

Preparation of Single-Atom Tips and Their Field Emission Behaviors*

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We have developed a simple and reliable method for preparing single-atom tips. Electrochemical techniques are applied to deposit a noble metal film on the $W < 111 >$ tip. With the protection of the metal film, the tip can be stored and transferred in the ambient condition. After a gentle annealing of the plated tip in vacuum, a thermally and chemically stable nano-pyramid with single atom sharpness can be generated at the tip apex. The atomic structure of the tip is imaged by a field ion microscope (FIM) layer by layer through field evaporation. The corresponding field emission patterns can also be determined by the field emission microscopy (FEM). Most importantly, the single atom sharpness as well as the pyramidal structure can be regenerated for tens of times in vacuum simply by annealing if the apex is accidentally damaged. Field emission measurements indicate that the single-atom tips can emit stable electron beams of high brightness with a small extension angle. These desirable features make the single-atom tips very promising for future applications. [DOI: 10.1380/ejsnt.2006.233]

Keywords: single-atom tip; field emission; field ion microscopy; faceting; and electrochemical methods

I. INTRODUCTION

Single-atom tips are metal tips ending with only one atom. They are of great interest because they are able to produce coherent and bright electron beams and may greatly improve the resolution of current electron microscopy. They can also produce highly focused ion beams for fabrication of nanostructures. Single-atom tips can also be wonderful probes for scanning probe microscopy, as they can achieve the highest spatial resolution and allow for manipulation of single atoms. In spite of these desirable features, single-atom tips were very difficult to prepare. Traditional methods [1–4] require special equipments and tedious procedures in ultra-high vacuum (UHV). Moreover, single-atom tips could not be produced reliably. Even if a single-atom tip was obtained, the tip did not last long because its structure was not thermodynamically or chemically stable. Thus, the application of single-atom tips has so far been very limited.

Recently Fu and Tsong demonstrated a reliable way to prepare a Pd-covered $W(111)$ single-atom tip [5]. This tip is thermodynamically stable, and thus can be regenerated by annealing if it is destroyed. Most importantly, the stacking of the single-atom tip remains the same after each regeneration. The thermodynamic driving force for the formation of this single-atom tip is the faceting process for Pd on $W(111)$. It has been known that ultrathin Pd, Pt, Au, Ir, or Rh films grown on the $W(111)$ surface can form three-sided pyramids with $\{211\}$ facets upon annealing in UHV [6–11]. The success of the Pd-covered W single-atom tip implies that other noble metals (such as Pt, Ir, Rh, and Au) covered $W(111)$ tips may also form

single-atom tips through a similar procedure. However, two requirements in this preparation procedure make its application less convenient. First, a clean W surface has to be prepared prior to the noble metal deposition. This requires applying either a very high electric field or a very high temperature to remove surface contaminants. However, most equipments do not allow application of such a high voltage, and the tip shape may not survive such a high temperature treatment. Moreover, an evaporator for noble metal deposition has to be installed in the vacuum chamber, which is also difficult to fulfill for many systems.

Now we have developed a new method for simultaneously preparing a clean W tip surface and the deposition of a noble metal film in an electrochemical cell [12]. This tip can be stored in the ambient condition for a long time. After the tip is transferred into a vacuum chamber and treated by a gentle annealing, a single-atom tip with the atomic structure identical to the one prepared by the vacuum method can be obtained. Annealing is a standard procedure in most applications using electron field emission (FE) tips. Therefore, our new method removes the final obstacles that hinder the application of single-atom tips.

II. EXPERIMENTAL PROCEDURES

The preparation process for electroplated single-atom tip is schematically depicted in Fig. 1. It starts with an electrochemical process, as illustrated in Figs. 1(a)-(d). A $< 111 >$ oriented single crystal W wire of 0.1 mm in diameter is electrochemical polished to a needle shape in KOH solution [Fig. 1(a)]. The tip shape can be inspected by either an optical microscope or an electron microscope. The tip apex has a typical radius of 50 nm, as shown in Fig. 2(a). Note that the tip surface is covered by a thin native oxide after the etching.

A potentiostat (M366A, Princeton Applied Research,

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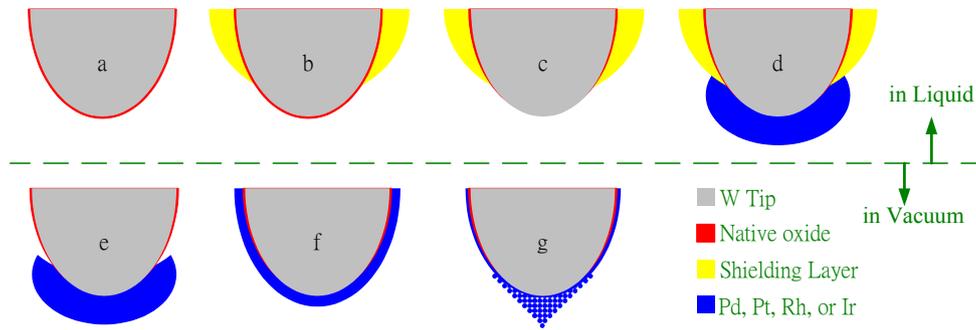


FIG. 1: Schematic diagram showing the procedures for preparation of single atom tips. (a) Etch a single crystal W $\langle 111 \rangle$ wire to a sharp tip. (b) Cover the tip with a nail polish except at the apex. (c) Reduce the native oxide by a cathodic polarization. (d) Electroplate a noble metal film on the tip. (e) Remove the nail polish and transfer the tip to a vacuum chamber. (f) Anneal the tip to diffuse the noble metal atoms to other part of the tip. (g) When the tip is covered by only one physical layer of the noble metal, a pyramidal single-atom tip builds up simply by further annealing.

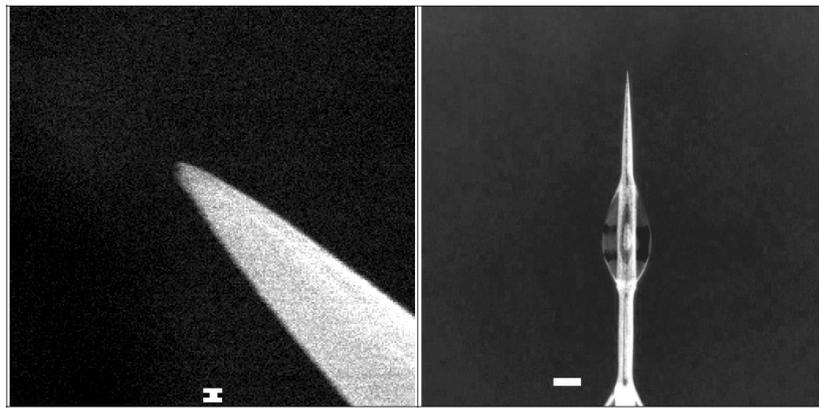


FIG. 2: (a) SEM micrograph of a W $\langle 111 \rangle$ tip after electrochemical etching. (Scale bar: 100 nm). (b) Optical micrograph of a W $\langle 111 \rangle$ tip after it is covered with a nail polish. (Scale bar: 0.1 mm)

USA) and a conventional 3-electrode electrochemical cell are used for the following electrolytic processes, including cathodic reduction [Fig. 1(c)] and electroplating [Fig. 1(d)]. In our electrochemical cell, which has a Pt counter electrode and a saturated calomel reference electrode (SCE), the W tip is placed at the working electrode. To decrease the area for metal deposition, we use a nail polish to shield the tip from the electrolyte except for the apex, as illustrated in Fig. 1(b) and shown in Fig. 2(b). After that, the tip is immersed into 0.1 M HCl of 20 ml and held at -0.6 V (SCE) to reduce the surface oxide for about 3 minutes [Fig. 1(c)]. Then, a small amount of plating electrolyte [13] ($15 \mu\text{l}$) is dropped into the electrochemical cell under the same cathodic polarization. The Faradic current was monitored during the electrochemical process, and the deposition time was controlled to about 10 – 15 s [Fig. 1(d)]. With protection of a noble metal film, the tip can be stored even in a humid ambient for a long period without any problem of corrosion or oxidation.

Before the vacuum process, acetone is used to remove the nail polish on the tip [Fig. 1(e)]. The plated tip was then loaded in our homemade UHV-FIM/FEM chamber [14]. The base pressure of the chamber is about 2×10^{-10} Torr. In the chamber, only heating is applied for de-

gassing as well as for facet formation [Figs. 1(f) and (g)]. The tip temperature is measured by an optic pyrometer. After a proper heat treatment, a mixture of He and Ne gases is admitted to a pressure of 2×10^{-5} Torr to act as the image gas for an FIM observation. For FIM imaging and field evaporation, a positive high voltage is applied to the tip. For observation of the field emission pattern, a negative high voltage is applied in an UHV condition (pressure $< 5 \times 10^{-10}$ Torr). The emitted ion or electron beam is amplified by a microchannel plate (MCP, Hamamatsu, Japan) and clear images can be seen on the attached phosphor screen. We use a digital camera to capture all images. We note that the temperature of the tip during the FIM and FEM observations is about 30 K.

III. RESULTS AND DISCUSSION

A. Atomic Structure of Single-Atom Tips

After degassed at 700 K for 5 min in our vacuum chamber, the as-deposited Pd-plated tip is imaged by our FIM, as shown in Fig. 3(a). Randomly scattered image spots indicate a rough tip surface. An ordered smooth tip surface gradually appears after annealing the tip to 1000 K

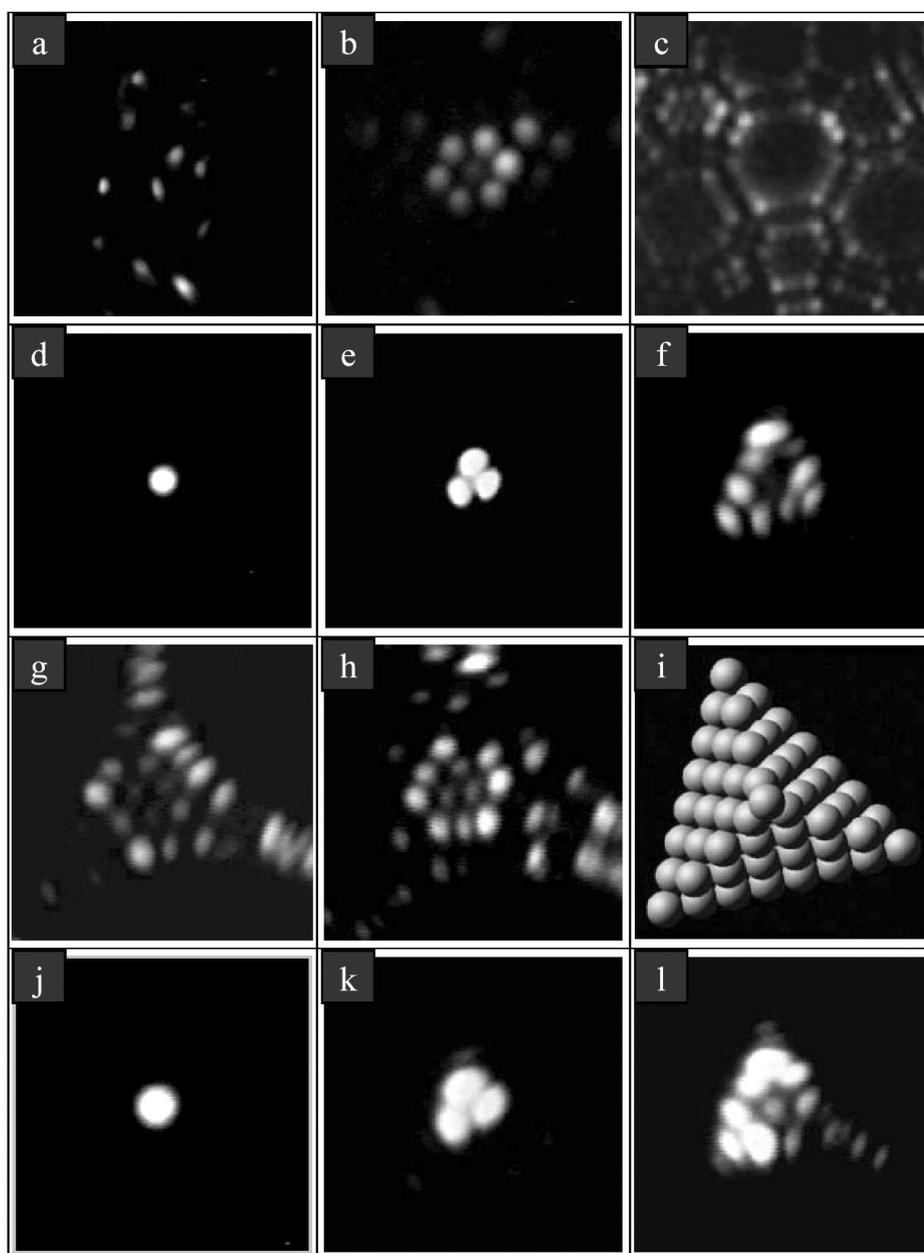


FIG. 3: FIM images showing the structure of a Pd-covered W(111) tip. (a) As-deposited tip. (b) The tip after annealing at 1000 K for 20 min. (c) The tip after annealing at 1000 K for 25 min. (d) A Pd-covered W(111) single-atom tip is formed after annealing at 1000 K for 30 min. (e) The second layer consists of three atoms. (f) The third layer consists of ten atoms. (g) The fourth layer consists of 15 atoms. (h) The pyramidal structure is destroyed by a series of field evaporations. (i) 3-D hardball model of the nano-pyramid. (j) A regenerated single-atom tip by annealing to 1000 K for 5 min. (k) The second layer consists of 3 atoms. (l) The third layer consists of only nine atoms, because the atom at the right-bottom corner is also evaporated with the second layer.

for 20 min [Fig. 3(b)]. If the tip is annealed for another 5 min, the tip surface exhibits a $\langle 111 \rangle$ surface surrounded by other planes [Fig. 3(c)], which is a typical smooth tip surface seen on a bcc metal. This suggests that a Pd pseudomorphic overlayer is formed on the W tip [15, 16]. A single-atom tip shows up after further annealing to 1000 K for 5 min. Fig. 3(d) shows an image of the topmost atom. This atom can be field evaporated away by increasing the positive voltage on the tip. Once the topmost atom is removed, the atomic structure of the second layer is exposed. We can apply an even higher volt-

age to remove the second layer and allow the third layer to be imaged. Therefore, the atomic structure of the single-atom tip can be imaged layer by layer with a series of field evaporations. Figures 3(e) and (f) show 3 atoms on the second layer and 10 atoms on the third layer. Figure 3(g) shows only 15 atoms on the fourth layer, rather than 21 atoms as expected, because a few corner atoms are field evaporated together with the 3rd layer of atoms. After the above procedure, the tip apex is destroyed [Fig. 3(h)]. A hardball model based on the above FIM observations is illustrated in Fig. 3(i), which shows a pyramidal tip with

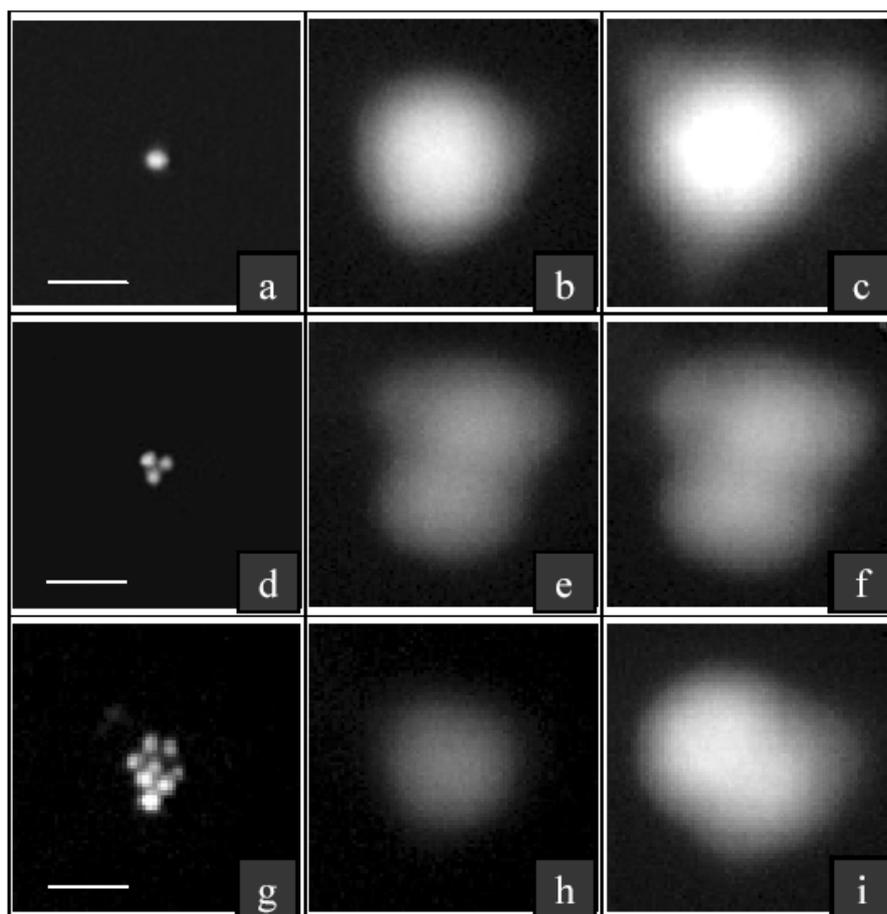


FIG. 4: The FIM and FEM images show the atomic structures and their corresponding field emission patterns of Pd faceted tip at various applied voltages: (a) FIM image of single-atom tip. (b) FE pattern at -1100 V (c) FE pattern at -1200 V. (d) FIM image of the trimer tip. (e) FE pattern of a trimer at -1200 V. (f) FE pattern of the trimer tip at -1300 V. (g) FIM image of the third layer, which consists of 8 atoms at the tip apex. Two corner atoms are also field evaporated with the second layer. (h) FE pattern of the 8-atom tip at -1100 V. (i) FE pattern of 8-atom tip at -1200 V. Scale bar indicates a length of 1 nm on the phosphor screen, corresponding to 4° in the opening angle of the electron beam.

three $\{211\}$ facets. Interestingly, the single-atom sharpness can be recovered simply by annealing the destroyed tip at 1000 K for 5 min. Figures 3(j)-(l) show the regenerated pyramidal structure, which has an atomic stacking identical to the one before the field evaporation. Our experiments show that this pyramidal single-atom tip can be destroyed by the field evaporations and regenerated through annealing for tens of times.

For the case of a Pt-plated W(111) tip, a single-atom tip can also be obtained simply by annealing at 1100 K in vacuum. The atomic stacking of the Pt-covered W single-atom tip is also observed with our FIM with the procedure described above for the Pd-coated W tip. It consists of one atom on the first layer, three atoms on the second layer, 10 on the third layer, etc., same as the Pd-coated W(111) tip [12]. The Pt-coated W single-atom tips can also be regenerated. These results further indicate that our electroplating approach can be applied to other faceting systems to produce single-atom tips.

Madey, *et al.* pointed out that a proper coverage (~ 1 physical monolayer, PML) of a noble metal film on the W(111) surface is one of the prerequisites in inducing the faceting transition [6–11]. However, it is very difficult to

control the coverage to exactly 1 PML due to the rather high deposition rate. This is because the electroplating has to be carried out at the same potential for the native oxide reduction, which inevitably leads to a very high plating rate and a coverage much higher than 1 PML. To reduce the total amount of the plating material, we confine the plated area on a very small area around the tip apex with a nail polish. This technique has been widely used in the tip preparation for operation of STM in an electrochemical cell. We estimate a noble metal film of tens to hundreds of PMLs is deposited on a W(111) single crystal tip apex. During annealing in vacuum, excess Pd (or Pt) atoms may diffuse to other parts of the tip surface which have not been plated [17, 18]. Therefore, in our approach, the coverage of the noble metal film is not as critical as what Madey, *et al.* have found on flat W(111) surfaces. Moreover, this thicker noble metal film can provide a better protection of the W(111) tip surface against further oxidation or corrosion than 1 PML of the film. Clearly, our electroplating method greatly simplifies the deposition process, and provides a better protection before the tip is transferred into vacuum for some applications.

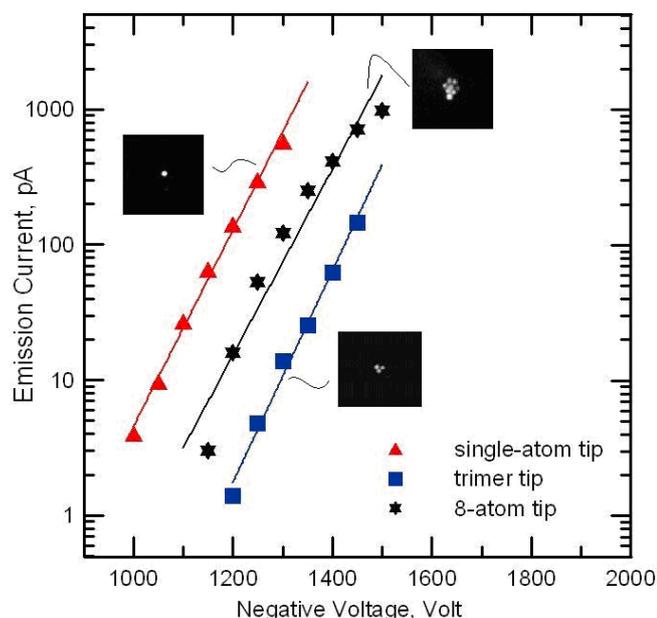


FIG. 5: Field emission currents of Pd-covered single-atom tip, trimer tip and 8-atom tip as a function of the applied voltage.

B. Field Emission through the pyramidal tip

This kind of single-atom tips may have an important application as field emission electron sources. After checking the single-atom sharpness of the Pd-covered tip with the FIM mode [Fig. 4(a)], we switch to the FEM mode to study the field emission (FE) behavior. The FE pattern of the single-atom tip exhibits a circular spot extending an angle of $\sim 4^\circ$ (at FWHM), indicating that the electron emission is originated from the topmost atom of the tip [Fig. 4(b)]. Increasing the applied voltage to -1200 V, the circular spot becomes brighter and meanwhile a dim and broad triangular pattern appears around the circular spot [Fig. 4(c)]. This suggests that, not only the topmost atom, the underlying trimer and the pyramidal base tip also contribute to the field emission if the applied voltage is high enough. We can remove the topmost atom by field evaporation to obtain a trimer tip [Fig. 4(d)] and measure its corresponding field emission pattern, which exhibits a triangular shape [Figs. 4(e) and 4(f)]. Obviously, the field emission pattern accurately reflects the geometry of the nano-pyramid. Similarly, the third layer can be exposed by another field evaporation. In this case, only 8 atoms instead of 10 atoms remain on the third layer [Fig. 4(g)]. Two corner atoms are field evaporated together with the second layer. Interestingly, the angular FE pattern is smaller than that of the trimer tip, as shown in Figs. 4(h) and (i).

For the three tips shown in Fig. 4, we also measure their FE currents as a function of the applied voltage (Fig. 5). The three insets in Fig. 5 show the corresponding FIM images of the tips. Our measurements indicate that the single-atom tip emits the largest FE current at the same applied voltage. The brightness at 100 keV is estimated to be 2.2×10^{13} A/m²·sr for this single-atom tip, which is at least one order of magnitude larger than that of a regular tungsten field emitter (1.4×10^{12} A/m²·sr)

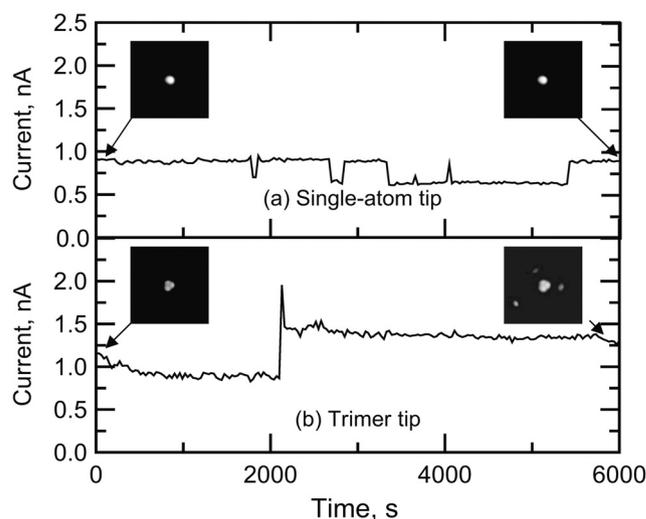


FIG. 6: (a) Time variation of the electron current field emitted from a Pt-covered single-atom tip. (b) Time variation of the current field emitted from a Pt-covered trimer tip. The atomic structures before and after the FE current measurements are also examined with the FIM mode. Their corresponding FIM images are shown at the left and the right insets, respectively.

[19]. Clearly, our pyramidal single-atom tips can provide a brighter source for electron microscopes. We find that these tips are very stable against the field emission measurements. They maintain the original single atom structure after switching back to the FIM mode.

For the cases of the trimer and 8-atom tips, the emission current also increases exponentially with voltage. Interestingly, the emission current from the trimer tip is one order of magnitude smaller than that from the 8-atom tip at the same applied voltage. One may expect that a trimer tip can emit a higher emission current than the 8-atom tip because of its sharper tip shape and thus a higher field enhancement at the tip apex. We guess the different electronic structure and the larger emission area of the 8-atom tip may contribute to its larger emission current. This would require theoretical calculations to understand our measurements.

As good electron sources, a great concern about these tips is the stability of their emission currents. We have prepared a Pt-covered W single-atom tip and a Pt-covered W trimer tip with the above method. We then measure the time dependence of their FE currents. Figure 6(a) shows the FE current of a single-atom tip at about 1 nA and -1500 V. The current is very stable and occasionally jumps to another value. The current fluctuation between two stable values was also seen in other kinds of nanotips [21]. After measuring the field emission for 100 minutes, the current jumps back to the original value and the tip is found to maintain the single-atom sharpness by our FIM observation [Fig. 6(a)]. We believe the jump in current to a lower value is caused by adsorption of a residual gas on the topmost atom. For the field emission of the trimer tip, a higher extraction voltage is required (at -1725 V) to reach a FE current of ~ 1 nA. Similar to the case of the single-atom tip, the FE current is very stable and jumps to a high current of ~ 1.5 nA at ~ 2000 s [Fig. 6(b)].

Then it stays at that value till the end of our measurement. When we recheck the atomic structure with the FIM mode, we find presence of three new spots at the vicinity of the trimer [Fig. 6(b)]. These unknown adsorbates have caused the emission current fluctuations.

IV. CONCLUSIONS

In summary, we have found a simple and reliable method for preparing single-atom tips. The method uses cathodic polarization to prepare a clean surface of the W(111) tip, followed by electroplating a thin layer of a noble metal. With the protection of a noble metal, the W(111) tips can survive in atmosphere for months before transferred into a vacuum chamber. After a gentle annealing in vacuum, a well-defined single-atom tip can be easily and reliably obtained. The tips are both chemically

and thermally stable and can be regenerated for tens of times.

In this study, we also have characterized the field emission behavior of the pyramidal tips. The electron beams field emitted from these tips possesses many desirable features, including small extension angles, smallest emitting areas, high brightness, high spatial coherence, and high stability. Therefore, it can be expected that applications of these single-atom tips to advanced instruments and devices will occur in the near future.

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