Fabrication of high-aspect-ratio platinum probes by two-step electrochemical etching

Z. Yi, and M. Zhang

Citation: Review of Scientific Instruments **86**, 085105 (2015); doi: 10.1063/1.4928119
View online: https://doi.org/10.1063/1.4928119
View Table of Contents: http://aip.scitation.org/toc/rsi/86/8
Published by the American Institute of Physics

REVIEW OF SCIENTIFIC INSTRUMENTS **86**, 085105 (2015)

Fabrication of high-aspect-ratio platinum probes by two-step electrochemical etching

Z. Yi and M. Zhang[a)]
Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, China

(Received 28 April 2015; accepted 24 July 2015; published online 7 August 2015)

In this paper, a two-step AC electrochemical etching process was investigated for the fabrication of platinum probes with controllable aspect ratio from 10 to 30, and tip apex radius less than 300 nm. Experiment results show that the shape of the obtained probes is quite sensitive to the etching time of the first step and the voltage applied in the second step. A graphite crucible was used as the counter electrode during etching. It is proved that the shape of the counter electrode also play a key role for realizing high-aspect-ratio probes. The method presented here provides a simple way in the fabrication of micro-tool for the construction of high-aspect-ratio microstructures, especially for the 3D electrochemical micromachining. © *2015 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4928119]

I. INTRODUCTION

Probes with micro/nano tips have been widely used in nanolithography, scanning probe microscopy, multipoint contact measurements, micro/nanomanipulation and electrochemical micromachining.[1–4] The size and the shape of the tips play important roles in enabling various tasks.[5–7] Different techniques can be used to fabricate sharp tips, including cutting,[8,9] grinding,[10,11] mechanical pulling,[12,13] ion milling,[14,15] and electrochemical etching.[5,16–20] Among these methods, electrochemical etching is the most widely investigated technique for microprobe fabrication because of its low-cost, reproducibility, and ease of implementation.[21] Tungsten is the most commonly used probe material when using electrochemical etching due to its high strength and the simple fabrication process. However, a tungsten tip obtained through a typical electrochemical etching process is always easy to be contaminated and oxidized.[22] This limits their application in the situation where conductivity and chemical stability play important roles in the process, such as electrochemical micromachining. Fabrication of microprobes with inert materials, such as platinum and gold, has been studied by a number of researchers and sharp tips with low aspect ratio can be obtained reproducibly.[23,24] However, few studies have been conducted on Pt probes with high aspect ratio.

Electrochemical machining with submicrometer resolution can be realized by the application of ultrashort voltage pulses.[25] One of the determinant factors that the spatial resolution of electrochemical micromachining could be improved is the apex radius of the microelectrodes.[26] Electrodes with high-aspect-ratio tip are particularly needed in the fabrication of 3D structures with sharp resolution.

In this paper, we present a simple and reproducible method to fabricate sharp and smooth Pt probes with aspect ratio up to 30. This was achieved by using a two-step AC electrochemical etching technique with a graphite crucible as the counter electrode. The method presented here provides a simple and efficient way to fabricate high-aspect-ratio probes for 3D electrochemical micromachining.

a)Author to whom correspondence should be addressed. Electronic mail: zhang.min@sz.tsinghua.edu.cn.

II. EXPERIMENTAL

The schematic of the experiment setup is shown in Fig. 1. The tip material used is a 0.3 mm diameter Pt wire, cut into pieces 15 mm long and then ultrasonically cleaned in acetone or alcohol and deionized (DI) water prior to etching. A translation stage was used to control the position of the Pt wire in the electrolyte. Instead of a glass beaker, a high-purity graphite crucible is used as the container of the electrolyte and also, the counter electrode for the etching process. The graphite crucible has a purity of 99.95% and an electrical resistivity of 13 $\mu\Omega$ m. $CaCl_2$ solution with a concentration of 20 wt. % was used as the etching electrolyte. All the solutions were prepared with DI water.

The probes are formed in a two-step process at two different AC voltages. In order to ensure a quick switch between two voltage values, two variacs were connected in parallel to the Pt wire and the graphite crucible, and a Microcontroller Unit (MCU) controlled relay was used to adjust the two variacs automatically. All the experiments were conducted under room temperature.

In the first step, the Pt wire is immersed pointing downwards about 3 mm into the solution. An AC voltage of 35 V is applied to the Pt wire and the counter electrode. After 60-90 s, the voltage is then reduced to the second stage rapidly. The etching reaction will stop automatically until all of the Pt wire immersed under the solution is etched out. By carefully controlling the etching time and voltages, sharp tips with high aspect ratio can be obtained at the air-liquid interface. The fabricated probe is then cleaned by deionized water immediately and dried in nitrogen flow.

III. RESULTS AND DISCUSSION

In the first step, the high voltage applied between the Pt wire and the graphite counter electrode results in a constant

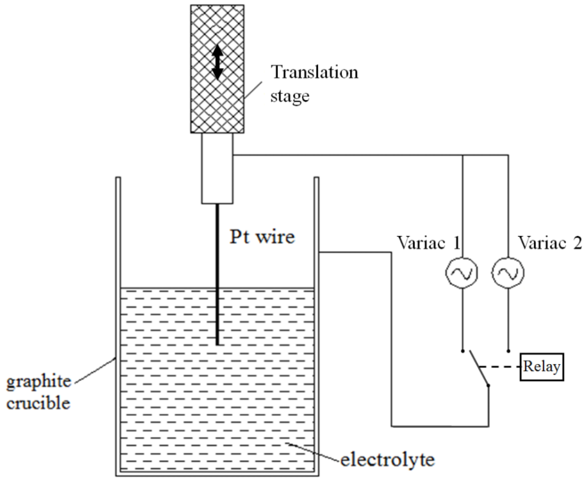

FIG. 1. The schematic of the experiment setup. The graphite crucible acts as the counter electrode as well as the container of the electrolyte.

sparking at the specimen-liquid-air interface. Meanwhile, the part of the Pt wire immersed in the solution is shortened rapidly by the electrochemical reaction between platinum and the electrolyte. Therefore, the etching process in the first step is a combination of the electrochemical etching from the bottom and the electrical discharge etching at the liquid surface. The etching principle of the first step is shown in Fig. 2(a). The etching rate at the liquid-air interface is dramatically enhanced by the electrical discharge process. As a result, a "neck-in" phenomenon occurs in the close vicinity of the liquid surface, where the etching rate is the highest, as shown in Fig. 2(b).

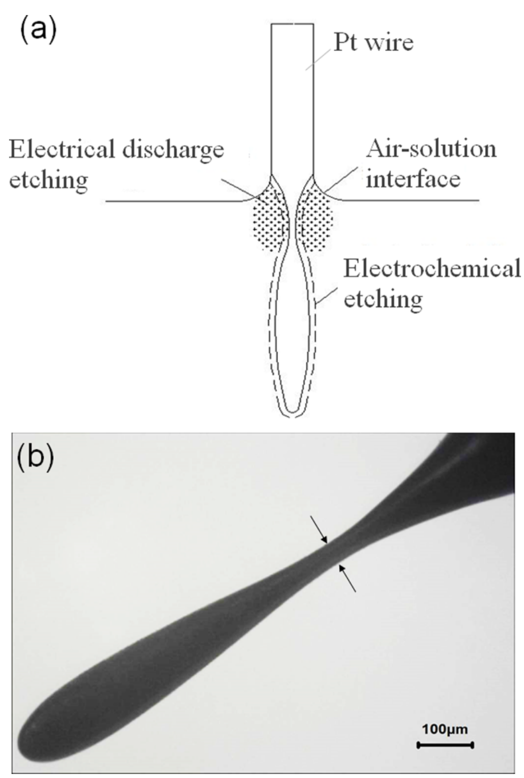

FIG. 2. (a) The schematic of the etching process of the first step. (b) The "neck-in" structure fabricated in the first etching step.

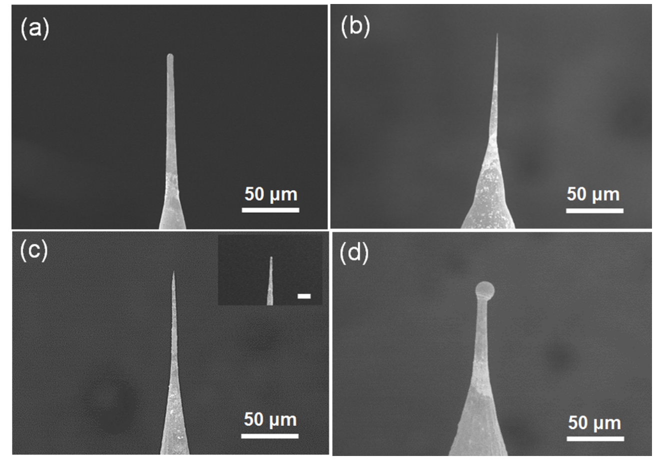

FIG. 3. SEM images of the probes fabricated by two-step etching process with different etching time of the first step. (a) 60 s, (b) 75 s, and (c) 90 s. The voltage of the second step is 20 V. The inset in (c) shows the enlarged probe tip. The scale bar is 2 μm. (d) is the probe obtained with the first step only.

It is necessary to have a second step with lower voltage than the first step to reduce the etching rate at the end of the whole etching process. When the voltage is reduced from 35 V to 22 V or below, the sparks on the air-liquid interface disappear and the etching process changes to pure electrochemical etching. Experiment results show that the duration of the first step and the voltage chose in the second step have strong effects on the aspect ratio and sharpness of the tips obtained.

Fig. 3 shows the influence of the duration of the first step on the length of the fabricated probes. The voltage of the second step is kept at 20 V. It is clear to see that rod-like probe tips with uniform diameter on a length more than 100 μm were obtained in all the used conditions. The aspect ratio of the tips increased from 20 to about 30 as the first-step etching time increased from 60 s to 90 s (Figs. 3(a)-3(c)). The tip apex radius of the probe fabricated with the first-step etching time of 90 s and the second-step voltage of 20 V is less than 300 nm, as shown in the inset of Fig. 3(c). Further increasing the duration of the first step to more than 100 s leads to a complete consumption of the Pt wire under the solution and an automatic stop of the etching process. At the moment when the tip leaving the solution, an arc between the tip and the solution is usually generated by the high voltage used in the first step. The high energy of the arc results in the melting of the Pt tip and leaves a melted ball on it, as shown in Fig. 3(d).

TABLE I. The relationship between the duration of the first step and yield rate of probes with high aspect ratio. 30 samples were fabricated for the calculation of the yield rate in each condition.

Yield rate of the probes with aspect ratios higher than 20 (%)	Duration of the first step (s)	Voltage of the second step (V)
20	60	
47	75	20
83	90	
40	>100	NA

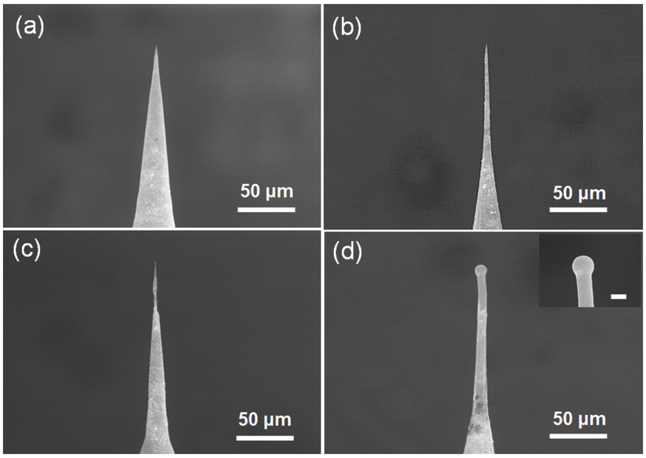

FIG. 4. SEM images of the as-fabricated Pt probes under different voltage of the second step. (a) 18 V, (b) 20 V, (c) 22 V, and (d) 24 V. The inset in (d) shows the melted tip caused by the arc discharge. The scale bar is 5 μm.

Due to the instability of the electrical discharge process, there is an uncertainty of the experiment results. Therefore, the relationship between the etching time of the first step and the yield rate of high-aspect-ratio probes is also investigated (Table I). When 60 s etching time was used, the yield rate of probes with aspect ratio higher than 20 is about 20%, that is, 6 out of 30 samples. As the etching duration increased to 75 s, the yield rate of qualified probes increased to around 47%. A yield rate of more than 83% was achieved when the etching time increased to 90 s. The condition with etching time higher than 100 s gives rise to a low yield rate of 40% with blunt tips.

Moreover, the voltage applied in the second step is also important to the final shape of the probes. As shown in Fig. 4 and Table II, the aspect ratio of the probes achieved a peak value of about 30 at the second step voltage of 20 V. Voltages higher than 22 V or lower than 18 V result in blunt tips as well as very low aspect ratio. Obviously, the probe fabrication process is quiet sensitive to the second step voltage. Only the voltage value between 20 and 22 V can be used for the successful fabrication of the probes. Voltage lower than 20 V leads to a longer etching time and, therefore, the disappearance of the long neck fabricated in the first step. Voltage higher than 22 V results in sparking during the etching process and melting balls at the end of the tips.

It is also worth to note that the shape of the graphite counter electrode also plays an important role on the shape of the fabricated probes. If a graphite rod is used instead of a graphite cylinder, only low aspect ratio tips can be obtained, which is in agreed with the results from other groups.[21,27]

TABLE II. The relationship between the voltage of the second step and yield rate of probes with high aspect ratio.

Yield rate of the probes with aspect ratios higher than 20 (%)	Duration of the first step (s)	Voltage of the second step (V)
0		15
0		18
83	90	20
40		22
0		24

IV. CONCLUSIONS

A two-step AC electrochemical etching process was investigated for the fabrication of Pt probes with high aspect ratio and sub-micro tip apex radius. The first step is a rapid electrochemical reaction combined with electrical discharge etching at a voltage of 35 V. A long neck is formed on the Pt wire at the air-liquid interface by the composite etching process. A second step with more gentle electrochemical etching is then applied to form a sharp tip on the probe. Experiment results show that the duration of the first step and the voltage of the second step are the key roles in obtaining of high aspect ratio probes. Long sharp Pt probes with aspect ratio as high as 30 and tip apex radius of 300 nm can be realized using the proposed technique. This method provides a simple and low-cost way to obtain micro-tools for the fabrication of 3D microstructure with high aspect ratio, especially for electrochemical micromachining process.

ACKNOWLEDGMENTS

This work was supported by Shenzhen Fundamental Research Funds (No. JCYJ20120616215627623) and the Shenzhen Peacock Plan (No. KQCX20130628155525050).

[1] Y. F. Lu, Z. H. Mai, G. Qiu, and W. K. Chim, Appl. Phys. Lett. **75**, 2359 (1999).
[2] C. Albonetti, I. Bergenti, M. Cavallini, V. Dediu, M. Massi, J. F. Moulin, and F. Biscarini, Rev. Sci. Instrum. **73**, 4254 (2002).
[3] M. Cavallini and F. Biscarini, Rev. Sci. Instrum. **71**, 4457 (2000).
[4] X. Sun, T. Masuzawa, and M. Fujino, in *Proceedings of the IEEE Workshop of MEMS, San Diego, CA* (IEEE, Piscataway, NJ, 1996).
[5] J. P. Ibe, P. P. Bey, S. L. Brandow, R. A. Brizzolara, N. A. Burnham, D. P. DiLella, K. P. Lee, C. R. K. Marrian, and R. J. Colton, J. Vac. Sci. Technol., A **8**, 3570 (1990).
[6] A. S. Walton, C. S. Allen, K. Critchley, M. L. Gorzny, J. E. Mc Kendy, R. M. D. Brydson, B. J. Hickey, and S. D. Evans, Nanotechnology **18**, 065204 (2007).
[7] B. Guenther, M. Maier, J. Koeble, A. Bettac, F. Matthes, C. M. Schneider, and A. Feltz, in *Atomic Scale Interconnection Machines*, edited by C. Joachim (Springer, Berlin, 2012), pp. 1–8.
[8] J. Garnaes, F. Kragh, K. A. Mørch, and A. R. Tholen, J. Vac. Sci. Technol., A **8**, 441 (1990).
[9] G. W. Stupian and M. S. Leung, Rev. Sci. Instrum. **60**, 181 (1989).
[10] G. Binning, H. Rohrer, C. Gerber, and E. Weibel, Phys. Rev. Lett. **49**, 57 (1982).
[11] T. Held, S. Emonin, O. Marti, and O. Hollricher, Rev. Sci. Instrum. **71**, 3118 (2000).
[12] Y. Yakobson, P. J. Moyer, and M. A. Paesler, J. Appl. Phys. **73**, 7984 (1993).
[13] G. A. Valaskovic, M. Holton, and G. H. Morrison, Appl. Opt. **34**, 1215 (1995).
[14] K. Akiyama, T. Eguchi, T. An, Y. Fujikawa, Y. Yamada-Takamura, T. Sakurai, and Y. Hasegawa, Rev. Sci. Instrum. **76**, 033705 (2005).
[15] D. K. Biegelsen, F. A. Ponce, J. C. Tramontana, and S. M. Koch, Appl. Phys. Lett. **50**, 696 (1987).
[16] P. J. Bryant, H. S. Kim, Y. C. Zheng, and R. Yang, Rev. Sci. Instrum. **58**, 1115 (1987).
[17] J. P. Song, N. H. Pryds, K. Glejbøl, K. A. Mørch, A. R. Tholen, and L. N. Christensen, Rev. Sci. Instrum. **64**, 900 (1993).

[18]H. Lemke, T. Goddenhenrich, H. P. Bochem, U. Hartmann, and C. Heiden, Rev. Sci. Instrum. **61**, 2538 (1990).
[19]H. Muramatsu, K. Homma, N. Chiba, N. Yamamoto, and A. Egawa, J. Microsc. **194**, 383 (1999).
[20]M. H. Kang, C. S. Park, B. Y. Choi, and D. W. Lee, in *4th IEEE International Conference Proceedings of the Nano/Micro Engineered and Molecular Systems (NEMS)* (IEEE, Shenzhen, China, 2009), pp. 1069–1072.
[21]A. J. Melmed, J. Vac. Sci. Technol., B **9**, 601 (1991).
[22]A. Cricenti, E. Paparazzo, M. A. Scarselli, L. Moretto, and S. Selci, Rev. Sci. Instrum. **65**, 1558 (1994).
[23]U. J. Quaade and L. Oddershede, Europhys. Lett. **57**(4), 611 (2002).
[24]I. H. Musselman and P. E. Russell, J. Vac. Sci. Technol., A **8**, 3558 (1990).
[25]R. Schuster, V. Kirchner, P. Allongue, and G. Ertl, Science **289**, 98 (2000).
[26]R. Schuster, ChemPhysChem **8**, 34 (2007).
[27]J. Lindahl, T. Takanen, and L. Montelius, J. Vac. Sci. Technol., B **16**, 3077 (1998).