Surface Science 602 (2008) 2508–2512

Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

Field emission spectra of single-atom tips with thermodynamically stable structures

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ARTICLE INFO

Article history:
Received 21 December 2007
Accepted for publication 24 May 2008
Available online 8 June 2008

Keywords:
Field emission spectroscopy
Surface electronic phenomena
Metallic monolayer films
Facet

ABSTRACT

Energy spectra of field emitted electrons from well-characterized tungsten nanoemitters covered with different metals have been measured in detail while changing the electric field and the topmost atomic structure. At very high electric fields, additional humps appear in the spectra of a single-atom tip. Their energy positions depend on both the coated material and structure termination but not on the electric field. On the other hand, their intensities increase with increasing field. The current spectra did not include either peculiar features attributable to resonant tunneling or electric-field penetration, or significantly narrow FWHM, but are rather analogous to those of the conventional metallic field emitters. The spectral features along with a recent *ab-initio* theory indicate a large reduction in the tunneling barrier height in front of the single-atom electron source.

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1. Introduction

Field emitted electrons from a single-atom emitter have attracted attention from the viewpoint of practical application and fundamental quantum physics. After the development of the tungsten (W) single-atom tips [1], there have been a considerable number of experimental and theoretical studies of this subject. Many useful characteristics of electron beams such as high collimation, large current at low electric fields, and high brightness have been verified for the W single-atom tips across these studies [1,2]. By carrying out an *ab-initio* self-consistent field calculation, Lang et al. concluded that these excellent characteristics were due to a considerable reduction in the tunneling barrier height in front of the source atom [3]. In contrast to these consistent findings about the spatial profiles of the electron beams, earlier studies of the energy distributions have not necessarily met a good convergence [4,5]. To our best knowledge, although the energy distributions are important information, field emission spectra (FES) of the single-atom tips have not been obtained with appropriate reproducibility.

In general, the FES of nanoemitters are very sensitive to the various conditions of the emission site such as the atomic structure, chemical composition, and contamination [5–8]. We suppose that the poor reproducibility of the FES stems from the notably extreme sensitivity compared to the other experimental techniques. Additionally, it should be noticed that the previous single-atom tips were fabricated via non-equilibrium processes. This means that their atomic structures were not thermodynamically stable, and must have varied from sample to sample. As a joint result of the extreme sensitivity and the structural variation, the FES were considered to be not as reproducible as the spatial-profile characteristics. In order to validate the FES of the single-atom tips, it is necessary that the tips are thermodynamically stable and well-characterized so that data can be collected reliably.

Previously, Maedy and coworkers found that proper heating treatment on W(1 1 1) covered with monolayer films of platinum-group metal formed numerous nanometer-scale pyramids with three sides of the {2 1 1}-equivalent facets [9]. This finding together with theoretical study [10] elucidated that the pyramid formation was a result of free energy lowering that is induced by the monolayer film growth. Later, Fu et al. demonstrated that the equivalent pyramids were fabricated on the end of sharpened W⟨1 1 1⟩ tips [11]. In addition, their field ion microscopy (FIM) experiments revealed that the top of the nanopyramids was a single atom.

The above-cited studies indicate that the nanopyramids on the W⟨1 1 1⟩-tip ends are thermodynamically stable, covered with the monolayer films of the noble metals, and terminated with a single atom. These features are appropriate for an ideal single-atom field emission tip. In this paper, we report the FE spectra obtained from these well-characterized nanoemitters while systematically changing the topmost structure, electric field, and covering metal.

2. Experimental

Preparation procedures of such nanoemitters have been described in detail elsewhere [12]. Briefly, an ultrathin layer of a

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doi:10.1016/j.susc.2008.05.038

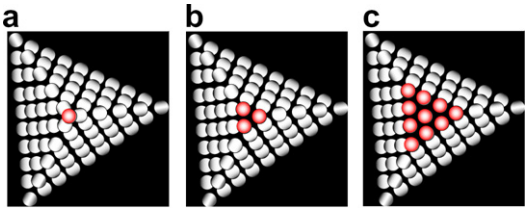

Fig. 1. Schematic depiction of the structures of the present nanoemitters with different terminations: (a) single atom, (b) trimer, and (c) decamer terminations.

noble metal, M (M = Pd, Pt, Ir, or Rh), is electrochemically plated on the apex of a sharpened W⟨1 1 1⟩ tip. A nanopyramid with three {2 1 1}-faceted sides at the tip apex is spontaneously grown by a proper heat treatment in UHV. FIM observations show that the termination of the nanopyramid eventually turns into a single atom after cyclic heating at 1000 K for all the covering metals studied. Furthermore, by combining the heating with a field evaporation treatment, the termination can be varied from a single atom to the buried third layer, repetitively. Therefore, the nanoemitters are further specified by the termination structure and are called "single-atom tip," "trimer tip" (i.e., the field emission tip terminated at the second layer), and "decamer tip" (terminated at the third layer); the models of these structures are shown in Fig. 1. The tip temperature is maintained at ~55 K in our FIM and FE experiments, and a stable emission is maintained during the period of the FE measurements [13].

3. Results and discussion

Fig. 2 represents typical field emission microscope (FEM) patterns of the three different terminations of the Pd-plated nanoemitter as a function of the field emission current. There are two important observations. First, all the FEM patterns feature well-collimated emission spots. Opening angles of these beams are measured at 1 nA as 2.0° for the single-atom tip at FWHM, 2.8° for the trimer tip, and 3.2° for the decamer tip. These values are the lowest among all the reported values [1,7,8,14–17]. Second, the single-atom tip exhibits circular FEM patterns, whereas both the trimer and decamer tips show a triangular shape. The narrowest circular FEM patterns prove that most of the electrons are emitted from the topmost single atom, but not from the underneath layers having threefold rotational symmetry, and that diffraction effects do not occur.[1]

Fig. 3 shows typical FES of the nanoemitters as a function of the three parameters of the covering metal, the applied voltage (the electric field), and the structure termination. For the decamer tips, the spectra are featureless, and the characteristics are explainable within the framework of the well-known Fowler–Nordheim (FN) theory [18]. For the trimer tips, the spectra are also featureless at low electric fields. However, as the field is increased, subtle but clearly detectable humps appear. For the single atom tips, more pronounced humps appear in the spectra. These characteristics are commonly seen for all the covering metals.

Energy of the hump for the single atom tip varies from sample to sample for all the covering metal within an energy range of −0.5 to −1.2 eV, presumably due to either intermixing of the two constituent atoms [19] which may occur slightly apart from the top region, or different size of the nanopyramids.[2] In the present study,

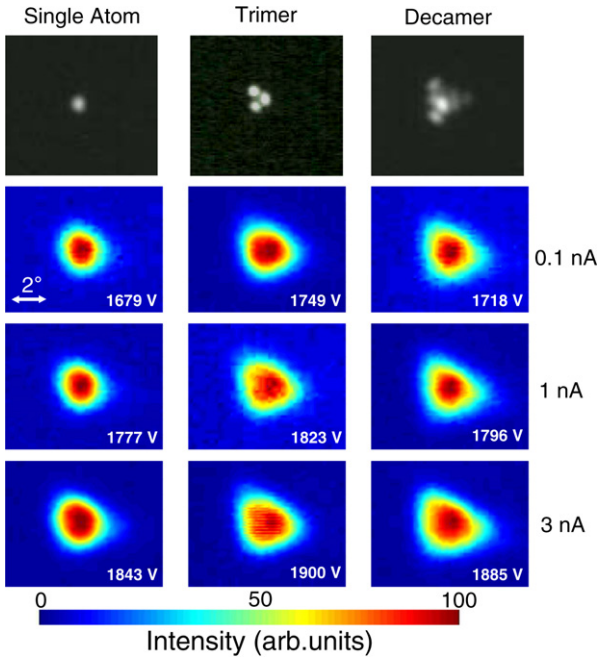

Fig. 2. FEM profiles of the Pd-covered nanopyramids with different terminations. Results of the preliminary FIM observations mentioned to the top of each column. In the left column, FEM of the single-atom tip is shown as a function of emission current. In the middle and right columns, the counterparts of the trimer and decamer, respectively, are shown. The intensity of the FE beam normalized with respect to the maximum is represented by color representation, where the entire range is represented by the linear color scale shown at the bottom. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

since the nanopyramid used in the FES measurements for every covering metal was the same except for the termination structure, minor cause of the slight energy shift can be regarded as constant for the sequential FES measurements.

Fig. 3 also shows that the energy of the hump for each covering metal does not shift when the electric field is changed, whereas its appearance becomes more conspicuous, and its intensity grows faster than that of the Fermi-level peak.[3] It is important to find that the Fermi-level peak is the dominant structure in any spectra regardless of the coated elements, the electric field, or the termination. These features imply that neither resonant tunneling emission nor penetration of the electric field is present, which is in disagreement with previous reports [8,17,20,21].

In the conventional FN theories, total energy distribution (TED) of field emitted electrons is expressed as

$$\frac{\mathrm{d}j}{\mathrm{d}E} = \int_0^E N(E, E_z) D(E_z, F) \mathrm{d}E_z, \tag{1}$$

where j is total current; $N(E, E_z)$, supply function; $D(E_z, F)$, tunneling probability; E, total energy; E_z, usually referred to as a normal energy associated with momentum normal to emission plane; and F, electric field [22]. The supply function is a product of density of states (DOSs) $\rho(E)$, group velocity v_z, and the Fermi–Dirac function $f(E)$. In a one-dimensional system, the DOSs are expressed as $\rho(E) \sim (\partial E/\partial k_z)^{-1}$ and the group velocity v_z is given by $\hbar^{-1}(\partial E/\partial k_z)$. As was pointed out by Harrison [23], information on the energy

[1] In the current observation, size of the FEM pattern increases as area of the termination increases. This finding means that diffraction effects are negligible as far as an assumption that electron wavelengths are comparable to the termination dimension is true.

[2] Number of stacking of (1 1 1)-equivalent layers consisting of each nanopyramid ranges from six to eight although difficult to determine precisely due to the obscured FIM images around the bottom regions. This approximately corresponds to 8–10 nm for one side of the base triangle of the nanopyramid.

[3] The Fermi-level peak is not practically located at the Fermi level due to thermally blurred step edge of the Fermi–Dirac function. The intensity at the Fermi level is approximately 65% of the maximum at the present temperature of 55 K. In the present text, we referred to these peaks in this manner for simplicity.

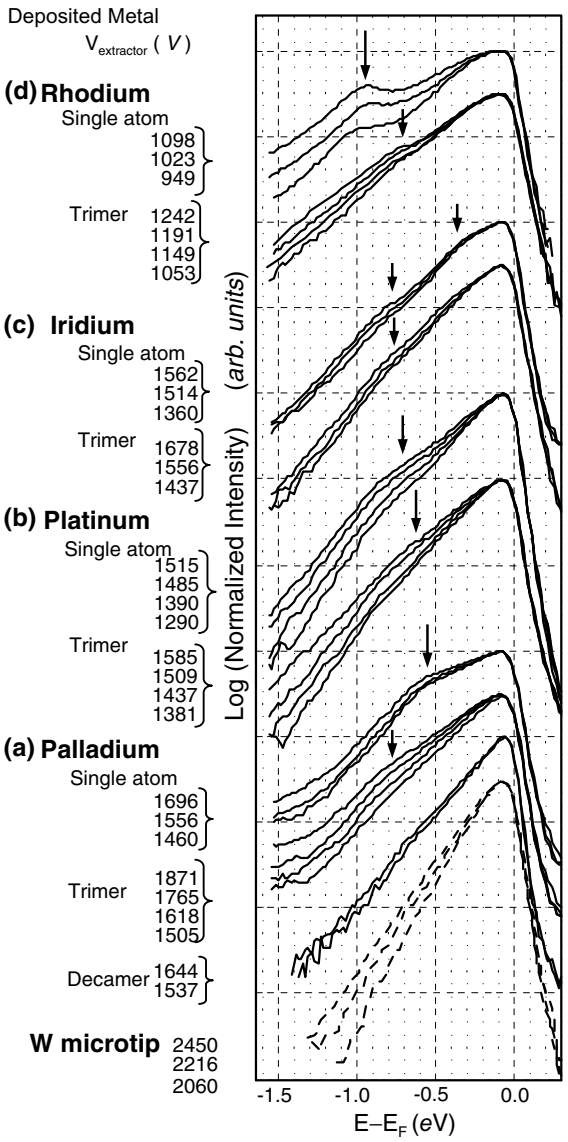

Fig. 3. FE spectra of the single-atom tips and trimer tips for different covering metals of Rh, Ir, Pt, and Pd. Spectral intensities (vertical axis) are normalized by being divided with the maximum intensity in each spectrum, and represented logarithmically, while energies relative to the Fermi level (horizontal axis) are shown linearly. Each set of the FE spectra is shifted vertically for visual simplicity. The FE spectra of the decamer tip are shown only for Pd. Equivalent featureless TED curves are obtained for the decamer tips of the other metals. For comparison, the TED curves obtained using the conventional W emitters are shown. Attached arrows are a rough indication of energy position of the humps.

dispersion relation disappears from Eq. (1) owing to the cancellation of the DOSs and the group velocity. In an actual system, although the expression is modified, the foregoing cancellation survives appreciably [24]. If the functional forms of the transverse electron energy dispersions are the same as the longitudinal one, the TED curves are determined by integral of the tunneling probability, as modulated by the Fermi–Dirac function. Therefore, at low temperatures, the TED curves are well-represented by the exponential form, which exponentially descends below the Fermi level with decreasing energy [25]. In other words, within the framework of the semi-classical electronic band theory, the electronic band effects are unobservable.

The featureless spectra of the decamer tips in Fig. 3, i.e., the invisible electronic-state effect, indicate that the DOSs and the group velocities cancel each other, similar to the case of the quantum point contact (QPC) conductors[4] and ultra-slow photoemission [26]. Namely, the electronic transport phenomena observed in the decamer tip and these other systems are expressible within the same theoretical model. In contrast, the FE spectra of both the trimer and single-atom tips cannot be explained merely on the basis of the FN theory; hence, we attempt to interpret the present data based on more elaborate theory that is introduced in the following sections.

Gohda et al. performed *ab-initio* self-consistent field simulations for systems of an Al atomic pyramid on an Al slab surface having a jellium substrate, which were embedded in a high electric field [27]. Instead of carrying out an integral analogous to Eq. (1), they directly obtained electron current densities by using current operator on acquired wave functions. In the calculated FES, a dominant peak and a secondary hump arose from the delocalized states and the localized states at the apex, respectively. They were found at and below the Fermi level, respectively. These spectral features are the same as our experimental results as discussed above. Since the conduction bands of our nanopyramids consist of d electrons of the constituent atoms, the topmost atoms are more likely to generate such localized states than the Al atom used in the calculation. Hence, the Fermi-level peaks seen in the current FES are attributable to delocalized states, while the humps are to localized states characteristic of the nanopyramids. In the earlier FES study of the pure W nanotips, similar, and even more peculiar, humps were also seen [8,20], and they have been supposed to arise from similar localized states. These independent studies may indicate that appearance of the spectral humps depends largely on the atomically sharp shape of the tip. If we interpret our data based on the Gohdas' theory, we find it reasonable to think that the energies of the humps do not vary with changing the electric fields, because the localized states are hardly influenced by the external electric field due to screening of conduction electrons of the delocalized states at Fermi level. Furthermore, the field-dependent growth of the secondary humps may be explicable from their theory, as contained in the following paragraph [28].

When we apply electric fields, the fields are most concentrated at the topmost atom, and, simultaneously, the most significant barrier reduction due to the Schottky effect occurs before the same atom. Owing to a constructive combination of the two effects, therefore, it is the topmost atom that most of the emission issue from. That's why the electronic states related with the topmost atom are considered as the most influential in the FES. Roughly mentioning on the basis of a calculation for electron scattering in one-dimensional model potential, the tunneling probability from metal to the vacuum increases exponentially with the electron energy in case that the electron energy is much lower than the tunneling barrier maximum, but the probability becomes saturated as the electron energy becomes comparable to the barrier [29]. When electric fields are moderate, a reduction in the tunneling barrier is not so large before the topmost atom that the barrier maximum is located sufficiently above the Fermi level. In this field region, the tunneling probability grows exponentially with an increase in the electric fields, both at the Fermi level and at deeper localized-states level. For higher fields, on the other hand, the local barrier reduces in front of the topmost atom, and become comparable to the Fermi level there. Eventually, the tunneling probability at the Fermi level saturates. However, it still increases at the energy of the localized-states level that is much low in comparison with the barrier maximum. As a result, the hump grows more pronouncedly than the Fermi-level peak. This is an intuitive explanation for the energy-dependent growth of the spectral features retrieved from the Gohdas' theory, of which the FES results agree well with our data.

[4] According to the Landauer formula from which the universal conductance quantum is derived, the information inherent in the electronic states of the material is eliminated due to the cancellation between the group velocity and density of states.

Such a large reduction in the tunneling barrier is also supported by FES measured under unusual conditions of considerably low electric fields. In Fig. 4, the FES of the Rh-coated single-atom tips are shown. Main peak intensity is only 3 cps at the lowest field, which are at least three orders of magnitude less than those acquired in conventional measurements. As shown in the spectra of the three lowest applied voltages, only straight descending slopes are clearly observed. As the field is increased, a faint hump appears, showing that the spectral features are in agreement with the results of Fig. 3. This apparent transition from disappearance to appearance of the hump is in perfect accordance with the prediction of the Gohdas' theory [27], and suggests the interpretation that the tunneling barrier maximum decreased to such an extent that the growth of the tunneling probability saturate at the Fermi level. Thus, the interpretation relying on the large barrier reduction may give general consistency between the theory and experiment. However, there still remain some inquiries if we view the present data of each specimen individually. For instance, the preceding interpretation does not explain why the remarkable field sensitivity has been observed only in the FES of the Rh-coated single-atom tip (Fig. 3d), but not in the rest single-atom tips. Theoretically, the intensity of the FES should be determined from the transmission probability, and it is derived by solving the scattering problem for the actual systems. Therefore, in order to clarify the phenomena in detail, it is necessary to deal with the scattering problems for the realistic systems individually by carrying out an *ab-initio* self-consistent field calculation as shown by Gohda et. al.

Finally, we mention about peculiar phenomenon of "negative tunneling barrier", i.e., a reversal of the energy level of the Fermi level and the barrier maximum, which was first predicted by Lang et al. [3]. According to the theory of both Lang et al. and Gohda et al., the negative barrier were found to occur at an electric field ranging approximately from 1 to 1.3 V/Å, and would lead to a deceleration of the increase of the FE current with increasing the extractor voltage [3]. In the present experiments, however, this sort of the saturation was not seen, and, hence, we suppose that the negative tunneling barrier does not occur.

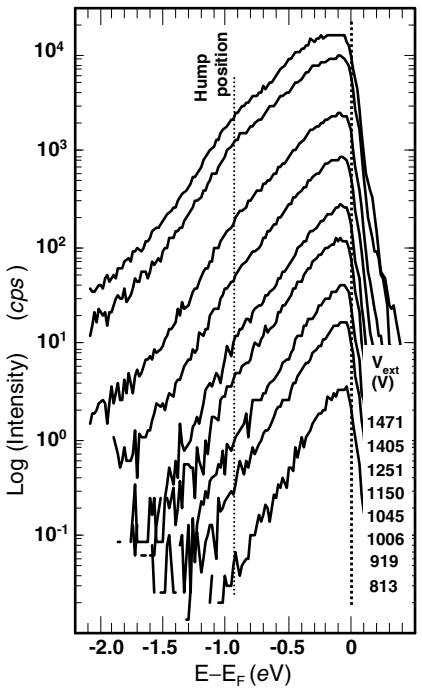

Fig. 4. FE spectra obtained by applying significantly low electric fields. Notice that a unit of the intensity is counts per second, but not arbitrary units. In the lowest three FE spectra, no secondary humps are visible. A hump grows gradually as the electric field is increased. These behaviors indicate that not only the localized electronic states, but also the significant lowering of the potential barriers, are responsible for the appearance of the hump.

4. Summary

We have investigated FE patterns and spectra of thermodynamically stable and well-characterized W nanoemitters covered with four types of late-transition metals (Pd, Pt, Ir, and Rh). The FE patterns indicate electron beams issue from a top most atom of the single-atom FE tips. The FE spectra exhibit characteristic humps due to localized electronic states, which is in qualitative agreement with a recent *ab-initio* self-consistent field theory. In order to analyze these humps accurately, *ab-initio* calculation should be undertaken on the realistic nanostructures, but not on a simple-metal systems.

The FE spectra at very high electric fields presented in this paper provide new information concerning the localized electronic states of nanoemitters with the different covering metals and the structural terminations. In principle, FE spectroscopy yields energy spectra over a wide dynamic range in various directions without being coupled to the counter electrode. In these regards, the FE spectroscopy should be distinguished from scanning tunneling spectroscopy and QPC transport measurements. The present results suggest a new fruitful field of research in probing the electronic states of nanostructures and their transport phenomena at high electric fields. We hope that this study will stimulate further detailed theoretical and experimental studies of these subjects.

Acknowledgement

We wish to thank Dr. Y. Gohda for his helpful comments on an interpretation of the FES data.

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