

Materials Science and Technology Nanoscience

Probing the evolution and stability of thin ice films on solids with molecular-layer resolution.

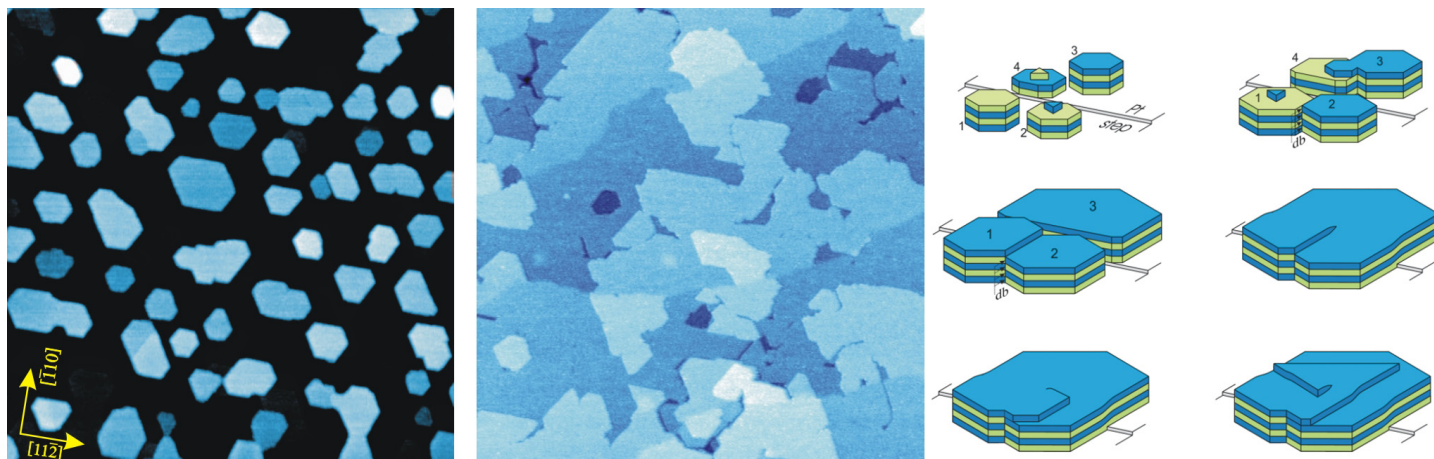


Figure 1: The two $500 \times 500 \text{ nm}^2$ STM images (left and center) of ice films grown on Pt(111) at 140 K demonstrate the capability of STM to investigate ice multilayers nondestructively. Left: 0.8 nm thick ice film with individual $\approx 3 \text{ nm}$ high crystallites. Center: 4 nm thick continuous ice film. The abrupt contrast changes are ice surface steps of molecular height, which have never been imaged before. Right: schematic of a coalescence scenario leading to cubic-ice formation.

Scanning tunneling microscopy is used to decipher what governs the morphology and structure of ice films.

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The interaction of water with solid surfaces plays a key role in applications like catalysis, corrosion, water purification and fuel cells. It is also important in many natural processes that occur in the earth's atmosphere or in the outer solar system. For example, rainfall is triggered by nucleation of ice crystals on micron-sized particles in clouds. Despite its importance, little is known about water-solid interactions. In fact, to this day, the best theoretical models fail to reproduce even the most basic phenomena.

Two examples of basic unsolved questions concern the growth of ice on metals. First-principles calculations predict that ice forms 3D crystals that grow directly on the bare metal substrate, whereas multiple experiments indicate that water first forms a molecularly-thin wetting layer on which 3D crystals grow. Settling this discrepancy could provide much insight into ice-film energetics in particular or water-solid interaction in general. Another basic unsolved question concerns the metastable, low-temperature

phase of cubic ice, which had been discovered in the 1940's, but whose origin remains puzzling.

Electron microscopy techniques have been powerful in solving similar puzzles for metal growth; however, they all failed in studying multilayer ice because the imaging electrons immediately damage the insulating ice. Up to now, scanning tunneling microscopy (STM) has also not been successful because it requires an electric current to flow between STM tip and sample, and ice generally cannot supply the electrons needed for imaging. However, at Sandia we recently discovered conditions where the needed electrons are extracted from the ice valence band, thus making nondestructive imaging possible.

Figure 1 illustrates the success of this novel approach. The left picture shows a 0.8 nm thick ice film grown on a Pt substrate at 140K. Individual nanometer-sized ice crystals are embedded in a molecularly-thin wetting layer (black). Upon depositing more water, these crystals coalesce into a

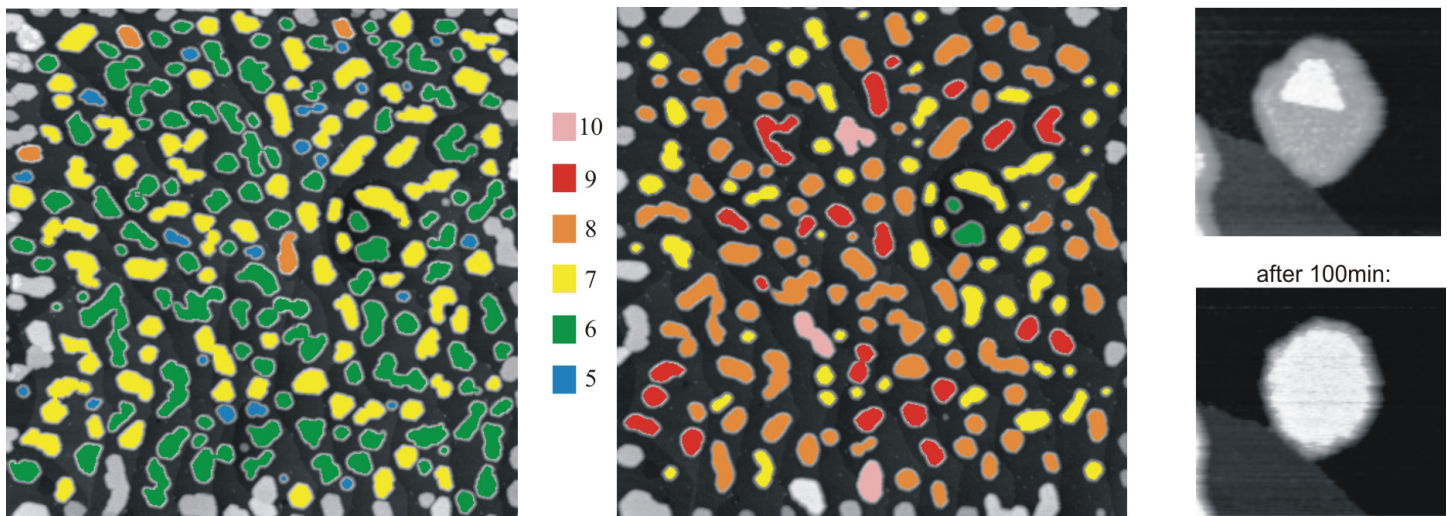


Figure 2: Nucleation-limited dewetting. Left: $1 \times 1 \mu\text{m}^2$ image of an 0.8 nm thick ice film grown at 140 K with the height of each three-dimensional crystallite colored differently. The colors represent the height in molecular layers of ice (one layer = 0.37nm). Center: Image of the same surface region after annealing at 140 K for one hour. Right: individual nucleation event.

continuous film at around 4 nm average thickness (center picture). By deciphering the exact nature of this coalescence we are able to determine the origin of the metastable cubic ice. It is steps in the substrate that modify how the molecular layers of merging crystallites connect. As a result, screw dislocations are created that, in turn, form growth spirals where cubic ice is being produced.

To probe the stability of the ice film, we monitored changes in morphology when the 0.8 nm thick film is annealed for 1 hour at 140K. The image sequence in Figure 2 reveals that the ice crystals grow thicker and consequently expose more of the wetting-layer covered Pt surface. The results show that it is the rate at which new layers nucleate, and not diffusion along the surface, that determines how fast individual crystallite shapes equilibrate. Applying nucleation theory to measured growth rates vs. crystallite dimensions, we obtain new bounds on the energetics both of step formation on ice and of the Pt-ice interface.

This new insight into ice-film energetics provides a benchmark against which first-principles calculations can be further tested and enhanced. Improving the still unsatisfactory theoretical models would help address a variety of unsolved questions in the general field of water-solid interactions.

References:

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