Electrochemical etching of metal wires in low-stress electric contact using a liquid metal electrode to fabricate tips for scanning tunneling microscopy

Takashi Nishimura, Amer Mahmoud Amer Hassan and *Masahiko Tomitori

School of Materials Science, Japan Advanced Institute of Science and Technology

1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan

*Corresponding author; e-mail, tomitori@jaist.ac.jp

Keywords: STM; tip fabrication, liquid metal electrode; FEM

Abstract

A liquid metal electrode of Ga was used to reproducibly fabricate a sharpened metal tip with an elongated shank by electrochemical etching for scanning tunneling microscopy (STM). The electrode was in contact with the wire for the tip in low stress; it was prevented that the tip end from being rugged owing to mechanical tear-off on splitting into two pieces by etching. The wire was vertically penetrated down through a film of an electrolyte solution held in meniscus onto a platinum (Pt) ring, and the lower part of the wire under the film was softly in contact with an electrode of the liquid metal having high wettability and viscosity, resulting in a good electric contact. A tip with a radius less than 20 nm and an elongated tip length of order of 1 μm was obtained, which was preferable for the build-up process in a thermal-field treatment. The tip was evaluated by scanning electron microscopy and field emission microscopy, and used in STM observation.

1. Introduction

Scanning tunneling microscopy (STM) is powerful to observe surface topography on an atomic scale using tunneling current depending on the separation between a sample and a sharpened tip in close proximity [1]. Since the spatial resolution of STM is dominated by the sharpness of the tip, a number of methods to fabricate a sharpened tip were reported [2, 3, 4, 5, 6]. In general, the STM tips are made by electrochemical etching of various metal wires [7]: for example, W [8], Ni [9], Co [10], Pt, Ir, Au, Pd, Rh [11]; in these reports apparatuses for electrochemical etching were developed to obtain sharpened tips.

Development of methods to prepare tips with controllable profiles by electrochemical etching has continued for a wide variety of technical applications including electron emitter, ion-beam emitter, point contacts in conductance measurements, etc. The conditions for electrochemical etching were systematically examined using a metal ring electrode to obtain better profiles of the tip, while the tension on the wire affected the sharpness of obtained tips [12]. A small contact potential difference between the wire and the electrode also changed the blunt shape of the tip [13]. Furthermore, by applying pulse trains of bias voltage between the wire and the electrode using a function generator, the tip profiles were controlled owing to anion distribution change surrounding the wire in an electrolyte solution [14]. In order to prepare tips in desired profiles, there has still been room to be examined in electrochemical etching methods.

In this study, a novel method is presented to fabricate a sharpened tip with an elongated shank by electrochemical etching using liquid metal gallium (Ga) as an electrode without specific electronic circuits. The one end of wire is in touch to the liquid metal electrode with a good electrical contact due to its wettability and lightly supported with damping by its viscosity, which prevents the wire from mechanically tearing-off. The electrochemical etching is automatically stopped just after the wire breaks into two pieces, resulting in leaving a sharpened tip end. The tips prepared by this method are examined by scanning electron microscopy (SEM) and field

emission microscopy (FEM), and used in STM observation.

2. Method

First, a typical setup for electrochemical etching of the tip is shown in Fig. 1, which was used before in our lab. A ring of Pt wire was placed horizontally, in which an electrolyte solution was held in meniscus under surface tension onto the ring. A cut of metal wire for the tip was inserted into the solution by pinching its top end with a metal clamp. As the etching progressed by passing current between the ring and the clamp, a part of the metal wire immersed in the solution became thin, and finally broke into two pieces; both of which were used for an STM tip. To catch the dropped piece, a receiver of a small tubular container was placed under the wire. Immediately after the wire broke into the two pieces, the electrochemical etching for the dropped piece automatically stopped, because this piece came off from the loop of etching current through the Pt ring, the solution, the clamp, and an electric power supply.

To quickly drop the piece from the solution to avoid further chemical corrosion in the etching solution, a long cut of metal wire or a weight was attached at the bottom of the wire [10, 15]. There was, however, a tendency that the end of broken piece exhibited slightly rugged after the piece was torn off; the wire broke into the two pieces before the thinning part was completely electrochemically etched. An example of a bent tip mechanically torn-off in the setup is shown in SEM images in Fig. 1(b).

Next, the schematic diagram of the present setup developed in this study and its photos are shown in Fig. 2 and Fig. 3, respectively. This apparatus is similar to that shown in Fig. 1, except for the bottom part, where the cut of metal wire is in contact with a liquid metal electrode of Ga having high wettability to the wire. Mercury (Hg) is also usable as a liquid metal electrode but should be avoided because of the toxicity of Hg. A Pt wire of ring was wounded with a polyimide-coated Cu fine wire of 0.15 mm in diameter, which was employed as a small heater,

shown in Fig. 3(b). At first we soaked the Pt ring in a melting Ga lump slightly heated at a temperature higher than the Ga melting temperature of 29 °C, and pulled up the ring from the lump, resulting in a film of Ga held onto the ring. To keep the Ga film in a liquid state, a current of about 0.2 A at 0.1 V into the Cu wire was passed to heat it above 29 °C. A cut of metal wire for the tip was inserted into the liquid metal film, and the film was broken. Subsequently, the Pt ring, on which the small droplets of liquid Ga remained, was positioned to touch the bottom of the wire to the droplet, shown in Fig. 3(c). The droplet can maintain the contact with the surface tension and viscosity of melting Ga. Then, the wire was held in very low stress and in good electric contact with the Pt ring at the bottom of the wire.

In our practical way, the cut of the wire was mounted on a tip holder of STM, located at the top of Fig. 2 (the detail is not shown), after the wire was spot welded to a metal loop of W wire; the loop was used to heat the tip in ultra-high vacuum (UHV) for degas and build-up process by passing current into the loop and applying a high voltage before STM observation, as mentioned in Experiment section. When the wire was electrochemically etched, the wire pointed downward, penetrated the film of etching solution in the upper Pt ring, and the bottom end of the wire touched the liquid metal electrode on the lower Pt ring. When the electrochemical etching was completed, that is, the wire split into two pieces, the circuit of electrochemical etching of the upper piece opened instantaneously, and no further etching current passed to the upper piece. Thus, no additional switching circuit was required to stop the etching current. Since the upper piece was mounted on the STM tip holder, the tip for STM observation can be used immediately without resetting it into other holders. In practice, an overplus lengthy part of the wire, about 10 mm longer than a finally desired length as the STM tip, was required for the etching. In the case of a shorter metal wire used in this etching process, an additional length of wire was attached at the end of the metal wire with a bit of silver paste; the bottom of additional wire was in contact with the liquid metal electrode.

3. Experiment

A [111]-oriented single crystal W rod (FEI Company) of 0.13 mm in diameter was used to prepare an STM tip using the setup shown in Fig. 2. The rod was electrochemically etched in a solution of 4 mol/l KOH at a DC voltage of 3 V applied to the rod, and split into the two pieces in about 5 min. Subsequently, the upper piece on the STM tip holder was soon retracted and used in the following experiments. After the tip was rinsed in hot water and ethanol to remove salt residues out of the etching solution, the tip was observed by SEM and FEM. A field emission SEM (S-5200, Hitachi High-Technologies Corporation) and a home-made FEM combined with a home-made STM operated in a UHV chamber with a base pressure of $2x10^{-11}$ Torr were used; FEM/STM observations and tip treatments were conducted in the same stage without tip transfer [16, 17, 18]. Before the FEM observation the tip was heated at about 600 °C for 6 hours in the UHV chamber to remove overlayers covering the tip. Furthermore, the tip was treated to be sharpened in a build-up process of applying 3 kV and simultaneously heating at about 2000 °C by passing an AC current into the W loop as a thermal-field treatment [18]; the W atoms on the tip apex are polarized owing to the high electric field and diffuse at the high temperature towards the apex of the [111] direction at higher electric field, resulting in a sharper end of the tip. Using the treated tip, STM images of a clean Si(111)-7×7 and a Si(001)-2×1 reconstructed surface were observed, which were prepared by flashing at 1250 °C in the UHV chamber.

4. Results and discussion

Fig. 4 shows SEM images of the W tip electrochemically etched using the setup in Figs. 2 and 3. The tip radius was evaluated to be less than 20 nm within the accuracy limited by a narrow focus depth of the SEM (S-5200) for the three dimensional shape of the tip and by the growth of contamination layers deposited with a focused electron beam at high magnification. Just after

etching current was shut off, the tip end was probably sharper than 20 nm; the radius of tip apex slightly became larger owing to overlayers growth such as oxides covering the tip apex while being transferred in air. The diameter of the shank was less than about 100 nm over a length of 1 μm from the tip end, which looks elongated compared with that fabricated by conventional etching methods. This elongated fine shank indicates that use of the liquid metal electrode reduces the effect of tear-off during the electrochemical etching.

The tip was treated in the build-up process in the UHV chamber and observed by FEM [19]; a typical FEM image obtained after the treatment is shown in Fig. 5(a), which was observed at an applying voltage of -1.0 kV. The [111]-oriented W tip has a three-fold symmetry in crystallography, and a facet of (111) at the center and three facets of {013} around the (111) facet on the tip end have work functions lower than those of the other facets, from where electrons are easily field-emitted. Consequently, FEM images of a dull tip of [111]-oriented W usually show a bright wide pattern around the center of a FEM screen with three-fold symmetry. For facetted sharper tips prepared by applying a high voltage at a high temperature the FEM patterns show one bright spot at the center of the image, corresponding to the field emission from the [111]-oriented protrusion, accompanied by three bright spots surrounding the center spot with the three-fold symmetry, corresponding to the <013>-oriented protrusions. On the other hand, in the FEM image in Fig. 5, only one prominent bright spot of the [111]-oriented protrusion at the center was observed after an optimizing build-up process [19]. This indicates that the W tip atomically protruded to only the [111] direction of the tip axis; a small pyramidal atomic structure as a protrusion to the [111] orientation was probably formed, as shown in Fig. 5(b). The build-up process of the tip was achieved reproducibly and easily with the tip fabricated in the process using the liquid metal electrode. It is probable that the fine tip elongated over 1 μm, as shown in Fig. 4 of the SEM image, is preferable to carry out the build-up process, because the high electric field is easily concentrated at the apex of the elongated tip. Using this tip after the FEM observation we

brought the tip closer to sample surfaces and succeeded in observing stable atom-resolved STM images of Si(111)-7×7 and Si(001)-2×1, as shown in Fig. 6.

Using the method with the liquid metal electrode demonstrated in this study, an elongated W tip with a diameter less than 100 nm and as long as 1 μm was obtained. It is expected that the diameter of the thinning elongated part can be as small as 1 nm just before the wire is split. Since the Fermi wavelength of metals is of the order of Angstrom, the quantum mechanical quantized conductance [20] may emerge in the thinning part. The quantized conductance was reported by methods of electroplating combined with etching [21], mechanically controlled break junctions [22], STM [23] and so on. Those methods were applied to detection of quantized conductance for soft or polycrystalline metals such as Au, but not for brittle metals as W. It is worth while pointing out that this method using the liquid metal electrode is applicable to the formation of a fine wire of brittle metals where the conductance is quantized due to the quantum mechanical effect. The conductance in the wire even during etching is possibly detected by electrochemical techniques using a potentiostat or a lock-in amplifier with AC modulation to separate the electrochemical etching current.

5. Summary

A liquid metal electrode for electrochemical etching was used to reproducibly fabricate a sharpened W tip with an elongated shank for STM. The metal wire for the tip was in contact with the liquid metal electrode in low stress but in good electric contact, leading to less mechanical tear-off. An elongated sharp W tip with a diameter of 100 nm over a length of 1 μm was formed; this is preferable to apply the build-up process to prepare an atomically sharpened tip for STM.

ACKNOWLEDGMENT

This work was supported by Grants-in-Aid for Scientific Research from the Japanese Society for the Promotion of Science.

References

[1] C. J. Chen: *Introduction to Scanning Tunneling Microscopy*, Oxford Science Publication, New York, 2008.

[2] I. Ekvall, E. Wahlstrom, D. Claesson, H. Olin, E. Olsson: Meas. Sci. Technol., **10** (1999) 11.

[3] T.T. Tsong : *Atom-Probe Field Ion Microscopy*, Cambridge University Press, Cambridge, 1990.

[4] H.W. Fink: IBM Journal of Research and Development, **30** (1986) 460.

[5] V.T. Binh: Surf. Sci., **202** (1988) L539.

[6] V.T. Binh, N. Garcia: Ultramicroscopy, **42-44** (1992) 154.

[7] R. Kazinezi, E. Szocs, E. Kalman, P. Nagy: Appl. Phys. A, **66** (1998) S536.

[8] A.J. Melmed : J. Vac. Sci. Technol. B, **9** (1992) 601.

[9] M. Cavallini, F. Biscarini: Rev. Sci. Instrum., **71** (2000) 4457.

[10] C. Albonetti, I. Bergenti, M. Cavallini, V. Dediu, M. Massi, J.F. Moulin, F. Biscarini: Rev. Sci. Instrum., **73** (2002) 4254.

[11] A.J. Nam, A.Teren, T.A. Lusby, A.J. Melmed: J. Vac. Sci. Technol. B, **13** (1995) 1556.

[12] S. Kerfriden, A. H. Nahlé, S. A. Campbell, F. C. Walsh, J. R. Smith: Electrochimica Acta, **43** (1998) 1939.

[13] O. L. Guise, J. W. Ahner, M.-C. Jung, P. C. Goughnour, J. T. Yates, Jr.: Nano Lett., **2** (2002) 191.

[14] W.-T. Chang, I.-S. Hwang, M.-T. Chang, C.-Y. Lin, W.-H. Hsu, J.-L. Hou: Rev. Sci. Instrum. **83** (2012) 083704.

[15] A.D. Muller, F. Muller, M. Hietschold: Rev. Sci. Instrum., **70** (1999) 3970.

[16] M. Tomitori, M. Hirade, Y. Suganuma, T. Arai: Surf. Sci. **493** (2001) 49.

[17] M. Tomitori, M. Hirade, Y. Suganuma, T. Arai: J. Surf. Anal. **9** (2003) 359.

[18] M. Tomitori, K. Sugata, G. Okuyama, H. Kimata: Surf. Sci., **355** (1996) 21.

[19] M. Nagai, M. Tomitori and O. Nishikawa: Jpn. J. Appl. Phys. **36** Pt. 1 (1997) 3844.

[20] H.X. He, S. Boussaad, B.Q. Xu, C.Z. Li, N.J. Tao: J. Electroanal. Chem., **522** (2002) 167.

[21] S. Sahoo, C.S. Yang, B. Doudin: Phys. Lett. A, **352** (2006) 331.

[22] J.M. Ruitenbeek, A. Alvarez, I. Pineyro, C. Grahmann, P. Joyez, M.H. Devoret, D. Esteve, C. Urbina: Rev. Sci. Instrum., **67** (1996) 108.

[23] J.I. Pascual, J. Mendez, J.G. Herrero, A.M. Baro, N. Garcia, V.T. Binh: Phys. Rev. Lett., **71** (1993) 1852.

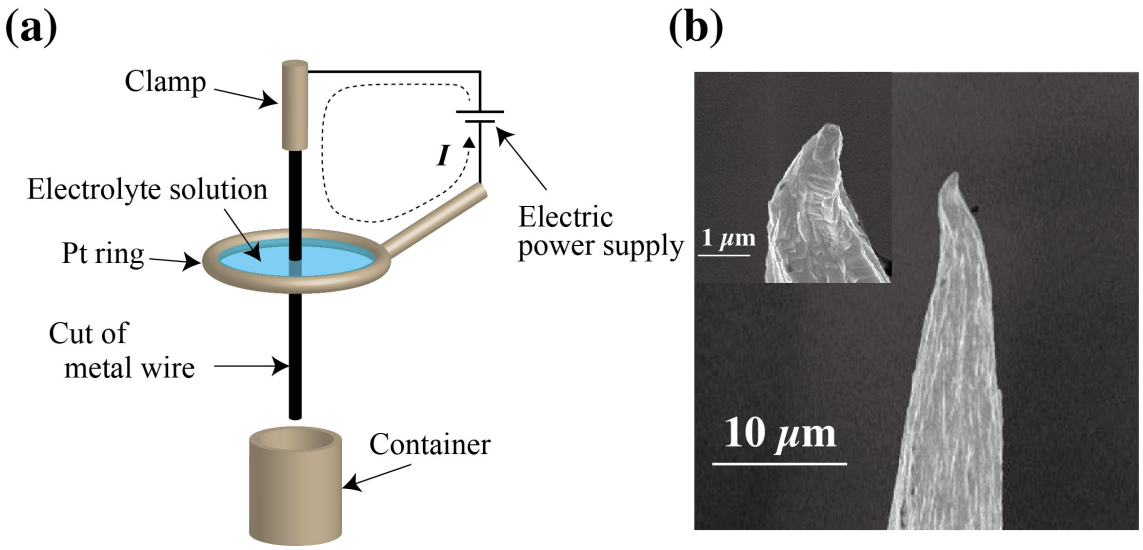

Figure 1 (a) Schematic of a typical setup to fabricate STM tips by electrochemical etching in a meniscus solution in a Pt ring. (b) SEM image of a bent tip of polycrystalline W wire prepared using this setup, as an example. Inset shows a magnified image of the tip.

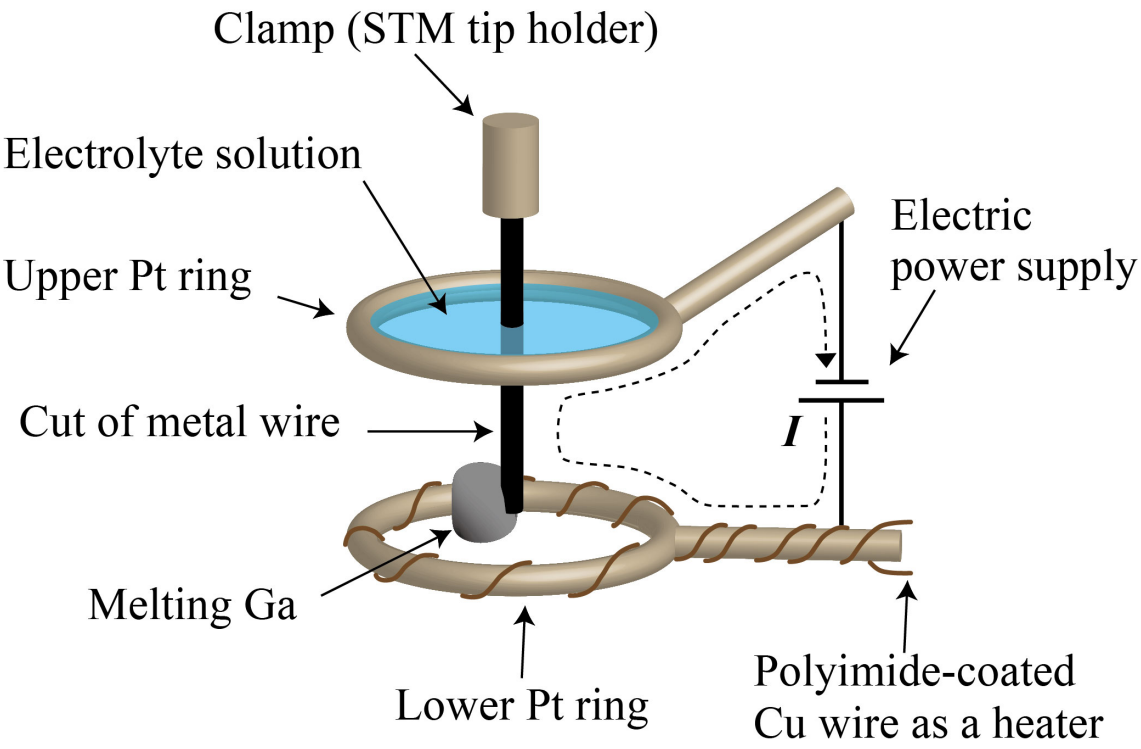

Figure 2 Schematic of the setup of electrochemical etching with a liquid metal electrode.

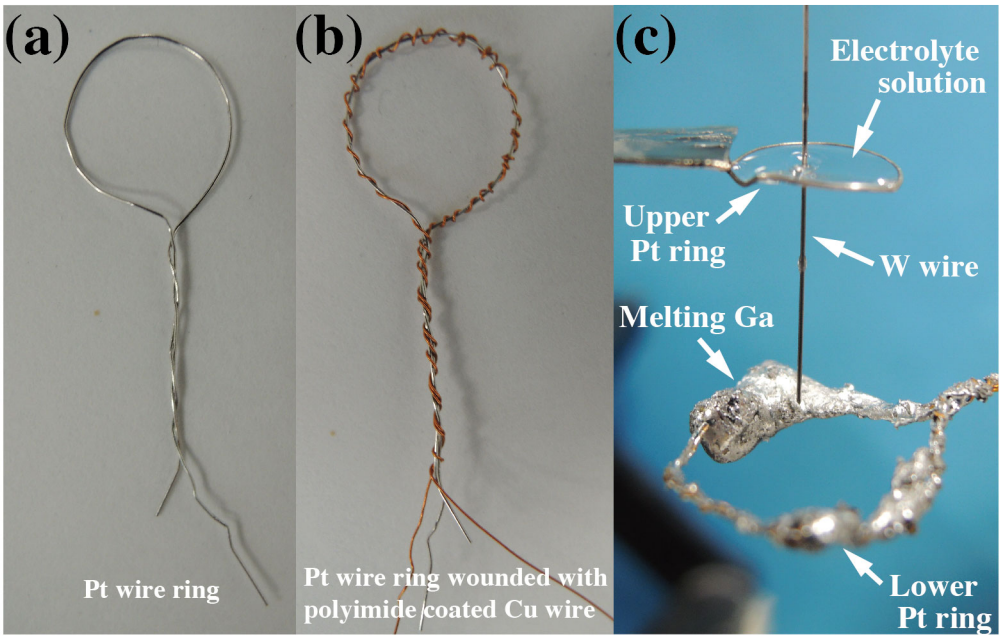

Figure 3 (a) Pt wire ring, (b) Pt wire of the ring is wounded with a polyimide-coated Cu fine wire of 0.15 mm in diameter as a heater, and (c) photo of the setup with a Pt ring (upper) and a Pt ring wounded the Cu wire (lower) covered with liquid metal Ga.

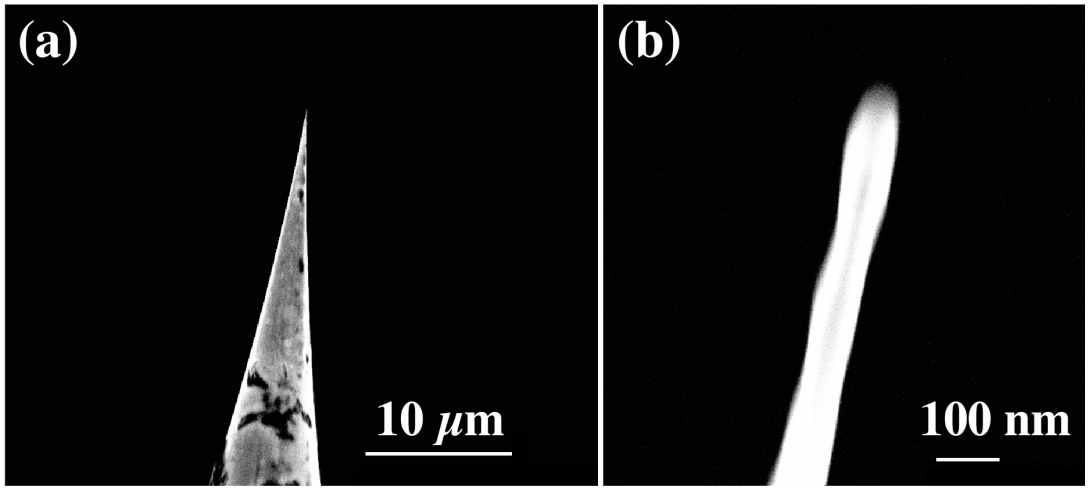

Figure 4 (a) SEM image of a W tip fabricated in the procedure using the liquid metal electrode.

(b) Magnified SEM image of the apex in (a).

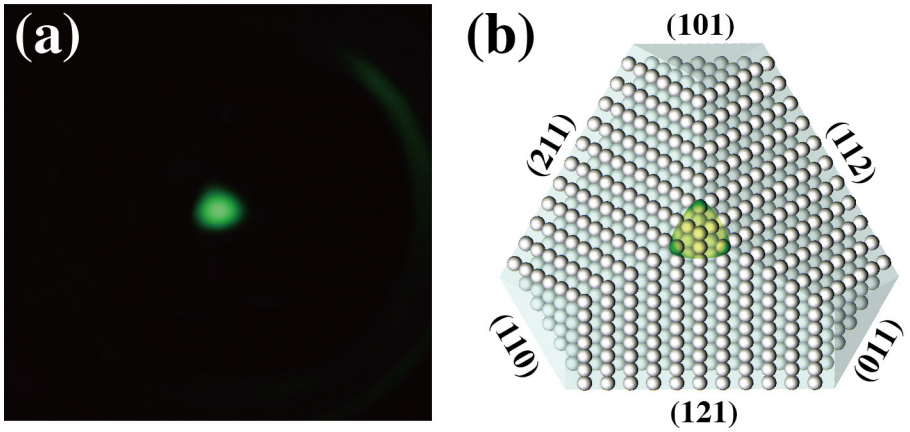

Figure 5 (a) FEM image at -1.0 kV of a build-up W tip fabricated in the procedure using the liquid metal electrode. A faint bright arch on upper right is the discharge of peripheral area of a micro-channel plate with a phosphor screen for FEM. (b) model of a [111]-oriented build-up W tip surrounded with facets of {110} and {211}. The confined sharp region of (111) plane with a low work function, depicted in green at the center, can easily field-emit electrons, which corresponds to the bright spot at the center in (a).

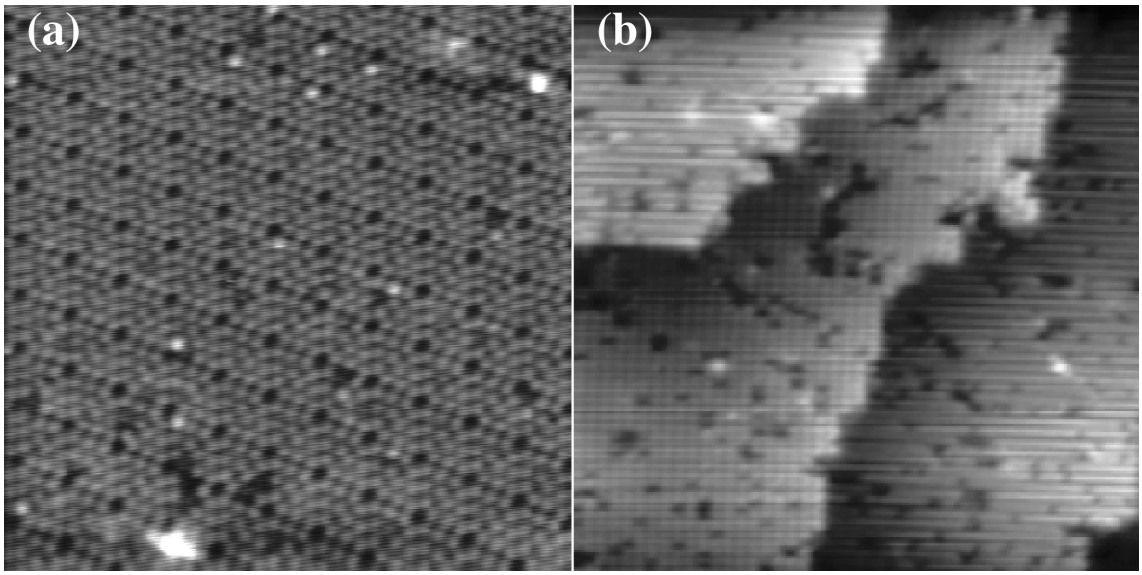

Figure 6　STM images taken with W tips fabricated using the liquid metal electrode. (a) STM image of a Si(111)-7×7 surface; scanning area: about 18 nm to 27 nm, tunneling current: 0.05 nA, tip voltage: -1.5 V. (b) Si(001)-2×1 surface; scanning area: about 36 nm to 38 nm; tunneling current: 0.1 nA, tip voltage: 1.5 V.