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Preliminary evidence of field induced rhenium etching by XeF$_2$ at high vacuum

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Preliminary evidence of enhanced etching of rhenium by XeF$_2$ under the influence of an electric field (3.36 GV/m) is presented. Scanning electron microscope photographs of sharp rhenium tips show etching of at least 0.40 μm ± 0.07 in 32 min at the point of maximum electric field, indicating a field enhanced etching rate of 13 nm/min ± 2. A control experiment shows a maximum spontaneous etching of rhenium by XeF$_2$ of 0.1 μm ± 0.07 in 30 min, indicating a maximum possible spontaneous etching rate of rhenium by XeF$_2$ of 3 nm/min ± 2. The spontaneous rate of tungsten by XeF$_2$ reported in the literature is 0.2 nm/min. © *2008 American Institute of Physics.*
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INTRODUCTION

Electric fields of the order of V/Å are of the same order of magnitude as fields experienced by valence electrons inside atoms and molecules. Such electric fields can occur at field emission tips, zeolite cavities, and electrode-electrolyte interfaces.[1] In the presence of fields of this magnitude, redistribution of the valence electrons of atoms and molecules adsorbed in surfaces takes place. The redistribution affects both internal and surface bonds of the molecule. The redistribution of electrons can increase or decrease a bonds' strength depending if the bonding or antibonding orbitals in the molecule are more affected.[2] This phenomenon is called field induced chemistry. The electric field becomes then just another state variable such as temperature (T) or pressure (P), which can alter chemical equilibrium[3] and kinetics.[4]

Surfaces under the effect of high electric fields have been studied for many years. There have been two main approaches. One is electrochemistry, where the metal surface and the ions solvated at closest approach form a sort of capacitor of molecular dimensions: the double layer. Assuming the distance to the inner Helmholtz plane to be 0.3 nm, and a voltage drop of 1 V (with respect to the plane of zero charge), values of electric field at the double layer of ~3 GV/m should be achieved. Such a simplified model is not always valid and the values of electric field are not so easy to estimate.[5]

The second approach corresponds to high electric field at the surface-vacuum interface. field electron and field ion microscopes work on this principle, where sharp tips enhance the surface electric field near the apex of the tip (radius of ~50 nm). At fields of tens of GV/m field induced desorption is possible.[6] The concept of surface electrochemistry or the combination of both approaches has experienced a period of scientific and technological revolution in the last 10–20 years, with the incorporation of newer techniques such as infrared reflection spectroscopy, synchrotron x-ray diffraction and absorption, electroreflectance, and scanning probe microscopy among others.[7]

In the present paper we present preliminary evidence of enhanced etching of sharp tips made of rhenium exposed to high vacuum with residual XeF$_2$. The original objective in studying the system was to find a system where points of concentration of electric field could be preferentially etched such that electric breakdown could be prevented.[8] Rhenium was selected because it is a refractory metal that when combined with fluorine forms volatile compounds at all stoichiometries [boiling point (BP) ReF$_7$=73.7 °C, BP ReF$_6$=33.8 °C, BP ReF$_5$=221.3 °C, BP ReF$_4$=300 °C (Ref. 9)] such that vaporization of microprotrusions under fluorine ion bombardment is likely.

EXPERIMENT

The experimental setup consist of an anode formed as a sharp tip and facing a broad area plane cathode electrode with a polished Rogowski profile.[10] The electrodes are inside a vacuum chamber evacuated using a BOC Edwards turbomolecular pump model EXT250/100CF backed by a Duo Seal vacuum pump, model 1397 from Welch Scientific. The chamber achieves ultimate pressures down to 4.1 $\times 10^{-8}$ Torr measured with a glass Alpert-Ballard ionization gauge. The voltage of the high voltage electrode is recorded using a PHV 4002-3 0,6 ppm/V 1000$\times$ high voltage probe. The probe was calibrated in December of 2003 in the range of 2–20 kV dc providing a minimum accuracy of 0.083%. The gap between broad area electrode and the tip is controlled using a Huntington® Laboratories micrometer linear motion feedthrough model L-2141-2-A with a maximum stroke of 5.08 cm (2 in.). The power supply consists of a EMCO general purpose negative high voltage supply, model 4330N. Which allows output voltage from 0 to 33 kV and a current at maximum voltage of 0.3 mA. This power supply incorporates arc and reverse polarity protection.[11] The microphotographs of the electrodes were taken using a JEOL JSM-

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6060LV low vacuum scanning electron microscope in the Frederick Seitz Materials Research Laboratory.

The rhenium tips were obtained by electropolishing a 0.1 mm diameter rhenium wire, 99.97%.[12] To obtain tip radii below 1 μm a double layer electrolyte is necessary. The bottom layer is required to be denser than the top layer and that it does not participate in the reaction. Historically CCl_4 was used for this purpose, but now it is a suspected carcinogen and is not recommended. We used instead Galden HT-200 (Perfluoropolyether Cas 69991-67-9).[13]

The top layer is the real electrolyte and consists of a thin (5–7 mm) floating layer of 50% H_2SO_4 solution. The conditions for the electrolysis are 2.5 V dc with a current of ~20–35 mA for approximately 3 min. The thin wire to be formed into a tip penetrates through the top electrolyte layer and reaches the bottom inert layer. During the process the wire is moved up and down to prevent preferential attack at the air-electrolyte interface. This produces a necked region in the center of the wire until the weight of the lower part of the wire is too heavy to be supported by the neck formed. Further details of this experimental technique can be reviewed elsewhere.[14]

A rhenium tip was polarized positive to 4000 ± 10 V (for a maximum field of 3.36 GV/m, see discussion), while exposed to XeF_2 at a pressure of 8.0×10^{-6} Torr. There was no emission current and no breakdown present during 32 min. The tips before and after the procedure described are shown in Fig. 1. The presence of particles in the postmortem tip is not considered significant and is likely due to a weak argon glow discharge struck in the chamber during a different test. Tip annealing is performed in vacuum before every experiment at 1355 °C ($0.47 T_m$) for 3 min. This annealing has always been too mild to change the geometry of the tips.

The first impression from Fig. 1 is that there must be an erroneous assignment of the micron marker from the microscope software. We have found in repeated experiments that the value of the marker is only approximated. Here we will use the distance from the hole defect (top left) to the grain boundary near the apex of the tip (16.60 ± 0.05 μm) as our invariant marker between experiments. Normalizing both pictures conservatively (16.60 μm hole-grain boundary distance), the distance from the grain boundary to the apex of the tip in Fig. 1(b) is actually 6.35 ± 0.05 μm. Therefore, we etched at least 0.40 μm from the apex of the tip in 32 min, thus etching approximately 13 ± 2 nm/min.

The same tip was used for a control experiment. After annealing at the same temperature for an identical amount of time, the tip was exposed to XeF_2 for 30 min but without an electric field present. The control experiment tip is shown in Fig. 2. The micron markers in Fig. 2 are again only approximate. Therefore normalizing the values again to 16.60 μm hole-grain boundary distance, the tip of Fig. 2(a) is 6.20 ± 0.05 μm, and the tip of Fig. 2(b) is 6.10 ± 0.05 μm. Therefore the observed change in the tip was 0.1 ± 0.07 μm corresponding to a maximum possible spontaneous etching rate of rhenium by XeF_2 of 3 ± 2 nm/min. Table I summarizes the results for the normalized grain boundary to apex distance after normalization for both experiments.
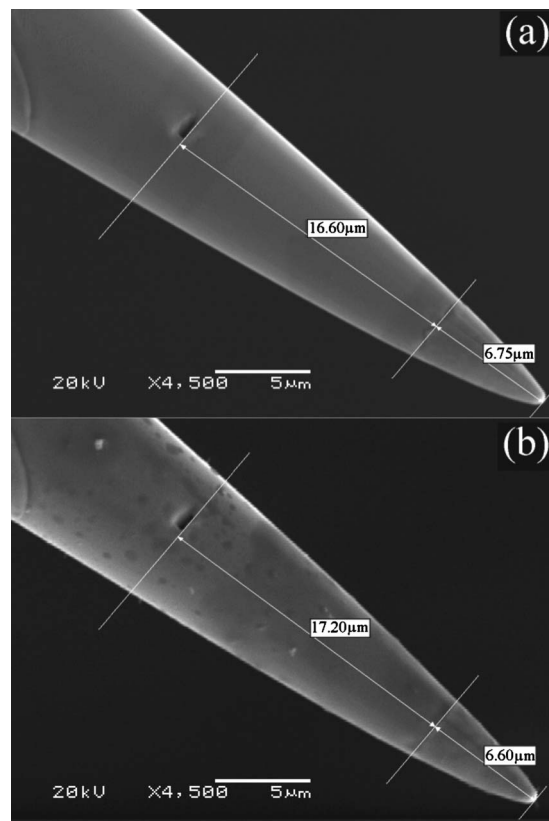

FIG. 1. (a) Virgin rhenium tip and (b) same tip after polarization to positive 4 kV (3.36 GV/m) while exposed to 8.0×10^{-6} Torr of XeF_2 for 32 min. We used the distance from the hole defect to the grain boundary as an invariant marker of 16.60 ± 0.05 μm such that the tip of (b) measures 6.35 ± 0.05 μm.

DISCUSSION

To estimate the maximum electric field (E) at the apex of our tips, we used an empirical equation provided elsewhere,[15]

$$E = \frac{V}{kR_t}, \tag{1}$$

where V is the applied voltage, R_t is the radius of the tip, and k is defined as

$$k = 0.59\varepsilon^{1/3}\left(\frac{d}{R_t}\right)^{0.13}, \tag{2}$$

where ε is the emitter-cone half-angle and d is the distance to the other electrode. Analysis of the scanning electron microscope (SEM) images, using the SCALE 2.0 program,[16] gives $R_t \approx 0.40 \pm 0.05$ μm and $\varepsilon \approx 6.1 \pm 0.1°$. Since the gap $d \approx 1 \pm 0.1$ mm, Eq. (2) gives $k = 2.98 \pm 0.22$. Finally, using Eq. (1), the maximum electric field at the apex of the tip is 3.36 ± 0.49 GV/m.

To illustrate the electric field distribution on the anode such that an educated guess of the etching profile can be made, we used Ansoft Maxwell™.[16] The approximate distribution of electric field for a simulated two dimensional (2D) equivalent case to our experiment is shown in Fig. 3. From Fig. 3 it is clear that the location of the maximum electric field is located near the apex of the tip as expected, but also
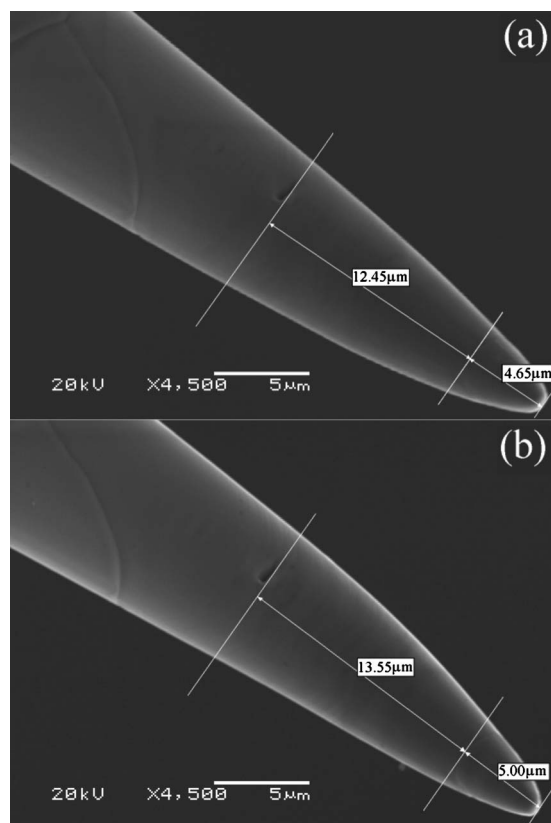
FIG. 2. (a) Freshly annealed rhenium tip and (b) same tip after exposure to 8.0×10^{-6} Torr of XeF_2 for 30 min without electric field. Using the distance from the hole defect to the grain boundary as an invariant marker of 16.60 ± 0.05 μm, such that the normalized tip lengths for (a) are 6.20 ± 0.05 μm and (b) 6.10 ± 0.05 μm.

that the electric field decreases quickly away from the tip. In our case, the field has dropped about one order of magnitude 7 diameters away from the apex of the tip. That is about 6 μm from the tip in Fig. 1. Notice, however, that the equilibrium constant of a field induced chemically reaction is affected by the field according to the well known van't Hoff Equation,[17]

$$\frac{\partial \ln K}{\partial E} = \frac{\Delta M}{RT},$$ (3)

where K is the equilibrium constant, E is the electric field strength, R is the gas constant, and T is temperature. ΔM is partial molar energy related to the change in electric moment
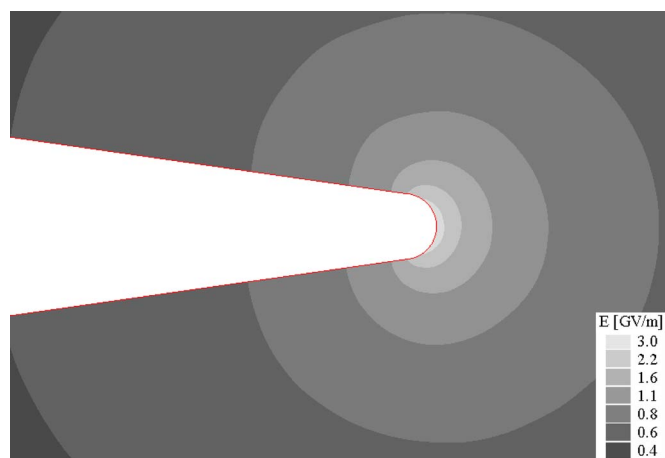

FIG. 3. (Color online) 2D simulation of the field distribution near the apex of the tip, illustrating the fast drop of electric field strength away from the point of maximum electric field.

and includes dipole moments, polarizabilities, and hyperpolarizabilities for reactants and products.

Equation (3) basically indicates that the change the equilibrium constant K is exponential on the change of electric field. While the equilibrium constant or its change does not give any information about kinetic behavior, we can at least know that if the reaction happens at all, it is likely to happen exclusively at the point of maximum electric field. So we should expect etching only at the apex of the tip.

The spontaneous rate of tungsten (also a refractory metal) etching by XeF_2 is reported elsewhere as approximately 0.2 nm/min.[18] Here the Re rate was estimated as 5.6 nm/min. Due to slight change in perspective between the SEM pictures the exact etching rate is hard to determine accurately and further study is required.

ACKNOWLEDGMENTS

TABLE I. Normalized distance between the grain boundary and apex of the tip, change, and etch rate for the experiments presented in Figs. 1 and 2.

Experiment	Figure	Normalized[a] length (± 0.05 μm)	Change (± 0.07 μm)	Etch rate (± 2 nm/min)
Etch (32 min)	Fig. 1(a)	6.75	0.40	13
	Fig. 1(b)	6.35		
Control (30 min)	Fig. 2(a)	6.20	0.10	3
	Fig. 2(b)	6.10		

[a]Normalization of all pictures using the distance from the defect hole to the grain boundary as an invariable marker of 16.60 μm.

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