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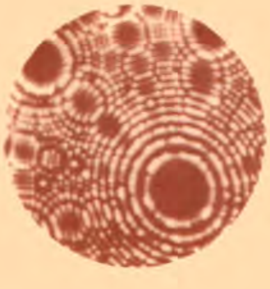

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Imaging atom-probe analysis of a vitreous ice interface

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The imaging atom-probe (IAP) mass spectrometer has been used to examine the interface between a metal surface and aqueous solutions of potassium chloride. The interface is preserved for IAP analysis by rapidly freezing a thin layer of the aqueous solution on the apex of a field-emitter tip. Cooling rates in excess of 10^6 K/s can be achieved by plunging the liquid-coated tip into liquid propane in an inert argon atmosphere. A novel anode assembly allows the frozen interface to be transferred into the IAP without contamination and maintained at 80 K until field-desorption exposes the interface for analysis. The desorption process occurs at a field strength of ~ 10 V/nm, and removes the entire layer of ice from the tip apex as though it were an insulating film. Spatially resolved images of H_2O^+ and K^+ (the dominant ions resulting from the desorption process) show no order on a nanometer scale. Desorption images suggest that the frozen layer exists on the tip surface in the vitreous state. No evidence for hexagonal epitaxy of the liquid layer prior to the freezing event has been observed on tungsten or gold surfaces.

1. Introduction

Modern techniques of surface analysis can provide a detailed picture of the solid–vacuum interface. The morphology of a surface can be visualized in atomic resolution and the chemical identity of species can be probed with precision. Knowledge of catalytic processes, studies of wear and lubrication, and the assembly of novel microelectronic devices have benefited from studying the surface of metals and semiconductors exposed to a vacuum environment. The solid–liquid interface provides the opportunity to study these processes under equally interesting conditions, but experiments have been constrained by the vacuum requirements imposed by most techniques. In particular, the removal of a liquid from the surface of a solid requires that the surface remains undisturbed as it dries and is transferred into high vacuum for analysis.

Enormous pressures can be exerted at the surface of a solid when it is removed from a liquid environment and dried, prior to transfer into high vacuum. Surface morphology can be distorted and adsorbates can be rearranged by the surface tension forces that act on the surface as it dries [1]. Aqueous solutions present a particular problem because of the high surface tension of water ($\gamma \approx 77$ dynes/cm) at the water–air interface. The problem is shown schematically in fig. 1. A cylindrical structure of radius, $R \approx 100$ nm is depicted as it is removed from water and dried in air. High pressures ($\sim 2\gamma/R = 1$ ton/inch^2) are easily ex-

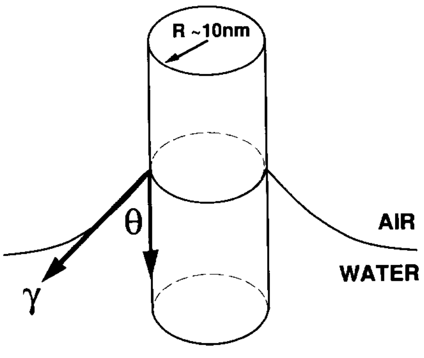

Fig. 1. A schematic drawing of the pressure exerted on a small cylindrical object (due to surface tension forces) as the object crosses a water–air interface. A worst case scenario ($\cos\theta = 1$) is assumed. $P = F/A = 2\gamma\cos\theta/R \sim 2\gamma/R$. $P \sim 10^8$ dynes/cm$^2 \sim 1$ ton/inch^2.

erted on structures of this size as they cross the water–air interface. Critical point drying can be used to avoid the surface tension problem, but immersion in acetone is required to insure reasonable temperature and pressure profiles, and this precludes analysis from a pure aqueous environment [2].

An approach that eliminates the surface tension problem involves embedding the interface between a surface and a liquid within a thin layer of vitreous ice formed from the liquid environment [3]. The vitreous state is unique in that freezing occurs so rapidly that ice crystal formation and solute partition in the frozen solid is absent. Species within the liquid (and adsorbates at a surface in contact with the liquid) are preserved within a sample of the native liquid environment as it existed just prior to freezing. If the embedded interface is transferred intact into the imaging atom-probe mass spectrometer without contamination, field-desorption can be used to remove the covering layer of ice. The composition of the layer can be measured by time-of-flight (TOF) mass spectroscopy, and the species within the layer can be visualized on a nanometer scale [4].

2. The imaging atom-probe

The Imaging Atom-Probe (IAP) is shown schematically in fig. 2. During operation, a positive high voltage pulse and a DC bias are applied to the surface of a field emitter tip having an apex radius of curvature, R. Each pulse has an amplitude of ~ 1 kV, a width of ~ 40 ns, and a rise time of ~ 1 ns. The voltage developed at the tip surface ($V_t = V_{\text{pulse}} + V_{\text{dc}}$) creates a high electric field, $F \sim V_t/R$, at its apex. The electric field can be used to ionize gas molecules (i.e. helium) above the apex to image the surface below by "field-ion microscopy", or to remove species adsorbed at the tip apex as positive ions by a process called "field-desorption". At higher field strengths the surface of the tip apex will erode away in a controlled fashion by a process called "field evaporation". Field evaporation produces positive ions that can be used to determine the chemical composition of the tip apex. A good estimate of the field strength at the tip apex can be made because the electric field, $F_{\text{biv}} \approx 45$ V/nm, corresponding to the measured "best-image" voltage for field-ion imaging in helium, V_{biv}, is known. If V_t is the total bias voltage at the tip, the electric field, F, at its apex (in volts per nanometer) will be approximately given by: $F = 45(V_t/V_{\text{biv}})$.

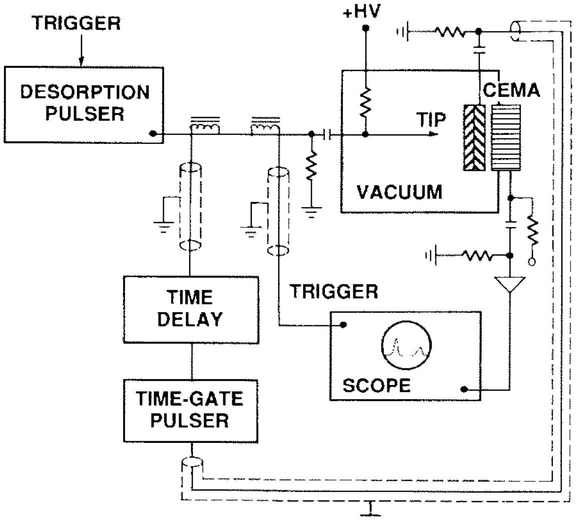

Fig. 2. A schematic drawing of the imaging atom-probe mass spectrometer. Time-of-flight mass spectra of species desorbing from the apex of a field-emitter tip (as positive ions) can be obtained with a mass resolution of $\Delta m/m \approx 0.05$ amu. The desorbing species can be imaged at any desired magnification, with a lateral resolution of ~ 1 nm.

The IAP has an intrinsic advantage over other TOF mass spectrometers because the ions produced at the tip surface are essentially monoenergetic and spatially localized [5]. Ions acquire their final kinetic energy ($\frac{1}{2}mv^2 = zeV_t$) within several tip radii from its apex. Their well-defined point of origin in space means that the ions will drift for a measurable time, t, over a known distance, d, between the tip and a detector. An accurate measurement of an ion's travel time, $t = d/v$, is possible because the desorption event is limited to the risetime of the high voltage pulse which is much faster than the sequential arrival of two ions at the detector. The risetime of the pulse can also be used as a "fiducial" mark to indicate $t = 0$ in the mass spectra.

All of the parameters needed to determine the chemical identity of a surface species of mass, m, desorbed from the tip apex as a positive ion of charge, $z = ne$, can be measured, or are known: $m/z = 2e(V_{\mathrm{pulse}} + V_{\mathrm{dc}})t^2/d^2$. Since the ions will accelerate almost radially from the tip apex they will diverge into space, producing a highly magnified image of their point of origin at the tip surface when they reach the detector. The magnification of the image, $M \approx d/R$, can be varied by changing the tip-to-detector distance. The resolution of the image is always much better than one nanometer if the tip is cooled to ~ 80 K. A chevron channel electron multiplier array (CEMA) can be used to detect the ions, and to visualize their point of origin on the apex by video imaging [6].

3. Experimental considerations

The vitreous state of water can be achieved if the cooling rate of the liquid exceeds ~ 10^6 K/s at the liquid–solid interface. The vitreous state can be maintained provided the temperature of the interface remains below 130 K (which is the approximate phase transition temperature between vitreous and cubic water–ice). Slam-freezing techniques will achieve the vitreous state reliably, but cannot be used to cool IAP specimens because of the fragile nature of a field-emitter tip which must be used as a substrate [7]. The alternative is to rapidly plunge the liquid-coated tip into a cryogenic liquid, or "cryogen". In theory, rapid cooling of the tip is limited by the heat capacity of the tip and its support, and by heat conduction to the cryogenic liquid. In practice, the cooling rate is determined by poor heat transfer to the liquid caused by the formation of a thin, insulating layer of gas at the tip surface as it cools below room temperature. This phenomenon is known as the "Leidenfrost" effect. It was first described in 1756 by Johann Gottlied Leidenfrost to explain the anomalous stability of water drops deposited on metal surfaces that were heated well above the boiling point of water [8]. The formation of an insulating gas layer is minimized when a warm object is plunged into liquid ethane or liquid propane [9]. Although liquid ethane is the cryogen of choice, it cannot be used in the present application because a thin film of ethane will remain on the tip surface under the experimental conditions dictated by a successful IAP transfer.

4. Tip preparation

Field-emitter tips are electrochemically etched at one end of 12 mm lengths of 0.2 mm diameter tungsten and gold wires using procedures described in the literature [10]. The radius of the tip apex formed by electrochemical etching is typically between 60 nm and 100 nm. The other end of each wire is etched to a blunt point. After etching, a wire is inserted into a length of 1.5 mm O.D. × 0.3 mm I.D. stainless steel capillary tubing for structural support. The wire is held by friction in the bore of the tube and is adjusted so that the tip and the sharp point protrude ~ 2 mm from opposite ends of the tube. Cleaning and smoothing of the tip apex is accomplished by field-evaporation at 80 K. Field-evaporation is continued until metal ions from the tip apex dominate the mass spectra obtained during IAP analysis. A typical mass spectrum of a clean tungsten tip is shown in fig. 3. Field-ion imaging in helium is used to evaluate the crystallography and the morphology of the surface on an atomic scale. These procedures insure that the apex of a tip is clean and smooth on a nanometer scale, with clearly delineated defects.

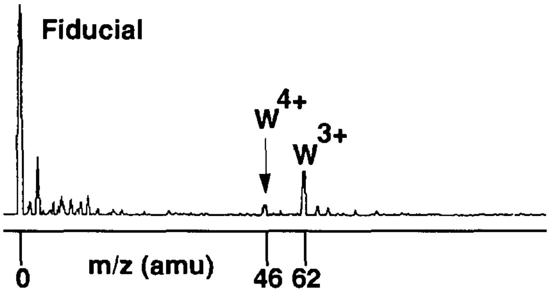

Fig. 3. A time-of-flight mass spectrum of a tungsten tip taken in the imaging atom-probe at 80 K to insure tip cleanliness. $V_{\mathrm{pulse}} = 1.5$ kV. $V_{\mathrm{dc}} = 12.5$ kV.

5. Plunge-freezing

After field-evaporation, field-emitter tips are removed from the IAP and immersed into a 20 μl droplet of aqueous KCl using a fixture described previously [11]. The tip support is held in the fixture by a spring and is oriented vertically, with the tip pointed upward and the other end of the tip wire pointed downward toward a container of liquid propane. The propane is cooled close to its freezing point by placing the container in a Dewar of liquid argon. Argon vapors from the evaporating liquid surround the tip and fixture, effectively eliminating contamination from laboratory ambient. After a suitable immersion time has passed, the tip support is released from the fixture and falls vertically downward (under the influence of gravity) into the propane container. The support retains its vertical orientation as it falls, and remains vertical when it comes to rest within the container of propane. The support sticks into a layer of foam at the bottom of the container as shown in fig. 4. The plunge-freezing procedure will be described elsewhere in detail [12].

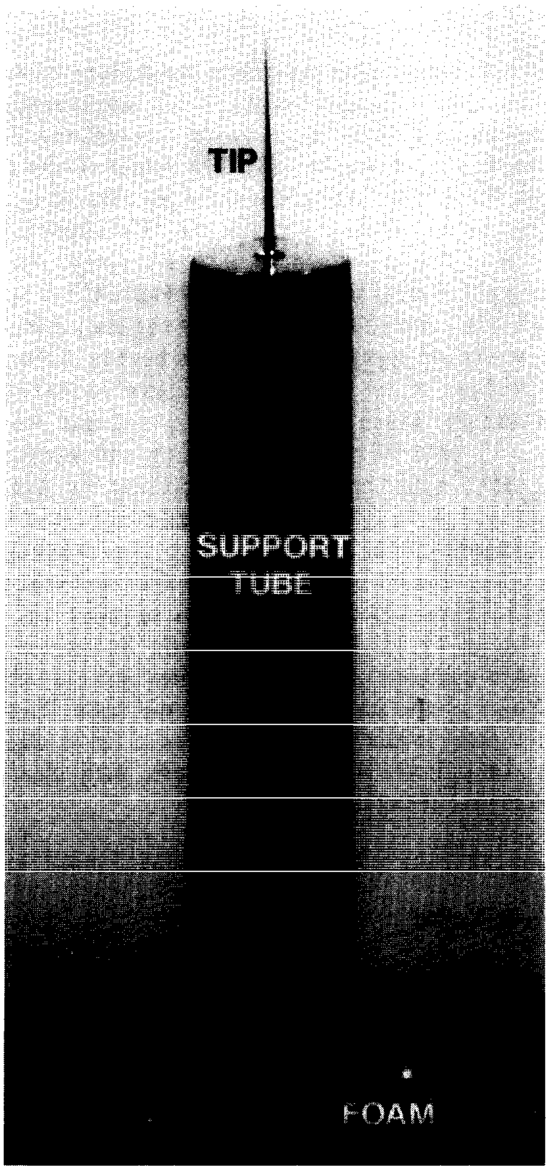

Fig. 4. A field-emitter tip supported by a stainless steel capillary tube within a container of liquid propane. One end of a tip wire protrudes from a tubular support and sticks in a layer of foam at the bottom of the container.

6. Cryotransfer

The tip and its support must be transferred through laboratory ambient and into the IAP without contamination. The temperature of the tip must also be kept below 130 K during the transfer to preserve the vitreous state of the frozen interface. Finally, the tip must remain cold and contaminant free until the IAP has been evacuated to a typical operating pressure of ~ 10^{-8} Torr. These objectives have been met by a unique IAP anode assembly, shown schematically in fig. 5. The anode assembly is precooled to ~ 87 K in the same Dewar containing the propane container. A removable cathode cap contains an aperture that can be closed by a steel ball. The purpose of the anode assembly is to isolate and protect a tip from contamination in an inert atmosphere of argon, within cryogenically cooled walls, until IAP analysis can be initiated.

After a tip and its support reach thermal equilibrium with the liquid propane in the container, they are removed from the propane with precooled tweezers and inserted into the anode assembly by removing the cathode cap. Tip transfer (from the propane container to the anode assembly) is accomplished under the argon atmosphere in the Dewar. After the cathode cap and the steel

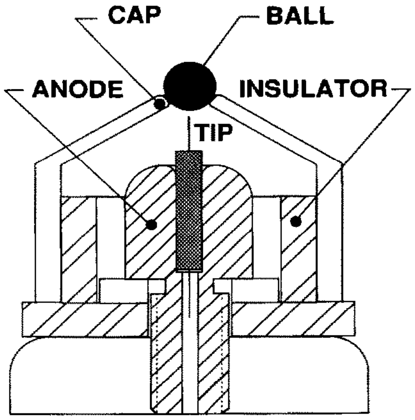

Fig. 5. The IAP anode assembly. A field-emitter tip is inserted into a copper anode block and covered with a cathode cap. The assembly is typically precooled to 87 K in liquid argon prior to tip insertion. A precooled steel ball covers an aperture in the wall of the cap, shielding the cold tip from gas-phase contamination as the IAP vacuum chamber is evacuated. When a suitable operating pressure is reached, the ball is removed from the aperture in an external magnetic field.

ball are put in place, the tip is isolated in an environment of pure argon vapor and surrounded by walls at 87 K. A special cryotransfer tool is used to pick up the anode assembly and to transfer the assembly into the IAP at 87 K without contamination. Complete details of the transfer procedure will be published elsewhere [12].

7. IAP analysis

The glass vacuum chamber of the IAP is purged with argon vapor and surrounded by liquid argon prior to transfer of the anode assembly. After the transfer is completed the vacuum chamber is attached to the body of the IAP (which contains the CEMA detector and access to the vacuum system). The chamber, still cooled by liquid argon, is evacuated with turbomolecular and ion pumps until a pressure of ~ 10^{-6} Torr or better is obtained. At this time the vacuum chamber is cooled to ~ 80 K by replacing the liquid argon (in which it was immersed) with liquid nitrogen. Liquid argon is used to cool the vacuum chamber during evacuation to minimize the chance of condensing a layer of argon on the tip from the argon vapor trapped in the interior of the cathode cap. During evacuation, the argon atmosphere in the cap is gradually pumped away through the aperture that is loosely covered by the steel ball.

The steel ball is removed (magnetically) from the aperture when an operating pressure of ~ 10^{-8} Torr is obtained. When the ball is removed the tip "sees" the ambient environment of the IAP for the first time. At 10^{-8} Torr the contamination rate from the IAP ambient will be ~ 10^{-2} monolayer/s. Since an IAP analysis can be performed in less than 100 s, a maximum of one monolayer of contamination will condense on the tip apex during a typical experiment. Analysis proceeds by raising the DC bias at the tip by ~ 0.5 kV after each pulse is applied until the ice layer desorbs.

8. Results and discussion

Mass spectra were recorded for tungsten and gold surfaces in contact with 1N aqueous KCl. Typical mass spectra display dominant mass peaks at m/z 18 amu and m/z 40 amu, corresponding to H_2O^+ and K^+, respectively. These peaks, together with the absence of peaks at $m/z = 14$ (N^+), and at $m/z = 28$ (CO^+) in the mass spectra suggest that a frozen layer of aqueous KCl was retained on the tip apex, and was not subject to atmospheric contamination during transfer into the IAP. Control experiments (performed without immersing tips in aqueous KCl) never show mass peaks characteristic of a desorbing ice layer. More complete details of these experiments are published elsewhere [13].

Desorption of the ice layer is abrupt and occurs during a single desorption pulse when the field strength at the tip apex reaches ~ 10 V/nm. The desorption event appears to be qualitatively similar to DC field-desorption of thin insulating layers of LiF from the apex of field-emitter tips [14]. A typical video image of H_2O^+ and K^+ taken as an ice layer containing IN KCl desorbs is shown in fig. 6. No ordering of species within the layer is observed, indicating that the vitreous state of the liquid was achieved and preserved on a nanometer scale. No evidence for epitaxial growth of hexago-

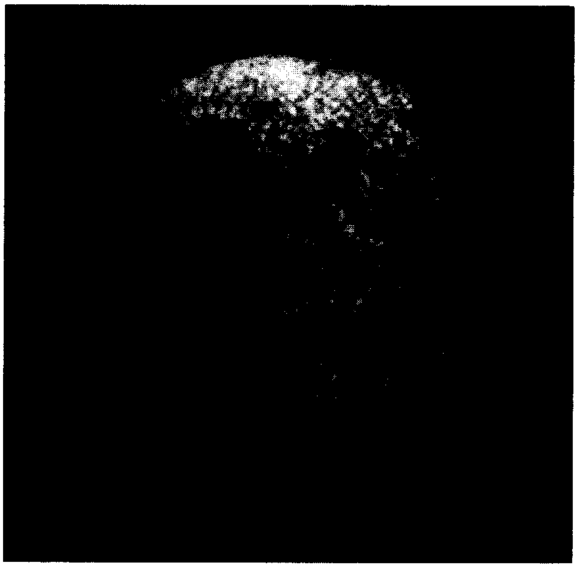

Fig. 6. A video image of H_2O^+ and K^+ from 1N KCl in water, frozen on a tungsten tip and field-desorbed from the tip apex. The image shows no order in the liquid indicating that the vitreous state was achieved and maintained during IAP analysis. No evidence for epitaxial growth of hexagonal ice at the interface is seen. Scale marker = 30 nm.

nal ice at the interface has been seen in the desorption images.

9. Summary and perspectives

Tungsten and gold surfaces in contact with 1N aqueous KCl were examined in the imaging atom probe mass spectrometer by freezing a thin layer of the aqueous solution on the apex of a field-emitter tip. Mass spectra taken as the layer desorbed from the tip apex were dominated by peaks at $m/z = 18$ amu, and $m/z = 40$ amu. Images of the desorbing ions showed no order in the ice layer on a nanometer scale. The data suggests that the ice layer is vitreous in nature. Future research will address the problem of how organic monolayers form at metal surfaces by adsorption from solution. Studies will be initiated to investigate the feasibility of using the IAP to determine the molecular weight of biological macromolecules.

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