Fabrication of Coherent Electron Sources with Palladium Oxide Reservoirs*

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(Received 24 January 2018; Accepted 28 May 2018; Published 21 June 2018)

Tungsten (W) nanopyramids coated with noble metal films can function as highly coherent electron sources. This study aims to grow nanopyramids by employing long-distance surface diffusion of palladium (Pd) atoms. Collodion (also known as nitrocellulose) containing PdO powder was coated on the regions far from the W tip and was used as a source of Pd atoms. Annealing the W tip in UHV resulted in a change in the field ion microscopy (FIM) pattern. The resultant FIM images showed three equivalent (211) planes adjacent to the (111) planes of the W tips. However, with the proposed method, the apex of the W tip was not a single atom, but a wide triangle corresponding to the subsurface of an ideal nanopyramid. [DOI: 10.1380/ejssnt.2018.306]

Keywords: Field emission; Single-atom emitters; Field ion microscopy; Tungsten; Palladium

I. INTRODUCTION

Ultrasharp metal tips are highly coherent electron sources capable of improving electron optics devices such as electron microscopes and electron beam lithography systems. A basic strategy for developing the electron sources is to reduce the apex areas. In principle, the smaller the area, the higher the coherence of the electrons released from the tip.

A tungsten (W) pyramid (nanopyramid) coated with a monolayer film of noble metal (NM) was grown on the apex of a W tip. The nanopyramids show unusual characteristics associated with field emission, such as a narrow angular spread of the electron beam, narrow source areas, and a stable emitted current [1, 2]. The nanopyramids also exhibit important properties with respect to their application. That is, due to their thermodynamic stability, the nanopyramids are able to easily regenerate, which elongates the lifetime of electron source containing the nanopyramids. These characteristics make the nanopyramids potentially suitable as a next-generation coherent electron source. However, there are problems related to the growth yield ratio and the number of nanopyramid regenerations.

The number of regenerations (i.e., lifetime of the W nanopyramids used as an electron source) is limited by the number of NM atoms on the tip. In conventional methods [3–5], however, the total number of NM atoms reserved for nanopyramid regeneration is small. To address this problem, Nakagawa et al. developed another method, in which Pd atoms were supplied to the W tip from the rear of the W wire [6]. This study indicated that it is possible to supply an unlimited number of NM atoms from the NM reservoir via surface diffusion even if the reservoir is located on surface regions of the W needle that are far from the nanopyramids. Following Nakagawa’s study, we applied a modified version of this method by employing the surface diffusion of platinum and gold [7, 8].

In this study, collodion containing PdO powder was used as the Pd source rather than the electroplated thin films of NM atoms used in previous studies. The composition of the present specimen is analogous to those of the ZrO/W Schottky emitter [9], although the aimed overlayer totally differs from each other: Substance of the overlayer is an oxide for Schottky emitter, while it is metal oxides, but pristine Pd for the present specimens. Formation of the pristine metal films require PdO to be thermally reduced.

Experimental data of PdO reduction in ultrahigh vacuum have not been reported in our best knowledge, although Zhang et al. researched decomposition temperature of PdO under oxygen partial pressures ranging from $1.013 \times 10^5$ Pa to $1.013 \times 10^5$ Pa. They showed that, even in an oxygen atmosphere with the partial pressure of $1.013 \times 10^5$ Pa, PdO turned into Pd [10]. Also, they demonstrated that PdO is reduced at 1124 K in $1.013 \times 10^5$ Pa of oxygen. According to the results of Zhang’s experiment, transition from PdO to Pd is plausible at high temperature. We expected that PdO reduction occurs at 1000 K which required nanoparamid formation.

Structural changes in the W tip associated with this method are reported in this paper.

II. EXPERIMENTAL

Specimens of W tips, on which the apex of the nanopyramid grows, were made from polycrystalline W wire with a diameter and length of 0.1 mm and 4 mm, respectively. One end of the W wire was etched in 2 M aqueous potassium hydroxide to make it sharp enough for field emission. After etching, collodion, in which palladium oxide (PdO) powder was dispersed, was placed on the side face of the needle, which was approximately 2 mm from the W tip.

After the atmospheric treatment, the specimens were annealed in an ultrahigh vacuum (UHV) at about 1000 K. The atomic structures of the W tips were observed by...

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* This paper was presented at the 11th International Symposium on Atomic Level Characterizations for New Materials and Devices ’17, Aqua Kauai Beach Resort, Kauai, Hawaii, USA, December 3–8, 2017.
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means of field ion microscopy (FIM) at 100 K. All the imaging gases are helium (He) with the pressures around $2 \times 10^{-3}$ Pa.

### III. RESULTS AND DISCUSSION

#### A. Atomic structure of a W tip with PdO reservoir

Figure 1(a–c) shows the structure of the W tip as a function of the total annealing time. A typical FIM image of a BCC tip is shown in Fig. 1(a). Every bright spot involved in Fig. 1(a) was almost equal in intensity, and was scattered in the entire region of a fluorescence screen. Homogeneous distribution of the FI-beam spots suggests that electric fields were homogeneous on the whole region of the surface of the tip. After 1 min annealing, a countable number of bright spots were seen only in the central region of the image [Fig. 1(b)]. The concentrated ion beams are an implication that electric fields were anisotropically high on the end of the tip. By additional annealing for 3 min, the FIM changes from Fig. 1(b) to Fig. 1(c). Comparison between Fig. 1(c) and Fig. 1(a) recognized that three monoatomic-chains directed along equivalent <311> direction are formed. In other words, the three sided nanopyramid with {211} faceted faces formed. If the surface of the tip was not contaminated with any adsorbate, temperatures higher than 1500 K are necessary to develop the faceting of the {211} faces [3]. Therefore, this change did not occur on a pristine W tip at 1000 K, indicating that numerous Pd atoms moved from the Pd reservoir to the proximity of the tip and started to coat this region with monolayer films of Pd. The top of the nanopyramid is triangle consisting of fifteen atoms. Figure 1(d) shows schematic model of the top of the nanopyramid.

Figure 2(a–c) shows changes of the atomic structure by annealing at 1000 K done additionally on the specimen corresponding to that of Fig. 1(c). After annealing for 1 min (total annealing time is 5 min), the three ridges were no longer monoatomic chains, and the top of the nanopyramid became broad [Fig. 2(a)]. As for the completeness of the ideal structure, further annealing did not change for the better, as show in Fig. 2(b, c). As removing the surface layers by means of field evaporation [Fig. 2(d)], we successfully regenerated the nanopyramid with three ridges of monoatomic chains by annealing the specimen at 1000 K for 3 min [Fig. 2(e)], although the imaging biases became higher. Changes represented by Figs. 1 and 2 are very typical for the specimen prepared by the present production method.

In spite of prolonging annealing treatment, the single atom top of the nanopyramid has not been attained so far. In case of using Pd as an overlayer metal, nanopyramids with a single atom top are thermally equilibrated. The observed structures different from the ideal one is an implication that the specimens differ in composition. Even if very tiny amount of impurities like carbon and oxygen were incorporated into the nanopyramid, we suppose that the impurity effects prevent the growth from completing in an ideal way of producing the nanopyramid. Simultaneously, however, we suppose that the impurity effects are not a dominant, fatal one, considering the novel recipe in an ideal way of producing the nanopyramid. The structural changes observed in this study are largely different from those seen when carbon was incorporated on surface layers of the W tip [11, 12]. The incorporation of carbon atoms did not result in the {211} facet. According to previous studies, it does not look like oxygen are the cause of the present structural changes. Temperatures at which the {211} faces facet are much higher in case of the structural changes due to oxygen incorporation (1260 K to 1580 K) [13–15]. Rather than the explanations based on such impurity incorporation, the present structural change is close to those seen in the conventional growth processes [1–6]. The fact that a single atom top does not achieve may suggest that the thermal equilibrium shape is sensitive for small amount of oxygen and carbon contamination. In order to form the nanopyramid with single atom top, it is necessary to reduce contamination of these impurities.
FIG. 3. FEM images and emission pattern intensity profile of W nanopyramid with fifteen atom termination. (a) Field emission pattern of nanopyramid at extractor voltage of 711 V. The emission current is 0.588 nA. (b) Intensity profile of the emission pattern along solid line AB in (a) fitted to a Gaussian distribution.

B. Field emission pattern of a nanopyramid with a top consisting of fifteen atoms

Figure 3(a) shows the field emission pattern of the nanopyramid shown in Fig. 1(c), whose top was terminated with fifteen atoms. The emission pattern intensity profile along solid line AB in Fig. 3(a) was fitted with a Gaussian distribution function as shown in Fig. 3(b). The opening angle corresponding to the FWHM of the beam profile is about $\pm 4.7^\circ$, which is consistent with the atomic structure shown in Fig. 1(c).

C. Characteristics of Fowler-Nordheim plot

Figure 4 shows the Fowler-Nordheim (FN) plots obtained for the bare W tip [solid circles, Fig. 1(a)], the faceted W tip after annealing at 1000 K for 1 min [solid triangles, Fig. 1(b)], the W nanopyramid terminated with fifteen atoms [open squares, Fig. 1(c)], and the repaired nanopyramid [open triangles, Fig. 2(e)]. As shown experimentally by Ishikawa et al., we suppose that, when nanopyramid growth conditions are undoubtedly valid except for annealing time, the successful growth would depend on finding the correct sample-annealing time. While developing low-voltage scanning electron microscopy, Ishikawa used FN curves to determine whether nanopyramid growth was completed [5]. He found that all the tested specimens exhibited the following identical behavior: The FN plot shifted to the left during nanopyramid growth and reached the leftmost position when the growth stopped. Although our FN data are not as detailed as those of Ishikawa et al., the movement seen in Fig. 4 is applicable to the previous findings.

IV. CONCLUSION

In this study, we fabricated a W nanopyramid coated with Pd film by employing the surface diffusion of Pd atoms, which were supplied from powdered PdO located at a far distance from the W tip.

The findings are summarized as follows:

1. Three equivalent \{211\} planes of the tungsten tips appeared around the \{111\} pole.

2. Pd atoms were supplied to the W tip end via surface diffusion from PdO at the rear of the W tip.

3. Termination with a single atom was not achieved in this study.
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