Imaging Ice Step Edges with Differential Interference Contrast Microscopy

Motivation

Single-crystal surfaces give surface scientists the ability to study the properties of specific arrangements of atoms and, in particular, the reactivity of each crystalline face. Perhaps the best example of this comes from studies done on the faces of bcc single-crystal iron to reveal that the (111) face is over 16 times as reactive as the (100) or (110) faces.[1] This insight allowed industrial chemists to maximize the production of ammonia fertilizer in the Haber-Bosch process, which is single-handedly responsible for the exponential increase in Earth's sustainable human population. Although such insights are overwhelmingly common in metal surface studies, for ice—one of the most fundamental hydrogen-bonding surfaces—very little is known.

The limiting step to performing surface studies on ice is the inability to produce desired ice faces. While it is straightforward to "manufacture" a given crystallographic face of a metal, there is no well-established method for generating a specific face of ice. In fact, there are very few research groups even capable of producing single-crystal ice to begin with. At Tufts University, the Shultz group has overcome this difficulty by perfecting a method for growing single-crystal hexagonal ice from the melt.[2] In a recent publication, we described a technique to locate the crystalline lattice within a macroscopic ice sample; this knowledge leads to the ability to define the rotations needed to produce any crystallographic face. Our method is accurate within ±5°.[3] This work leads the way for surface scientists to begin studies of reactivity on the major ice faces.
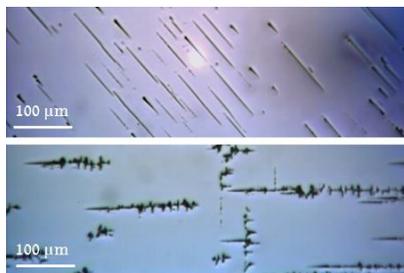
Figure 1. Micrographs of the (a) primary and (b) secondary prism faces after extended self-anneal.

While verifying this method, I discovered that if I allowed a primary prism face surface to self-anneal over the course of multiple days, then contrary to forming a flat surface, it would instead develop surface defects (Figure 1a). My hypothesis is that these defects are step edges and are visual evidence of the tendency for a system to minimize its surface energy. Due to the limited accuracy associated with cutting a desired face, the surface that is produced is not a true primary prism face. When left to self-anneal, the molecules that impose a high surface energy on the system are the first to leave; as a result, the system undergoes a minimization of energy. The final product is a surface of primary prism face terraces and basal face step edges. This theory is further validated by the secondary prism face (Figure 1b), which forms perpendicular defects after extended self-anneal. Indeed, these perpendicular marks can be construed to be step edges along the primary prism and basal faces, which are both perpendicular to the secondary prism face and to one other.

This discovery is particularly exciting due to its relevance to reactivity studies on surfaces. Although it is true that certain faces are more reactive than others, defects—such as step edges and corners—remain the most reactive due to the low coordination number of the atoms in those positions. The ability to produce step edges on ice in a controlled laboratory environment would allow scientists to study the interactions of molecules at the most reactive surfaces.

Research Plan

To ascertain whether there are step edges present on the surface of ice, I propose to use differential interference contrast microscopy (DIM). DIM is a modified optical microscopy technique in which interferometry is used to enhance the contrast seen in an image. In reflective-mode DIM, incident light is separated into two orthogonal components when it passes through a Nomarski prism that functions as a beam splitter. The two beams are reflected by the sample surface, and when they are recombined in the Nomarski prism, an optical path length difference between the two beams

manifests as constructive or destructive interference. The intensity of the resulting beam is used to calculate the path length difference imparted upon the beams due to the height of the sample at the position that was imaged. Since commercial DIMs require a Nomarski prism for every unique objective and distances between optical components cannot be easily manipulated, I propose to circumvent the high cost and inflexibility of a commerical DIM by constructing a DIM in the laboratory. This arrangement will allow for easy optical element replacement and position adjustment so that the configuration can be easily adapted for multiple experiments.

An etched ice surface will be used as a reference to confirm the functionality of the DIM. Etching is done by coating the surface with a solution containing polyvinyl formvar; the resulting etch pits have a distinctive shape that reveals the orientation of the crystalline lattice.[4] Etch pit shapes have been well explored, so the qualitative result expected from DIM is clear. However, DIM analysis of an etched surface will provide the depth of an individual etch pit; this is a parameter that cannot be determined from a pictomicrograph of the etched surface. It will provide insight into the structure of the etch pits, useful knowledge due to the relation between etch pit structure and ice face energies.

With the enhanced resolution of DIM, it should be possible to visualize etch pit formation more quickly and watch its evolution with greater precision. This is not possible with regular microscopy, as surface defects take four days to form and are coupled with such large changes in sample thickness that it is not possible to follow their formation. DIM should enhance my analysis by allowing me to ascertain the time scale required for a step edge to appear and calculate the height of the first step edges. It is possible that the smallest step edges will correspond to one bilayer (0.37 nm), unlike the >1 μm step edges seen with regular microscopy. Bilayer step edges have been seen before, but (i) the studies were not done on macroscopic samples, and (ii) the studies are difficult to replicate considering the arbitrary nature of the ice face investigated.[5]

Intellectual Merit

With ice, simple concepts such as surface energies act as obstacles to complex studies, and elegant experiments cannot occur simply because the foundation for their implementation is not present. This work builds upon the new ability to generate ice surfaces via the investigation of potential step edges. If my work reveals step edges on the surface of ice, it will transform scientists' view of aqueous interfaces in a way analogous to how scientists currently understand metal surfaces.

Broader Impact

This work expands on the quest to create a solid foundation for ice studies and will allow future scientists to enter the field without being intimidated by the complexities of ice. Though the community of ice researchers is small, our work impacts every field of science due to the ubiquity of ice on our planet and its role in hydrogen bonding.

The most remarkable part of this research is the visual connection between macroscopic samples and microscopic crystal structure. One of the greatest difficulties that chemistry students experience is relating macroscopic properties to microscopic features, because so often there is not a visual relationship. The fact that with ice, such a connection is present means that this work can serve to deepen students' understanding of how chemists look to microscopic properties such as electronic configuration and crystal structure to determine how macroscopic samples behave.

References

(1)   Spencer, N. D.; Schoonmaker, R. C.; Somorjai, G. A. *J. Catal.* **1982**, *74* (1), 129–135.
(2)   Shultz, M. J.; Bisson, P. J.; Brumberg, A. *J. Phys. Chem. B* **2014**, *118* (28), 7972–7980.
(3)   Shultz, M. J.; Brumberg, A.; Bisson, P. J.; Shultz, R. *PNAS* 10.1073/pnas.1513173112.
(4)   Higuchi, K. *Acta Metall.* **1958**, *6*, 636–642.
(5)   Sazaki, G.; Zepeda, S.; Nakatsubo, S.; Yokoyama, E.; Furukawa, Y. *PNAS* **2010**, *107* (46), 19702–19707.