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Dynamic electrochemical-etching technique for tungsten tips suitable for multi-tip scanning tunneling microscopes

Rei Hobara,* Shinya Yoshimoto, and Shuji Hasegawa
Department of Physics, School of Science, The University of Tokyo, Hongo 7-3-1, Bunkyo-ku, Tokyo, 113-0033, Japan

Katsuyoshi Sakamoto
Department of Electronic Engineering, The University of Electro-Communications, Chofugaoka 1-5-1, Chofu-shi, Tokyo, 182-8585, Japan
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We present a method to prepare tungsten tips for use in multi-tip scanning tunneling microscopes. The motivation behind the development comes from a requirement to make very long and conical-shape tips with controlling the cone angle. The method is based on a combination of a "drop-off" method and dynamic electrochemical etching, in which the tip is continuously and slowly drawn up from the electrolyte during etching. Its reproducibility was confirmed by scanning electron microscopy. Comparison in tip shape between the dynamic and static methods was shown. [DOI: 10.1380/ejssnt.2007.94]

Keywords: Scanning Tunneling Microscopy; Multi Probe; Tip; Tungsten; Electrochemical etching

I. INTRODUCTION

Since the invention of field ion microscope (FIM) by Erwin W. Müller in 1937 [1], the fabrication techniques of atomically sharp tips have been actively investigated. The invention of scanning tunneling microscope (STM) by Gerd Binnig and Heinrich Rohrer in 1981 [2] has further promoted the investigation. Sharp and hard tips are now an important component of many of scanning probe microscopes (SPM) [3–11]. The size, shape, physical and chemical identity of the tip apex influence not only the resolution of microscopes but also the interpretation of images and data.

Huge number of works on the fabrication of sharp tips have been performed and several techniques have been developed, such as grinding [2, 12], cutting [13–16], mechanical pulling [17–27], chemical or electrochemical etching [28–71], field evaporation or other field-induced methods [72–76], beam deposition [77–83], ion milling [15, 84–94], and others [95].

Among these methods, the etching technique is most widely used as a fast, cheap, convenient and reliable method and also as a pre-treatment method for further fine fabrications such as gluing carbon nanotubes on the metal tip [96–101]. One of the common and reliable methods is so called a "drop-off" method, in which etching occurs at the air-electrolyte interface, causing the portion of wire immersed in the solution to "drop off" when its weight exceeds the tensile strength of the etched wire metal neck [28–41, 54–57].

Tips of different kinds of materials can now be made by the etching methods [41–53]. Especially, electrochemical etching of a tungsten wire is widely used for STM tips [54–66]. Thanks to contributions from many researchers, sharp tungsten tips having around 20-nm diameter at the apex can now be acquired routinely [64–66].

In recent years, optical fiber tips for near-field scanning optical microscopes have attracted much interest. There are also several kinds of methods in the fabrication of fiber probes [12, 17–27, 67–71]. Among them, a dynamic etching method has advantages in reliability and controllability of the taper angle of probe apex [69–71]. But the fiber probes usually do not need to be atomically sharp at the apex.

Since tips and probes are essential for the SPM, a new fabrication technique of probes suitable for a new kind of SPM has to be developed in some cases [8, 10, 62, 63]. We have developed four-tip STM, which has four independently driven STM tips [102, 103]. Since the main aim of this instrument is to measure electrical conductivity by four-point probe method in nanometer-scale region using plurality of probes, the spacing between the tips is required to be as small as possible. Although tungsten tips made by usual etching techniques are sharp only at the apex, which is enough for single-tip STM, its short concave shape in macroscopic scale sometimes becomes an obstacle to achieve the small spacing between tips in multi-tip STM. A conical shaped tip with a small cone angle is needed for the purpose.

In this short report, we present a fabrication technique of metal tips suitable for multi-tip STM aiming nanometer scale probing. Our method is a combination of a drop-off method and a dynamic electrochemical etching method. The dynamic etching enables one to make the whole shape of tip conical with a controlled cone angle, and the drop-off method ensures the sharpness at the apex. The reproducibility and the reliability are as high as usual drop-off or dynamic chemical etching technique.

II. EXPERIMENTAL

The experimental setup is sketched in Fig. 1(a). A coarse mechanical positioner (B) and a fine stepper motor stage (F) were placed on a simple vibration isolator stage that was made of a heavy stainless steel plate on thick rubbers. A tip was etched from a polycrystalline tungsten drawn wire in diameter of 0.20 ∼ 0.55 mm. The wire was cut into pieces about 30 mm long, and then ultrasonically cleaned by aceton prior to etching. The

*Corresponding author: rei@surface.phys.s.u-tokyo.ac.jp

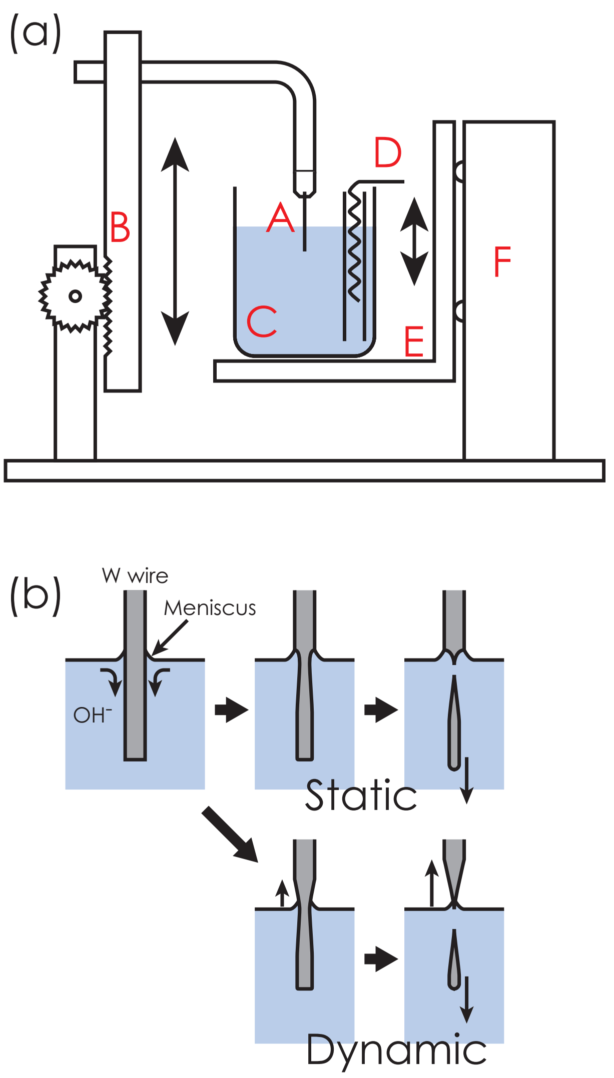

FIG. 1: (a) A schematic drawing of the experimental setup for the dynamic electrochemical etching. Tungsten wire (A) is mounted at the top of a coarse positioner (B). The wire is immersed into an electrolyte solution (C) in a beaker, and etched between a counter electrode (D) placed in a glass tube. The whole of electro cell are set on an optical stage (E) connected to a piezo stepper motor (F). During the etching, the optical stage moves downward slowly and continuously, and therefore the tip is slowly pulled off from the electrolyte. (b) Schematic drawings of etching process around the air-solution interface. The etching occurs most rapidly below the meniscus due to the convection of OH^- ion. The dynamic etching method makes a long conical tip while the static etching method makes a short tip.

tungsten wire (A) was fixed at the top of the mechanical positioner (B) and dipped 7 to 10 mm into the electrolyte (C) in a beaker. The beaker was placed on an optical z stage (E), which was connected to a stepper motor (F). For dynamic etching, the stepper motor was continuously driven by an etching controller to lower the z stage, and thus the wire was pulled off from the electrolyte gradually during the etching. We usually chose about 2 to 10 μm/s for the speed of pulling off, which could be also controlled in the range from 0.01 μm/s to 100 μm/s.

The etching voltage and the shut-off current were controlled by a conventional constant voltage and shut-off control circuit [37–41]. When the wire was almost cut off by etching and the current quickly fell below the pre-set limit, the circuit automatically shut off the etching voltage. The shut-off time, which is important for controlling the sharpness of tip apex, was set to be less than 100 ns.

The simplified process of the anodic oxidation of metal tungsten in a KOH or NaOH solution can be expressed by the following two steps [104–106]:

$$W + 6OH^- \rightarrow WO_{3(S)} + 3H_2O + 6e^- \quad (1)$$

$$WO_{3(S)} + 2OH^- \rightarrow WO_4^{2-} + H_2O \quad (2)$$

First, by OH^- ions and the etching potential, the metal tungsten is oxidized to tungstate (WO_3) (reaction (1)). The production rate of tungstate is proportional to the etching current. Next, tungstate reacts with OH^- again, dissolving into the solution (reaction (2)). The reaction (2) does not depend on the current or voltage, and proceeds spontaneously. If proper voltage is applied, the rate-controlling reaction becomes (2).

We applied 3 to 10 V to process the electrochemical reaction. This etching voltage was determined by potentiostatic polarization curves [53, 54, 76, 88]. The final tip shape or etching speed was kept constant in this voltage range. The voltage lower than this range made tips ragged because local non-uniformity of the potential affected the speed of etching locally. Higher voltage resulted in the formation of a large quantity of a surface oxide. Since, after the etching, the oxidation in air must occur, further processing in vacuum is needed in any way for oxide free tips for use of STM and conductivity measurements in vacuum.

Since only the reaction (2) affects the etching rate in our etching voltage range, the concentration of solution is only the parameter to control the rate of etching. As a result of some trials, we decided to use 2.5 N KOH or NaOH solution for etching the tungsten wires in 0.20 $\sim$ 0.35 mm diameter. In case of thicker wires such as 0.55 mm in diameter, the solution of 10 N concentration was used.

We used an arbitrary shaped Pt wire (D in Fig. 1(a)) in a glass tube as a counter (cathode) electrode. In some etching methods, surface tension or meniscus at the cathode plays an important role in the etching process [44, 63, 65]. The active use of surface tension at the cathode increases the degree-of-freedom of etching, together with troublesome complexity. We tried various sizes and shapes of cathodes (rings, cylinders, plates, rods, etc) at various positions (near or far from the tip, at the surface or bottom of electrolyte) to optimize the shape and the reproducibility of the tip. We have confirmed that the shape and position of cathode hardly affect the shape of etched tip because the electric field is high enough everywhere around the anode in the electrolyte. Rather than the cathode itself, bubbles evolving at the cathode are a disturbance to make high quality tips with good reproducibility. Finally, we placed the counter electrode far away from the tip and surrounded it with a glass tube to confine the bubbles inside the tube.

Figure 1(b) illustrates processes of dc etching with and without pulling up the tip from the electrolyte. Because the convection of ions provides new hydroxide at the meniscus and surrounds tips with WO_3, the etching rate is the maximum just below the air-solution interface. So, in principle, the dc drop-off method produces two tips simultaneously: the upper tip in the air and the lower tip in the solution. However, we use the upper tip only. Although the lower tip made by either the static method or the dynamic method has a small cone angle [29, 30, 58, 65], it is not suitable for our multi-tip STM application. The wire diameter of lower tip becomes much smaller than the original wire because it is totally immersed in the electrolyte during the etching process. The total tip length in the electrolyte cannot be enough long because the weight of the lower tip affects the drop-off process. Together with the difficulties to collect the dropped tip in the electrolyte, these disadvantages made us give up using the lower tip.

After the etching process, the tips were rinsed immediately for 20 sec in hot (~ 95 °C) deionized water. This process significantly decreased the oxides sticking on the tip surface.

III. RESULTS AND DISCUSSION

Figure 2(a) is a SEM image of four W tips made by the present method and installed in our multi-tip STM [102, 103]. The inset show another SEM image of tips made by the usual static drop-off etching method. It clearly shows the difference in tip shape between the static etching and the dynamic etching methods. The dynamic-etched tips have very long conical shapes, while the static-etched tips are sharp but short and in concave shape. The static-etched tips have ledges derived from the meniscus, which is sometimes an obstacle for bringing the tips close to each other, as shown by a red circle in the inset. Since, on the other hand, the dynamic-etched tips have no such ledges, there are no obstacles to approach a plurality of tips: only the radius of apex determines the minimum distance between the tips. Thus, though the sharpness at the apex of static-etched tips is enough for usual single-tip STM, it is obvious that the static-etched tips are not appropriate for bring multi tips in a very small region. Since the controllability of probe spacing is an important parameter in multi-probe measurements, the dynamic-etched tips are essential for multi-tip STM.

Figure 2(b) is magnified images of the apex of the dynamic-etched tip with and without (inset) hot-water rinse after the etching. By the SEM, we estimated the radius of the tip apex is about 30 nm, which is similar to that of the static-etched tips we usually made. Without hot-water rinse, the surface looks very rough due to contamination (inset). This contamination disappeared when we anneal the tip over 800 °C. Low voltage etching (< 1.8 V) did not make the contamination. We guess that the contamination is a thick layer of tungsten oxides due to the high concentration of solution and the high electric field around the tip [38, 54, 57, 63, 106]. This contamination is easily removed from the tip by hot-water rinse.

A tip fabricated by the low-voltage (about 0.5 V) static etching is seen in Fig. 2(c). This method barely enables one to make a conical shaped tip without using the dynamic etching technique if one has a great patience because it takes quite long time for etching (about 60 min for our case). The tip surface, however, becomes quite ragged and the tip apex is frequently collapsed because of local

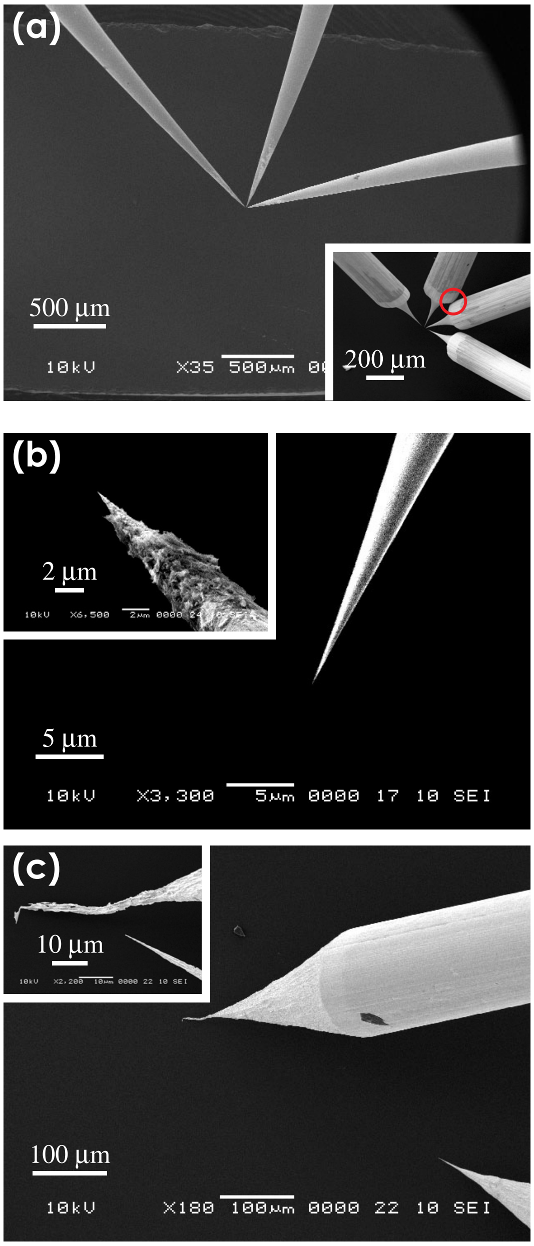

FIG. 2: (a) SEM image of the tips fabricated by the dynamic etching method. Inset shows the tips made by the static etching. A red circle indicates an accidental contact between the tips. (b) A close-up image of the tip apex fabricated by the dynamic etching method with hot water rinse. Inset is a tip without rinse. (c) A tip made by the static-etching method with a low voltage (0.5 V) and it apex (inset). Rugged surfaces can be seen.

non-uniformity of surface potential. No reproducibility and reliability are expected by this method. Since the dynamic etching method uses a higher voltage, the tip shape is stable and the fabrication is much faster (usually it takes only a few tens of minutes).

We have fabricated over several hundreds of tips using this etching method, and confirmed that the tip cone angle is controllable by changing the speed of pulling off the wire from the electrolyte solution. The success rate in making the sharp tips having a radius smaller than 50 nm at the apex is over 80 %, which is as high as by the usual static etching method.

IV. CONCLUSION

We show a method to prepare long conical-shape tungsten tips suitable for multi-tip STM. This method uses a dynamic etching technique and a drop-off method. The tip apex is as sharp as those made by the static etching. We can control the cone angle in macroscopic shape of tip by changing the speed of tip pulling-up from the electrolyte solution. This small cone angle tips without any ledges is suitable for applications to multi-probe measurements in nanometer scale.

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