Electrochemical preparation of tungsten tips for a scanning tunneling microscope

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We present experimental results obtained during the electrochemical preparation of tungsten tips for a scanning tunneling microscope. Experiments were done with direct current and two kinds of electrolytes widely reported in the literature: KOH and NaOH. We report the effects of the applied voltage, time of etching, tip length, electrolyte concentration, wire diameter, and immersed portion as relevant parameters in the process. From the images obtained by a metallurgical microscope and a scanning electron microscope as well as from Auger and electron diffraction x-ray analysis the best conditions for W tip preparation were obtained. We found that KOH is better than NaOH as an electrolyte to prepare tips for scanning tunneling microscopy and that tip quality increases as the wire diameter and the immersed portion increases. © 1996 American Institute of Physics. [S0034-6748(96)04004-4]

I. INTRODUCTION

The scanning tunneling microscope (STM)—invented by Binnig and Rohrer1 in the early 1980s—has become an important instrument in surface science. The STM uses the high sensitivity of tunnel current flowing through the gap formed between the sample and a tip.

The characteristics and composition of the tip play an important role in the resolution of the STM. Ideally, the tip needs to have one atom on its apex, but the method2 is very complicated and expensive. There are different methods to produce tips of high quality to obtain atomic resolution: electrochemical,3 mechanical,4 evaporation,5 cutting,6 and breaking off.7

The electrochemical method is the easiest and faster method to obtain cheap and reliable tips for STM applications (the drawback is the usual oxidation of the tip). Each laboratory or research group has its own conditions to prepare adequate tips, and they all verify the suitability of their method by obtaining satisfactory results, that is, good STM images. Obviously, this method to qualify tips is not quantitative but qualitative. Important exceptions are the works of Fotino,8 Garnaes,9 and Biegelsen10 where high resolution transmission electron microscope (TEM) images of the tip apex are used to quantify the tip sharpness. However, a systematic study to find out the best conditions for tip preparation is still lacking.

In this work, we present a study of tip preparation with the aim of finding the best conditions for tungsten tip etching.

We have determined the optimum conditions for tip preparation considering three basic requirements for tips: short length, high symmetry, and sharp apex. Short length is necessary to decrease mechanical vibrations that will blur the image. High symmetry will yield an electronic wave function symmetric that will yield an undistorted image (the image is the convolution of the electronic wave functions of tip and sample). Finally, a sharp apex will avoid changes of the microtip that is actually responsible for the tunnel current. Those changes produce ghost images from double tips and large differences between the images generated from the forward and the backward scan. The reason is the change of microtip in large surface steps.

II. EXPERIMENT

The experimental setup used for tip preparation consists of a glass beaker containing the electrolyte, a cylindrical stainless steel sheet lining the glass beaker in direct contact with the solution (cathode), and a tungsten wire mounted into a metallic tip holder. The wire is positioned into the solution and the electrical circuit is closed when it is immersed. The level of the solution is modified by capillary action around the wire. The wire length below the solution level can change tip morphology.11,12 For this reason we have systematically controlled this length with an optical microscope through a hole in the cylindrical stainless steel sheet. A voltage (from a dc power supply) is applied between electrodes. After etching is completed the tip is cleaned in distilled water by using an ultrasonic cleaner. The experimental setup was kept free of external vibrations during etching.

By electronically monitoring the etching current, the potential is shut off automatically when the immersed part of the wire dropped off into the bath and leave the usable tip on the tip holder. The electronic is similar to that described in Ref. 12.

We used for this study the two electrolytes most often used for tip preparation: NaOH and KOH. We prepared tips with one, two, three, and four normal electrolyte concentrations.

The electrochemical reaction during tip preparation involves anodic dissolution of tungsten in aqueous medium. The etching process occurs at the air/electrolyte interface.
when a voltage is applied to the tungsten wire (anode). The electrochemical reaction has been studied by several authors.\textsuperscript{12–14} It involves the oxidative dissolution of tungsten to tungstate anion ($\text{WO}_4^{2-}$), which is soluble in water.

For each concentration and tip, we experimentally determined the corresponding voltagram. As can be seen in Fig. 1, the $I$–$V$ curve shows three different regions: a fast increase in the current with the voltage up to a given voltage ($V_{\text{min}}$) where a “plateau” is reached, the plateau itself that finished when a new threshold voltage ($V_{\text{max}}$) is reached and the region which a very fast increase of current with voltage. The best region for polishing is the flat one. In fact, the first region requires very long times for polishing and at voltages above $V_{\text{max}}$, the electrochemical reaction becomes a violent one and produces cavities, holes, and large irregularities in the tip and a poor quality of its surface. Taking into account the $V_{\text{min}}$ and $V_{\text{max}}$ for each concentration, we prepared tips with intermediate voltages, i.e., values of the voltage in the plateau range. The etching times are between 20 and 50 min, smaller etching times are required for higher voltages.

As soon as each tip is made, it is observed in a metallographic microscope with a 50× magnification and a photograph is taken. From the photograph the tip length is obtained. All the photographs were compared to discern the best tips from the geometrical point of view. The next step was to obtain scanning electron microscope (SEM) images of the best tips (as decided in the previous step) at increasing resolutions to obtain the symmetry and tip radius. Finally, atomic resolution images of highly oriented pyrolytic graphite (HOPG) are obtained with the tips that have good geometrical shape. Only tips with good shape and that yield atomic resolution images of HOPG are considered as good tips.

A STM-SEM combined and integrated microscope has been used for tip imaging and performance. The SEM equipment is an HITACHI S-2700. A STM stage V-3000 from HITACHI has been installed in the SEM equipment. The STM has two different piezoelectric tripods. In this work we used the best one (atomic resolution and 10 Å/V for the $x$–$y$ scanner and 5 Å/V for the $z$ piezo). The STM and SEM control/scanning electronics and data acquisition systems as well as the software managing the whole system were developed in our laboratory based on an IBM workstation RISC/6000-340. Maximum data acquisition speed is 100 000 samples/s at 16-bit resolution. STM, performance has been checked by obtaining high-quality images of HOPG at atomic resolution. Images are analyzed in a digital image processing system (Altamira) that has also been developed on the IBM RISC workstation in our laboratory.

### III. RESULTS AND DISCUSSION

To obtain a standard method for tip preparation, we evaluate tip quality by measuring tip length and tip radius and also the tip symmetry.

First, we studied tip morphology when the immersed portion of the tip was 8 mm and the wire radius 0.8 mm. The tip length—defined as the distance from the apex to the point where the diameter returns to its original unetched value—is obtained from the optical microscope photograph. For voltages below 10 V, the tip lengths are located in a limited region without a clear dependence on concentration and voltage. Using NaOH, the region ranges between 300 and 1200 μm and with KOH between 600 and 1300 μm. Best results were obtained with KOH as electrolyte in the region between 2 and 3 N and 2 and 6 V.

The next step is to clarify the effect of the length of the submerged part of the wire on tip morphology. Thus, we have repeated the study described above but with only 1–2 mm of immersed part. This change in length represents a change in weight of the submerged part four to eight times smaller than in the previous case whereas the active surface for etching is the same.

Figures 2(a) and 2(b) show SEM images of a good tip at two resolutions: magnifications of 90× and 900×. The tip was obtained from a rod of 1 mm diameter and with an immersed part of 8 mm. By comparing with Figs. 2(c) and 2(d) (corresponding to a tip prepared by immersing the wire only 1 mm) we can see the large difference in tip quality. From images at a magnification of 30 000× we have obtained that the tip radius in the case of 8 mm of immersion is of about 25±5 nm (the error comes from the blurring and poor quality of the SEM image at this resolution when the STM is in the chamber), whereas for the case of 1–2 mm immersion it is larger than 1 μm. Similar results were obtained in all cases. They can be summarized as follows: a decrease in the submerged part produce an increase in the tip radius. Then, to obtain good quality (geometrical) tips, with small apex radius, a large submerged part should be used.

The next step is to study the relationship between tip morphology and wire diameter. There is no single hint about the possible effect of wire diameter on tip radius and quality in the literature. We used a wire of 0.35 mm on which we repeated the previous study with 1–2 and 8 mm submerged part. The optimum region in this case is 2–3 N and 3–5 V. In this case, we have decreased the weight of the submerged portion by a factor of about 50 with regard to the previous case and by a factor of 60–400 with regard to the first case (8 mm submerged part, 1 mm diameter). On the other
hand, the active region has changed in the same amount when comparing with the two previous cases (about four times smaller).

We have not obtained a clear relationship between the wire diameter and the tip radius. In fact, in images obtained at low resolution apparently the tip quality increases when wire diameter decreases. However, at high resolution we can see that tip radius does not change appreciably with wire diameter. As an example, Figs. 2(e) and 2(f) show images of a good tip (90× and 900× magnification) prepared from a 0.35-mm-diam wire and 8 mm of immersed part. By comparing Figs. 2(a) and 2(b) we can see that at high resolution the tip quality is similar. In fact, tip radius as measured at high resolution (30 000× magnification) is 35±5 nm. The main difference is in tip length. In fact, tip length increases as wire diameter decreases. Since a tip has to be as short as possible, an extremely thin wire rod should be avoided in tip preparation.

As a final characterization of the tips we have studied the oxygen contamination by Auger with the same experimental procedure as in Ref. 15 and using an ESCA/SAM Phi Model 560 Perkin–Elmer in an ultrahigh vacuum (UHV) equipment. Oxygen contamination plays an important role in STM because of the insulator layer that will avoid the tunnel current.

A W tip prepared under optimum conditions was introduced 20 min after preparation into the ultrahigh vacuum (5×10⁻⁹ Torr) of the ESCA/SAM system and analyzed with
the Auger technique. Figure 3(a) shows the Auger analysis of a freshly made tip. Quantitative analysis of the wire surface of this particular tip was 60% C, 11% O, and 29% tungsten (W). W concentration can change from about 20% up to 65% depending on the preparation conditions.

The tip was afterwards sputter-etched for a long time until the surface composition stabilized at 79% W [Fig. 3(b)]. Probably the final level of W, O, and C concentrations depends on the starting material from which the tip was prepared. The peak near 400 eV is due to nitrogen, a usual contaminant in metals.

To observe the distribution of the oxygen contamination we have obtained an electron diffraction x-ray (EDX) map of the oxygen concentration in tip. Since oxygen contamination is a surface feature, then an EDX study was made at the lowest possible acceleration voltage: 5 kV. From this study we obtained that in the case of the thin tip (0.35 mm wire diameter) the O concentration is uniform along the tip. However, in the case of thick tungsten wire (0.8 mm diameter) the oxygen concentration is much lower in the tip axis than around the region of interface with the air. In this last case, deposition of microcrystals (whose atomic composition is WO₃/K) occurs in the region of interface between air and liquid. However, the concentration of oxygen in the tip apex is similar in all cases. Important departure only occurs when the starting material was contaminated with oxygen (in some cases it can be as high as 20% atomic!). Thus, from the point of view of oxygen contamination, the rod diameter or the immersed part are not important. Then, tip shape is the important criterion to decide tip quality.

Cricenti et al.¹⁶ show that high vacuum annealing at 1800 K removes most of the oxide and they think that after exposure during ten days at air a new oxide layer probably appears. The assumption was made on the basis of the deformation of STM I–V curves obtained from a gold sample. To confirm their assumption we made a new Auger analysis of the tip after exposure to air during 15 min. Figure 4(c) shows the result: oxygen concentration has increased but still is much lower than after tip preparation. However, carbon concentration does not increase.

IV. CONCLUSIONS

In conclusion, a large immersed part (more than 5 mm) of a thick tungsten rod (wider than 0.6 mm diameter) will yield short and sharp tips: the optimum for STM use. The average tip length obtained under optimized etching conditions was 750 μm.

Auger electron spectroscopy (AES) and EDX results showed the presence of the oxides formed in the tip. Thus, electrochemically prepared tungsten tips are not recommended for tunnel spectroscopy because the oxide layer will probably produce a distortion of the information as observed by Cricenti et al.¹⁶ for I–V curves. Thus, for spectroscopy it is preferable to use PtIr tips on which no appreciable oxide layer is formed.

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