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Noble Metal/W(111) Single-Atom Tips and Their Field Electron and Ion Emission Characteristics

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We have developed a simple, reliable and reproducible method for preparing single-atom tips. With electrochemical techniques, a very small amount of a noble metal is plated on the surface of a clean W(111) tip. Upon annealing the tip at an appropriate temperature in vacuum, a three-sided {211} pyramid with a single-atom sharpness is formed spontaneously at the tip apex by adsorbate-induced faceting. This tip is both thermally and chemically stable, and can be regenerated several ten times when accidentally damaged. We use a field ion microscope to examine the atomic structure of the tip apex layer by layer and characterize the corresponding electron emission in the field emission mode. Some properties of Ne⁺ ions emitted from a single-atom tip are also measured, indicating a high brightness and a small extension angle. Many desirable features make the single-atom tips very promising for future particle beam applications in nanoscience and nanotechnology. [DOI: 10.1143/JJAP.45.8972]

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1. Introduction

Single-atom tips (SATs) are of great interest for producing coherent and bright electron beams, as well as for producing highly focused and bright ion beams. They can greatly improve the resolutions of current electron and ion microscopes, and become powerful tools for the fabrication of nanostructures. They can also be applied to scanning probe microscopes, as they can achieve the best spatial resolution and allow for the manipulation of single atoms. Despite their wide applications, only a few methods were proposed for their preparation. In 1986, Fink prepared a SAT by field ion microscopy (FIM).^{1,2)} He first prepared a W(111) tip ending with only three atoms and deposited several tungsten atoms on the tip. He then field-evaporated excess atoms until only one atom remains at the trimer top. In 1992, Binh and coworkers proposed a field-surface-melting method,^{3,4)} which involved repeated heating at a positive high electric field. FIM is also performed to monitor the atomic arrangement of the tip apex until a single atom stands on the top. Nagaoka et al. also fabricated a similar structure by applying a negative high electric field to a contaminated W(111) tip.⁵⁾ There were also reports on the use of an ion back bombardment^{6,7)} or thermal field method^{8–10)} to obtain ultrasharp tips terminated with a few atoms. All of these methods require tedious procedures and high technical skills. Moreover, special instruments, such as FIM and field emission microscopy (FEM), are required to monitor tip conditions in situ. Moreover, the SATs cannot be produced reliably. Even if a SAT is obtained, the tip cannot last long, because its structure is neither thermally nor chemically stable. Thus, the application of SATs is thus far very limited.

In the 1990s, Madey and coworkers have found that an ultrathin Pd, Pt, Au, Ir or Rh film grown on a W(111) surface can undergo massive reconstruction upon annealing to form three-sided pyramids with $\{211\}$ facets.^{11–14)} The driving

force of the facet formation was attributed to an increase in surface energy anisotropy as the metal films were adsorbed on the W(111) surface, which was later confirmed by theoretical calculation.^{15,16)} Inspired by this adsorbateinduced faceting process, Fu et al. demonstrated that Pdcovered W(111) SATs having atom-perfect wedges can be obtained by evaporating a Pd monolayer on a tungsten tip and then annealing the tip in ultra-high vacuum (UHV).¹⁷⁾ Because faceting is a thermodynamic process, the tip can be regenerated by simple annealing even if it is destroyed. This ensures a very long lifetime for the tip. The SAT is stable up to a temperature for its formation, i.e., ~ 1000 K. Most importantly, the stacking of the SAT remains the same after each regeneration. This indicates that the Pd/W(111) SAT can be a well-defined tip, in contrast with previous SATs that never showed the same atomic stacking for the final several atomic layers.

Although this tip possesses many desirable properties, there are several requirements for its preparation.^{11–17)} First, a clean (impurity and oxide free) W(111) surface has to be prepared. Second, a right amount of a noble metal (about one physical monolayer) has to be deposited on the clean tip surface. Third, the tip has to be annealed to an appropriate temperature for a certain period of time to induce surface faceting. This third requirement is a standard procedure in most instruments that use field emission (FE) tips. However, the other two requirements are difficult to be fulfilled in most situations, which make the application of this SAT less convenient. In this work, we propose an electrochemical method to achieve the above two processes in an electrolyte and carry out the annealing in a UHV chamber. Therefore, our new method removes the final obstacle that hinders the application of SATs. We also characterize the apex structure of several noble-metalcovered W(111) pyramidal tips by FIM, investigate their field electron/ion emission behaviors and evaluate their likelihood for practical applications. Finally, we report some abnormal conditions observed on these pyramidal tips after many times of regeneration.

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Fig. 1. Schematic diagram for preparation of SAT. (a) Etch a single crystal W(111) wire to a tip shape. (b) Cover the tip with nail polish except for the apex. (c) Reduce native oxide by cathodic polarization. (d) Electroplate a noble-metal film on the tip. (e) Remove the nail polish and transfer the tip into vacuum. (f) Anneal the tip to diffuse noble metal atoms to other parts of the tip. (g) When the tip is covered by only one physical layer of a noble metal, a pyramidal single-atom tip builds up spontaneously.

2. Experimental Procedure

2.1 Tip etching, cleaning, and electroplating: Liquid process

The procedure for preparing SATs using our new method is schematically depicted in Fig. 1. It can be divided into two parts: the liquid and vacuum processes. In the liquid process, as shown in Figs. 1(a)-1(d), a (111) orientated single crystal W wire of 0.13 mm diameter (purity 99.999%, FEI Co.) is electrochemically polished to a needle shape in KOH solution with an AC voltage [Fig. 1(a)]. The tip is inspected using either an optical microscope or an electron microscope to ensure sharpness. The apex of the needle is approximately hemispherical with an average radius of curvature of 50 nm. After polishing, the tip surface is covered with a thin native oxide layer, which has to be removed before the plating of a noble metal film. To decrease the total amount of the material to be deposited (plating metal), we use nail polish to shield the tip from the electrolyte except for the apex part [Fig. 1(b)].

A potentiostat (M 366A, Princeton Applied Research, U.S.A.) and a conventional three-electrode electrochemical cell are used for all the electrolytic processes. The electrochemical cell has three electrodes: a W tip working electrode, a Pt counter electrode, and a saturated calomel reference electrode (SCE). The shielded tip is immersed into 0.1 M HCl (15 mL) and held at -0.6 V (SCE) to reduce the



Fig. 2. Current transient curve of electrochemical processes. The tip is cathodically polarized to -0.6 V in 0.1 M HCl until 180 s, when a drop of the plating electrolyte (0.1 M HCl + 0.1 mM PdCl₂, 15 µl) is added, and 15 s later, the tip is retrieved from the electrolyte to stop plating.

surface oxide for about 3 min [Fig. 1(c)]. Subsequently, a small amount of the plating electrolyte¹⁸ (15 μ L) is introduced into the electrochemical cell under the same cathodic polarization conditions. Faradic current is *in situ* monitored during the electrochemical process, and the deposition time is controlled to within 10–15 s [Fig. 1(d)]. Figure 2 shows a typical current–time (*I*–*t*) transient of the electrochemical sequence. During the period of cathodic cleaning (t = 0 to 180 s), background current (I_b) exists. During the second period (t = 180 to 195 s), the current increases markedly due to the electroplating of Pd. At t = 195 s, the tip is removed from the plating bath, and the current drops to zero, indicating the end of the electrochemical reaction.

2.2 SAT generation and regeneration: Vacuum process

With protection of the noble metal layer, the tip can be stored even in a humid ambient for a long period of time without any problem of corrosion. Before transferring the electroplated tip into our laboratory-built UHV FIM/FEM chamber,19) we use acetone to remove the nail polish covering on the tip [Fig. 1(e)]. The chamber has a base pressure of about 1×10^{-10} Torr. As depicted in Figs. 1(f) and 1(g), only heat treatments are used for degassing the tip as well as for faceting. The temperature of the tip is measured with an optical pyrometer. After a proper heat treatment (\sim 1000 K), a He–Ne gas mixture with a pressure of 2×10^{-5} Torr is utilized as an image gas for FIM observations. By FIM, we can examine the atomic structure of the tip surface. Typically, a positive high voltage is applied to the tip and carefully and slowly increased for observing atomic images as well as for field evaporating surface atoms. To switch to the field emission mode, the image gas has to be evacuated to a pressure $<5 \times 10^{-10}$ Torr, and then a negative high voltage has to be applied to the tip. Both ions and electrons emitted are amplified using a microchannel plate (MCP; Hamamatsu, Japan), and images are observed on the attached phosphor screen. A digital



Fig. 3. FIM image showing structure of Pd-plated W(111) tip: (a) As-deposited tip. (b) Tip after annealing at 1000 K for 20 min. (c) Tip after annealing at 1000 K for 25 min. (d) Tip after annealing at 1000 K for 30 min. The top layer ends with only 1 atom. (e) The second layer consists of 3 atoms. (f) The third layer consists of 10 atoms. (g) The fourth layer consists of 15 atoms. (h) The pyramidal structure is destroyed by continuous field evaporation. (i) 3D hardball model of nanopyramid. (j) Regenerated single-atom tip after annealing at 1000 K for 5 min. (k) The second layer consists of 3 atoms. (l) The third layer consists of 9 atoms.

camera is used to capture all the images during the experiment. We note that the temperature of the tip during the FIM and FEM observations is fixed at about 40 K.

3. Results

3.1 Apex structure identification

3.1.1 Pd-induced faceting

After degassing a Pd-plated tip in UHV at 700 K for 5 min, we obtain an FIM image of the tip, as shown in Fig. 3(a). Scattered image spots indicate that Pd atoms are deposited randomly on the tip surface. Since the tip apex is covered with a Pd multilayer, a longer period of annealing than that for the vacuum evaporation of Pd is required for extra Pd atoms to diffuse to the tip shank. After annealing at 1000 K for 20 min, an ordered atomic structure starts to appear [Fig. 3(b)]. If the tip is annealed for additional 5 min,

a perfect bcc atomic structure centered around (111) can be clearly identified [Fig. 3(c)], suggesting that a Pd pseudomorphic overlayer is formed on the W(111) tip surface.^{20,21)} The tip is further annealed to 1000 K for 5 min, and the image of a single-atom tip is observed [Fig. 3(d)]. This topmost atom can be field-ionized and field-evaporated by further increasing the positive voltage of the tip, known as field evaporation. Once the top-layer atom is removed, the atomic structure of the second atomic layer is revealed. With field evaporation, the atomic structure of the tip can be examined layer by layer. Figures 3(e) and 3(f) show that 3 atoms constitute the second layer, while 10 atoms constitute the third layer, respectively. The fourth layer is expected to contain 21 atoms, but only 15 atoms are observed after field evaporation, because some corner atoms have been fieldevaporated along with third-layer atoms [Fig. 3(g)]. From



Fig. 4. FIM images showing two types of Rh-covered W(111) single-atom tip: (a) The first layer consists of one atom. (b) The second layer consists of 3 atoms. (c) The third layer consists of 10 atoms. (d) Top view model of tip with 1-3-10 stacking sequence. (e) The first layer consists of 1 atom. (f) The second layer consists of 6 atoms. (g) The third layer consists of 15 atoms; (h) Top view model of tip with 1-6-15 stacking sequence.

these observations, a hardball model of the tip apex can be constructed, as illustrated in Fig. 3(i). The apex is gradually shrunk by three {211} facets until only one atom sits on the top, similar to a nanosized pyramid. This structure is identical to that prepared by vacuum evaporation.¹⁷⁾ After these field evaporations, the sharp tip apex is destroyed, as shown in Fig. 3(h). Interestingly, single-atom sharpness can be recovered only by annealing this tip. Figures 3(j)-3(1)show the images of the topmost three layers for the regenerated pyramidal tip, which has the same atomic stacking as the original pyramidal tip. Note that only 9 atoms, instead of 10 atoms, are observed on the third layer, because the lower right corner atom is also evaporated along with the second layer atoms. Because the SAT is covered with a physical Pd monolayer, such a corner atom is probably a Pd atom, which evaporates at a field lower than that of W atoms.¹⁷⁾

3.1.2 W(111) SATs covered with Pt, Rh, and other noble metals

For a Pt-plated W(111) tip, a SAT can also be obtained simply by annealing at 1100 K in vacuum. Our previous data clearly showed that the atomic stacking of the Pt/W(111) tip is the same as that of the Pd/W(111) tip, and both SATs can be regenerated.²²⁾ For Pd- and Pt-covered SATs, this is a major stacking sequence with 1, 3, and 10 atoms from the top to the deeper layer. However, there is a second stacking sequence with 1, 6, and 15 atoms. This sequence is seldom observed (<10%) for Pd/W(111) and Pt/W(111) SATs, but it is more often observed for Rh/W(111) and Ir/W(111) SATs. An example is shown in Fig. 4. After annealing, a Rh electroplated tip at 1100 K for 30 min, we obtain a Rhcovered SAT with a stacking sequence of 1, 3, and 10 atoms, as shown in Figs. 4(a)-4(c). After the field evaporations, the tip is annealed at 1100 K again to recover the single-atom sharpness. This time, as shown in Figs. 4(e)-4(g), the pyramid is stacked with a sequence of 1, 6, and 15 atoms. Interestingly, both pyramidal structures are terminated with one atom and bounded with the same {211} faceting. We find that the probability for either sequence is a function of annealing temperature. A 1-3-10 stacking sequence is favored for a high annealing temperature. For Rh-covered tips, the probability of 1-3-10 stacking is only 35% at 1100 K, but it increases to 72.5% at 1300 K.²³

3.1.3 Chemical stability of noble-metal/W(111) pyramidal SATs

Our noble-metal plated W(111) tips can be stored under ambient conditions for at least several months before transferring them in vacuum for the preparation of SATs. This is due to the protection of noble-metal thin films. To our surprise, SATs are also chemically inert even they are covered with only one physical monolayer of noble metals. We prepared a Pd/W(111) SAT, stored it under ambient conditions for about 1 h, and then placed it in vacuum again. The SAT was obtained immediately after mild annealing. Another Pd/W(111) SAT was stored under ambient conditions for a month and single atom sharpness was also recovered after simple annealing. These experiments indicate that the SAT prepared in a vacuum chamber can be transferred to air and then to another vacuum system.²⁴

3.2 Electron emission from pyramidal tip

After the preparation of the pyramidal tips as shown above, we can switch to the FEM mode to study field emission behaviors. Figure 5 shows the FIM images and corresponding FE patterns of a Pd-covered W(111) pyramidal tip. In the field emission mode, a negative high voltage is applied to the tip. After the preparation of a Pd-covered SAT [Fig. 5(a)], the FEM image taken at -1000 V shows only a circular spot, indicating that electron emission originates from the topmost atom of the tip. When the negative voltage



Fig. 5. FIM images showing atomic structures of Pd-faceted tip at various applied voltages and their corresponding field emission patterns. First row: (a) FIM image of single-atom tip; (b) its FE pattern at -1000 V; (c) its FE pattern at -1100 V; (d) its FE pattern at -1200 V; (e) FIM image after FE to determine whether single atom remains at tip apex. Second row: (f) FIM image of trimer tip; (g) its FE pattern at -1100 V; (h) its FE pattern at -1200 V; (i) its FE pattern at -1300 V; (j) FIM image after FE to determine whether the trimer remains at tip apex. Third row: (k) FIM image of third layer, which consists of 8 atoms at tip apex. Two corner atoms are also field-evaporated with the second layer; (l) its FE pattern at -1000 V; (m) its FE pattern at -1100 V; (n) its FE pattern at -1200 V; (o) FIM image after FE to determine whether original 8 atoms remain at tip apex. The scale bar indicates a length of 1 cm on the phosphor screen, corresponding to an opening angle of 4° for the electron beam.

is increased, the circular spot enlarges, and gradually, a triangular emission pattern appears, as observed in Figs. 5(b)-5(d). This pattern indicates that electron emission also originates from a triangular base. After field emission, single-atom sharpness is reconfirmed by our FIM observation [Fig. 5(e)], indicating that SAT is highly stable against electron field emission.

We can obtain a trimer tip by field evaporation [Fig. 5(f)]. Figures 5(g)-5(i) show a triangular FE pattern of the trimer tip at various applied voltages, indicating the geometry of the trimer tip. Noted that this pattern is much dimmer than that of the SAT for the same applied voltage. The trimer tip also has a higher onset voltage for field emission than the SAT. Figure 5(j) indicates that this tip is very stable against field emission. Similarly, the third layer can be exposed by another field evaporation process. In this case, only 8 atoms instead of 10 atoms remain on the third layer [Fig. 5(k)]. 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 observed in Figs. 5(1)-5(n).

During the observation of the FE patterns of the Pd/W(11) and Pt/W(111) pyramidal tips, FE currents as a function of the applied voltage are also measured (Fig. 6). Well-fitted straight lines indicate that their emission behaviors obey the Fowler–Nordheim (F–N) equation. Note that the SAT always emits a larger FE current than the other two tips at the same voltage. Interestingly, the emission current from the trimer tip is one order of magnitude smaller than



Fig. 6. F-N plot of single-atom and trimer tips.

that from the 8-atom tip at the same applied voltage. One may expect that the trimer tip can emit a higher emission current than the 8-atom tip because it is sharper and has a higher field enhancement at its apex. We hypothesize that the different electronic structure and large emission area of the 8-atom tip contribute to its large emission current. It would require theoretical calculations to understand our measurements.



Fig. 7. (a) Ne ion current vs voltage characteristics for Pt/W(111) singleatom tip at about 30 K. (b) Field ion image of 20th-generation SAT at 6800 V. (c) Field ion image of 20th-generation SAT at 7200 V. (d) Field ion image of 20th-generation SAT at 7600 V. The scale bar indicates a length of 5 mm on the phosphor screen, corresponding to an opening angle of 2° for the ion beam.

3.3 Ion emission from the faceted tip

The SAT can also serve as a point source of field ion beams, which can be focused for nanoscale imaging, nanomachining,25) nanoanalysis and precision doping in a material.²⁶⁾ To evaluate the possibility for these applications, we should characterize the field ion beams emitted from these pyramidal SATs. Figure 7(a) shows the ion current characteristics of two different generations of Pt/W(111) SATs as a function of extraction voltage. Since field ion current is in the range of 10^{-14} – 10^{-11} Å, we measure this small current by the amplification of the MCP using the calibration procedure described by Purcell and Binh.²⁷⁾ For $P_{\rm Ne} = 1 \times 10^{-4}$ Torr, the field ion current emitted from a first-generation SAT (the first SAT obtained after annealing the plated tip) steeply increases with the field (about 60th power of the voltage) in the low-field regime. As the voltage increases, the current increases at a slow rate, only about one tenth of the low-field regime. If the topmost atom is removed, the plot basically follows the same slope in both the low- and high-field regimes except that a high onset voltage is required.

We use another SAT that has been regenerated 19 times by repeated field evaporation and thermal annealing, as described in §3.1. The log *I*-log *V* plot shown in Fig. 7(a) resembles that of the first-generation SAT, indicating the high stability and reliability of the SAT. The 20th-generation SAT may be blunt, and thus a high voltage is required to emit the same ion current. Figure 7(a) also shows that the ion current basically varies linearly with gas pressure.²⁸⁾

The ion beam pattern of this SAT is very different from that of a normal field emission W tip.²⁹⁾ Figure 7(b) shows



Fig. 8. Typical Ne field ion current emitted from Pt/W(111) single-atom tip as function of time.

only one self-collimated ion beam (extension angle of ~1.6° at full-width half-maximum, FWHM) striking the screen, unlike the diverging scattering spots of the normal W tip. This small single bright spot indicates that the field ion beam has a high angular intensity. Angular intensity has been a major concern for traditional gas field ionization sources (GFISs). Another crucial issue for GFISs is the stability of the ion current over a reasonable operation time.³⁰⁾ Figure 8 shows a typical time evolution of the field ion current emitted from a Pt/W(111) SAT, which exhibits a very high stability (instability < 3%) throughout our measurement time.

3.4 Abnormal tips

3.4.1 Effect of base tip

Nanopyramidal tips with three {211} facets can always be obtained by annealing the noble-metal-plated W(111), but not all of them can be successfully terminated with one atom. Our extensive study shows that defects or impurities near the tip apex can affect the formation of the final stacking structure. In our experience, these defects can sometimes be removed by long annealing, and then the SAT can be obtained again.

Occasionally, we may see asymmetric FIM and FEM patterns for the pyramidal SATs. A typical example is shown in Fig. 9. A single bright spot representing the topmost atom is observed in Fig. 9(a). However, its FE pattern [Figs. 9(b) and 9(c)] does not appear circular as expected. Instead, an isosceles triangular shape is observed. We switch back to the FIM mode and remove the topmost atom to examine the atomic structure underneath. The trimer, as well as the bottom-left wedge, is observed [Fig. 9(d)]. Figures 9(e) and 9(f) also show an isosceles triangular pattern instead of an equilateral triangular pattern. Figures 9(g)-9(i) show that this pyramidal tip can be regenerated and has the same stacking sequence as the normal tip. We observe that this asymmetry in FIM and FEM patterns cannot be removed by adjusting the angle of bellows where the MCP and screen are attached, and thus, the case of a tilted tip is ruled out. We speculate that this asymmetry is caused by an asymmetry in the shape of the large base tip, inducing an asymmetric electric field pattern.

3.4.2 Degradation of SATs by repeated destructions and regenerations

A SAT can be regenerated tens of times, or even over 100 times occasionally. However, this field evaporation and



Fig. 9. FIM images showing atomic structures of asymmetric Pt/W(111)-faceted tip apex and corresponding FE patterns. (a) FIM image of single-atom tip. (b) FE pattern of single-atom tip at -1300 V. (c) FE pattern of single-atom tip at -1400 V. (d) Switch to FIM mode, field evaporate topmost atom and trimer tip formation. (e) FE pattern of trimer tip at -1400 V. (f) FE pattern of trimer tip at -1500 V. (g) Anneal tip at 1000 K for 5 min; FIM image shows a regenerated Pt/W(111) single-atom tip. (h) The second layer consists of 3 atoms. (i) The third layer consists of 7 atoms. In this case, 3 corner atoms are field-evaporated with the second layer. The scale bar indicates a length of 1 cm on the phosphor screen, corresponding to an opening angle of 4° for the electron beam.

regeneration cycle cannot be repeated forever. Field evaporation eventually depletes noble metal atoms, and prolonged cyclic thermal treatments increase tip radius. Figure 10(a) shows the FIM images of a truncated pyramid for a degraded Pt-covered W(111) tip after about 100 times of regenerations. Further annealing can only deteriorate the tip. We have deposited more Pt onto the tip by thermal evaporation. After annealing, apex size decreases [Fig. 10(b)]. Further Pt depositions are carried out, but singleatom sharpness is never recovered. The smallest apex area is shown in Fig. 10(c). Probably, the base tip is too blunt to form a SAT.

Another type of degradation commonly observed after long annealing is the formation of twin peaks on top of the tip. As can be observed in Figs. 11(a) and 11(b), an additional small pyramid is formed on the upper left part of the main pyramid. The minor one is stacked with a sequence of 6, 15 atoms and so on. From these observations, a schematic model of the tip apex is illustrated in Fig. 11(c). Interestingly, after annealing this tip again, the minor pyramid not only recovers but also ends with one atom, as shown in Figs. 11(d) and 11(e). However, it moves downwards after annealing, while the main pyramid remains at the original position.



Fig. 10. Degradation of Pt/W(111) single-atom tip. (a) After \sim 100 times of repeated field evaporation and regeneration, a truncated pyramid substitutes the sharpness of the original single-atom tip. (b) Redeposit Pt (dose \sim 1 ML) and anneal tip again, and decrease in top plane size. (c) After a series of deposition and annealing, the smallest apex size is achieved. (d) Model of tip apex.



Fig. 11. Twin pyramids of Pd/W(111)-faceted tip after long annealing. (a) FIM image of twin pyramids. (b) FIM image of second layer of twin pyramids. (c) Model of twin pyramids. (d) After annealing tip at 1000 K for 5 min, other twin pyramids are formed. (e) FIM image of second layer of twin pyramids. (f) Model of tip apex.

4. Discussion

4.1 Advantages of our method for preparation of noble-metal/W(111) SATs

An important trait of noble-metal/W(111) SATs is that they are thermally and chemically stable. Hence, a nanopyramid can be formed spontaneously by annealing. As mentioned in the introduction, three requirements for the preparation of a noble-metal/W(111) SAT have to be met: surface cleaning, the deposition of one physical monolayer of a noble metal film, and annealing. The first two requirements are difficult to be fulfilled in most instruments. For the case of surface cleaning in UHV, the major contaminations on tungsten surfaces are carbon and oxygen atoms. Carbon atoms can be removed by repeated hightemperature oxidation, and the oxide can be eliminated by high-temperature flashing.³¹⁾ However, this type of surface cleaning is suitable for flat tungsten surfaces, but not for sharp tips. This is due to the facts that the stress induced by oxidation easily destroys the crystal structure at the tip apex and that high-temperature flashing may blunt the tip. As shown in Fig. 10, the blunt tip induces the formation of a truncated pyramid. Another method of preparing a clean tip surface without losing its sharpness is field evaporation, which is a common tip treatment in FIM operation. The drawback of this method is that a field ion microscope has to be installed to monitor the field evaporation process, which is not convenient for most applications. As to the metal deposition in vacuum, the system has to be equipped with an evaporator.

A great advantage of our method is that we can achieve both surface cleaning and metal deposition in an electrochemical cell by several simple procedures. We perform only thermal annealing in vacuum. The plated tips can be stored under ambient conditions for at least several months. Furthermore, it is much easier to change the plating material to prepare different types of SAT than vacuum evaporation. We have succeeded in preparing Pd/W(111), Pt/W(111), Rh/W(111), Au/W(111), and Ir/W(111) SATs. We believe that our method can also be used for the preparation of noble-metal/Mo(111) pyramidal tips, as one physical monolayer of a noble metal also induces a similar faceting transition on a Mo(111) substrate.³¹⁾

4.2 Reduction of tungsten oxide layer and estimation of exposed tip area

The tungsten surface forms a native oxide layer in atmosphere at a very high rate. If Pd is deposited on the tungsten tip without reducing the native oxide first, faceting will not occur. The oxide layer can be removed by cathodic polarization.³²⁾ In our procedure, the tip is cathodically polarized to -0.6 V (SCE) for $3 \text{ min}^{33)}$ to prepare an oxide-free surface for subsequent electroplating.

Figure 2 shows a background current of -1.2 nA at -0.6 V (SCE), which is mainly produced by the hydrogen evolution. This current is proportional to the area of the exposed tip surface. We have determined that one square centimeter of the tungsten surface produces a Faradic current of *ca*. -3 mA in this environment. Thus, we have estimated the exposed tip area to be $\sim 4.6 \times 10^{-7} \text{ cm}^2$ (46 µm^2). This demonstrates that the nail polish is effective in limiting the exposed tip area.

4.3 Estimation of coverage of electroplating material

For the case in Fig. 2, the total amount of the plating material can be estimated by integrating the reaction current produced by the reduction of Pd^{2+} ions to Pd atoms on the tungsten surface with time. The total charge is calculated to be about 1.02×10^{-7} C, corresponding to 5.3×10^{-13} mole of Pd.³⁴) We have further estimated that about 400 PMLs of Pd (1 PML = 1 physical monolayer = 1.7×10^{15} atoms/ cm²) have been plated onto the exposed tip area of ~46 µm².

Electron source	Unit	LaB ₆ ^{a)}	CFE W ^{a)}	SAT
Log brightness	$\mathrm{A}\mathrm{m}^{-2}\mathrm{sr}^{-1}$	10	13	16 ^{b)}
Crossover size	μm	10	0.01	0.0002
Energy spread	eV	1.5	0.3	0.4 ^{b)}
Vacuum	Pa	10^{-4}	10^{-8}	10^{-8}
Maintenance		_	Frequent flashing ~5000 K	Repeated annealing ~1000 K
Lifetime	h	500	>1000	~ 100 regenerations

Table I. Characteristics of the electron sources operating at 100 keV.

a) Data adopted from D. B. Williams and C. B. Carter in *Transmission Electron Microscopy* (Plenum Press, New York, 1996) p. 77.

b) C. Oshima, E. Rokuta, T. Itagaki, T. Ishikawa, B. Cho, H. S. Kuo, I. S. Hwang and T. T. Tsong: e-J. Surf. Sci. Nanotechnol. 3 (2005) 412.

Madey and coworkers have demonstrated the importance of deposition coverage of noble metals, one physical monolayer, for adsorbate-induced faceting.^{11–14)} In our case, electroplating must be carried out under cathodic polarization conditions; otherwise, a native oxide layer would form immediately. This inevitably leads to a very high plating rate; and thus, it is difficult to control the deposition of such a small coverage. We have overcome this problem by confining the plating area merely around the tip apex, reducing the amount of the plating metal. The multilayered noble-metal film may provide a very good protection for the W(111) surface against further oxidation or corrosion during storage under ambient conditions.

The requirement of 1 PML of a noble-metal film can be fulfilled easily by annealing in vacuum. Excess Pd atoms may diffuse to the shank of the tip surface that has not been plated^{35,36)} until only one monolayer is left. Probably due to the plated tip having a much thicker film than the tip prepared by vacuum deposition, it usually takes a long annealing time for the first appearance of a SAT. Another advantage of our new method is that the coverage of the noble-metal film is not as critical as that observed on flat W(111) surfaces by Madey and coworkers. Clearly, our method greatly simplifies the preparation procedure and provides a good protection before the tip is transferred into vacuum for applications.

During electroplating, some other electrochemical reactions may also occur simultaneously, including hydrogen evolution, dissolved oxygen reduction, hydride formation, and chloride adsorption. However, these reactions do not seem to have any deleterious effect on the formation of SATs.

4.4 Formation of pyramidal single-atom tips

For Pt-induced faceting on a flat W(111) surface, it has been found that pyramids formed by {110} facets coexist with pyramids formed by {211} facets.³⁷⁾ This is due to the fact that the surface energy anisotropy and formation barriers are compatible between these two facets on the flat W(111) surface. However, we have never observed the formation of {110} facets at the apex of the W(111) tip. Only {211} facets are observed, probably because three {211} planes are only 19° away from a {111} plane.

Several abnormal pyramids are found here. Most of them are related to the tip apex. It is crucial that the purity levels of tungsten tips, water, and chemicals used should be very high. In addition, if the base tip is not hemispherical, asymmetric FIM and FEM patterns are observed. In many occasions, thermal annealing can be used to remove these imperfections and a SAT can be generated again. However, repeated annealing inevitably blunts the base tip and consumes the plating metal. As we have shown in Figs. 10 and 11, a large base tip usually results in a truncated pyramid or a twin pyramid. These undesirable situations can occur either for a blunt new tip or a sharp tip after being regenerated many times.

4.5 Field electron emission

A SAT can produce bright and coherent electron beams. As shown in Fig. 5, SATs emit electron beams with a extension angle of only $\sim 6^{\circ}$ (at FWHM), which is much smaller than 80° for normal FE tips^{38,39)} and 100° for carbon nanotube tips.40) The self-collimation property originates from the very small pyramidal structure grown on a base tip with a large radius of curvature.⁴¹⁾ The brightness at 100 keV is estimated to be $\sim 10^{13}$ A m⁻² sr⁻¹ (beam current ~ 1 nA), which is at least one order of magnitude larger than that for a regular tungsten field emitter $(1.4 \times 10^{12} \text{ Am}^{-2} \text{ sr}^{-1}).^{42} \text{ A}$ comparison of conventional electron sources with our SATs is shown in Table I. Our pyramidal SATs are better than the conventional electron sources in terms of brightness and emitting area; however, they exhibit a slightly larger energy spread than a CFE tungsten tip. From the recent measurements of the FE spectrum of a Rh/W(111) SAT,⁴¹⁾ an additional shoulder at 0.8 eV below the Fermi level was detected. This would result in a small reduction in temporal coherence. Nevertheless, spatial coherence is expected to be higher than that of a conventional FE tip by a factor of 10-50 due to a small emission area.⁴¹⁾

The stability of emission current is an important factor for an electron emitter. In general, the fluctuations of FE current result from the adsorption of residual gas or ion bombardment from residual gas. For a normal tungsten field emitter, emission current usually decreases with time. Our earlier report showed that the emission currents of a Pt/W(111) SAT and a Pt/W(111) trimer tip are almost constant except for occasional spikes and steplike fluctuations.⁴³⁾ The high stability is mainly due to their small emission area; thus, only the adsorption of residual gas near the topmost atom can cause current fluctuation. These spikes and steplike noises are typical features of nanotip emitters.⁵⁾ An interesting observation is that the adsorption of gas molecules decreases emission current in some occasions; however, it increases emission current in other occasions. It appears that some adsorbates are good emitters, but others are not. It would be interesting to determine which gas molecules enhance/suppress electron field emission.

It has been known that an oxygen layer can also induce $\{211\}$ faceting on a W(111) plane [as well as on a Mo(111) plane].^{31,44–46)} Recently, Szczepkowicz and coworkers have reported the preparation of W(111) pyramidal tips by oxygen-induced faceting.^{47–49)} The tips may end with one or three atoms at their apex.⁵⁰⁾ Their atomic stacking is the same as that of noble-metal/W(111) SATs. The FE pattern from such a tip also exhibits a small extension angle, and the electron beam emitted from it may also possess a high spatial coherence. However, before oxygen exposure, the preparation of a clean W tip surface requires flashing at very high temperatures for several times. High-temperature treatments always make the base tip blunt, and a high voltage is required for extracting electrons.

Several reports have shown that carbon nanotubes (CNTs) can also be used as stable, bright, and coherent electron sources.⁵¹⁾ However, it is not trivial to control a tip ended with only one CNT. Typically, a bundle of CNTs is observed.⁵²⁾ Moreover, there are many different types of CNT, including multiwalled, single-walled, chiral, armchair, capped, and uncapped. These CNTs have different atomic and electronic structures at the end. This remains a great challenge in controlling the tip structure and FE energy spread.⁵³⁾ Furthermore, the FE pattern from a CNT usually exhibits more than one spots,⁵⁴⁾ and thus, a CNT cannot be considered as a perfect point source. Nevertheless, carbon nanotubes can still be considered as good candidates for replacing traditional cold FE tungsten emitters.⁵⁵⁾

4.6 Field ion emission

Focused ion beams (FIBs) have been used in numerous applications in submicron technology, ranging from microor nano-machining, device inspections to material modifications. Currently, the most widely used focused ion beam systems employ liquid metal ion sources (LMISs) due to their high stability, simplicity and high angular intensity. However, LMISs are found to have some limitations. For example, liquid metal ions are inevitably implanted into samples, which may change the physical (such as electrical, magnetic, mechanical, and optical) or chemical properties of the material. The energy distribution of LMISs is large (5-50 eV).⁵⁶⁾ This is mainly due to the Coulomb interaction between the emitted particles, because a large emission current (at least several µA) is required for the operation of a stable LMIS beam. The large energy spread causes a large chromatic aberration. In addition, the opening angle of the emitted ion beams is also large, which causes a large spherical aberration. The virtual source size of LMISs is about 50 nm. Therefore, the resolution of the focused beam is limited to 20-50 nm.

The ion beams emitted from the topmost atom of a noblemetal/W(111) SAT have the potential to become ideal ion sources for FIB systems. There are two major advantages of using these SATs. First, the resolution of the FIB systems can be improved significantly. One factor is the small source size, which is about two orders of magnitude smaller than that of LMISs. Another factor is the small opening angle ($\sim 1^{\circ}$), which is at least one order of magnitude smaller than that of LMISs. Moreover, energy spread can be expected to be small,⁵⁷⁾ because emission current is several orders of magnitude smaller than that of LMISs; thus, the effect of the Coulomb interaction is negligible. The second advantage is a wide selection of ion sources, including gas-phase field ion sources (GFISs) and metal field ion sources. The implantation of metal ions can be avoided if noble gas ion sources are used.

A major concern about the field ion sources (FISs) produced using noble-metal/W(111) SATs is the low angular intensity. The angular intensity estimated from our Ne ion emission at a gas pressure of 2×10^{-4} Torr is $\sim 2 \times 10^{-2} \,\mu$ A/sr, which is three orders of magnitude lower than the typical value of LMISs. The estimated brightness of Ne ion emission is about 1×10^{11} A m⁻² sr⁻¹, which is two to three orders of magnitude larger than that of LMISs. We believe that the angular intensity and brightness of GFISs produced by noble-metal/W(111) SATs can be improved by at least three orders of magnitude. One method of achieving this is to increase gas pressure, because these two values increase linearly with the gas pressure. In our current setup, we can only achieve a Ne gas pressure of 2×10^{-4} Torr. If we increase gas pressure further, the mean free path of Ne ions would be shorter than the spacing between our tip and MCP (14 cm), and the scattering of Ne ions from Ne would become significant. This problem can be overcome by differential pumping,^{58,59)} which has been adopted in a conventional GFIS. Another method of improving angular intensity and brightness is to operate SATs at an optimum temperature. It has been found that the gas-field ion beam emitted from a tip is strongly temperature-dependent and a sharp maximum ion current is produced at an optimum temperature. The temperature is 21 K for the Ne ion current emitted from a tungsten tip.60) Our SATs are W(111) tips covered with one physical layer of a noble metal. The optimum temperature for the maximum Ne ion current may be lower than 21 K because of the small adsorption energies and diffusion barriers for Ne atoms on the noble metal film. The tip temperature is fixed at ~ 40 K in our current setup. Currently, we are modifying our system to carry out temperature-dependence measurements.

Our pyramidal SATs can be considered as a special type of nanotip or supertip (a tiny protrusion of the order of 1-2 nm grown on top of a base tip). Börret and coworkers demonstrated that GFISs emitted from their supertips have an exceptionally high angular intensity $(35 \mu A/sr)$ and brightness $(10^{14} \text{ Am}^{-2} \text{ sr}^{-1})$.⁷⁾ Edinger and coworkers also demonstrated that GFIS emitted from their nanotips have an angular intensity up to $10 \mu A/sr$.¹⁰⁾ These results indicate that a nano-protrusion on a base tip can be an ideal field ion emitter. Börret et al. prepared their supertips by ion back bombardment, and Edinger et al. prepared their nanotips by a thermal field method. Even though these methods can produce 1-2 nm protrusions on a base tip, they are much more complex than our method for the preparation of SATs. Moreover, they require a FEM or a FIM to monitor tip conditions during the process, which would not be convenient for real applications. Moreover, their tips are not thermally stable; thus, cannot be regenerated as our SATs.

In *I*–V characteristics (Fig. 7), the slopes of region 1 $(m_1 \sim 60)$ and region 2 $(m_2 \sim 6)$ are higher than those of a

Table II. Characteristics of various ion sources.

Ion source	Unit	Plasma source	LMIS	$\begin{array}{c} GFIS^{a)} \\ (H_2, \ 2\times 10^{-2} \ Torr) \end{array}$	$\frac{\text{SAT}^{\text{b})}}{(\text{Ne, } 2 \times 10^{-2} \text{ Torr})}$
Semiangle	deg.	_	30	45	1
Angular intensity	µA/sr	3×10^3	20	1	2
Source size	nm	$\sim 3 \times 10^4$	$\sim 100^{c)}$	~1	~ 0.2 (single atom)
Brightness	$\mathrm{A}\mathrm{m}^{-2}\mathrm{sr}^{-1}$	1×10^{6}	6×10^8	3×10^{11}	1×10^{13}

a) Angular intensity is calculated from the sensitivity of $5 \times 10^{-5} \text{ A sr}^{-1} \text{ Torr}^{-1}$, obtained by J. H. Orloff and L. W. Swanson in J. Vac. Sci. Technol. **12** (1975) 1209. This value is valid when an Ir normal tip is used in hydrogen atmosphere over the range $3 \times 10^{-4} \sim 2 \times 10^{-2} \text{ Torr}$.

b) Angular intensity is estimated from the sensitivity of $8.5 \times 10^{-5} \,\text{A}\,\text{sr}^{-1} \,\text{Torr}^{-1}$.

c) This value was assumed by J. W. Ward, R. L. Seliger in J. Vac. Sci. Technol. 19 (1981) 1082.

normal tip $(m_1 \sim 30, m_2 \sim 3-4)$.^{61,62)} The slope of *I–V* characteristics has been considered to depend on tip cone angle, i.e., current steeply increases as cone angle decreases.⁵⁸⁾ The steep slope of our SATs may be due to the small radii of base tips. In addition, ion current is also determined from a dynamical balance between the gas supply coming from the tip shank and the gas flux escaping along the tip shank.⁶¹⁾ The three {211} facets of our SATs may provide efficient diffusion channels^{17,63)} for Ne atoms, and thus, steep slopes are obtained.

In Table II, we compare the characteristics of the LMIS, normal GFIS, and Ne gas ion source produced by our Pt/W(111) SAT. The performance characteristics of our SAT are calculated by Ne extrapolation to 2×10^{-2} Torr. As shown in this table, angular intensity may approach $2 \mu A/sr$, and brightness may exceed 10^{13} A m⁻² sr⁻¹ if our SAT can be operated in a differential pumping system. We believe that the angular current densities can be further increased if our tip can be controlled at an optimum temperature, differential pumping is adopted, and gas with a low ionization field (for example, H₂ and Ar) is used.

5. Conclusions

We have developed a method of preparing SATs. This method involves cathodic polarization for preparing a clean W tip surface, followed by electroplating a thin layer of a noble metal on it. Owing to the protection of the noble-metal layer, plated W(111) tips can be stored in atmosphere for months without corrosion. After simple annealing in vacuum, a well-defined SAT can be reliably obtained. The tips are both chemically and thermally stable and can be regenerated several ten times. We believe that this method can also be used for the preparation of noble-metal/Mo(111) pyramidal SATs.

In this study, we have also characterized the field electron and field ion emission behaviors of faceted tips by switching between FIM and FEM modes. As expected, these SATs possess many desirable features for next-generation ion and electron sources. The small extension angle, smallest emission area, high brightness, high wave coherence, and high stability of the particle beams emitted from these SATs make them very promising for many applications.

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