P H Y S I C A L   R E V I E W   L E T T E R S

Crystalline Ice Growth on Pt(111): Observation of a Hydrophobic Water Monolayer

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The growth of crystalline water films on Pt(111) is investigated using rare gas physisorption. The water monolayer wets Pt(111) at all temperatures investigated (20–155 K). At low temperatures ($T \leq 120$ K), additional water layers kinetically wet the monolayer surface. However, crystalline ice films grown at higher temperatures ($T > 135$ K) do not wet the water monolayer. These results are consistent with recent theory and experiments suggesting that the molecules in the water monolayer form a surface with no dangling OH bonds or lone pair electrons, giving rise to a hydrophobic water monolayer on Pt(111).

Water-surface interactions are ubiquitous in nature and play an important role in many technological applications such as catalysis and corrosion. To understand these interactions, numerous prior experiments have been done on thin water films grown on single crystal metals such as Ru(0001) and Pt(111) which are considered to be good templates for the epitaxial growth of crystalline ice (CI) [1,2]. However, despite years of effort, our understanding of fundamental aspects of water-surface interactions [3], and even the structure of bulk water [4], remains incomplete.

Water adsorbs molecularly on Pt(111) [1,2]. At temperatures above ~60 K, the adsorbed water monomers become mobile [5,6] and form hydrogen bonded clusters as the coverage increases [7,8]. Slow deposition at relatively high temperatures (e.g., ~0.01 ML/s and $T > 135$ K) produces a commensurate $(\sqrt{39} \times \sqrt{39})R16.1°$ structure for the complete monolayer (referred to hereafter as the "$\sqrt{39}$ structure") [9,10]. For typical water fluxes, CI films result for growth temperatures above ~125–135 K [10–12]. For multilayers of CI, the equilibrium structure has the lattice constant of bulk ice, is incommensurate with the substrate, and is rotated 30° relative to the close packed direction on the Pt(111) [10,11]. Multilayer CI films desorb with zero-order desorption kinetics [2,10,13]. Based on these and other experiments, the prevailing view has been that multilayer films of water wet Pt(111) [1,2,12,13].

Here, we investigate the growth of crystalline ice films on Pt(111) using temperature programed desorption (TPD) of both water and Kr adsorbed on the water films. As expected, the water monolayer wets the Pt(111) surface [6,9,10]. However, for coverages greater than 1 ML, the additional water molecules form ice crystallites that do not wet the water monolayer, which remains exposed even for total coverages as large as ~45 ML. The structure of the water monolayer on Pt(111), which has no dangling OH bonds or lone pair electrons, is key to understanding the nonwetting growth of CI films [14,15]. The fully coordinated water monolayer results in a *hydrophobic* surface on which water diffusion is facile. At high temperatures where

large scale rearrangement of the films is *kinetically* accessible, the low surface energy of the hydrophobic water monolayer relative to the crystalline ice surface *thermodynamically* favors the formation of nonwetting, 3D ice crystallites. The hydrophobic character of the water monolayer is further supported by the observation that kinetically wetted, amorphous films dewet upon heating, exposing the water monolayer. We have also obtained results similar to the D_2O data presented here for H_2O on two different Pt(111) crystals, and for H_2O films grown on a thin epitaxial Pd(111) film deposited on Pt(111).

The experiments were performed in an ultrahigh vacuum chamber with a base pressure of $\sim 1 \times 10^{-10}$ Torr that is equipped with a molecular beam, a quadrupole mass spectrometer, a closed-cycle helium cryostat, and an Auger electron spectrometer. The Pt(111) sample was cleaned using standard sputtering and annealing cycles. D_2O films were grown at normal incidence using a molecular beam that is smaller than and centered on the Pt(111) with a flux corresponding to ~0.2 ML/s. Water TPD spectra indicative of a clean surface with few defects were routinely observed [10]. After water deposition, the samples were cooled to low temperature (typically 20–30 K) and dosed with Kr using the same molecular beam.

Figure 1 shows a typical series of TPD spectra for crystalline D_2O on Pt(111). The multilayer ice films desorb with zero-order kinetics, resulting in the low temperature peak that shifts to higher temperature with increasing coverage. The water monolayer desorbs at higher temperature (~ 170 K). We define 1 ML as the water coverage at which the monolayer peak in TPD saturates, corresponding to the $\sqrt{39}$ structure observed by both He atom scattering [11] and LEED [10] for films grown at high temperatures. Water TPD spectra similar to these have been obtained on a variety of metal surfaces [1,2], and presented as evidence for the wetting growth of the multilayer water films on these metals [13].

The van der Waals interaction of a rare gas atom with a metal surface is a sensitive function of the distance between them. As a result, the TPD spectra of multilayers of
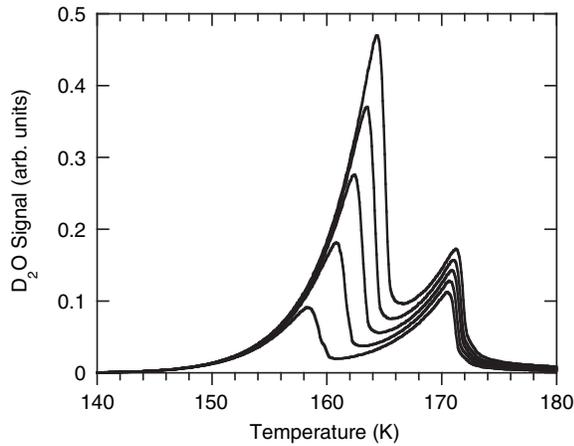
FIG. 1. D_2O TPD spectra for 2, 3, 4, 5, and 6 ML CI films. The temperature ramp rate was 1 K/s. The spectra exhibit zero-order desorption from the CI multilayers (i.e., the leading edges of the low temperature peaks are aligned), and the monolayer desorbs at higher temperature. These characteristics are typically believed to indicate that the water films wet the substrate.

FIG. 2 (color).   TPD spectra for ~1 ML of Kr on various coverages of D_2O deposited on Pt(111) at 100 K where the films kinetically wet the surface. The solid blue, red, green, and black lines are the spectra for 0, 1, 2, and 3 ML of D_2O, respectively. The dashed (blue and red) lines show Kr TPD spectra for partial coverages $\theta = 0.2, 0.4, 0.6,$ and 0.8 ML. The schematic illustrates Kr adsorption on various thicknesses of water films associated with the $W0$, $W1$, $W2$, and $W3$ desorption peaks.

rare gas atoms adsorbed on a metal surface typically have a series of peaks at ascending temperatures due to desorption of adlayers successively closer to the substrate [16,17]. Thus the TPD spectra can be used to assess the height of a desorbing atom above a metal surface. This same approach can also be used to determine the height distribution of a thin water film grown on a metal substrate: the solid blue, red, green, and black lines in Fig. 2 with peaks labeled $W0$, $W1$, $W2$, and $W3$ show the TPD spectra of ~1 ML of Kr adsorbed on clean Pt(111) and 1, 2, and 3 ML of water deposited at 100 K, respectively. Clearly, adsorption of Kr on 1 ML of water can be easily distinguished from 2 or more layers of water or from the bare Pt(111). Hence, as we show below, TPD of physisorbed Kr can be used to probe the growth of water films on Pt(111).

As the water coverage, θ, increases from 0 to 1 ML, the $W0$ Kr TPD peak systematically decreases and $W1$ increases (Fig. 2, dashed lines). This behavior is observed at all growth temperatures (20–155 K). Integration of the $W0$ and $W1$ peaks can be used to determine the fractional areas of the Pt(111) substrate that are bare, $F0$, and covered with *only* 1 ML of water, $F1$. Figure 3(a) shows $F0$ (circles) and $F1$ (triangles) for water deposited at 120 K (open symbols) and 152 K (closed symbols). For both cases, $F0$ decreases linearly and $F1$ increases linearly as the water coverage increases from 0 to 1 ML, indicating that the water monolayer wets the Pt(111) surface. For larger coverages (1 ML $< \theta <$ ~2.1 ML) and growth temperatures below ~125 K, $F1$ decreases ~ linearly indicating that the second layer wets the water monolayer [Fig. 3(a), open triangles]. Analogous data (not shown) demonstrate that the third layer fully covers the second layer. For all growth temperatures below ~125 K and our fluxes, multilayer water films, which are predominantly

amorphous solid water (ASW), wet the Pt(111). We believe this behavior is due to limited mobility and thus kinetic in origin. The morphology of these ASW films will be the subject of a future publication.

In contrast to low temperature ASW growth, CI films grown at higher temperatures, where the water mobility is higher, are dramatically different. For $\theta > 1$ ML the CI films do not wet the water monolayer on Pt(111). The inset of Fig. 3(b) shows the Kr TPD spectra for ~1 ML of Kr on various coverages of water ranging from 1 ML to 50 ML grown at 152 K. For CI films, the $W1$ peak is readily distinguished from the Kr desorbing from the multilayer ice crystallites, CI (inset). The $W1$ TPD peak indicative of Pt covered with only one layer of water does not completely disappear even for total water coverages as high as ~45 ML. CI films grown at other temperatures (140–155 K) also do not wet the water monolayer on Pt(111). The coverage at which the $W1$ TPD peak disappears depends on the growth temperature and flux: at higher growth temperatures or lower fluxes, higher total water coverages are required to completely cover the water monolayer (data not shown). The fraction of the surface covered by only one monolayer of water, $F1$, highlights the different grow mode for CI for $\theta > 1$ ML: at 152 K, $F1$ decreases over a much longer length scale, not vanishing until $\theta \sim 50$ ML [Fig. 3(b), triangles].

Thick films of ASW which wet the Pt(111) can be grown at low temperatures [18]. Here we investigate the morphology of these ASW films as they are annealed to higher temperatures by monitoring the $W1$ Kr TPD peak. For
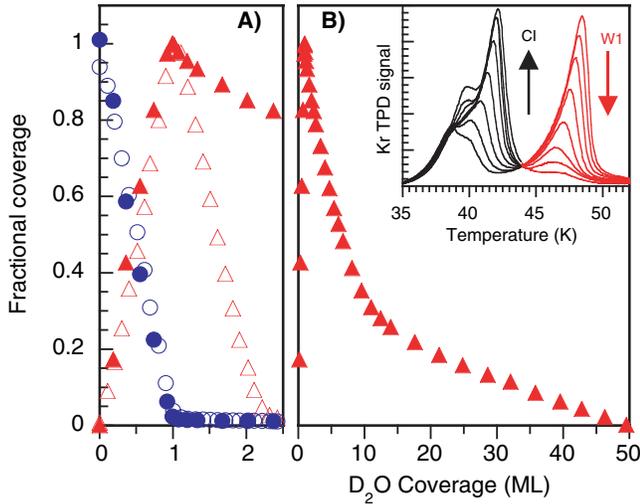
FIG. 3 (color). Fraction of the surface covered with no water, $F0$ (circles), or only 1 ML of water, $F1$ (triangles), vs D_2O coverage. (a) $F0$ and $F1$ for $0 \leq \theta \leq 2.5$ ML for films deposited at 120 K (open symbols) and 152 K (solid symbols). At both temperatures, the first water layer wets the surface. (b) $F1$ for CI films (deposited at 152 K) for $0 \leq \theta \leq 50$ ML. The ice crystallites do not wet the water monolayer. Inset: Kr TPD's from crystalline D_2O for $\theta = 1, 2, 3.4, 5.4, 8, 12.5, 25,$ and 50 ML. The arrows indicate how the Kr TPD peaks associated with the monolayer and ice crystallites evolve as the D_2O coverage increases.

isothermal annealing at lower temperatures ($T < 140$ K), the films typically crack during crystallization but do not substantially dewet the surface [19,20]. However, at higher annealing temperatures, the films crystallize and dewet *exposing the water monolayer but not the bare Pt(111).* Figure 4 shows the isothermal desorption of an initially amorphous 75 ML D_2O film (black line). At 155 K, the film rapidly crystallizes as indicated by the decrease in the desorption rate [12]. After the crystallization is complete ($t > 75$ s), the desorption rate remains constant until $t \sim$ 800 s indicating zero-order desorption from the crystalline ice film. In a separate set of experiments, the isothermal desorption was stopped after various annealing intervals and the films were examined with Kr TPD to determine the fraction of the surface covered by only 1 ML of water, $F1$ (Fig. 4, triangles). Immediately after the film has crystallized, the entire surface remains covered with more than 1 ML of water. However, further annealing results in additional water desorption and concomitant dewetting of the film: after ~ 350 s, when ~ 45 ML of water remain, the water monolayer is exposed and its fractional area, $F1$, increases with time until ~ 950 s when all of the multilayer ice crystallites have desorbed. The water monolayer subsequently desorbs and the fraction of Pt(111) not covered by any water, $F0$, increases (Fig. 4, circles). Zero-order isothermal desorption is also observed for initially nonwetting CI films (i.e., films deposited at higher tempera-
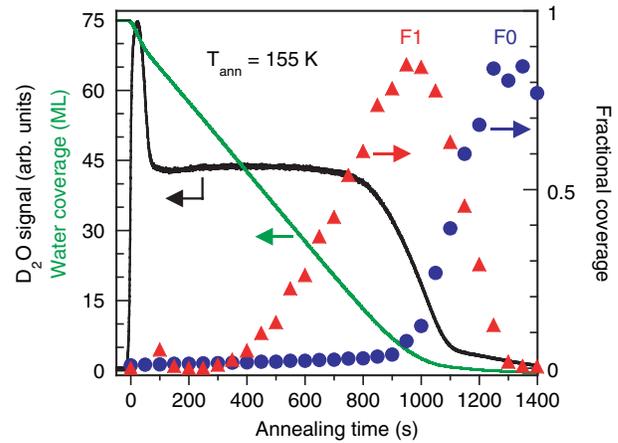
FIG. 4 (color). D_2O desorption rate (black line), D_2O coverage (green line), $F0$ (circles), and $F1$ (triangles) vs annealing time for a 75 ML film deposited at 80 K and annealed at 155 K. After crystallizing, the D_2O desorption rate is constant indicating zero-order desorption kinetics. However, the fraction of the surface covered with only 1 ML of water, $F1$, increases as the film dewets.

tures, data not shown). The data in Figs. 3 and 4 show that the minimum energy configuration for multilayer CI films is nonwetting ice crystallites on top of a hydrophobic water monolayer that wets the Pt(111) surface.

To understand the nonwetting growth of CI films, consider the structure of the water monolayer on Pt(111): for years, it was believed that a water monolayer was similar to a bilayer plane from crystalline ice, with half of the molecules bonded to the substrate and half further from, and not bonded to, the substrate [1,2]. Recent experimental and theoretical results indicate that the actual structures of water films for $\theta \leq 1$ ML on Pt(111) [and other metals such as Pd(111)] are quite different: all the molecules in the first layer interact significantly with the metal substrate, and the oxygen atoms are nearly coplanar with O-O vertical separation of ~ 0.02 nm (versus ~ 0.1 nm in a traditional bilayer structure) [8,14,15]. Here, half the molecules bind to the surface through the oxygen lone pair, half have a hydrogen atom pointing toward the metal, and all the molecules form hydrogen bonds to 3 neighboring water molecules. Therefore, each molecule in the monolayer forms four bonds, leaving no dangling OH bonds or lone pair electrons protruding into the vacuum [8,14,15,21].

Heuristically, the water monolayer is expected to be hydrophobic with a low surface free energy owing to its fully coordinated bonding configuration. The $\sqrt{39}$ monolayer is compressed $\sim 3\%$ relative to bulk ice [10], such that epitaxial growth on the monolayer will produce strain in the films. To reduce this strain, the films relax to an incommensurate $R30°$ structure with the lattice constant for bulk CI [11]. If strain relief were the only energetic driving force, then the relaxed films could still wet the water monolayer [22]. We believe it is the large surface

free energy difference between the hydrophobic monolayer and CI which, in the absence of kinetic bottlenecks, gives rise to the observed dewetting [23]. Since the physisorption data are insensitive to the structure of buried water layers, whether the CI lattice extends all the way to the water/metal interface or the ice crystallites grow on top of an unreconstructed $\sqrt{39}$ monolayer is unresolved.

Zero-order desorption kinetics, such as those observed for multilayer CI films (Figs. 1 and 4), have long been considered a good indicator that water films wet the substrate [1,2,12,13]. However, zero-order desorption kinetics can clearly be obtained from incomplete or nonwetting water films. For example, in Fig. 4, the isothermal desorption rate is constant while the fraction of the surface covered with only 1 ML of water, $F1$, increases. Analogous to the case for submonolayer adsorbate coverages on many surfaces [6,24], zero-order desorption kinetics are obtained for the nonwetting CI films so long as quasiequilibrium is maintained between the ice crystallites and the water monolayer via a mobile 2D gaslike phase, with the chemical potential set by the crystallites.

The results presented here help clarify several reports in the literature. For example, in helium atom scattering no intensity oscillations were observed during the growth of CI films on Pt(111) indicating that the growth is not layer-by-layer [11]. However, the absence of layer-by-layer growth can be due to thermodynamics (i.e., nonwetting or incomplete wetting of the substrate) or can arise from kinetic limitations. It is now clear that the nonwetting growth of 3D ice crystallites on the water monolyayer is thermodynamically favored. In another example, CI films grown on Pt(111) were found to have an abundance of dangling OH bonds which were nearly isotropically distributed [25] which is inconsistent with a perfectly terminated flat ice surface. However, the abundance of dangling OHs and their angular distribution probably results from the molecules on the various facets of the 3D ice crystallites. Finally, the persistence of the $(\sqrt{39} \times \sqrt{39})R16.1°$ structure observed by LEED for up to ~5 ML [10] can be understood since at that coverage only ~50% of the surface is covered by 3D ice crystallites with the rest covered by only the water monolayer.

In summary, we have used rare gas physisorption to investigate water growth on Pt(111). In accord with previous results [6,9,10], the first water layer wets Pt(111). Surprisingly, this monolayer is hydrophobic and gives rise to nonwetting growth for subsequent crystalline layers. These results indicate that Pt(111) is not a good template for growing smooth, epitaxial crystalline ice films. Furthermore, the observation of zero-order water desorption kinetics cannot be used to infer that multilayer water films wet the substrate. Based on these results, the morphology of multilayer water films on many other substrates may be different than previously believed.

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