Vitreous ice as a cryoprotectant for imaging atom-probe studies of adsorption phenomena at a solid–liquid interface

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A novel approach is outlined for studying adsoption phenomena at a solid–liquid interface in the imaging atom-probe mass spectrometer. An interface is preserved for analysis by embedding it within a thin, conducting layer of vitreous ice formed from its native environment. The ice is controllably sublimed at 20 K using a high electric field to dissect the layer, and to map the distribution of species within the layer as a function of depth from its surface. Procedures are described for creating a layer of ice believed to be vitreous in nature, and for transporting an interface embedded within the ice layer into high vacuum without damage (and without contamination from laboratory ambient). Field-ion imaging suggests these procedures are effective for preserving the surface structure of a solid on a subnanometer scale.

I. INTRODUCTION

The first few atomic layers of a solid can form a barrier between its interior and an often hostile environment. Although adsorption at the vacuum–solid interface has been studied in great detail, little is known about adsorption at the liquid–solid interface. In particular, we do not understand how species in solution interact with a surface that is exposed to an aqueous environment. The liquid–solid interface has been difficult to study because the majority of techniques that are sensitive to surface morphology and composition operate most effectively in high vacuum. Removing a solid–liquid interface from a liquid environment for study in high vacuum (without perturbing the chemistry and the morphology of the surface it contacts), has proved to be a major obstacle. Consequently, our knowledge of surface morphology within a liquid environment is fragmentary, and detailed knowledge of adsorption phenomena at a liquid–solid interface is virtually nonexistent.

In addition to its intrinsic scientific interest, adsorption phenomena at a solid–liquid inteface may have important technological consequences. For example, adsorption from a liquid environment may provide a convenient way to coat a surface with a monolayer of organic material.[1] If a pinhole free, organic monolayer could be produced with a reasonable dielectric constant, molecular-sized capacitors with reasonable energy storage characteristics could be envisioned. Adsorption phenomena could also be used to passivate a surface from external modification, or to change the properties of a surface to reflect new and useful attributes (i.e., increased wear or lubrication[2]). Insight into the processes that occur at an interface during adsorption from a liquid environment may lead to new types of molecular electronic devices, or to smart sensors with novel characteristics.[3,4]

At the present time, the scanning tunneling microscope is the only instrument that has the potential to visualize adsorption phenomenon at a solid–liquid interface within a liquid environment.[5] We are developing a complementary approach to the study of adsorption phenomena at a solid–liquid surface. Our goal is to freeze the interface within its liquid environment at a rate sufficient to create an encasing layer of vitreous (viz. amorphous) ice.[6] The interface, rapidly frozen in time, is then transferred under liquid nitrogen into a high vacuum environment for anaylsis in the imaging atom-probe (IAP) without damage or modification. Our aim is to use the IAP to provide two-dimensional, mass-resolved, spatial maps of species within the ice layer as a function of distance from the interface.[7] Previous experience with spatial mapping of species as a function of depth within metallic solids suggests that the IAP procedure can provide a spatial resolution better than 1 nm, and a mass resolution of $\Delta m/m \sim 1/100$ for $m/n \sim 50$ amu.[8] The IAP provides the capability of subliming a conducting layer of ice at a cryogenic temperature, in a controlled fashion, to provide positive ions of all species within the layer for analysis. As the ice layer sublimes and the interface is exposed, a three-dimensional image of isolated macromolecules and monolayer structures adsorbed at its surface can be obtained on a nanometer scale.[9] This paper describes the procedures we have developed for creating a layer of ice believed to be vitreous in nature, for embedding an interface within the layer, and for transporting the embedded interface through laboratory ambient for analysis in high vacuum.

II. EXPERIMENTAL TECHNIQUE

In our approach *in situ* analysis of an interface is provided by rapidly freezing the interface within a layer of vitreous ice created from its liquid environment. The vitreous state is unique in that crystal formation and solute partition (in frozen aqueous solutions) is absent on a nonameter scale.[10] The importance of vitreous ice for this study lies in its value as a cryoprotectant. For example, biological structures have been imaged in the transmission electron microscope (TEM) on a scale of ~4 nm by preserving the structure in vitreous ice.[11] The interaction of the electron beam with the vitreous ice layer during imaging can induce artifacts that may limit the structural preservation of species embedded within the layer. Since an electron beam is not used for IAP analysis, structural detail on a much smaller scale may be

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preserved. The nature of the problem during TEM imaging is illustrated by an example cited in the literature:

> "...taking the value of 5×10^3 e nm^{-2} as the [electron] dose which induces severe bubbling [of a vitreous ice layer]... it is found that a cube of pure protein must have a side length of at least 6 nm to be correctly visible ($S/N=5$) before being destroyed".[12]

To obtain the vitreous state in an aqueous environment, the liquid in the immediate vicinity of the interface must be rapidly frozen. A freezing rate of $\sim10^5$ Ks^{-1} is required until a temperature of ~135 K is reached.[13] Below this temperature water exists in the vitreous state, which is stable if the temperature is not increased. The rapid cooling required for creating the vitreous state is an advantage for adsorption studies because the morphology of individual adsorbates at a liquid–solid interface will be frozen in time, typically within tens of microseconds.[14] As a result, a *snapshot* of the microenvironment at the interface can be preserved for analysis at a later time. One can even envision the preparation of several identical samples, frozen sequentially in time, for subsequent anaylsis of a dynamic process occurring within a liquid environment.

The procedure we have developed for optimizing the production of a layer of vitreous ice is an adaptation of the *plunge freezing* method developed by biologists to prepare biological specimens for observation by cryoelectron microscopy in the TEM.[15] The object of our procedure is to provide an IAP substrate with a minimum covering of aqueous solution at room temperature, and a way to insure the liquid layer on the substrate will be rapidly frozen when the substrate is plunged into a suitable cryogenic liquid. When an object at room temperature is plunged into a cryogenic liquid, it will cool at a rate determined by its mass, and by the thermal transfer properties of the insulating layer of gas that initially forms at the object's surface. The reduction in the cooling rate produced by the insulating properties of the gas layer is known as the *Leidenfrost* phenomenon. Cryogenic liquids (or *cryogens*), can be rated in terms of their ability to minimize the Leidenfrost phenomenon. Table I compares the efficiency of several common cryogens (relative to ethane) in eliminating the Leidenfrost phenomenon.[16] Liquid nitrogen was used in this study.

III. SUBSTRATE CONSIDERATIONS

The substrate required for IAP analysis is a slender, needlelike, field-emitter *tip*. Imaging and analysis is perfomed at the tip apex which is spherically shaped, and has a radius of curvature typically <1000 nm. Tips can be fabricated from almost any material. However, the vitreous ice layer (and the substrate below) must have a minimum resistivity of $\sim10^{11}$ Ω for IAP analysis to be successful with short duration, high-voltage pulses. High-voltage pulsing (rather than thermal pulsing with a laser) insures that the substrate will remain at the lowest possible temperature throughout the IAP analysis procedure.[17] In general, the conductivity requirement places a limit on the insulating properties of the liquid. A reasonably conducting liquid (or a conductive solution such as NaCl in water), may be required for successful IAP analysis.

TABLE I. Common cryogens and their efficiency (relative to ethane) in minimizing the Leidenfrost phenomenon.

Cryogen	Freezing point (K)	Efficiency (%)
Ethane	102	100
Propane	83	77
Freon 13	88	62
Freon 22	118	55
Freon 12	121	38
Isopentane	113	38
LN_2 (frozen)	63	15
LN_2 (boiling)	77	8

Field-emitter tips are prepared by forming a wire or a rod of the selected material to the required dimensions, usually by chemical or electropolishing techniques.[18] For example, tungsten tips are quickly formed by polishing a small diameter tungsten wire in 1 N NaOH, at a few volts ac. Large radius tips that result from the polishing process can be cleaned and made smooth on an atomic scale by surface self-diffusion, performed by heating a tip close to its melting point in high vacuum.[19] Small radius tips can be field evaporated in vacuum.[20] Field evaporation is the most effective cleaning and smoothing procedure known because the surface of any solid can be dissolved in a controlled fashion until the desired degree of surface perfection is achieved.

IV. VITREOUS ICE FORMATION

Figure 1 is an enlargement showing the end of a plunging mechanism developed for accelerating a tip, through a vol-

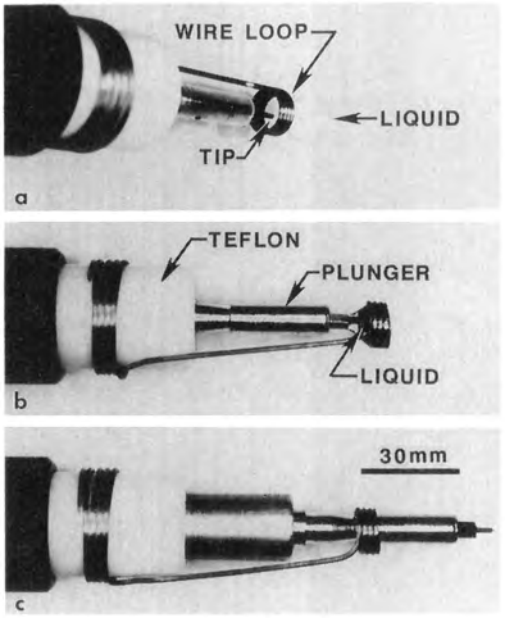

FIG. 1. A mechanism designed for plunging a tip into a cryogenic liquid (cryogen). (a) The plunger is positioned above a 20 μL droplet of liquid. (b) The tip is immersed in the droplet of liquid retained by a wire loop. (c) The tip has been accelerated through the droplet of liquid by the release of a spring mechanism.

ume of liquid, into a suitable cryogen. Figure 1(a) shows a tip, surrounded by a wire loop, positioned above a 20 μl droplet of the desired liquid. In Fig. 1(b) the liquid has contacted the wire loop, and is held in place by surface tension forces. The tip (immersed in liquid at the center of the loop), experiences adsorption from the liquid with a surface coverage that depends on the concentration of species in solution, and the time of immersion.[21] To prevent possible galvanic corrosion of the tip surface during the adsorption process, a teflon block electrically insulates the tip from the wire loop.

When a spring in the plunger mechanism is tripped, the tip rapidly accelerates forward (through the wire loop and the liquid volume), as shown in Fig. 1(c). A very thin layer of liquid is maintained on the tip apex as it exits the drop of liquid held by the wire loop. For plunge freezing, the plunging mechanism is held just above the surface of a suitable cryogen before the spring is released. This step in the procedure is shown in Fig. 2.

Figure 2 shows a small volume of cryogen ($\sim$10 cc), and an IAP anode assembly immersed in a dewar of liquid nitrogen. The cryogen is kept at its melting point by inserting a glass rod (at room temperature) into its frozen surface just before tip immersion. After immersing the tip in the liquid droplet held by the wire loop, the plunging mechanism is quickly positioned just above the liquid surface of the cryogen. When the spring is tripped, the tip accelerates through the wire loop into the cryogen where the thin layer of liquid remaining on the tip apex freezes to form a layer of ice, believed to be vitreous in nature.

In the next step of the procedure, tweezers cooled with liquid nitrogen are used to remove the tip from the plunging mechanism through the surface of the cryogen. The tip is then placed into a blind hole in the anode assembly of the IAP where it is immersed just under the surface of the liquid nitrogen in the dewar. The tip is protected from gas phase contamination during transfer from the cryogen to the anode assembly by the atmosphere of pure nitrogen gas that exists above the surface of the liquid nitrogen in the dewar.

The procedure used to transfer the anode assembly into the high vaccum environment of the IAP is shown in Fig. 3. A tweezers precooled by liquid nitrogen lifts the IAP anode assembly out of the liquid nitrogen in the dewar and into laboratory ambient where it is transferred onto the cold stage of the IAP, precooled to 80 K. Contamination from laboratory ambient during transfer into the IAP is prevented by a continuous supply of nitrogen gas that flows from the surface of the liquid nitrogen in the anode assembly, up over its edge, and down over the outside of the anode assembly. Frost does not condense on the anode assembly during the transfer operation (even with a high humidity environment in the laboratory), provided rapid movements that could disrupt the flow of nitrogen gas are avoided.

V. FIELD-ION IMAGING

Field-ion microscopy is an integral part of the IAP technique. As a result of the tip preparation technique, the surface of the tip apex will display many different crystal planes of low and high Miller indices. These will be smoothly joined into an approximately hemispherical contour, and will be symmetrically placed about the tip axis. Field-ion microscopy displays the symmetry of the tip apex by imaging atoms on its surface with a magnification typically greater than 10^6. During the imaging process, positive ions created in space directly above the most protruding surface atoms accelerate almost radially from the tip apex. Image resolution is determined by the spread in the kinetic energy of the imaging gas ions parallel to the tip surface, the spatial extent of the ionization region, and the finite de Broglie wavelength of the ion. In practice, a subnanometer spatial resolution is obtained in a field-ion image under normal imaging conditions.

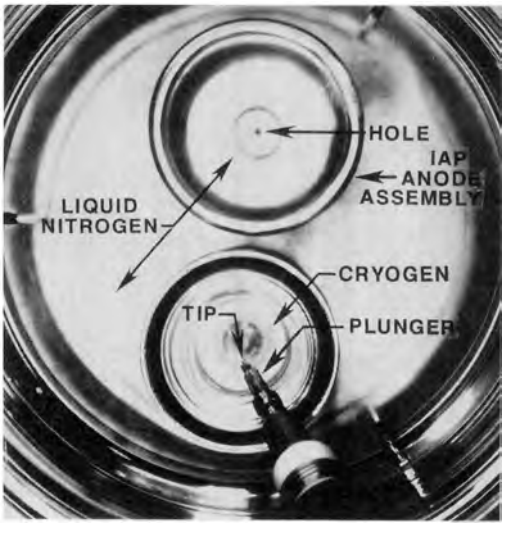

FIG. 2. The formation of vitreous ice at the tip apex. A tip has been accelerated by a plunger into a cryogen, cooled by liquid nitrogen in a dewar. An IAP anode assembly has been placed under the surface of the liquid nitrogen in the dewar. The tip is ready to be transferred into a hole in the IAP anode assembly.

FIG. 3. The transfer of a tip in an IAP anode assembly through laboratory ambient. The tip is immersed in liquid nitrogen. Nitrogen gas from the liquid surface flows up, travels over the edge of the IAP anode assembly, and flows down over its external surface. The flow of nitrogen gas prevents frost buildup on the IAP anode assembly during transfer into high vacuum.

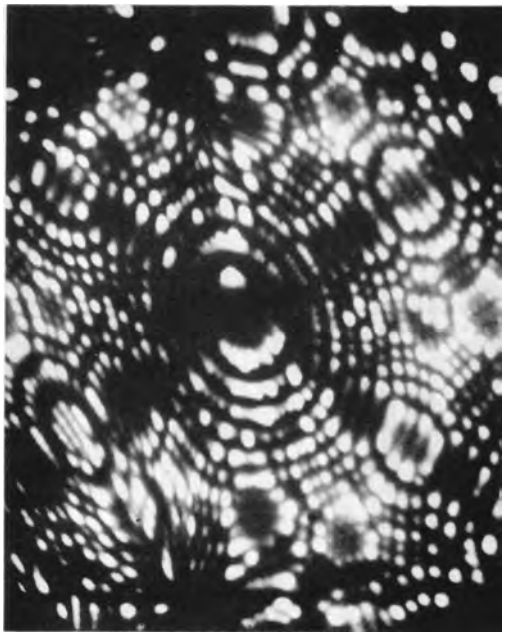

FIG. 4. A field-ion image of the apex of a tungsten tip after plunge freezing a tip in liquid nitrogen at 80 K.

Field-ion imaging was used in this study to assess the effect of freezing the apex of several tungsten tips. Field-ion images taken before and after the plunge freezing procedure were compared to evaluate lattice damage resulting from the freezing process. Figure 4 shows the apex of a typical tungsten tip used in this study, imaged by field-ion microscopy after plunge freezing the tip in liquid nitrogen. Although the results of the field-ion study are still being evaluated, it appears that the lattice structure of a tungsten surface is preserved on a subnanometer scale during the freezing process.

VI. SUMMARY AND CONCLUSIONS

A novel approach has been outlined for studying adsorption phenomena at a solid–liquid interface in the imaging atom-probe mass spectrometer. A solid–liquid interface is preserved at an instant of time for subsequent analysis in the IAP, by encasing and embedding the interface within a thin layer of vitreous ice formed from the liquid in its immediate vicinity. The vitreous ice layer is created at the apex of a field-emitter tip by quicky immersing a tip, coated with a thin layer of liquid, into a suitable cryogen held at its freezing point in a dewar of liquid nitrogen. After immersion in the cryogen, the tip is tranferred to the anode assembly of the IAP which is immersed in liquid nitrogen. The transfer is made in the atmosphere of pure nitrogen gas, existing above the surface of liquid nitrogen in the dewar. The tip is immersed within liquid nitrogen, contained within the cuplike anode assembly of the IAP. During transport through laboratory ambient into high vacuum, the anode assembly is protected from contamination and frost condensation by a protective layer of nitrogen gas produced by the liquid nitrogen retained by the anode assembly.

Field-ion microscopy of the tip apex suggests that the freezing protocol and the transport technique discussed in this paper do not cause lattice damage of the tip apex on a subnanometer scale. Unfortunately, field-ion microscopy cannot be used to verify the vitreous nature of the ice layer believed to be present on the tip apex. Indirect evidence for the formation of vitreous ice may come from IAP analysis of the ice layer. Ultimately, the formation of vitreous ice on the tip apex may have to be verified by electron diffraction anaylsis of the ice layer in the TEM. Adapting a conventional TEM cryostage for this purpose will be initiated in the near future.

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