

# Imaging atom-probe analysis of an aqueous interface

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Aqueous solutions of KCl in contact with tungsten and gold surfaces have been examined for the first time by imaging atom-probe (IAP) mass spectroscopy. The liquid is preserved for IAP analysis by rapidly freezing it on the surface of a field-emitter tip. The tip and the resulting vitreous layer of ice are cryogenically transferred into vacuum where an electric field of  $\sim 10$  V/nm is used to field desorb the ice layer from the tip apex at 80 K. Mass spectra of the resulting ions are dominated by peaks at  $m/z = 18$  amu ( $\text{H}_2\text{O}^+$ ) and  $m/z = 40$  amu ( $\text{K}^+$ ). The desorption process is characterized by an abrupt onset of ionization during which the entire layer is removed from the tip apex. Desorption characteristics suggest that a layer of vitreous water ice behaves like an insulating film on the tip surface. Desorption images taken as the ice layer is removed show no ordering of water or salt molecules within the layer on a nanometer scale.

## I. INTRODUCTION

Although the liquid-solid interface is of practical and fundamental importance, little is known about the interaction of liquids with solids on a nanometer scale. In particular, it is difficult to determine the chemical identity of species adsorbed at an interface despite the importance of adsorption phenomena to a wide range of problems in catalysis, lubrication, corrosion, and the fabrication of molecular electronic devices.<sup>1,2</sup> It is difficult to extract the chemical identity of species at a liquid-solid interface because conventional surface analytical techniques cannot operate in a liquid environment. For instance, it is impossible to use focused ion or electron beams to probe a liquid environment because their mean free path is too short (and their kinetic energy is too large) for meaningful information to be extracted. Scanning tip microscopes can examine the topography of a liquid-solid interface, but cannot provide a precise chemical description of the species that reside at a surface in contact with a liquid.<sup>3</sup> A tip that scans within a few angstroms of a surface may also move or distort the distribution of liquid molecules or solvents contained in the liquid near the solid surface making this type of analysis often difficult to interpret.<sup>4</sup> These considerations have led us to explore an alternate approach for determining the chemical identity and the distribution of species at a liquid-solid interface. Our approach uses the imaging atom-probe (IAP) mass spectrometer and a novel specimen preparation technique adapted from the biological literature.<sup>5,6</sup> This paper describes the first experimental observations of aqueous salt solutions in contact with tungsten and gold surfaces using the IAP technique.

## II. SUBSTRATE PREPARATION

IAP analysis is performed by field desorbing an ice layer formed on the surface of a field-emitter "tip." For this study, tips were prepared from 0.2 mm diam tungsten and gold wire. Although the wires are polycrystalline, the tips tended

to be oriented at  $\langle 110 \rangle$  for tungsten, and  $\langle 100 \rangle$  or  $\langle 111 \rangle$  for gold. Standard etching procedures produce tips with an apex radius of curvature of 40 nm–100 nm.<sup>7</sup> After etching, the tips are cooled to  $\sim 80$  K and field evaporated in vacuum to clean and smooth their surface.<sup>8</sup> The total voltage,  $V$ , applied to the tip to evaporate its surface provides an estimate of the radius of the tip,  $R$ , since the evaporation field,  $E$ , of the tip material is known and  $R \sim V/5E$ .<sup>9</sup>

## III. CRYOPREPARATION OF THE SUBSTRATE

To preserve an aqueous layer for IAP analysis the layer (in contact with the surface of a tip), is rapidly cooled below 130 K at a rate of  $\sim 10^6$  K/s.<sup>10</sup> The cooling process transforms the liquid layer into a layer of vitreous (namely, amorphous) ice, preserving the composition of the liquid in contact with the tip surface on a microsecond timescale. The tip wire is inserted into a small cylindrical support with the apex of the tip protruding  $\sim 2$  mm from one end. After immersing the tip apex into a droplet of salt solution for  $\sim 30$  s, the tip and its support are quickly plunged into liquid propane kept just above its freezing point (83 K). Plunging into liquid propane is known from the biological literature to maximize the cooling rate of room temperature substrates.<sup>11</sup> A complete description of the plunge-freezing technique will be given in detail in another publication.<sup>12</sup>

## IV. CRYOTRANSFER OF THE SPECIMEN

After creating a vitreous ice layer on the tip surface, the tip must be cryogenically transferred into the vacuum chamber of the IAP without contamination, and kept below 130 K to preserve its integrity. To achieve a rapid transfer, the anode assembly of the IAP is removed and precooled to  $\sim 87$  K. The anode assembly is constructed so that a tip can be inserted under an inert atmosphere of cold argon gas in the same Dewar where plunge freezing is accomplished. After inser-

tion, a precooled cathode cap is positioned on the anode assembly enclosing the tip within a cryogenic environment. A small steel ball covers the aperture in the cap through which ions will be extracted. With the ball in place, the anode assembly is picked up within the interior of a special tool that is cooled by liquid argon. The tool allows the anode assembly to be transferred through laboratory ambient and into the IAP vacuum chamber without moisture condensation on its surface.

The vacuum chamber of the IAP is a removable glass tube that is closed at one end. During the transfer procedure, the vacuum chamber is immersed in a Dewar of liquid argon and purged with cold argon gas. After the transfer is completed, the vacuum chamber is quickly attached to the body of the IAP and the IAP is evacuated (with a turbomolecular and an ion pump) until a pressure of  $\sim 10^{-8}$  Torr is obtained. At this time, the Dewar of liquid argon that cools the vacuum chamber is replaced with a Dewar of liquid nitrogen and the steel ball that covers the aperture in the cathode cap of the anode assembly is magnetically removed. When the ball is removed the tip is exposed to the ambient vacuum of the IAP for the first time. IAP analysis must now be performed within  $\sim 100$  s (the monolayer adsorption time at this pressure) to ensure that condensation of gas phase contaminants on the vitreous ice layer covering the tip surface will be minimal. Details of the anode transfer technique are given elsewhere.<sup>13</sup>

## V. IAP ANALYSIS

During IAP analysis a desorption field is established at the apex of a tip by applying a high voltage pulse with a rapid rise time to its surface. Ions created at the tip apex by this field are accelerated into space almost radially from its surface and intercepted by a channel-electron-multiplier array (CEMA) placed several centimeters away. The ion image that is formed by the CEMA detector is a highly magnified map of the spatial distribution of the ions at the tip apex. An image resolution better than 1 nm can be obtained at magnifications of  $\sim 10^6$ . A video camera and video digitizer captures the ion image on videotape.<sup>14</sup> Since the ionization event at the tip apex is initiated by a pulse with a rapid rise time, the travel time of ions between the tip and the CEMA detector can also be measured. From the travel time of the ions, the known distance of travel and their kinetic energy ( $= qV_{\text{pulse}}$ ), the mass-to-charge ratio ( $m/z$ ) of the ions can be determined. A complete description of the IAP technique can be found elsewhere.<sup>15</sup>

In our experiments the vitreous ice layer that covers the tip apex is removed by applying a series of high voltage pulses to the tip. Each pulse has a rise time of  $\sim 1$  ns, a width of  $\sim 40$  ns, and an amplitude of  $\sim 1$  kV. The pulses are superimposed on a dc bias. The dc bias is raised by 0.5 kV after each pulse is applied, until the total bias at the tip apex (pulse + dc) is sufficient to establish a field strength that will field evaporate the ice layer.

## VI. RESULTS AND DISCUSSION

Mass spectra were recorded for tungsten and gold surfaces in contact with a water droplet containing 1 N KCl. Freshly

(triple) distilled water was used to insure the cleanliness of the solutions. Typical mass spectra are shown in Fig. 1. The output of the photomultiplier (proportional to the number of ions) is plotted as a function of time from the initiation of the desorption event. The high voltage pulse is displayed as a "fiducial" marker to indicate the zero of time at the beginning of each spectrum. Its rise time (to maximum amplitude) defines the initiation of the desorption event. Mass peaks at  $m/z = 18$  amu, and  $m/z = 40$  amu dominate the mass spectra, and correspond to the arrival of  $\text{H}_2\text{O}^+$  and  $\text{K}^+$ , respectively. These peaks, together with the absence of peaks at  $m/z = 14$  amu ( $\text{N}^+$ ),  $m/z = 16$  amu ( $\text{O}^+$ ), and at  $m/z = 28$  amu ( $\text{CO}^+$ ), indicate that a frozen layer of the liquid was retained on the tip apex, and was essentially free of atmospheric contamination. A peak at  $m/z = 2$  amu ( $\text{H}_2^+$ ) may indicate that some of the water in the vitreous layer is field dissociating. The complementary species,  $\text{O}^+$  (at  $m/z = 16$  amu) would go unnoticed in the relatively poor rise time of the mass peaks. At the present time, the rise time of a mass peak is limited to  $\sim 80$  ns by the method used to record the arrival time of ions at the CEMA detector (a photomultiplier monitors the scintillations produced by arriving ions on its P47 phosphor screen).

Desorption of a vitreous ice layer is characterized by an abrupt onset of ionization when the entire layer is removed from the tip apex at a field strength of  $\sim 10$  V/nm. The field strength required for the ice layer to desorb,  $F$ , was determined from the known evaporation field of the metal,  $E$ , under the assumption that the tip radius does not appreciably change as the layer desorbs. In this case,  $F = (V/V_m)E$ , where  $V$  and  $V_m$  are the voltages at which the ice layer and the metal are removed, respectively. The abrupt onset of ionization suggests that a vitreous water ice layer (containing a high concentration of salt) behaves like an insulating film (e.g., of LiF) on the tip surface.<sup>16</sup> Video images taken as the

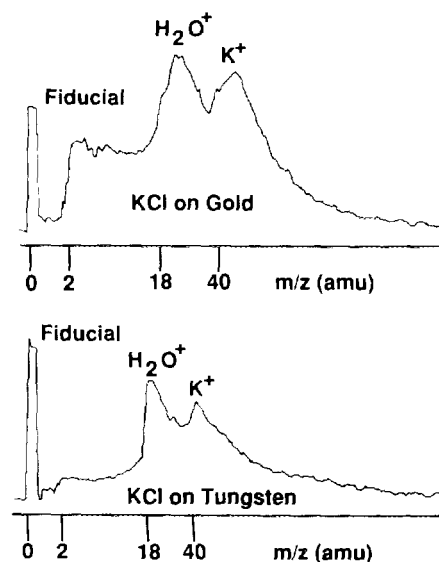


FIG. 1. Time-of-flight mass spectrum of 1 N aqueous KCl frozen as a vitreous ice layer on a gold tip (upper), and on a tungsten tip (lower). The fiducial that marks the zero-of-time is a display of the high voltage pulse used to initiate the desorption event.

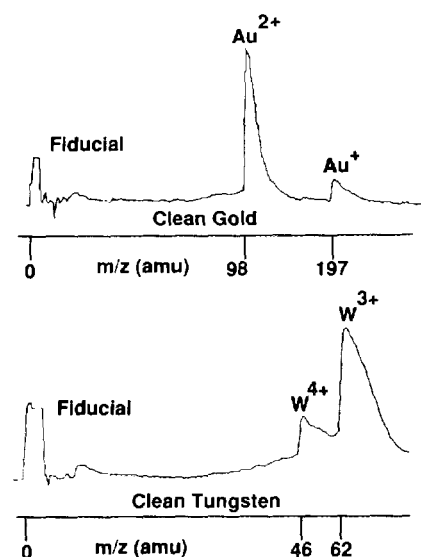


FIG. 2. Time-of-flight mass spectrum of control tips: gold tip (upper), and tungsten tip (lower). The fiducial that marks the zero-of-time is a display of the high voltage pulse used to initiate the desorption event. Ions of the substrate dominate the spectra as would be expected in the absence of atmospheric contamination.

ice layer desorbs show no order on a nanometer scale. The desorption images indicate that the vitreous state of the liquid was achieved and preserved during IAP analysis. Since the entire vitreous layer desorbs during one pulse it was not possible to visualize the layer as a function of depth, thereby examining the interface region for possible ordering of the liquid close to the metal surface. "Time gating" the CEMA coincidentally with the arrival of a preselected species will be implemented in the near future to visualize the spatial distribution of the dominant species in the mass spectra ( $\text{H}_2\text{O}^+$  and  $\text{K}^+$ ) independently. It is possible that the lack of order suggested by the video images reflects disorder in the distribution of only one of the two dominant species in the mass spectra.

Control experiments have been performed with the same tips (used to obtain mass spectra) plunged into propane and transferred into the IAP, but without contacting a water droplet during the immersion stage of the procedure. The voltage was raised as described previously until tungsten or gold ions were observed in the mass spectrum, indicating that the metal was field evaporating. Mass peaks corresponding to  $\text{H}_2\text{O}^+$  and  $\text{K}^+$  were never observed. Typical spectra are shown in Fig. 2. At the present time, ions characteristic of a frozen ice layer are not always observed after a tip is immersed into a drop of salt solution and prepared for IAP analysis. The problem appears to be associated with the sharp apex radius of curvature of tips required for cleaning by field evaporation at reasonable voltages. Tips with much larger radii of curvature ( $\sim 1 \mu\text{m}$ ) will be prepared and cleaned (by thermal annealing in high vacuum) to circumvent this difficulty.

## VII. SUMMARY AND PERSPECTIVES

Tungsten and gold surfaces in contact with 1 N aqueous KCL were examined by preserving the interface between the liquid and these materials within a thin layer of vitreous ice. The interface (with a frozen sample of its liquid environment) was successfully transferred into a vacuum system for analysis in the imaging atom probe mass spectrometer. Mass spectra from the frozen liquid were obtained as well as micrographs that showed no order in the ice layer. Future studies will concentrate on using larger radius tips, since vitreous ice layer formation on small radius tips is not consistently observed. It may also be desirable to lower the temperature of the tip to  $\sim 20 \text{ K}$  during IAP analysis to improve the image resolution and freeze out any possible motion within the ice layer initiated by the application of the electric field. A closed-cycle liquid helium refrigerator is being adapted for this purpose.<sup>17</sup> Finally the photomultiplier used to record the arrival of ions at the CEMA will be replaced by a direct electrical connection to the CEMA screen to improve the rise time of the mass peaks and the mass resolution of the spectrometer.

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