The art of electrochemical etching for preparing tungsten probes with controllable tip profile and characteristic parameters

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Using custom made experimental apparatus, the art of electrochemical etching was systematically studied for fabricating micro/nano tungsten probes with controllable tip profiles of exponential, conical, multidiameter, and calabashlike shapes. The characteristic parameters of probe including length, aspect ratio, and tip apex radius could also be well defined. By combining of static and dynamic etching, the conical-shape probe with length up to several millimeters, controllable tip apex radius, and cone angle could be fabricated. In addition, by continuously lifting the tungsten wire up during the electrochemical etching with different speeds and distances, the multidiameter shape probe could be fabricated. Finally by controlling the anodic flow, the multiple "neck-in" could be realized creating a calabashlike probe. The aspect ratio of probes depends on (i) the effective contact time between the surrounding electrolyte and the wire, (ii) the neck-in position of immersed tungsten wire. Under the optimized etching parameters, tungsten probes with a controllable aspect ratio from 20:1 to 450:1, apex radius less than 20 nm, and cone angle smaller than 3° could be achieved. The technique is well suited for the tungsten probe fabrication with a stabilized stylus contour, ultra-sharp apex radius, and high production reproducibility. The art for preparing microprobes will facilitate the application of such microprobes in diverse fields such as dip-pen nanolithography, scanning probe microscopy, micromachining, and biological cellular studies. *© 2011 American Institute of Physics*.
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I. INTRODUCTION

The demand for microprobes has been growing in diverse fields such as nanolithography,[1] scanning probe microscopy,[2–4] micromachining,[5] and biological cellular studies.[6] Among the common methods used to produce microprobes, electrochemical etching is the most practical method for fabricating probes with desired quality, reproducibility, and reliability. The electrochemical etching procedure is dominated by various etching parameters such as applied voltage, immersion depth of wire, size and position of cathode, and electrolyte concentration. Different etching procedures produce different kinds of probes.[7] Recent studies were also carried out that by using electrochemical method to investigate high quality micrometallic probes fabrication. Kim *et al.* investigated the effects of the magnitude of an attached mass at the end of the immersed wire on the tip shape.[8,9] Sun *et al.* reported the optimum conditions for etching long and thin probes for AFM application.[10] Hobara *et al.* presented a method of combination of the drop-off method and dynamic etching for achieving long and conical-shape probes.[11]

The electrochemical etching method is so far the easiest and a fast method to obtain cheap and reliable metallic probes. Most laboratories or research groups have developed their own experimental conditions to prepare adequate probes, and methods to verify the probes suitability. However, the quality of the probes produced is highly dependent on the operators' skills and experience. Moreover, a systematic study to determine the best condition for fabricating micro/nanoprobes with the desired tip profiles as well as the characteristic parameters of length, aspect ratio, and tip apex radius is still lacking.

In this work, we have developed a well controlled electrochemical etching process to facilitate the fabrication of tungsten probes with the desired tip profiles and parameters. The micro/nanoprobes, profiles of exponential, conical, multidiameter, and calabashlike shapes could be fabricated. The characteristic parameters of probe including length, aspect ratio, and tip apex radius could also be well defined. The proposed art of electrochemical etching technique and process are experimentally confirmed to have advantages for the tungsten probe fabrication of the stabilized stylus contour, ultra-sharp apex radius, and high production reproducibility. It opened the way of batch customization of high quality metallic probes.

II. EXPERIMENTAL

A. Electrochemical etching technique

As shown in Fig. 1(a), surface tension of the aqueous solution causes a meniscus to form around the tungsten wire once it is placed into the electrolyte. The electrochemical etching involves the anodic dissolution of tungsten in the aqueous base, therefore anodic flow was driven and vortex was generated in the meniscus.[12] As a result, the electrochemical etching in this area was dramatically enhanced. The electrochemical etching reaction involves the anodic dissolution of tungsten in the alkaline solution which is most commonly

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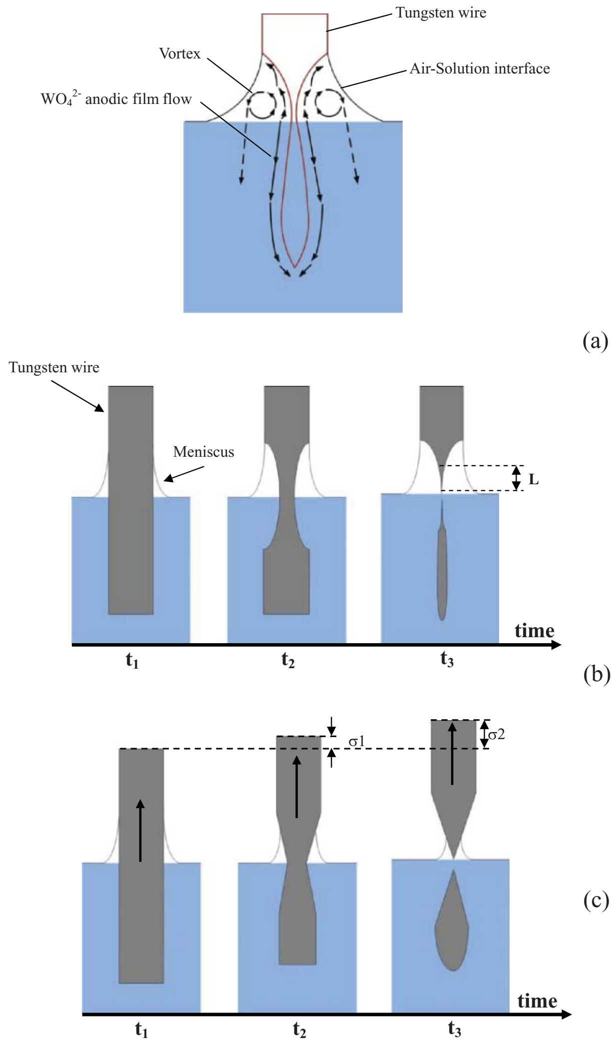


FIG. 1. (Color online) Schematic views of (a) the detailed anodic film flow during electrochemical etching of tungsten wires, (b) static electrochemical etching, and (c) dynamic electrochemical etching. The dynamic electrochemical etching is a combination of static etching with the lifting-up process, in which lifting-up speed and distance define the final shape of the fabricated probes.

used for tip preparation: NaOH or KOH. The etching process occurs at the surface of the wire inside the meniscus and below the nominal air/electrolyte interface when a positive voltage is applied to the tungsten wire. The respective and overall electrochemical reactions at the electrodes can be expressed as[13]

Cathode (negative polarity):

$$6H_2O + 6e^- \rightarrow 3H_2(g) + 6OH^-, \tag{1}$$

Anode (positive polarity):

$$W(s) + 8OH^- \rightarrow WO_4^{2-} + 4H_2O + 6e^-, \tag{2}$$

Overall:

$$W(s) + 2OH^- + 2H_2O \rightarrow WO_4^{2-} + 3H_2(g). \tag{3}$$

Although electrochemical etching can take place over the entire surface of immersed tungsten wire, the reaction near the surface of electrolyte solution is crucial for the purpose of fabricating probe with sharp tip. The formation of a meniscus of solution around the tungsten wire plays an important role in determining the final shape and aspect ratio of the probe.[14] Since the concentration of OH^- ions near the top of the meniscus is lower than that of the bulk solution, etching rate decreases along the meniscus. On the other hand, the etching of wire produces soluble tungsten anions that flow down on its surface. This layer of tungstate anions over the immersed tungsten wire actually hinders the etching of the immersed wire below the meniscus, causing the etching rate to be reduced, for the lower portion of the wire. As a result, a "neck-in" phenomenon occurs in the close vicinity of the bottom of the meniscus, where etching rate is the highest. When the tensile strength cannot sustain the weight of the immersed portion of the tungsten wire, a "drop-off" appears. The tungsten probe with sharp tip could then be eventually fabricated at the breaking point.

The electrochemical reaction was caused by the gradient of the flow thickness along axial direction and showed extremely violent in the meniscus area. Since the gradient of the flow thickness and streamline of the anodic flow define the profile and tip apex radius of the probe, it is possible to fabricate the probe with different tip profiles, shapes, and aspect ratios by controlling the moving direction and trail of the anodic flow.

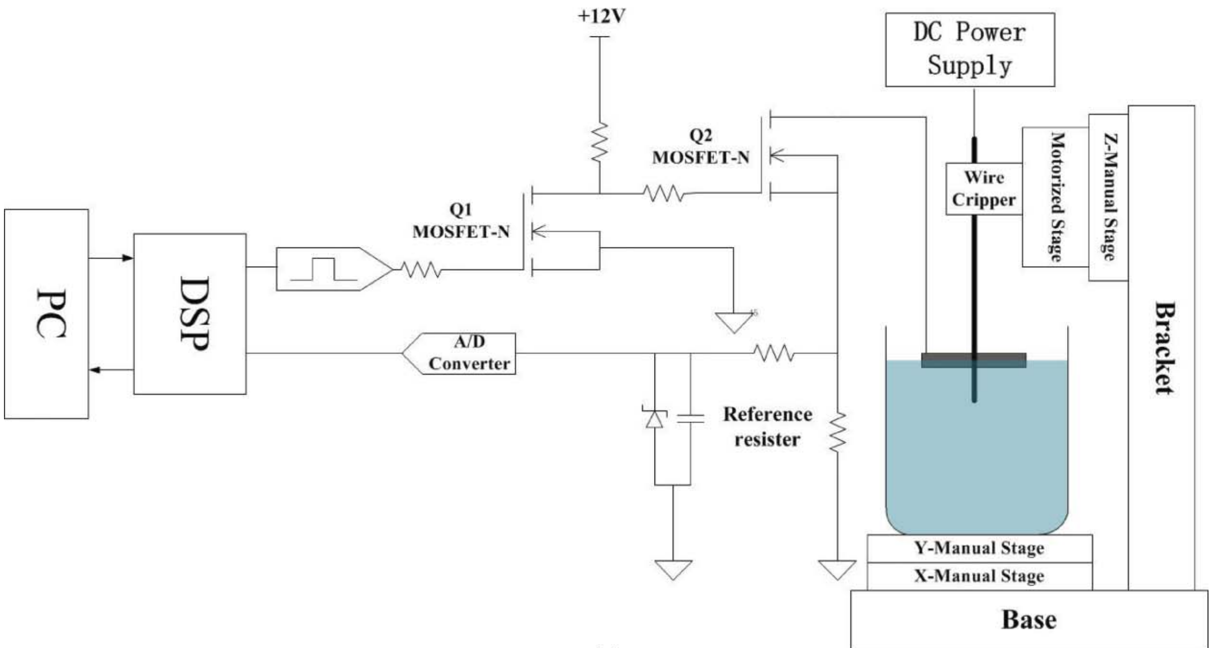
There are two methods to achieve the anodic flow control, namely static [Fig. 1(b)] and dynamic [Fig. 1(c)]. Both of them are meniscus-based methods. The meniscus acts on an original position in static etching to get an exponential shaped probe; while during dynamic etching, the meniscus imposes the effect to the tungsten wire during the entire lifting-up process. During the lifting-up process, the meniscus drops down continuously due to the thinning of immersed wire, and this mechanism creates the long and cone shaped probe.

By controlling the lifting speed and distances of $\sigma 1$, $\sigma 2$, various shapes and radial dimensions of probes can be customized.

B. Experimental apparatus for electrochemical etching

A custom made experimental setup is schematically shown in Fig. 2, which facilitate proper control of the electrochemical etching. The setup consists of a control unit, a 99.95% pure tungsten wire with diameter of 250 μm (The Nilaco Corporation, Japan) mounted with adjustable vertical positioning and a platinum ring with diameter of 12.0 mm serving as the cathode. A glass beaker was used to contain 50 ml of KOH as the electrolyte, whose concentration varied from 1.0 to 3.0 mol./L for the different experiments. Vertical coarse and fine positioning of the tungsten wire holder in the z-direction are achieved by a precision motorized stage (M-112, PI, Germany), which has a revolution of 0.007 μm and a travel range of 25.0 mm. Horizontal positioning of the tungsten wire inside the platinum ring is adjusted by a manual XY-stage to enable the immersed wire to be positioned at the center of the platinum ring.

A dc power supply (GPS-1850D, GWinstek, Taiwan, China) with range of 0–18.0 V, resolution of 0.1 mV was



(a)

(b)

FIG. 2. (Color online) The experimental apparatus for electrochemical etching with controllable tip profile and characteristic parameters. (a) Schematic view of the apparatus, (b) apparatus photo during the electrochemical etching.

applied to initiate the electrochemical reaction. A compact digital signal processing (DSP) based control circuit has been custom made for high speed data acquisition and cutting-off the control of the etching current. From our previous work,[7] we have noted a sudden current drop-down that could last for several milliseconds, in which the decreasing amplitude changed dramatically, the etching current cut-off at this instant, the probe with sharpest tip eventually results.

The variation of the etching current is monitored by a reference resistor and acquired by the DSP after RC low-pass filter and analog/digital converter. When there is a sudden drop-down of the etching current, the DSP would emit a triggering signal sequentially through the MOSFET transistor Q1 and Q2 to cut off the etching circuit loop for stopping the etching process instead of cutting off the power supply. The novel use of this circuit design has been testified to be with faster response and higher reliability which are very important in sharp tip fabrication.

III. PREPARING PROBES WITH CONTROLLED TIP PROFILE

A. Tip etching for exponential shape probe with controllable aspect ratio

Probe with exponential shape is preferred for quick and stable profile measurement during scanning. In addition, its good dynamic characteristic dominates the stability and response time of scanning tunneling microscope (STM) measuring system. Moreover, probes with various aspect ratios are the prerequisite to complex microstructures measurement, particularly for high aspect ratio microstructures measurement. Therefore, techniques for fabricating probe not only with well defined exponential shape, but also with controllable aspect ratio are commonly required.

Figure 3 shows the exponential shape probes with controllable aspect ratio from 20:1 to 450:1 by applying the newly developed electrochemical etching set-up and

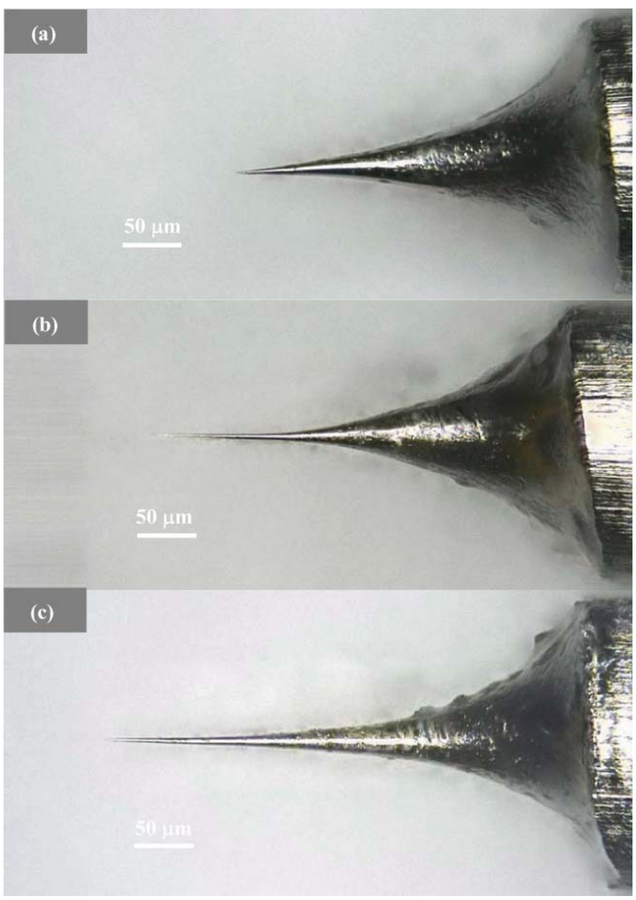


FIG. 3. Images of the fabricated exponential shape probe under different etching conditions: (a) etching time 950 s, voltage 5.0 V, electrolyte concentration 2.5 mol./L, immersed depth 1.0 mm, aspect ratio 20:1; (b) etching time 1200 s, voltage 4.5 V, electrolyte concentration 2.0 mol./L, immersed depth 800 μm, aspect ratio 130:1; (c) etching time 1620 s, voltage 3.0 V, electrolyte concentration 1.0 mol./L, immersed depth 600 μm, aspect ratio 450:1.

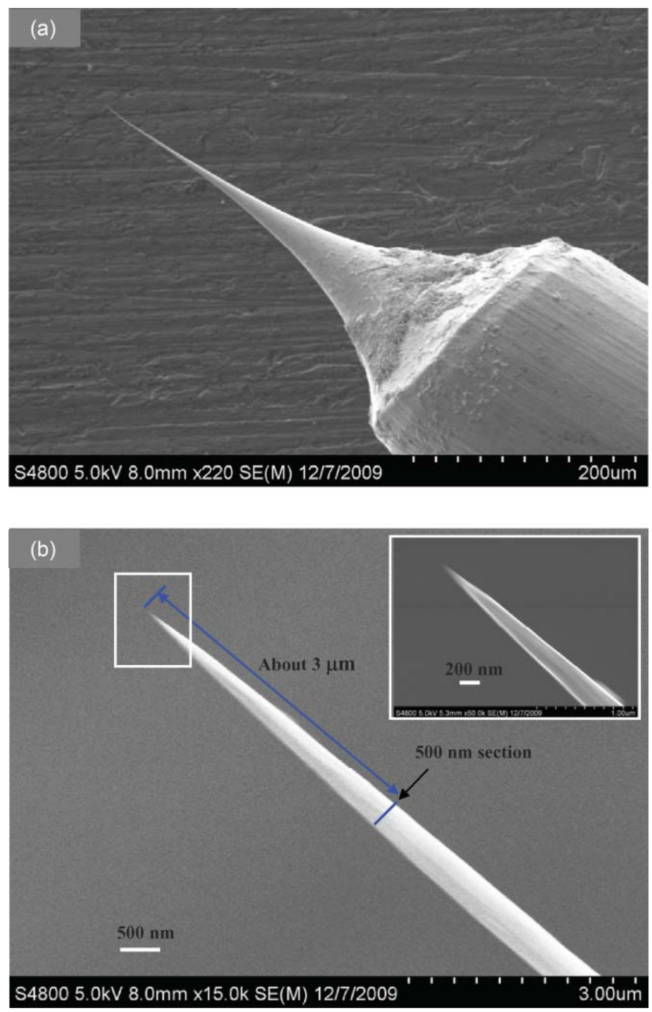


FIG. 4. (Color online) Scanning electron microscope (SEM) images of the fabricated probe under the optimized experimental condition which is suitable for high aspect ratio probe of voltage 3.0 V, electrolyte concentration 1.0 mol./L, immersed depth of 600 μm. (a) the finally patterned probe with high aspect ratio nanometric tip; (b) the detailed characteristics of the tip. The inset shows its radius and conical angle, $\times$50 000.

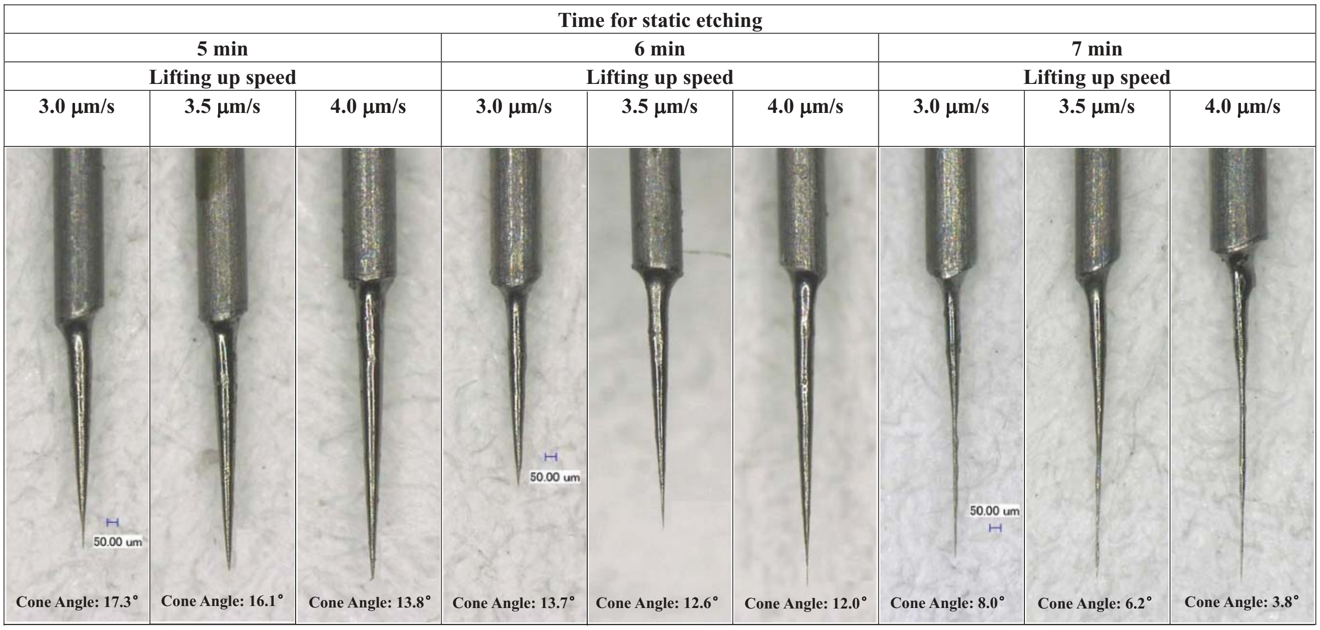


FIG. 5. Probes fabricated by the combination of static and dynamic electrochemical etching. Initially, the static etching was applied, and after 5, 6, and 7 min respectively, dynamic etching was used to achieve long and conical shape probes. The tungsten wire was lifted up at the velocities of (1) 3.0 μm/s, (2) 3.5 μm/s, and (3) 4.0 μm/s.

techniques. Figure 4 shows the SEM images of the customized exponential shape tungsten STM probe with aspect ratio of 300:1. It can be found that its profile can be well defined and complies well with exponential contour and the shape is symmetrical. The radius of the tip is less than 20 nm and conical angle is smaller than 3.0°. From the 500 nm section to the tip apex, there is still 3 μm long.

B. Probe etching for controllable conical shape

Figure 5 shows the probes with controllable conical shapes. First, static etching was applied to the immersed wire for 6, 7, and 8 min, as shown in Fig. 5, respectively. This is followed by dynamic etching to achieve the long and conical shape probes by controlling the motorized stage (in Fig. 2) at different velocities of 3.0, 3.5, and 4.0 μm/s. The final shape of the fabricated probe was produced by combining both static and dynamic etchings.

Referring to the Fig. 5, conical angle of the probe is inversely related to the velocity of lifting up motion. It also clearly showed that if static etching lasted longer, the aspect ratio of the probe would be higher, as it offered longer time for the immersed tungsten wire to be etched. As shown in Fig. 5, the aspect ratio up to 60:1 could be achieved. In order to obtain long and conical shape probe, sufficient time is needed for dynamic etching by pulling the tungsten wire out toward the air–solution interface before the drop-off phenomenon occurs.

C. Tip etching for controllable multidiameter shape

The multidiameter shape probes were fabricated and shown in Fig. 6. By continuously lifting up the tungsten wire during the electrochemical etching process at different speeds and different step distances σ, the multidiameter shape probes could be customized.

By lifting up the immersed wire in steps toward the flat air–electrolyte interface, the meniscus plays effect along the part which is lifted. The number of the terraces is equal to the number of times the wire is lifted. As that shown in Fig. 6, it took four "lifting-up" procedures to get the corresponding probes, respectively. It is worth pointing out that the lifting-up technique could only define the appearance, while the tip profile, length (L, shown in figure), and radius were solely dominated by the final static etching process.

The well defined multidiameter shape probe will facilitate the deep holes fabrication by applying electrical discharge machining technology, precision drilling, other applications

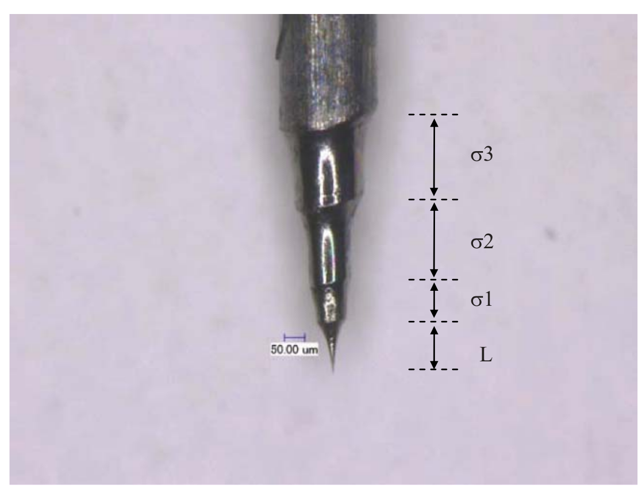


FIG. 6. The image of multidiameters shape probe that fabricated by four lifting-up procedures. The tungsten wire was lifted up at the velocity of 10.0 μm/s.

such as nanomanipulation, biological cellular studies, and so on.

IV. RESULTS AND DISCUSSIONS

A. Key factors influencing on aspect ratio and tip apex radius of probe

The imaging capability and resolution of STM are highly dependent on the tip profile, apex radius as well as aspect ratio.[8] Sharp apex and contour could be achieved by most probe fabrication techniques. Nonetheless, controlling the aspect ratio of the probe is extremely difficult to be realized even for the electrochemical etching method. It is therefore necessary to investigate the three basic working parameters of electrochemical etching, i.e., etching voltage, electrolyte concentration, and immersion depth and their contribution to aspect ratio.

The relationship between etching voltage and aspect ratio as well as the tip apex radius was shown in Fig. 7(a). The impact of the initial electrochemical etching voltage to be varied from 2.8 to 6.0 V was determined to be the most proper for both probe quality and efficiency. With increasing of voltage, the etching rate was enhanced and the effective contact time between the surrounding electrolyte and tungsten wire was decreased. Hence the neck-in was prematurely formed and the remaining part would break off before the whole immersed part become thin enough. Therefore the aspect ratio of probe deceases with the increasing etching voltage. In the range from 2.8 to 4.5 V, the aspect ratio of probe demonstrated a decreasing trend. Once the voltage exceeds 4.5 V, electrochemical etching would be saturated and the effect of the etching voltage was not so evident. Another important outcome that could be deduced from Fig. 8 was that the tip apex radius shows no direct relationship with the etching voltage.

Electrolyte concentration ranging from 1.0 to 3.0 mol./L was investigated and the relationship between the tip apex radius and electrolyte concentration is as shown in Fig. 7(b). There was no evident relationship between tip apex radius and electrolyte concentration, whereas high aspect ratio of tips could be achieved by using lower electrolyte concentrations. As shown in our previous work, the electrolyte concentration range between 1.0 and 3.0 mol./L was proved in our previous work to be the most suitable for electrochemical etching of tungsten wire.[7]

Figure 7(c) is the relationship curve of the immersion depth and aspect ratio as well as the tip apex radius. It was found that the immersion depth could change the electrical field distribution during the electrochemical etching process and cause the subsequent neck-in position variation. Consequently, the aspect ratio of the probe changes along with the neck-in position variation. In our experiments, it was found that increasing immersion depth would lead to lower aspect ratio. On the contrary, for the purpose of obtaining sharp apex tips using tungsten wire of 250 μm diameter, immersion depth less than 1.0 mm is recommended. For the longer portion that inserted into the solution, the neck-in will break off before the tip matures due to the heavier weight and the swing motion of the lower portion.[13]

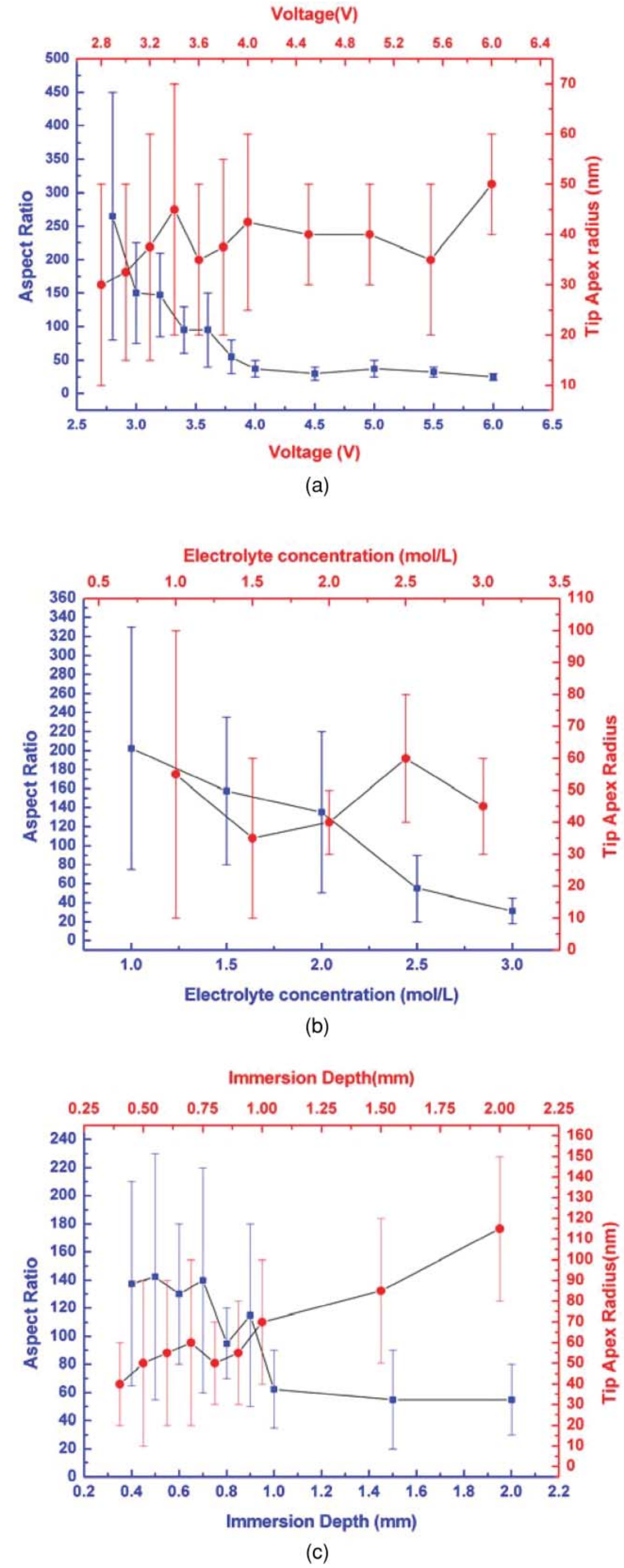


FIG. 7. (Color online) (a) The relationship of aspect ratio as well as tip apex radius with applied etching voltage during the electrochemical etching under the experimental condition of electrolyte concentration of 1.5 mol./L, immersed depth of 600 μm. (b) The relationship of aspect ratio as well as tip apex radius with electrolyte concentration during the electrochemical etching under the experimental condition of applied etching voltage of 3.3 V, immersed depth of 600 μm. (c) The relationship of aspect ratio as well as tip apex radius with immersion depth during the electrochemical etching under the experimental condition of applied etching voltage 3.3 V, electrolyte concentration of 1.5 mol./L.

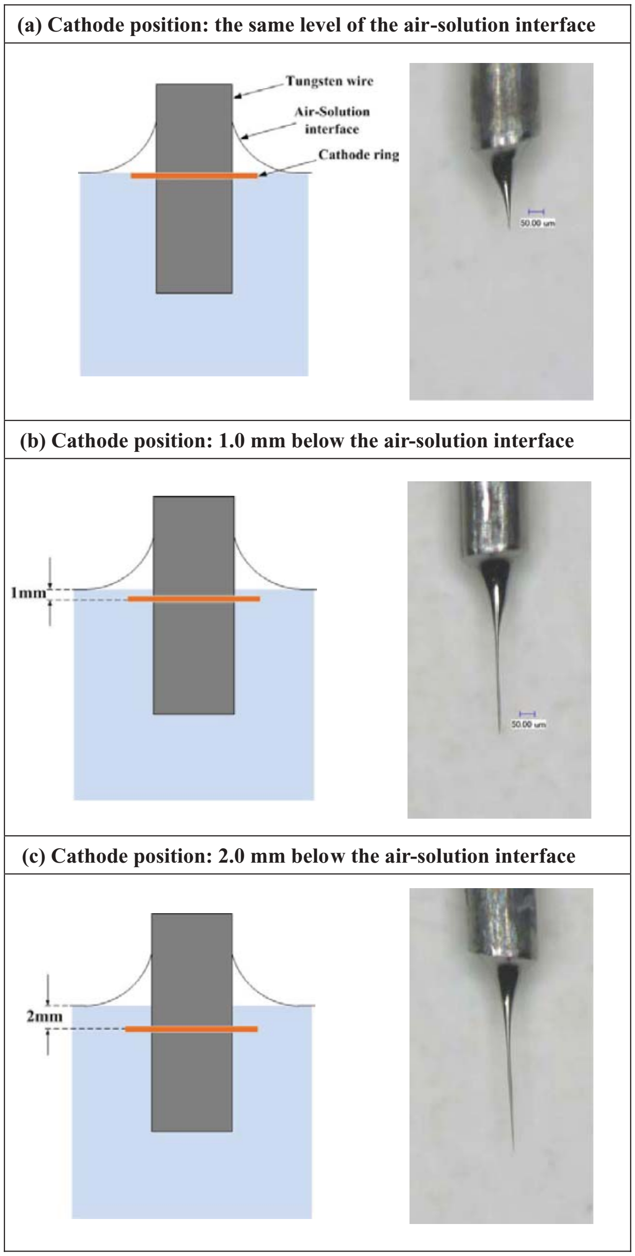


FIG. 8. (Color online) The effect of the cathode (platinum ring) position and its contribution to the final shape of probe (a) cathode position is at the same level of air–solution interface; (b) cathode position is 1.0 mm below the air–solution interface, and (c) cathode position is 2.0 mm below the air–solution interface.

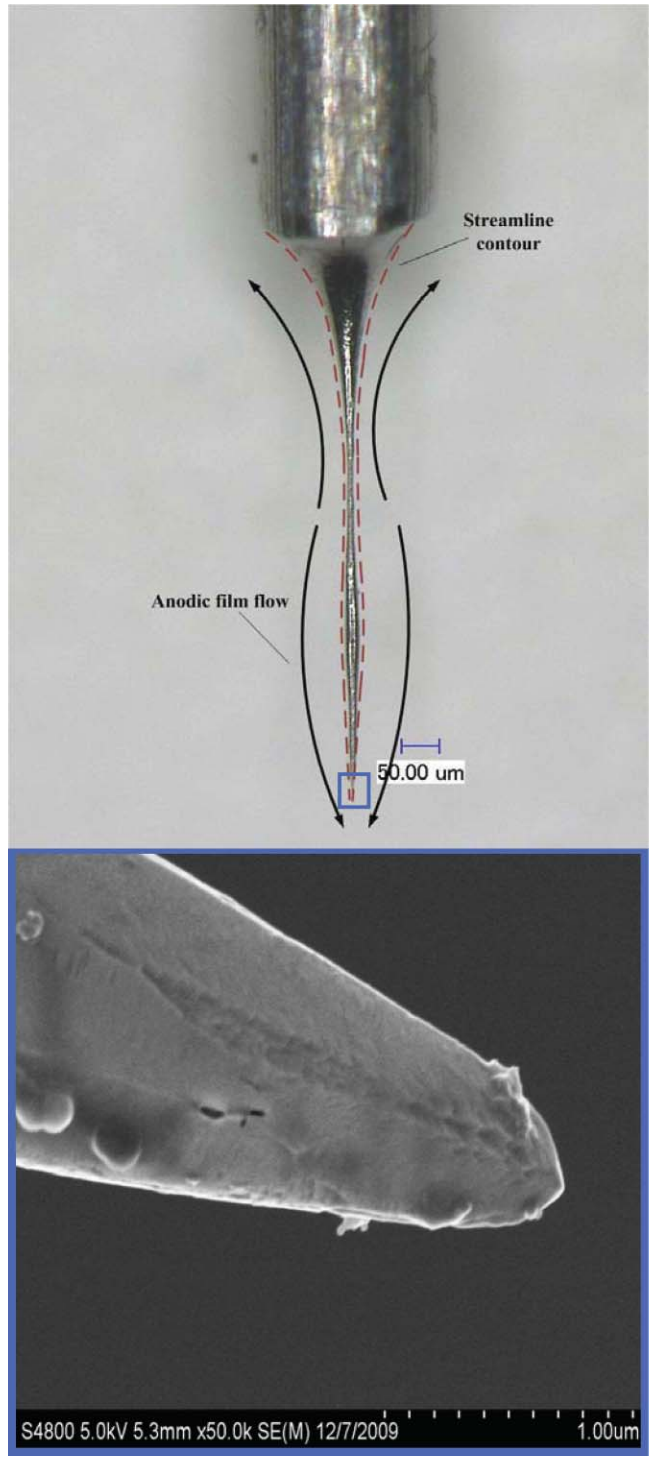


FIG. 9. (Color online) By controlling the anodic flow, the multitimes neck-in can be realized and calabashlike shape probe can be customized. The inset shows the SEM image of the detailed tip profile and functional characteristics of the calabashlike shape probe, ×50 000.

B. Effect of the cathode (platinum ring) position on the final shape of probe

Three different cathode positions were investigated. The cathode position at: (1) the same level of the air–solution interface, (2) 1.0 mm below the air–solution interface, and (3) 2.0 mm below the air–solution interface. The effect of the cathode position and its contribution to the final shape of probe is as shown in Fig. 8. It was found that the cathode position closely related to the length of final fabricated probe. As described in Figs. 8(a)–8(c), the lower the cathode position, the longer the probes can be produced.

During the electrochemical etching, the distribution and concentration of electrolyte within the meniscus, an exponential shaped tip can be obtained. However, the cathode position could change the electrical field distribution during the electrochemical etching process and cause the subsequent aspect ratio variation of the final probes. As shown in Fig. 8(a), when the electrical field around the tungsten wire is at the same level as the cathode position, the etching rate will increase due to the stronger electrical field. In the case of the cathode position lower than the air–solution interface, the nonuniformity in electrical field will lead to the neck-in position to be dropped. The immediate consequence of the low cathode position is an elongating probe, as shown in Figs. 8(b) and 8(c), respectively.

It is worth pointing out that using this method to control the aspect ratio of probe is not reproducible since the redistribution and nonuniformity of the electrical field will cause malformed probes.

C. The anodic film flow control for probe etching

As shown in Fig. 9(a), by controlling the anodic flow, several neck-in could be created thus forming a calabashlike probe. The neck-in position presumably coincides with a region where the anodic flow splits into upward and downward parts. The lower part of the flow goes downward, and the variation of electrochemical reaction is likely caused by the gradient of anodic flow. The upper part of the fluid partially follows a circular flow pattern. According to this phenomenon, streamline shape probe could be obtained by lifting up the wire at the time before it breaks off at the neck-in position, and the tungsten wire was pulled out of the electrolyte at a low etching current that was about 0.8–1.0 mA to avoid the occurrence of breaking off at the anticipated neck-in position. Therefore, the probe shape could comply well with the track of the anodic film flow and the calabashlike probe can be customized.

Figure 9 shows the SEM images of the tip apex that is selected randomly among the yield probes by using the above mentioned method. It was found that the profile of the tip apex complies well with a cone shape and its apex radius was very sharp whereas the drop-off did not occur. For this reason, it could provide an alternative to achieve sharp tips instead of using the traditional drop-off method.

V. CONCLUSION

We have demonstrated a novel electrochemical etching apparatus and technique to fabricate tungsten probes with well-controlled tip profile, aspect ratio, and tip radius.

- **Tip profile.** The meniscus behavior is the core factor that determines the probe profile. Static meniscus results in exponential shape, continuous dynamic movement of meniscus leads to the conical shape and step dynamic movement of meniscus causes multidiameter shape probes. By controlling the anodic flow, the multitimes neck-in could be realized and calabashlike probe could be customized.
- **Aspect ratio.** The resultant aspect ratio of probe tip is determined by the effective contact time between the electrolyte and tungsten as well as the neck-in position of immersed wire. The effective contact time could be adjusted by applying different process parameters, which will define the overall geometry of the tip profile at the tip apex. Through combination of different etching conditions, probes with a controllable aspect ratio of 5:1–450:1, in the meantime, apex radius less than 20 nm and conical angle smaller than 3° could be achieved.
- **Tip radius.** A relatively low immersion depth wire (for 250 μm tungsten wire, less than 1 mm) was proposed to develop ultra-sharp tips. The sharp tip is formed by breaking off at the neck-in position when its tensile strength cannot sustain the weight of the immersed portion of the wire.

The art of electrochemical etching for preparing microprobes with controlled tip profile can be applied to diverse fields such as dip-pen nanolithography, scanning probe microscopy, micromachining, and biological cellular studies.

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