH_3{}^+$ intensities in Fig. 1(a). These phenomena should be ascribed to the reorganization of the

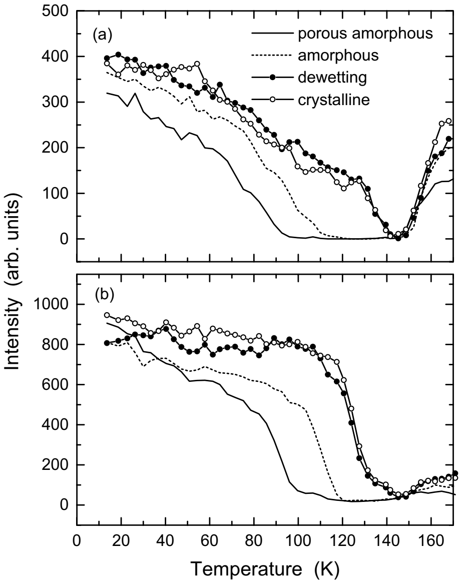

FIG. 2. (a) The temperature-programed TOF-SIMS intensities of CD_3^+ ions sputtered from the 1-ML CD_3OD molecules adsorbed on the 50-ML CH_3OH films. The films deposited at 15 K (porous-amorphous film), heated at 100 K (amorphous film), heated at 120 K (dewetting film), and heated at 120 K for 30 min (crystalline film) are compared to each other. (b) The temperature-programed TOF-SIMS intensities of H_3O^+ ions sputtered from the 1-ML H_2O molecules adsorbed on the 50-ML CD_3OD films prepared by the same procedure described above.

methanol molecules at the surface. Thus, the diffusion of methanol commences at temperatures well below the conventional glass-transition temperature and then the morphological change takes place as a consequence of the increased fluidity of the film. The results for the dewetting and crystalline films are essentially the same: the CD_3OD molecule stays at the surface up to 140 K.

Figure 2(b) shows the temperature evolutions of the $H^+(H_2O)$ intensity sputtered from the 1-ML H_2O molecules adsorbed on the CD_3OD films (50 ML). A similar tendency to the self-diffusion of methanol is observed, but the uptake of the water molecules in the methanol film occurs more steeply. On the porous-amorphous film, the water molecule disappears from the surface at temperatures less than 100 K, whereas it survives on the amorphous film until the morphological change occurs at 115 K. No appreciable differences are observed in the results between the dewetting and crystalline films.

Figure 3(a) shows the temperature evolutions of TOF-SIMS intensities from the binary film prepared by deposition of 25 ML of H_2O on 25 ML of CD_3OD at 15 K. The intermixing is found to occur abruptly at the conventional glass-transition temperature of water (136 K). As seen in the TPD spectra shown in the inset, the main desorption peak of the heavy-methanol occurs at 156 K, but the CD_3^+ intensity in TOF-SIMS is not changed at this temperature. This is because at least 1 ML of methanol stays on the surface until the water molecules desorb completely at 173 K. The dominance of the CD_3OH molecules in TPD, as well as the $H^+(CD_3OH)$ ions in TOF-SIMS (not shown explicitly), indicates that the CD_3OD molecule undergoes considerable H/D exchange with H_2O above 136 K. The intermixing is independent of the properties of the underlying heavy-methanol layer; i.e., the porous-amorphous, amorphous, dewetting, and crystalline films give the same onset temperatures for intermixing. In Fig. 3(b) is shown the similar experimental result for the film prepared by deposition of 50-ML H_2O on 2-ML CD_3OD at 15 K [14]. The methanol molecules segregate to the surface gradually and form a monolayer above 145 K. These two experimental results clearly show that the properties of water films change drastically at around 140 K. The penetration of methanol through the amorphous water film can be interpreted by the emergence of the liquidlike phase. Although no experimental evidence for the morphological change of the film is obtained in the water/methanol systems, it does occur for the pure amorphous water film as shown in Fig. 3(b): the Ni^+ intensity evolves abruptly above 160 K by heating the 50-ML amorphous water film. This phenomenon cannot be ascribed to the desorption of water molecules since only 5% of the water desorbs from the surface up to this temperature. The morphological change of the film is quenched by the monolayer of methanol since it plays a role as a surfactant to reduce the surface tension, indicating the liquidlike behavior of amorphous water above 160 K.

So far, there is significant debate about the properties of amorphous water above the glass-transition temperature.

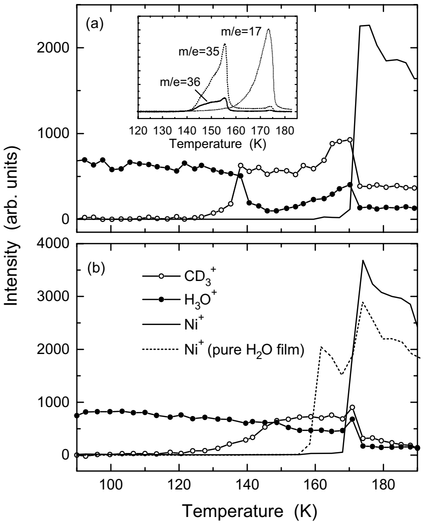

FIG. 3. The temperature-programed TOF-SIMS intensities from the films of (a) 25-ML H_2O grown on top of 25-ML CD_3OD and (b) 50-ML H_2O on 2-ML CD_3OD. Inset: TPD spectra of CD_3OD ($m/e = 36$), CD_3OH (35), and OH (17) from the H_2O (25 ML)/CD_3OD (25 ML) film. Since the ion mass of H_2O^+ overlaps with CD_3^+, OH was monitored for H_2O desorption. The Ni^+ intensity in TOF-SIMS of the pure H_2O layer (50 ML) is shown by a broken line in (b).

Fisher and Devlin [2] assumed that the amorphous solid water freezes directly to crystalline ice near 150 K without passing through the intermediate liquid state, whereas Jenniskens *et al.* [4] suggested that the viscous-liquid water coexists with cubic crystalline ice in the temperature range 140–210 K. Smith and co-workers observed a bump in the TPD spectra at 155–160 K where isotope scrambling occurs abruptly [5,15]. They ascribed this phenomenon to the abrupt phase transformation from the amorphous water into crystalline ice and the diffusivity of water molecules is estimated by assuming that the liquid phase evolves at a narrow temperature range ($150 < T < 159$ K) just before the crystallization. We observed such a bump in the TPD spectra of the pure amorphous water film at the same temperature for the emergence of the hump of the Ni^+ intensity in TOF-SIMS [16]. Therefore, these phenomena should be attributed to the morphological change of the liquidlike film rather than the crystallization. The liquidlike behavior of water films above 160 K seems to be consistent with the claim by Velikov *et al.* [3] who reassigned the glass-transition temperature of water to 165 ± 5 K. However, the properties of amorphous water film apparently change at 136 K in terms of the diffusivity of molecules or the surface segregation of methanol by penetrating the water film. Therefore, the event above 160 K can basically be attributed to a surface tension effect assisted by a strong decrease in viscosity of the liquid water (softening). Regarding the crystallization, it is suggested that only 30% of the molecules are transformed to ice Ic and the growth rate of cubic ice decreases abruptly above 163 K [4]. The short-range hexagonal stacking order may prevent the amorphous water from the complete crystallization to cubic ice [4]. In the case of amorphous methanol, the morphological change of the film (115 K) is also preceded by the liquidlike state characterized by the occurrence of self-diffusion of the methanol molecules (80 K). The crystallization of amorphous methanol would proceed gradually in the liquidlike phase above 115 K. These behaviors may be characteristic for weak glass forming systems like water and methanol. The glass-transition phenomena can be dependent on the heating rate. Indeed, the morphological change of the water-ice film has been suggested to occur even at 140–150 K from the measurement of the isothermal desorption rate in the TPD experiment [17]. More direct evidence for such a possibility would be obtained from the isothermal TOF-SIMS experiments.

It should be noted that the intermixing of the binary films of water and methanol occurs at 136 K independent of the morphological change or the crystallinity of the methanol layer, indicating that the intermixing is mainly controlled by the properties of the amorphous water film. The degree of the H/D exchange between the H_2O and CD_3OD molecules can be a good experimental measure of the hydrogen-bond formation in the mixture. The TPD intensity of CD_3OH relative to CD_3OD increases from 1 (140 K) to 5 (156 K) almost linearly with temperature, indicating that the mixing between water and methanol occurs completely at the molecular level. The liquid phase discussed here would be thermodynamically distinct from the real liquid, but the present result is apparently inconsistent with the claim that the mixing between water and methanol is imperfect at the molecular level [9].

In summary, the properties of glassy water and methanol films are highly controversial in terms of the crystallization and glass-liquid transition. The TOF-SIMS analysis of the mobility of molecules, as well as the morphological change of the films, concludes that the liquid phase is dominant for both water and methanol above their glass-transition temperatures.

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