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Preparation and Characterization of Single-Atom Tips

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ABSTRACT

A new, simple, and easily reproducible method of preparing single-atom tips by electroplating Pd or Pt on single-crystal W(111) tips followed by thermal annealing in a vacuum is reported. These tips are both thermally and chemically stable and can also be regenerated when accidentally damaged. The atomic structures of the tips are identical to those prepared by vacuum evaporation, as observed by field ion microscopy. The corresponding field emission characteristics are investigated with field emission microscopy.

Well-defined field emission (FE) tips with single-atom sharpness are of great interest for producing coherent and bright electron beams.[1] They can greatly improve the resolution of electron microscopy. Single-atom tips are also highly desirable for scanning tunneling microscopes (STMs),[2] since they can achieve the optimum lateral resolution and provide well-defined tips for measurement of surface electronic structures. Despite many applications of single-atom tips, they were very difficult to prepare. Several groups[3−7] have proposed different approaches to create single-atom tips, but these methods require special equipment and tedious procedures in ultrahigh vacuum (UHV). Moreover, the nanoprotrusions obtained are not thermodynamically or chemically stable, so the structure may not remain after an extended period of field emission. Furthermore, they can neither be regenerated nor be taken out of the UHV chamber. These problems seriously hinder the application of single-atom tips.

Madey et al. have found that ultrathin Pd, Pt, Au, Ir, or Rh films grown on the W(111) surface can undergo massive reconstruction upon annealing to form three-sided pyramids with {211} facets.[8−11] The driving force of the facet formation was attributed to the increase of the surface energy anisotropy as the metal films are adsorbed on the W(111) surface, which was later confirmed by theoretical calculations.[12,13] Recently, Fu and Tsong demonstrated that Pd-covered W(111) single-atom tips, having atom-perfect wedges, could be created by the same faceting process after annealing in UHV.[14] The major advantage of this method is that the faceting is a thermodynamic process. The tip is stable up to the temperature of its formation, i.e., ∼1000 K. When the tip is destroyed, it can be regenerated through a simple annealing. Most importantly, the stacking of the single-atom tips remains the same after each regeneration. This ensures a long lifetime of this kind of single-atom tip. Although such tips possess many desirable properties, the Pd evaporation in UHV still makes its application less convenient.

In this study, a new method with electroplating a Pd (or Pt) film on the single-crystal W(111) tip is proposed. Electroplating of a metal film is easier and more convenient than evaporation in a vacuum. Simply by annealing the Pd (or Pt)-wrapped W(111) tip in a vacuum chamber, a regenerable single-atom tip with atomically perfect stacking is prepared. The atomic stacking is examined with the field ion microscopy (FIM), and the field emission pattern is studied with field emission microscopy (FEM).

A tungsten tip is prepared from a ⟨111⟩ orientated single-crystal wire of 0.35 mm in diameter by electrochemical etching[15] followed by coating with ethyl acetate, except for the apex. A potentiostat and a 3-electrode electrochemical cell are used for cathodic cleaning and electroplating. To prepare a clean and defect-free surface for deposition, the tip is immersed into the base electrolyte (0.1 M HCl) and held at −0.6 V (SCE) for 3 min to reduce the native oxide.[16] For electroplating a Pd film, a small drop (15 μL) of Pd plating electrolyte (0.1 M HCl + 0.1 mM $PdCl_2$) is introduced into the base electrolyte. For electroplating a Pt film, then a drop of Pt plating electrolyte (0.1 M HCl + 0.01 mM $PtCl_2$) is added into the base electrolyte.[17] Instantly, the cathodic current increases dramatically to manifest that the electroplating is taking place on the tip apex. After plating about 15 s, the tip is withdrawn to stop plating. In the above procedures, we estimate tens to hundreds of physical monolayers (PMLs) of Pd (or Pt) are plated on the tip apex.

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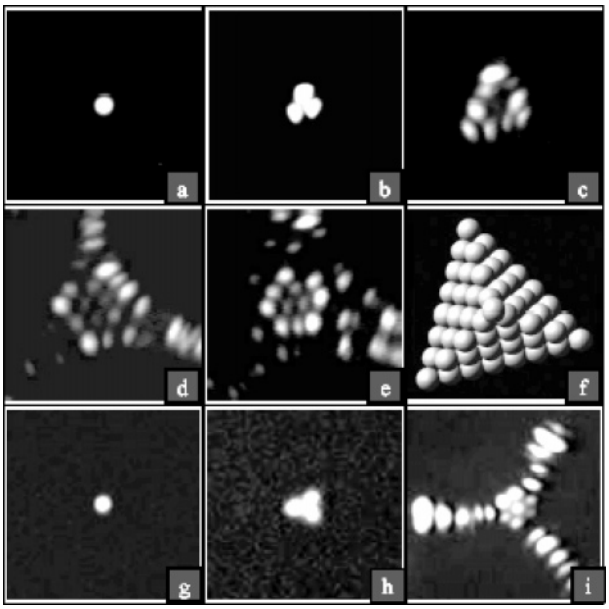

Figure 1. (a−e) FIM images showing the structure of a Pd-covered W(111) single-atom tip: (a) the top layer consists of only one atom; (b) the second layer consists of three atoms; (c) the third layer consists of 10 atoms; (d) the fourth layer consists of 15 atoms; (e) the pyramidal structure is destroyed by the continuous field evaporation; (f) a 3-D hardball model of the nanopyramid. (g−i) FIM images showing the structure of a Pt-covered W(111) single-atom tip: (g) the top layer comprises only one atom; (h) the second layer comprises three atoms; (i) the third layer shows only 7 atoms, rather than 10 atoms, because three corner atoms are removed together with the second layer during the field evaporation.

After cleaning in acetone (to remove ethyl acetate) and then in DI water, the Pd-plated tip is loaded in a homemade UHV−FIM/FEM chamber, which has already been described in detail elsewhere.[15] Inside the UHV chamber, the tip is directly heated to about 1000 K for 30 min to induce faceting. A pyramid ending with one atom is formed on top of the tip apex. For the operation of the FIM, neon gas of 2×10^{-5} Torr is admitted as an image gas. An FIM image of the pyramidal single-atom tip is shown in Figure 1a. One can further study the atomic structures underneath the topmost atom using field evaporation.[15] The entire layer of atoms at the tip apex can be evaporated by applying a stronger electric field. The next layer exposed is then imaged with the FIM. With this method, the second layer consisting of 3 atoms and the third layer consisting of 10 atoms are observed (Figures 1b and c). Figure 1d showing only 15 atoms on the fourth layer, rather than 21 atoms, because a few corner atoms are field evaporated together with the third layer of atoms. After the above procedure, the tip apex is destroyed. Nevertheless, the single-atom tip can be regenerated simply by annealing to 1000 K, as demonstrated in the previous study by Fu et al.[14] This process can be repeated many times, and we find that the regenerated tip is identical to the first one. A hard sphere model of the pyramidal single-atom tip is illustrated in Figure 1f. Figures 1a−f also prove that the Pd-covered W(111) single-atom tip prepared by electroplating is identical to that prepared by the Pd evaporation in a vacuum.[14] This is simply due to the fact that formation of the Pd-covered W(111) single-atom tip is a thermodynamic process.

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 a vacuum. Figures 1g−i show the top three layers of the Pt-coated W single-atom tip. The atomic structure is very similar to that of the Pd-coated W(111) tip and both single-atom tips are regenerable. These results further indicate that our electroplating approach can also be applied to other faceting systems to produce single-atom tips.

Madey et al. pointed out that proper coverage (∼1 physical monolayer (PML)) of a metal film on W(111) is one of the prerequisites in inducing the faceting transition.[8−11] However, it is very difficult to control electroplating of only 1 PML due to the rather high deposition rate.[18] Moreover, the as-deposited tip has to be rinsed and left in atmosphere for a period of time. One physical monolayer may not be sufficient to protect the W tip from oxidation or corrosion in the ambient condition. In our approach, a noble metal film of tens to hundreds of PMLs is deposited on a W(111) single crystal tip. The coverage of the metal film is far beyond 1 PML and not as critical as what Madey et al. have claimed on flat W(111) surfaces. Actually, this thicker metal film can provide a better protection of the W(111) surface against further oxidation or corrosion. The coverage of the metal films is not so critical, probably because the Pd (or Pt) layer is deposited on a very small area at the tip apex only. During annealing in a vacuum, excess Pd (or Pt) atoms may diffuse to other parts of the tip surface that have not been plated.[19−20] Clearly, our electroplating method greatly simplifies the deposition process and provides better protection before the tip is transferred into vacuum for real applications.

It has also been expected that a single-atom tip can serve as a perfect point source of electron beams.[1] After checking the atomic structure of the tip with the FIM mode, we can switch to the FEM mode by pumping out the image gas and inverting the polarity of the tip. With the FEM mode, we can study the field emission behaviors of our single-atom tips. Local field enhancement will confine the topmost atoms to emit electrons at the smallest negative voltage.[21] For a Pd-covered W(111) single-atom tip (Figure 2a), a circular spot subtending an angle of ∼6.6° (at fwhm) is seen with the FEM mode (Figure 2b). The beam intensity profile, approximately Gaussian, is also superimposed on the emission pattern. This indicates that the electron emission is originated from the topmost atom of the tip. After observing the field emission pattern, we recheck the atomic arrangement with the FIM mode. The original single atom remains intact at the tip apex.

When the topmost atom is removed by field evaporation, the second layer of a trimer is exposed, as in Figure 2c. The corresponding field emission pattern also exhibits a triangular shape (Figure 2d), indicating that the field emission mainly comes from the trimer. After the field emission operation, the trimer remains intact, as confirmed with the FIM mode. By switching between the FIM and FEM modes, the atomic structures of the tip and their corresponding FE patterns can be examined.

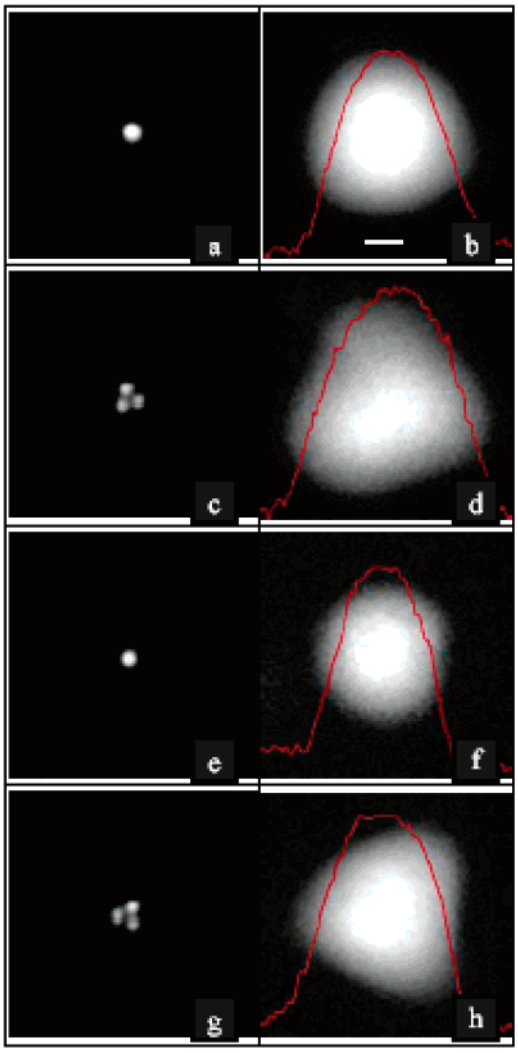

Figure 2. FIM and FEM images showing the atomic structures of the tip apex and the corresponding FE patterns, respectively. (a) FIM image of a Pd-covered single-atom tip. (b) FE pattern and beam intensity distribution of the Pd-covered single-atom tip at −1100 V. (c) FIM image of a Pd-covered trimer tip. (d) FE pattern and beam intensity distribution of the Pd-covered trimer tip at −1300 V. (e) FIM image of a Pt-covered single-atom tip. (f) FE pattern and beam intensity distribution of the Pt-covered single-atom tip at −1300V. (g) FIM image of a Pt-covered trimer tip. (h) FE pattern and beam intensity distribution of the Pt-covered trimer tip at −1500 V. A voltage of 900 V is applied to the channel plate for taking FIM images, but 700 V is applied for taking field emission patterns. Scale bar indicates a length of 0.5 cm on the phosphor screen, corresponding to 2° in the opening angle of the electron beam.

For the case of the Pt-covered W(111) single-atom tip, the FIM and the corresponding FEM images are shown in Figures 2e−h. The tip is very stable against the field emission, as in the case of Pd-covered W(111) tips. A major difference is that a higher voltage is needed to achieve the same field emission current because of its higher work function. In addition, the field emission pattern for the Pt-covered W(111) single-atom tip has an extension angle ~5.6°, slightly smaller than that of the Pd-covered W(111) single-atom tip.

Figure 3a plots the field emission current as a function of the applied voltage for the above tips. The FE current

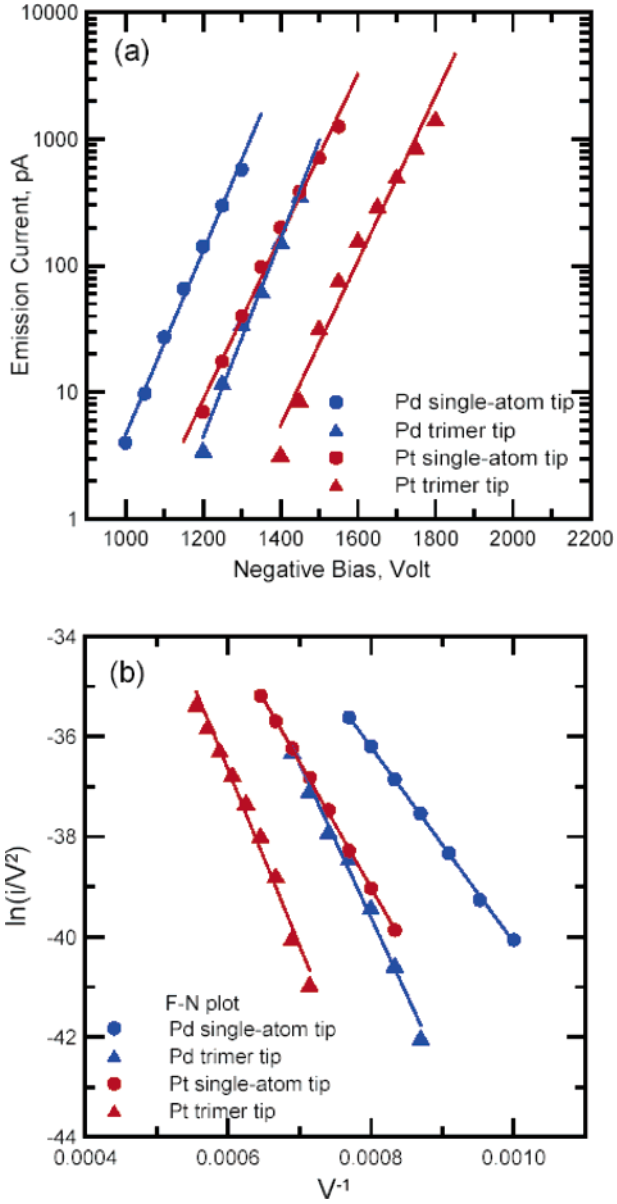

Figure 3. (a) Field emission currents of single-atom tips and trimer tips as a function of the applied voltage. (b) Fowler−Nordheim (FN) plot of the single atom tips and trimer tips.

increases exponentially with the applied voltages, so the FE current is plotted in the logarithmic scale. For the case of the Pd-coated tip (as well as for the case of the Pt-coated tip), the single-atom tip has a lower threshold voltage for field emission to occur than the trimer tip and the former has a larger FE current than the latter at the same voltage. We attribute these effects to the local field enhancement[21] and the resonant tunneling.[5,7,22] The reduced brightness (B_r)[23] of single-atom tips also increases with the applied voltage. It is calculated to be 2.2×10^8 A/m^2·sr·V for Pd-covered W(111) tips at 1300 V and 3.5×10^8 A/m^2·sr·V for Pt-covered W(111) tips at 1550 V. In fact, we are able to measure a higher brightness at a total current of several nanoamperes without destroying the tip apex. It has been confirmed that brightness is proportional to the accelerating voltage.[24] If a 100 keV is used as an accelerating voltage, the brightness of such emitters will scale up to 2.2×10^{13}

$A/m^2 \cdot sr$ for the Pd-covered single-atom tip and 3.5×10^{13} $A/m^2 \cdot sr$ for the Pt-covered single-atom tip. Compared with 1.4×10^{12} $A/m^2 \cdot sr$ of the W⟨111⟩ build-up field emission gun at 100 keV,[25] clearly our pyramidal single-atom tips provide a brighter source for electron microscopy. Fowler−Nordheim (F−N) plots of the tips are also shown in Figure 3b. The well-fitted straight lines indicate that the FE currents obey the F−N theory.[26] In addition, our measurements show that the FE currents of single-atom tips are very stable (peak-to-peak noise is less than 8% of the total current at a given field) even at the vacuum pressure of 5×10^{-10} Torr. Probably the small emitting area of single-atom tips significantly reduces the probability of gas molecular adsorption, which is the major cause for the instability of FE currents from normal W field emitters.[27] Most importantly, coherence of electron beams will be greatly improved because field emission occurs one electron at a time from the single apex atom.[1,28]

Several reports have shown that current emitted from carbon nanotubes can also be used as a stable electron source of high brightness and good coherence.[29] However, it is not trivial to prepare a tip ending with a single nanotube. Usually, a bundle of nanotube emitters are seen.[30,31] Also, there are many different kinds of nanotubes, including multiwalled, single-walled, metallic, semiconducting, capped, uncapped, etc., and they exhibit different field emission behaviors.[32] It remains a great difficulty in controlling the tip structure. Furthermore, field emission patterns from single carbon nanotubes exhibit more than one spot,[29−31,33] and thus cannot be considered as a perfect point source. Nevertheless, carbon nanotubes can still be considered as good candidates to replace the traditional cold field emission tungsten emitters.

In summary, we have demonstrated a new electroplating method to prepare single-atom tips. The atomic structure and field emission of the tips are also characterized. Pd (Pt) multilayer electroplating can replace the in-situ deposition process in UHV. The Pd (Pt)-plated tips can survive in the ambient condition for months before transferred into a vacuum system. Single-atom tips can be obtained easily by annealing the plated tips in a vacuum. These single-atom tips can be easily regenerated when accidentally damaged after prolonged use, guaranteeing the long lifetime of their operation. The small extension angle, smallest emitting area, high brightness, high wave coherence, and high stability of the electron beams field emitted from these single-atom tips make their application to electron microscopy,[34] electron spectroscopy, and electron holography[35−37] become very attractive.

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