Field Emission from W Tips Sharpened by Field-Assisted Nitrogen and Oxygen Etching

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Field emission properties were studied for tips sharpened using field-assisted nitrogen and oxygen etching. Sharp single crystal tungsten <111>-oriented tips were fabricated and evaluated by Fowler-Nordheim plots and field-ion microscopy observations. The results demonstrated emissions at lower bias voltages due to the sharpening of the tip apex using the etching. The field emission properties and tip shapes after nitrogen etching were compared with those obtained after oxygen etching. [DOI: 10.1380/ejssnt.2008.152]

Keywords: Field emission; Field ion microscopy; Field evaporation; Tungsten

I. INTRODUCTION

The fabrication of ultra-sharp tips is very important both for fundamental science and for field applications since highly collimated and coherent electron beams or nanometer-scale probes are required for many purposes. Several methods of preparing a sharp apex on a single crystal W<111>-oriented tip have been developed in the last two decades. Fink developed an atomically sharp tip by depositing tungsten atoms on the clean apex of the tip [1, 2]. Binh et al. produced nano-tips by heat treatment under a high negative electric field [3, 4]. Nagaoka et al. studied a field-enhanced diffusion growth technique, in which a negative field was applied to form a nano-protrusion on the contaminated tip [5]. Fu et al. and Kuo et al. reported methods of fabricating reproducible single-atom tips by vacuum deposition or electroplating of Pd or Pt followed by thermal annealing in a vacuum [6, 7]. Bryl et al. fabricated a three-sided pyramidal apex by annealing after oxygen adsorption [8].

Recent studies have employed field-assisted nitrogen (N2)- and oxygen (O2)-etching techniques. Rezeq et al. recently reported a field-assisted N2-etching technique [9]. In this method, N2 gas was introduced during FIM observation. The nitrogen molecules dissociated and adsorbed onto the shank of the W tip under the electric field, and an atomic-scale protrusion was formed due to the N-incorporated W displacement. This protrusion led to a higher electric field locally and thus evaporated. With careful reduction of the FIM bias, the periphery of the tip apex was etched away and the fabrication of the ultra-sharp tips was carried out. Rahman et al. reported a field-assisted O2-etching technique [10]. Both techniques allow the production of very sharp tips because thermal treatment is not necessary prior to the N2- or O2-etching processes.

In this report, we present the relations between field emissions (FE) and the geometries of tips prepared by field-assisted N2 and O2 etching. Such detailed data are indispensable for the successful application of tips fabricated by this method in fields such as electron microscopy, projection microscopy [11, 12], scanning Auger electron microscopy [13], point-reflection electron microscopy [14], and field emission low-energy electron diffraction [15]. We fabricated sharp tips using N2 and O2 etching because these fabrications enabled us to control the tip sharpness. Then, we modeled the tip apex to estimate the radius of curvature, investigated the FE property using a Fowler-Nordheim (FN) plot, and thereby determined the effect of field-assisted N2 or O2 etching.

II. EXPERIMENTAL

Tips were made from single crystal tungsten wire (0.25 mmø). It was electrochemically sharpened in 2N NaOH, and then spot-welded onto a tantalum wire that was attached to a tip holder. The tip holder was placed into an ultra-high vacuum chamber (5 × 10⁻⁸ Pa) and set 35 mm away from a microchannel plate (MCP) equipped with a phosphor screen. The input electrode of MCP was grounded and +1.3 kV was applied on the output electrode. FE beams were obtained by applying a negative bias to the tip. In addition, we carried out field-ion microscopy (FIM) applying a positive bias under a He-environment (1 × 10⁻³ Pa) at liquid-N2 temperature. Emitted electrons or ions from the tip apex went straight to the MCP, which created FE patterns or FIM images representing the atomic structure of the apex. The images were captured by an intensified charge-coupled device camera and stored on a computer.

In order to sharpen the tip by field-assisted N2 etching, we initially cleaned the tungsten tip apex by field evaporation under the FIM condition. After helium gas was reduced to 5 × 10⁻⁴ Pa, nitrogen gas was introduced to readjust the pressure to 1 × 10⁻³ Pa. These conditions led to the evaporation of tungsten atoms from the shank of the tip. Since the field in front of the tip apex was gradually enhanced by the sharpening process, we reduced the applied voltage accordingly to avoid evaporation of the apex atoms. As this controlled reaction continued, the apex became increasingly sharp. When the apex consisted of only several atoms at the end, the N2 etching was stopped by turning off the N2 gas supply. For the field-assisted O2 etching we reduced the He gas to 5 × 10⁻⁴ Pa and introduced O2 gas to an overall pressure of 6 × 10⁻⁴ Pa. The O2 etching proceeded in the form of explosion-like evaporation as described in our previous paper [10]. The evaporation occurred in a fraction of a second after an incubation period (10-20 min). Several

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peripheral layers of the tip were etched away at once to sharpen the tip. We quickly reduced the applied voltage after each sudden sharpening event. At the final stage, we decreased the O$_2$ pressure to slow down the etching reactions.

To evaluate the FE characteristics of the sharpened tips, we used the Fowler-Nordheim (FN) plots [16–18]. If a plot of ln($I/V^2$) versus $I/V$ yields a straight line, the slope of the FN plot is known to be $-6.8\phi^{1/2}\alpha k R$, where \(\phi\) is the work function of the tip in eV, \(\alpha\) is the image correction factor, \(k\) is the field reduction factor because of the presence of the shank, and \(R\) is the radius of curvature of the tip in nm. Since most of the electrons were emitted from the (111) plane in the present experiment, we used the work function \(\phi = 4.5\) eV for W. Since the effect of the image potential can be ignored, the image correction factor \(\alpha\) is known to be close to unity. The field reduction factor \(k\) is an arbitrary value and is known to be 3-35 depending on the shape of the shank. We defined the combined product of the field reduction factor and the radius of curvature as \(\gamma \equiv kR\) (in nm) to investigate the trend of the tip sharpness. To obtain the \(\gamma\) from the FN plot, the total FE current was measured using a collector (applied bias of +8 V) placed between the tip and the MCP. The position and size of the collector were suitable for collecting all FE beams.

III. RESULTS AND DISCUSSIONS

A. N$_2$ etching

The relation between the FE property and the tip sharpness was studied using a sharp tip with a radius of curvature of several nanometers. We prepared different-state tip apexes with different levels of sharpness by field-assisted N$_2$ etching and field evaporation. Figure 1(a) is an FIM image of the initial state of the tip. Since high-temperature annealing makes the tip quite blunt, the tip was cleaned by field evaporation to maintain the sharpness. Threefold rotational symmetry was observed around the <111> direction. Three \{112\} and three outer \{110\} planes were clearly visible while the \{110\} planes were almost out of sight. Then, the sharpened tip was blunted by field evaporation without N$_2$ gas as shown in Figs. 1(c) and 1(d). Figure 1(d) was obtained with the same FIM bias as in the initial state. After the observation of each FIM image, we measured the FE current at the bias voltages shown in Fig. 2. We defined states (A)-(D) of the tip apex as the respective He-FIM images (a)-(d) of Fig. 1. The same FIM voltage as that applied at the initial state (A) was applied at the final state (D).

FE currents were measured over a range of applied biases (negative on the tip) for each state. It was very clear that the tip at the state (B) emitted electrons at the lowest bias voltage as shown in Fig. 2(a). The emission current of 100 pA was measured for an applied bias of −380 V at the state (B), while a bias voltage of −480 V was necessary at the initial state (A) and the final state (D) for the same current. The required bias voltage at the state (C) was between these two values. These emission properties were reasonable if indeed the electrons were emitted from the apex region that was modified by field-assisted N$_2$ etching and field evaporation. The measured range of current to obtain reproducible experimental results was less than 200 pA; larger FE currents deconstructed the structures of the apex.

The Fowler-Nordheim (FN) plots are shown in Fig. 2(b). Each plot fitted the straight line well. We then obtained \(\gamma\), the product of \(k\) and \(R\) as defined above, as (A) 157 nm, (B) 122 nm, (C) 154 nm and (D) 163 nm, re-

![FIG. 1: FIM images of (a) the initial state, (b) after field-assisted N$_2$ etching, (c) after the first field evaporation and (d) after the second field evaporation. White dotted circles separate the inner clean W apex and the outer region. (e)-(h): Ball models for the FIM images (a)-(d). The models were fitted to an inner clean W apex. (i)-(l): FE patterns of the states corresponding with the FIM images (a)-(d). Obtained FE biases are shown. Blue and yellow circles mark the three small \{112\} planes, respectively, in (a) and (e).](http://www.sssj.org/ejssnt (J-Stage: http://www.jstage.jst.go.jp/browse/ejssnt/))

| State | \(V\) (kV) | \(R_{ball}\) (nm) | \(\gamma\) (nm) | \(V/R_{ball}\) | \(k_{ball}\) |
|-------|-----------|----------------|--------------|-------------|-------------|
| (A)   | +6.0      | 11.3           | 157±2        | 0.53        | 13.9        |
| (B)   | +4.1      | 8.5            | 122±3        | 0.48        | 14.4        |
| (C)   | +5.3      | 11.1           | 154±3        | 0.48        | 13.9        |
| (D)   | +6.0      | 11.5           | 163±3        | 0.52        | 14.2        |

TABLE I: Summary of the obtained values at each state in the N$_2$-etching experiment.
spectively. The straight line in the state (B) was shifted to the rightmost side of the graph because of the increment of the FE current at low bias voltages. When current-voltage data are obtained, it is important to be aware of the influence of contamination on the apex. If contaminating gases in the chamber, such as N₂, O₂, H₂O, etc., are absorbed on the apex, the structure of the apex and the work function may be varied. In order to avoid this situation, we checked the tip apex by FIM before measuring the FE data.

If we compare FIM images (a) and (b) in Fig. 1, it is clear that the distance between the neighboring spots is longer in (b) than in (a). Since the magnification is higher for a sharper tip, this is direct evidence that field-assisted N₂ etching makes the tip sharper. The imaging voltages of He-FIM also indicated the sharpness of the tip. Since the imaging voltages were applied so as not to exceed the evaporation field of the W atoms, all the imaging fields at the apex were of almost equal strength. The equation \( F = V/kR \) establishes the relation among the imaging field \( (F) \), applied FIM voltage \( (V) \), the field reduction factor and radius of curvature [17]. The imaging voltage +6.0 kV at the state (A) was reduced to +4.1 kV at the state (B) due to sharpening by N₂ etching, and those at the states (C) and (D) were +5.3 kV and +6.0 kV, respectively, due to blunting caused by field evaporation.

We divided each FIM image into two regions using a white dotted circle as shown in Fig. 1. The parts inside the circles show clear He-FIM images of tungsten crystal structures. These regions have a spherical shape and possess the smallest radius of curvature in each state. We estimated the radii of curvature of the inner regions with ball models and compared them. The models (e)-(h) in Fig. 1 correspond to the FIM images (a)-(d), respectively. These models were obtained by assuming their radii to fit the targeted FIM images. We colored the brighter tungsten atoms with green and the darker ones with red. The estimated radii of curvature \( (R_{ball}) \) were (A) 11.3 nm, (B) 8.5 nm, (C) 11.1 nm and (D) 11.5 nm, respectively. The outer parts of the white dotted circle had structureless bright spots presumably originating from nitride or oxide contaminants.

The obtained values are listed in Table I. The ratios of the FIM imaging voltage to the radius of the ball model \( (V/R_{ball}) \) should be constant if the tips have a similar overall shape during N₂ etching and field evaporation. The obtained ratios \( V/R_{ball} \) were (A) 0.53, (B) 0.47, (C) 0.47 and (D) 0.52, i.e., similar. We also evaluated the reduction factors \( k_{ball} \) as the ratio \( \gamma/R_{ball} \), and they were (A) 13.9, (B) 14.4, (C) 13.9 and (D) 14.2. Therefore, the FN plots suggested that the shank of the tip did not change very much among the states (A)-(D).

The FE patterns for the states (A)-(D) are shown in Figs. 1(i)-(l), respectively. These FE patterns showed that most of the electrons emerged from inside the white dotted circle of the FIM images, since the field there was higher than in the outer region. After N₂ etching, the FE from the center (111) plane became dominant due to the etching of the periphery. After further field evaporation, the FE pattern was restored to the initial one. Therefore, the FE from the small and clean tungsten apex reflected the shape of the tip apex obtained from the field-assisted etching.
N₂ etching and field evaporation. The FE data fit the FN theory, and the obtained values were consistent with the FIM observations. The results suggest that field-assisted N₂ etching is valuable for improving emission properties as well as the tip sharpness.

B. O₂ etching

A similar procedure was carried out twice using field-assisted O₂ etching. We used the same tip used in the above N₂-etching experiment. After the first O₂ etching, the periphery of the tip apex was etched away. Therefore, the initial state of the second O₂-etching experiment was much different from the final state of the N₂ etching. The following are the results of the second O₂-etching experiment. Three [112] planes were clearly visible in Fig. 3(a), which was prepared by field evaporation after the first O₂-etching experiment. Since the O₂ etching progressed via several explosion-like evaporations [10], control of the O₂-etching process was difficult compared to the N₂ etching. The sharpest possible state we could obtain is shown in Fig. 3(b). Then, the tip was blunted by field evaporation under a He environment (without O₂ gas) as shown in Figs. 3(c)-(e). We defined states (A)-(E) as corresponding to FIM images (a)-(e) of Fig. 3.

The etched tip emitted electrons at the lowest bias voltage as shown in Fig. 4(a). To obtain 100 pA of FE current the necessary voltage was only ~330 V for the state (B) while it was ~550 V for the initial state (A). The FN plots of all states are shown in Fig. 4(b). Each plot fitted the straight line well. The \(\gamma\) values were (A) 182 nm, (B) 98 nm, (C) 104 nm, (D) 174 nm and (E) 194 nm. The FIM image of the state (B) revealed a drastic change in the tip sharpness induced by field-assisted O₂ etching as shown in Fig. 3(b). The magnification of the image (b) was quite high compared to that of the initial state (A). The imaging voltage of +6.3 kV at the state (A) decreased to +3.0 kV at the state (B). The ball models in Figs. 3(f)-(j) show the approximate representative apex structures during the serial drastic change in the radius of curvature from 10.2 nm for the state (A) to 3.1 nm for the state (B).

The results are listed in Table II. The \(V/R_{\text{ball}}\) ratios were (A) 0.62, (B) 0.97, (C) 1.11, (D) 0.85 and (E) 0.89. These were different from the case of N₂ etching and were all relatively close to 1 except for that of the state (A). The estimated field reduction factors \(k_{\text{ball}} = \gamma/R_{\text{ball}}\) were (A) 17.8, (B) 31.6, (C) 28.9, (D) 29.5 and (E) 27.3. The sudden increase in the \(k_{\text{ball}}\) value corresponded with the change in the shape of the periphery of the tip induced by O₂ etching. The bright spots outside the dotted white circle in Fig. 3(a) vanished in the FIM image in Fig. 3(b). This fact suggests that the contaminated periphery of the tip apex were thoroughly etched away by O₂ etching. The observed FE patterns were in accordance with this change. The FE took place only from the (111) plane as shown in Fig. 3 while the FE patterns after the N₂ etching had considerable intensities from other directions. Rough models of the shape of the tip apex and shank are shown in Fig. 5. These models were estimated from the FIM images in which we counted the layers removed by field evaporation. While the shape of the shank was not greatly changed in the N₂-etching process, the shank was highly etched in the O₂-etching process due to the explosion-like evaporations. Changing the shape of the shank caused a considerable increment in the field reduction factor \(k\). In the present experiment, the O₂ etching was more effective than the N₂ etching for removing the periphery of the tip apex. However, the shape of the etched tip may depend on controlling the etching voltage, the geometry of the tip and the extractor, the pressure of the N₂ or O₂ gases, and the initial shape of the tip. In fact, the N₂-etched tip in Ref. [9] had a narrow neck as Fig. 5(b). Further experiments are necessary to elucidate differences in the fabrication efficiency between N₂ and O₂ etching.

### Table II: Summary of the obtained values at each state in the second O₂-etching experiment.

| State | \(V/(kV)\) | \(R_{\text{ball}}\) (nm) | \(\gamma\) (nm) | \(V/R_{\text{ball}}\) | \(k_{\text{ball}}\) |
|-------|-------------|-----------------|---------|-----------------|-------|
| (A)   | +6.3        | 10.2            | 182±4   | 0.62            | 17.8  |
| (B)   | +3.0        | 3.1             | 98±2    | 0.97            | 31.6  |
| (C)   | +4.0        | 3.6             | 104±3   | 1.11            | 28.9  |
| (D)   | +5.0        | 5.9             | 174±4   | 0.85            | 29.5  |
| (E)   | +6.3        | 7.1             | 194±4   | 0.89            | 27.3  |
IV. CONCLUSIONS

We studied the FE property of a single crystal W <111>-oriented tip fabricated by field-assisted N$_2$ and O$_2$ etching. The FE current measurements with changing bias voltages were very well fitted to FN theory. The obtained slopes of the FN plot matched the sharpening process of the tip apex. The results were also in good agreement with FIM images and FE patterns. This experimental study revealed that O$_2$ etching was more effective than N$_2$-etching at removing shank materials of the tip towards sharpening the tip; and the resulting tips showed differences in FE property in terms of electron beam geometry and bias voltage. The sharpening of the electron beam and the lowering of the bias voltages for FE by N$_2$ and O$_2$ etching of tip apexes have been demonstrated.

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