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Electron Emission Characteristics of Au-covered Tungsten⟨111⟩ Nanotips *

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We have investigated emission properties of Au-covered W⟨111⟩ nanotips fabricated by means of an electroplating method. The stable nanotips possessed a three-sided pyramid structure terminated with three atoms, differing from the nanotips covered with the other noble metals such as Pd, Pt, Rh, and Ir, of which all the final structures are terminated with a single atom. The observed values of the Au-covered nanotips were comparable with those of single-atom tips covered with the other noble metals; they were the semi-cone angle of 2 degrees, the brightness of 5×10^8 A/cm^{2}sr, and the half maximum full-widths of spectra, 0.3 eV. In addition, the self-repairing function and the demountable characteristic have been confirmed. As compared with other metal-covered nanotips, the other different feature of the Au-covered nanotips was their high reproducibility of the energy spectra. The hump always appeared at about 0.7 eV below Fermi level. [DOI: 10.1380/ejssnt.2008.25]

Keywords: Nano-tip; Single-atom tip; Field emission microscopy; Field emission spectroscopy; Field ion microscopy; Gold; Tungsten

I. INTRODUCTION

Field emission (FE) nanotips have recently attracted much attention because the high brightness and the high coherence of their electron beams play an important role in high-resolution electron microscopes [1]. Using field ion microscopy (FIM) and field emission microscopy (FEM), twenty years ago, Fink *et al.* [2] observed tungsten (W) nano-pyramids fabricated at the apex of W⟨111⟩ tips by applying remolding vacuum evaporation and the other techniques, and demonstrated that electron beams emitted from the nano-pyramid terminated with a single atom were significantly collimated. Later, some W nanotips have been fabricated on the apex of macroscopic W tips with some kinds of techniques by some researchers [3–5]. Since there was no way to repair the conventional nanotips if the nano-pyramids were accidentally destroyed, however, their applications were extremely limited. The absence of the repairing treatment was the most serious problem relating with the practical lifetime of the nanotips.

Recently, Fu *et al.* [6] demonstrated that new nanotips of noble metal covered W⟨111⟩ were repaired repeatedly by annealing at feasible temperatures even if they were destroyed. The thickness of these noble metals is one physical monolayer. The three-sided pyramid is terminated with a single atom, of which the structure is thermodynamically stable.

In previous works [7–9], we have reported the attractive electron emission properties of the nanotips covered with Pd, Pt, Rh, and Ir, and discussed the peculiar emission mechanism of FE from these nanotips on the basis of energy spectra measured by field emission spectroscopy (FES). Although the emission properties of those nanotips were observed in detail, no clear dependence of covering metals was recognized clearly so far. In this work, therefore, we have fabricated the nanotips covered with Au, of which the emission properties were unknown. We have measured the emission properties to clarify the characteristic features of the Au-covered nanotips being different from the other nanotips.

II. EXPERIMENTAL

The experiments were done in an ultra high vacuum (UHV) chamber capable of FIM, FEM, and FES. The base pressure of the chamber was 2×10^{-8} Pa, and tip temperature was 50K during the measurements. Neon gas of a pressure 2×10^{-3} Pa was used as the image gas of FIM observation. Details of apparatus in the chamber were described elsewhere [5]. We cut single-crystalline ⟨111⟩-oriented W and polycrystalline W wires with diameters of 0.125 mm and 0.150 mm, respectively, and spot-welded them to tantalum supportive loops. One ends of the wires were sharpened electrochemically in a potassium hydroxide aqueous solution with 2 M concentration, and the etched surfaces were continuously electroplated in a 0.1 M hydrochloric solution with a dropped 0.1 mM gold chloride solution [10]. The fabricated tips were mounted in the vacuum chamber and heated at about 1000K by means of direct resistive annealing of the tantalum loop. The tip temperatures were measured by an optical pyrometer.

III. RESULTS AND DISCUSSION

Firstly, the structures of the nanotips were observed by FIM. Figure 1 (a) shows the typical FIM image of the nanotip after cyclic annealing at 1000 K. The three

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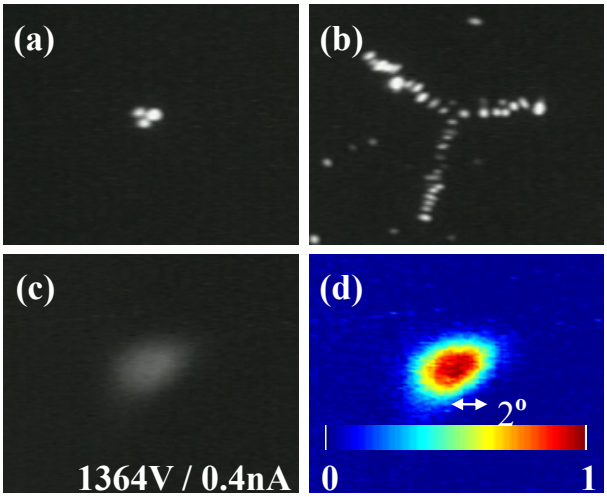

FIG. 1: (a) A typical FIM image of an Au trimer tip, (b) a typical FIM image of three ridges of an Au nano-pyramid, and (c) an FEM image of the Au trimer tip. The accelerating voltage and the emission current in the FEM observation were 1364 V and 0.4 nA, respectively. (d) Color representation of the normalized intensity distribution of (c). The color scale attached to the bottom represents the intensity range.

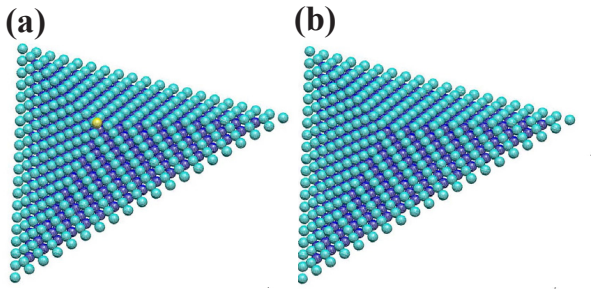

FIG. 2: Ball models of two nanotips; (a) A single-atom termination and (b) trimer-atom termination. A topmost atom, substrate W atoms and covering atoms in one physical monolayer are painted yellow, dark blue, and light blue, respectively.

bright spots indicate that the apex of the tip was terminated with three atoms: We call it "trimer" tip hereafter. With increasing the electric fields applied to the tip, some atoms are removed additionally by field evaporation, and eventually, the FIM images of the entire feature of the nanotip are observed as shown in Fig. 1 (b). Three ridges in Fig. 1 (b) reflect the structure of the three-sided pyramid surrounded by {211} facet faces as shown schematically in Fig. 2. In previous FIM works of the nanotips covered with the noble metals such as Pd, Pt, Rh, and Ir [8, 9], the pyramid structure was familiar. No matter how many times the tip was annealed, however, no single-atom termination was found in this experiment, which is much different from the previous nanotips covered with Pd, Pt, Rh, and Ir; the single-atom termination always occurs on the tips covered with the other metals after the annealing at 1000 K.

There are two possible explanations. One is that the "trimer" structure is the most stable thermodynamically among the various nanotips covered with Au; that is to say, the single-atom termination is not the most stable. Only the annealing in UHV might not be sufficient to fabricate a "single-atom" tip. The situation is similar to the nano-pyramids surrounded by {110} facet faces. The additional deposition is required to construct the single-atom termination.

The second one is as follows; the single-atom termination may be realized by annealing, but the topmost atom is evaporated immediately during the FIM observations owing to the low critical electric field of Au evaporation. In other words, the field strengths for the evaporation of the topmost Au atom are less than those of FIM observations. The best image field (BIF) of neon is well known to be 3.75 V/Å [11]. The topmost Au atom of Au nanotip may connect to the three underneath Au atoms mainly. As shown in Table I, the critical evaporation field of Au metal, 3.5 V/Å, is less than the BIF of neon, and weak as compared with those of the other noble metals, which means that the Au-Au bonds are broken easily by fields for FIM observations. In contrast, it is likely that the other Au atoms connect tightly to the substrate W atoms in this case, because Au atoms are located on W atoms as shown in Fig. 2. The structural models were proposed by Madey *et al.* [12] and Fu *et al.* [6]. The evaporation field strengths of the Au-W bonds should be stronger than those of the Au-Au bonds. This phenomenon is known as a "pseudomorphic structure" in case of Ga/W, for example [13]. The difference of nature might be the origin of the observed trimer termination. The evaporation field of Pd in Table I, however, is lower than the BIF of neon as well, which is consistent with the lists of cohesive energy. Since the Pd nanotips exhibit experimentally the single-atom terminations, the cohesive energy and the evaporation field strengths of bulk tips may not directly relate to the bond strengths between the topmost atom and three underneath atoms. The mixture in chemical composition in pyramids is presumably one reason of the difference between Au and Pd, which will be discussed later.

From the viewpoint of practical applications, the properties of the electron beam emitted from the trimer tips did not exhibit disadvantageous values to those of the single-atom nanotips. The observed semi-cone angle of the emitted beam was estimated to about 2 degrees from the intensity distribution of the FEM pattern in Fig. 1(c) and (d), and in addition, the observed brightness was estimated to be about 5×10^8 A/cm^{2}sr. These values are comparable with those of single-atom tips covered with the other noble metals [7]. Similarly to the single-atom nanotips of the other metals, furthermore, the apex destroyed by field evaporation can be repaired by the annealing at feasible temperatures thanks to its thermodynamically stable structure, and the Au nanotip also can be revived after air-exposure. Figure 3 shows typical FIM

TABLE I: Evaporation field strengths and cohesive energies of noble metals.

	Au	Pd	Pt	Rh	Ir
Experimental evapolation field (V/Å)[a]	3.5	3.2	4.8	4.8	5.3
Cohesive energy (eV/atom)[b]	3.81	3.89	5.84	5.75	6.94

[a]From Ref. [11]
[b]From Ref. [16]

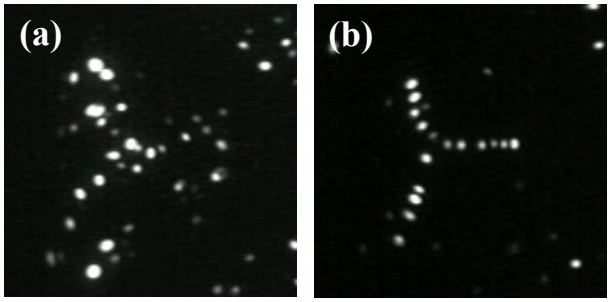

FIG. 3: Typical changes in FIM images during the annealing process of the air-exposed tip. (a) Just after air-exposure for 15 min, and (b) after annealing the air-exposed tip at 1000 K for 100 min.

images of the air-exposed nanotip and the revived nanotip. When a tip is contaminated by various gases in the air, the annealing in UHV restores it to the initial nano-pyramids without any other treatments. It is probably because the outermost layer of the nanostructure is composed of inert metal Au. These practically useful features such as "self-repairing function" and "demountable characteristic" are the specific properties common in all the nanotips covered with the noble metals [8].

Figure 4 shows experimental energy spectra of the electrons emitted from three different tips, the Au-covered trimer tip, the Pt-covered "single-atom" tip, and the clean W tip. Each spectrum was normalized with respect to the maximum intensity. The origin of the vertical axis of the Pt spectrum was different from others. The half maximum full-widths of the main peak of the Au-covered trimer tip, 0.3 eV, is almost the same as that of the Pt-covered single-atom tip. It means that the Au trimer tip is not much inferior to the single-atom tips from the view point of energy spread relating to temporal coherence. These values of FWHM are slightly larger than that of a conventional W tip, which originates from the small curvature radius of the nano-pyramid compared with that of a conventional W tip. The high fields generated at the apex of the nano-pyramid, owing to the small curvature radius, enable electrons at deep energies from EF to pass the tunneling barrier.

Figure 5 shows spectra of the Au-covered trimer tip and those of the Au-covered tip terminated with more than three atoms, which is called "flat-topped" nanotip in this paper. They are plotted in semi-log scale for various applied voltages. The spectra of the trimer tip have a subtle but clearly detectable hump structure below -0.7 eV, while those of flat-topped nanotip are featureless and well reproducible by Fowler-Nordheim (FN) theory [14]. Additionally, the humps become clearer as the applied field increases. These hump structures in the spectra are common characteristic features in all the single-atom and trimer tips covered with the noble metals [9]. According to the ab-initio calculation by Gohda *et al.* [15], the similar humps originating from localized states at the topmost atom appeared in the calculated spectra; they calculated electron density distribution around the single-atom terminated protrusion of Al four-sided pyramid on Al(100) slab surface plus jellium substrate, and pointed out the existence of localized states at the topmost atom. Since almost all the electrons are emitted through the topmost

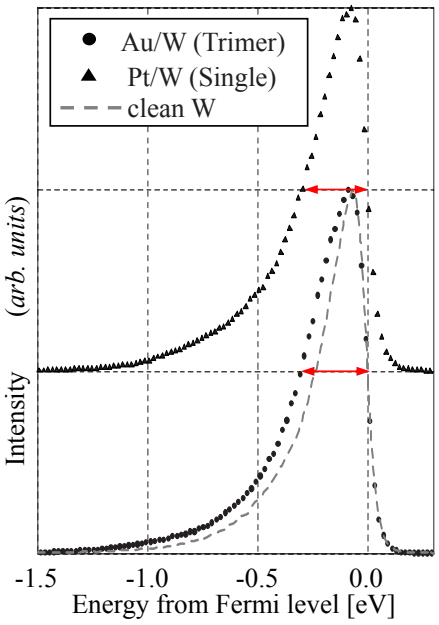

FIG. 4: A typical energy spectrum of an Au-covered trimer tip in a liner scale. For comparison, two spectra of a Pt-covered single-atom tip and a clean W(111) tip are shown.

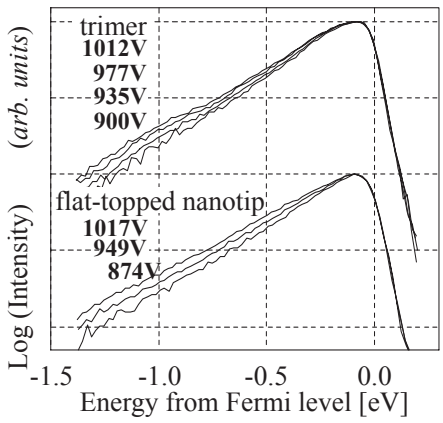

FIG. 5: Two kinds of spectra plotted in logarithmic scales as a function of applied voltage. Upper and lower ones were measured from a trimer tip and a flat-topped nanotip, respectively.

atom, the spectra are modified strongly by the localized states at the topmost atom. Regardless of the covering metals, on the other hand, the humps are observed in the spectra of the trimer tips as well as the single-atom tips [9]. The observed hump structures of the trimer tips including Au-covered ones seem to originate from the localized states at the three atoms.

It should be noted that the humps in the spectra of Au trimer tips always appear at the same energy position even if one specimen is changed to others. This is largely different from the nanotips covered with the other noble metals as well. In Fig. 6 (a) and (b), several spectra of Au trimer tips and those of Pt trimer tips are shown for comparison. As indicated by arrows, the humps of all the Au trimer spectra appeared in the range from 0.7 eV to 0.8 eV below Fermi level E_{F}, while those of Pt-covered trimer tips are distributed in the range from 0.5 eV to 0.7 eV below E_{F} depending on the different specimen.

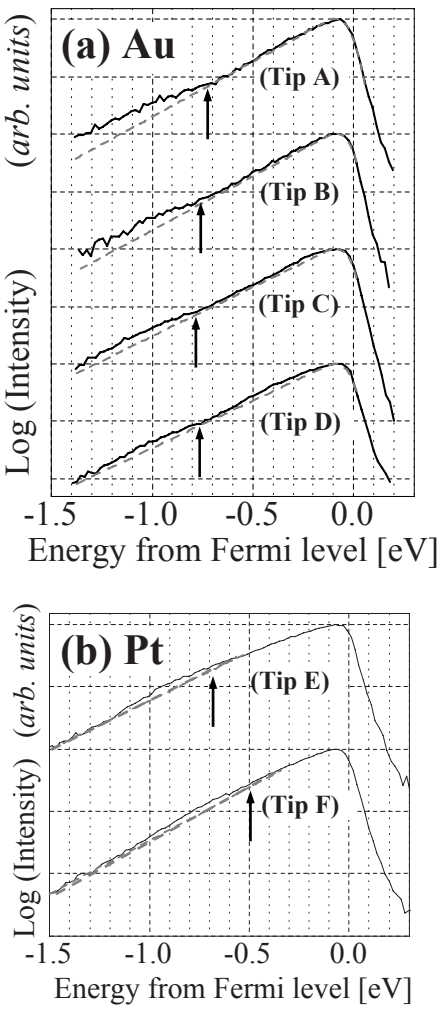

FIG. 6: Spectra of trimer tips covered with Au and Pt. The humps in the spectra of Au-covered trimer tips appeared at the range from 0.7 to 0.8 eV below E_F. In the case of the Pt-covered trimer tips, on the other hand, the energy position of humps shifted slightly depending on the different specimens.

The origin of the different emission properties between Au and the other noble metals is not clear now, but one finds the clear difference in the solid solubility with W: According to the phase diagrams of the binary W alloys [17], the W atoms are insoluble in Au, while they are soluble in the other noble metals. Consequently, the W atoms should not penetrate easily into the Au layer of one physical monolayer as compared with the other metal layers. One can expect that the reproducibility of the chemical compositions in the pyramids is higher in the Au-covered tips than the other tips, resulting in the high reproducibility of the spectra. In the other metal-covered tips, the random distribution of the W atoms in the noble metal layer affects the localized states at the topmost atom. This is presumably the reason why the high reproducibility of the hump energy appears in the spectra of Au nanotips. The difference of their terminations between Au and Pd in FIM observations, which is described above, presumably originates from the difference in the solubility as well, i.e. the topmost Pd atom strongly connects to the underneath three atoms containing solute W atoms.

IV. CONCLUSIONS

We have fabricated successfully the Au-electroplated W nanotips and investigated the electron emission properties and atomic structures. We found two peculiar features of the Au nanotips: (1) In the FIM observations, the final nanotips were terminated with three atoms, and the single-atom termination is not found only by annealing. (2) The humps in spectra always appear at the same energy position in the range from 0.7 eV to 0.8 eV below E_F.

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