A double lamellae dropoff etching procedure for tungsten tips attached to tuning fork atomic force microscopy/scanning tunneling microscopy sensors

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We present an electrochemical etching scheme for producing sharp tungsten tips for use in scanning probe microscopes. The motivation behind the development of this particular method comes from the need to have an etched probe attached to a quartz tuning fork. Comparisons with existing etching methods are made. This rather simple scheme incorporates the key advantages of previously established techniques to give reproducible and controlled etching cycles. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1532833]

I. INTRODUCTION

Sharp tungsten tips play a key role in field ion microscopy (FIM), scanning tunneling microscopy (STM), scanning force microscopy, and related techniques. Electrochemical etching procedures for producing atomically sharp tips from polycrystalline wires have been well established for more than 60 years and are described in several books and articles. In an early article, Müller[1] stated in 1937 that extraordinary fine tips for field emission microscopy could be made from tungsten and molybdenum by etching them in melted sodium nitrite, $NaNO_2$, and from copper and nickel by etching in nitric acid. Currently, especially motivated by the pursuit of high-resolution atomic force microscopy (AFM), etching techniques are being explored and further refined. In this article, a technique for etching a tip attached to a tuning fork is described.

II. BASIC ETCHING SCHEMES

A review of making sharp tips with different etching techniques is given by Melmed.[2] In a very simple procedure, the tungsten wire and a stainless steel counter electrode are dipped into an electrolyte of 2–3 M NaOH. For etching, a dc voltage of about 2.5–9 V is applied to the electrodes, the tungsten wire acts as the anode, the stainless steel electrode as the cathode. An etching current on the order of mA induces the following simplified reaction:[3]

$$W + 2H_2O + 2NaOH \rightarrow 3H_2 + Na_2WO_4.$$

In practice, the reaction is much more complicated, as intermediate oxidizing steps occur.[4] After an etching time of about 5–15 min, the wire at the air/electrolyte interface region becomes so thin that the lower portion of the tungsten wire falls down. The resultant etched wire terminates in a uniform taper since gravity is the only significant physical force felt by the wire. To prevent further etching of the upper part, the constant voltage power supply is equipped with a fast electronic switch set to break the current when it falls below a preset value. The etching current drops drastically when the lower end of the tungsten wire falls down. Sophisticated methods to switchoff the current have been developed.[5,6] The piece of the wire that falls into the solution is not usable due to the etching that occurs along its entire length, which makes it significantly thinner.

An improved and easy to use etching technique is the so called "lamellae dropoff technique," where a small ring electrode is used as a cathode [Fig. 1(a)].[7,8] A drop of NaOH in the ring creates an electrolytic cell in which the tungsten wire is etched. At the end of the etching process, the lower part of the tungsten wire falls down into a padded container. The etched end of this piece is very sharp and used as a tip. One advantage of using this scheme is that no switchoff control is needed. When the lower part of the wire falls down, the circuit breaks and the current is interrupted automatically. In this etching arrangement, the upper part of the wire cannot be used. Because the current is not interrupted at this part, the wire becomes blunt. Care has to be taken in this approach to ensure that the etched wire that falls does not break once having been caught. Our goal in creating a wire etching scheme was to have an automatic current cutoff that could take advantage of elements of the lamellae dropoff technique but in a geometry that would allow us to use the upper end of the wire as a tip. The main problem is how to make an electrical connection to the tungsten wire that will break once the tip etches. Niemeck *et al.* reported on a technique which makes a connection to the bottom portion of the wire through a spring made from high gauge wire [Fig. 1(b)].[9] This technique has the benefit of having an automatic current shutoff when the wire etches since the bottom part of the wire which has the electrical contact falls away. The main disadvantage of such an approach is the introduction of mechanical forces both lateral and vertical on the wire due to

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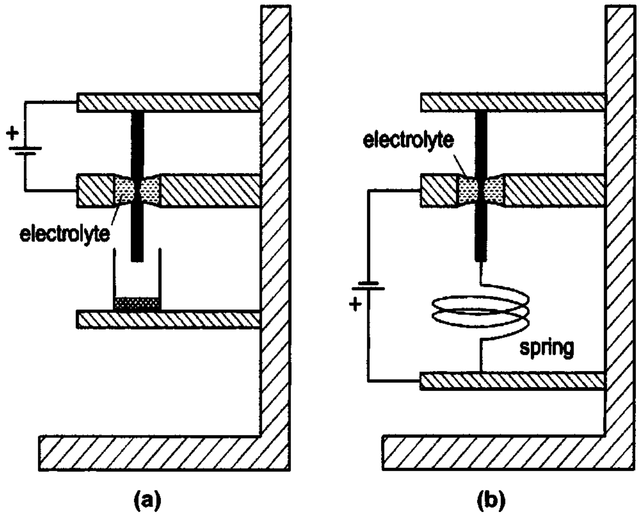

FIG. 1. By using a small ring electrode to carry the solution, the lamellae dropoff method utilizes the etching and wire dropoff event as the electrical switch that cuts the flow of current to the wire that will serve as a tip. If the voltage is applied to the upper portion of the wire (a), then the wire that falls is employed as a tip and if the voltage is applied to the lower part of the wire through a spring (b), then the upper portion of the wire can be used.

the spring tension that can distort the way the bottom of the wire drops. The method that we present in this article has an automatic current shutoff but with no additional forces applied to the end of the wire that falls.

III. qPLUS-SENSOR FOR AFM AND STM

Before we introduce our etching technique, we will discuss the motivation for etching tungsten tips for AFM tuning fork sensors. A major breakthrough in high-resolution atomic force microscopy was the invention of the qPlus-sensor by Giessibl.[10–12] This sensor is comprised of a quartz tuning fork, where one prong of the fork is bonded to a mount and the other prong is free and has a tip attached to it (Fig. 2). With this design, subatomic features were resolved on the Si(111)$-(7\times7)$ surface by using the tuning fork as a noncontact AFM sensor.[13] Tuning forks are being used more frequently in ultrahigh vacuum and low temperature environments due to the elimination of optical alignment requirements. Because the tungsten tip is an electrical conductor, this assembly can also be used for STM as well. We are going to use this tuning fork design in our low temperature

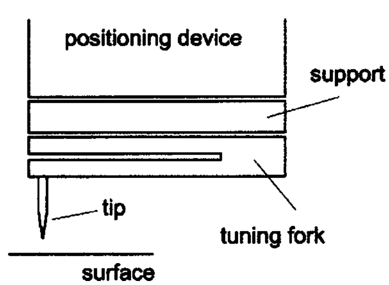

FIG. 2. Side view schematic of the qPlus sensor design. This scheme involves placing a conductive tip on one prong of a quartz tuning fork and rigidly attaching the other prong to a support that is subsequently affixed to a piezoelectric ceramic for positioning and tuning fork excitation.

scanning tunneling microscope[14,15] also to run it as a force microscope in order to investigate nonconductive oxide surfaces at low temperatures.

The steps we used to build up a qPlus sensor are the following. First, the tuning fork, which comes from a commercially available watch quartz,[16] is removed from its hermetically sealed canister. The sensors we have used have a fundamental resonance of 32 768 Hz. Then one prong of the tuning fork is affixed with Torr seal[17] to a Macor plate, which is fitted with wires for making connections to the two electrodes on the tuning fork. After the electrical connections are made to the tuning fork, a 10 mm long, 0.25 mm thick tungsten wire is glued with Torr seal at the very end of the free prong. The Torr seal is cured at 100 °C for 1 h. Then, the electrical contact between the tungsten wire and one of the tuning fork electrodes is made using silver epoxy,[18] which is cured at 150 °C for 1 h. The process of curing the vacuum compatible epoxies needed to make both the structural electrical contacts between the tungsten wire and the tuning fork preclude the option of etching a tungsten wire and then attaching it to the tuning fork. If an etched tip were generated then affixed to the tuning fork, the tip would oxidize rapidly in air at elevated temperatures rendering it less conductive and less sharp. This immediately prompted the investigation into etching a wire that has been attached to the tuning fork where the etching would be the last step before installation into the scanner assembly and evacuation of the system. We chose not to create a tip holder at the end of the tuning fork that would allow for *ex situ* etched tips to be used in order to minimize the mass load at the end of prong. The resonance frequency drops by as much as a factor of 2 with an etched wire attached directly and any additional material in the form of a tip holder would further decrease the fork resonance.

IV. DOUBLE LAMELLAE DROPOFF ETCHING TECHNIQUE

The tungsten wire of the premanufactured tuning fork sensor has to be etched to a sharp tip. For this reason, we developed the following etching technique [Fig. 3(a)], which eliminates the problems of the technique shown in Fig. 1(b). We replaced the spring in the etching configuration illustrated in Fig. 1(b) by a second ring electrode, which leads the current to the tungsten wire and acts as an electrolytic cell. We call this arrangement therefore the ‘‘double lamellae dropoff etching technique.’’ The additional electrode supplies a mechanical force free electrical connection to the tungsten wire. The positive pole of the dc voltage is fed to this lower electrode, the minus pole to the upper one, which acts similar to Fig. 1(a) as a counter electrode (cathode). The lower electrolytic cell is a nonlinear electrical resistor, feeding the positive potential to the tungsten wire (anode). Etching occurs at the portion of the wire that is encircled by the upper electrode. When the tungsten wire becomes thin, the lower part of the wire falls down and at this very moment, the current switches to zero. No circuit breaker is needed and no more etching is done at the upper part of the tungsten wire, which serves as the tip.

Our tip etching procedure is described step by step. The

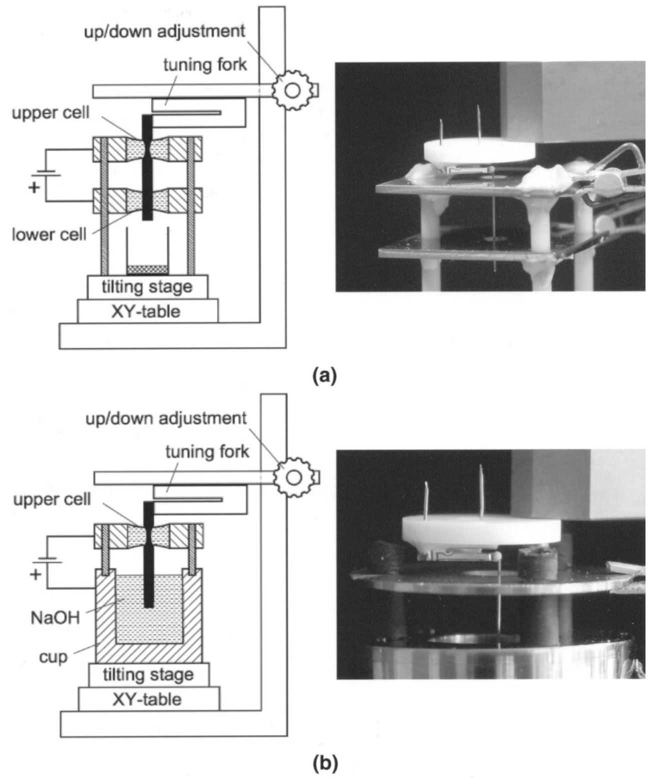

FIG. 3. Illustrated are two means of using the double lamellae dropoff etching technique. The positive pole of the dc supply is fed to the lower portion of the tungsten wire through electrolyte solution. This connection is made either by passing the wire through a second ring electrode containing the electrolyte solution (a) or by immersing the wire in a solution held in a conductive beaker (b).

tuning fork and wire assembly is attached to a translator with the free end of the tip wire to be etched pointing down. It is then lowered toward the stainless steel tip etching plates so that the tungsten wire passes through the center of the two concentric holes. The holes are tapered from 4 to 2 mm over a thickness of 1 mm. Care is taken to ensure that the wire is as vertical as possible and well centered in the two holes. Tilt stages are used on both the translator that lowers the tuning fork assembly and on the etching plates for alignment. By keeping the wire vertical and centered in the holes, there is less opportunity for the wire to tilt toward the edge of the bottom hole and get caught at the edge due to the solution surface tension and then not drop properly.

The etching height is set such that the tuning fork does not touch the top stainless steel plate and far more importantly such that any silver epoxy on the tungsten wire will not be immersed in the solution that will be placed into the hole. The silver in the epoxy will severely affect the electrochemical reaction and adversely influence the etching of the tungsten. A drop of freshly prepared 3 M NaOH solution is placed in the two holes so that the solution fills the small cavity and is not overflowing on the bottom or top of the stainless steel plates. We are using 3 M NaOH solution instead of the very often used 2 M to ensure proper etching during the entire etching period. The increase in concentration compensates for the smaller volume in which the reaction occurs as well as any loss of solution from the small

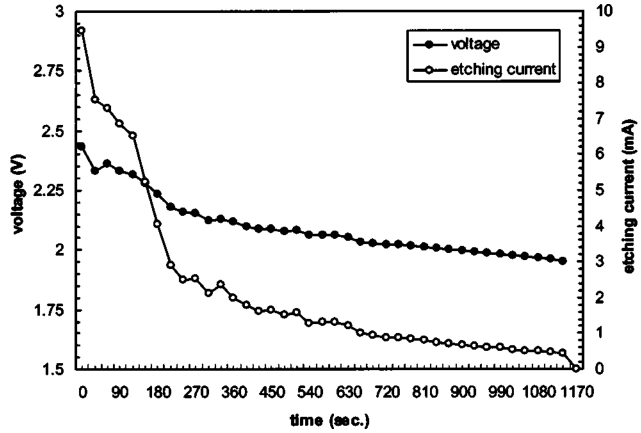

FIG. 4. Etching current and voltage across the upper electrolytic cell as a function of time.

holes from seeping on to the plates. The reaction is started with 4 V dc positive bias applied to the bottom plate. Etching current is measured on an ammeter in series from the top plate to the negative terminal on the dc power supply. At the start of reaction, the etching current starts at ~10 mA and drops as the wire is etched. The wire finishes etching in ~10–15 min and the bottom portion of the wire drops when the tip etching current is <1 mA. Once the tip is etched the assembly is rinsed in distilled water and then the tip is checked with an optical microscope. Finally, the Macor plate with the tuning fork and etched tip attached is mounted to the tripod piezo scanner of the STM and the system is evacuated to minimize oxidation of the etched tungsten.

The alignment of the tungsten wire has to be very carefully adjusted through the centers of the two holes of the electrodes to avoid lateral forces caused by surface tension.

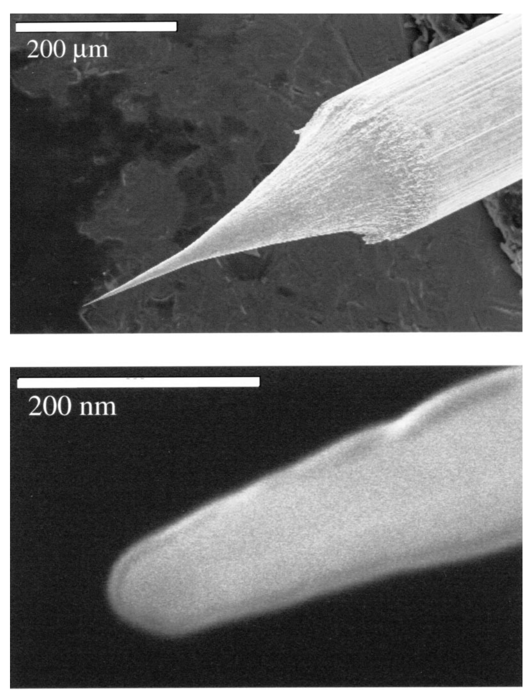

FIG. 5. Scanning electron microscope image of a tip etched by the double lamellae dropoff etching technique.

To make this process easier without giving up the principle of the double lamellae dropoff etching technique, one can replace the lower ring electrode by a conducting cup [Fig. 3(b)]. In that case, we are using an electrically insulated stainless steel cup on which the upper electrode is rested. The whole experimental setup is shown in Fig. 3(a). To monitor the etching parameters, the current through the cells and the voltage across the upper electrolytic cell have been measured during the etching process (Fig. 4). The potential of the wire against the cathode is determined by the ratio of the conductivities of the upper and lower electrolytic cells. It starts at ~50% of the supply voltage and drops slightly during the etching process, indicating an increase of conductivity at the upper cell and a decrease at the lower cell. The current falls nearly linearly with time and drops to zero when the lower part of the wire falls down. A scanning electron microscopy image of a typical tip etched with this procedure is shown in Fig. 5. With this technique we were able to make sharp tips in a reproducible manner.

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