Enhanced cold field emission from $\langle 100 \rangle$ oriented $\beta$–W nanoemitters

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(Received 7 July 2003; accepted 8 March 2004; published 5 May 2004)

Well-aligned $\beta$-phase W($100$) nanorods having square-base pyramidal apexes were grown on oxidized Si($100$) substrate using glancing angle deposition technique with substrate rotation. The field emission characteristics of nanorods were measured using scanning tunneling microscope (STM) tip as an extraction anode. A highly confined emission current of about 23 $\mu$A was obtained at a low extraction voltage of $\sim 260$ V at $\sim 280$ nm anode-cathode distance with $<$3% fluctuations over $\sim 2$ h. The Fowler–Nordheim plot of the field emission characteristics of nanorods is nonlinear compared with the linear behavior from a conventional W film. The STM topography after the field emission showed a type of nanolips structure grown over the pyramidal apex, which was suggested to enhance and stabilize the emission current. © 2004 American Vacuum Society.

[DOI: 10.1116/1.1736642]

I. INTRODUCTION

Cold field emitters have been the subject of intense research because of their technological applications, for example, flat panel displays and vacuum electronics.$^{1–4}$ For conventional thermally annealed field emission (FE) tips, several kilovolts are required to draw a useful amount of currents. For commercial applications, the field emitters must have a low turn-on voltage, high emission current density, and high stability over time. In the search of a better emitter, the microfabrication techniques led to the development of an array of field emitter tips such as “Spindt cathode” with an end radius of $\sim 20$ nm and an anode was positioned $\sim 500$ nm away from the tip.$^{4}$ Due to the proximity of the anode several microamperes of electron current could be extracted from these tips with a reduced extraction voltage of 200 V.$^{4}$ However, the fabrication of these sharp needle-type cathodes requires lithographic and multistep processes. On the other hand, the glancing angle deposition (GLAD) technique$^{5–7}$ is relatively straightforward and allows a single step fabrication of nanorods and other desired geometry. This is a physical vapor deposition in which flux arrives at a large oblique incidence angle ($>80^\circ$) from the substrate normal while the substrate is rotating. This results in the formation of isolated nanorods by the self-shadowing mechanisms. Colgan and Brett$^2$ studied the FE properties of GLAD columnar films of Si and C and compared them with conventional films of the same materials. They observed a reduction in the turn-on voltage for the columnar films. The FE properties from different nanostructures including carbon nanotube,$^8$ $\alpha$–W nanowires with flat tops,$^9$ AlN nanotube,$^{10}$ and MoS$_2$ nanoflowers$^{11}$ were reported to have relatively low turn-on voltages.

Most of the FE experiments have been conducted on emitters of unknown areas and on large numbers of emitters with some exception.$^{12}$ For the future development of nanoemitters with anode-cathode separation of a few tens to few hundreds of nanometers, knowledge of FE properties at a small distance is required. Also, until now little attention has been paid toward the study of modifications in the morphology of nanoemitter surface after the FE. There is a lack of experiments in the determination of current density limits in nanofabricated FE arrays, which is critical not only to the quantification of the maximum current density available but also to examine the possible effects due to field-assisted surface diffusion during the operation. To study this, scanning tunneling microscopy (STM) is an ideal tool in determining both the FE characteristics and the topography of an individual nanostructured cathode. In this article, we use a nonlithographic GLAD technique to fabricate $\beta$-phase W nanorods having square-base pyramidal apexes and investigated FE behavior and surface modification after FE using STM for their potential application as effective nanoemitters.

II. EXPERIMENT

Tungsten nanoemitters in the form of nanorods were deposited on the nativeoxide of polished $p$-Si($100$) (resistivity $12–25$ $\Omega$cm) substrates using a 99.95% pure W cathode in an dc planar magnetron sputtering chamber with a base pressure of $1.4 \times 10^{-6}$ Torr. The vapor flux arrived at an oblique incidence angle $\theta$ from the substrate normal. The angle $\theta$ has been repetitively changed from large to smaller angles to obtain a layered structure in vertical direction: $85^\circ$ (40 min), $75^\circ$ (10 min), and $60^\circ$ (5 min) for the first layer and then three layers of $88^\circ$, $80^\circ$, and $85^\circ$ (5 min), $75^\circ$ (10 min), and $60^\circ$ (3 min). The whole deposition process produced nanorods of $762 \pm 5$ nm thickness. The limited adatom mobility combined with the shadowing effects due to the extremely oblique incidence with the substrate rotating at 0.5 Hz resulted in the formation of isolated W nanorods having a pyramidal apex on each nanorod. The deposition rate in all the experiments lies within 7 to 10 nm/min. The sputtering power used was 200 W at an Ar pressure of 1.5 mTorr. The maximum temperature of the substrate during the deposition was 80 $^\circ$C. The W conventional film of $761 \pm 2$ nm thickness.

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was grown at normal incidence without substrate rotation under the similar sputter growth condition as that of nanorods.

III. RESULTS AND DISCUSSION

The scanning electron microscopy (SEM) images showing the top and side views of W nanorods and a conventional W film are illustrated in Fig. 1. The nanorods were observed to have square-base pyramidal apexes [see Fig. 1(a)] with an areal density of about 10^13 rods/m^2. All four sides of the pyramid had sharp boundaries with 88±11 nm side length. The sides were inclined with respect to the square base by an angle of about 45° determined from the cross-sectional SEM image in Fig. 1(b). The conventional film surface was observed to be relatively flat as shown in the top view in Fig. 1(c) and the side view in Fig. 1(d). No pyramidal structure was observed in this case, although the conventional film showed nanostructures on its surface. Formation of nanostructures on a conventional W film has been reported previously. The x-ray diffraction (XRD) spectrum of pyramidal W nanorods is shown in Fig. 2. The (200), (210), and (400) reflection planes show a simple cubic β-phase W with (100) preferred orientation. The β-phase is further supported by our ex situ reflection high-energy electron diffraction (RHEED), which shows a well-defined (200) texture. The lattice constant we extracted from the RHEED pattern for β-phase of W was 0.50±0.02 nm and is consistent with the literature. Figure 3(a) shows a STM image of pyramidal nanorods surface obtained in a constant current mode using a Pt–Ir tip (radius of curvature of about 10 nm) with a set current of 1 nA and a bias voltage of 0.5 V applied to the W nanorods surface. On some nanorods if we highlight dotted lines along dark boundaries we can see the boundaries do not intersect to one point. Instead an area that looks like pyramidal apex geometry exists. Our x-ray spectrum shows a preferred (100) orientation. The W(100) plane of pyramidal nanorods is known to be thermodynamically unstable and is faceted into energetically favored lower surface energy (110) planes. Based on the x-ray and STM images we suggest that a W nanorod apex is bound by four (110) facets and with a square base as shown in a schematic diagram in Fig. 3(b). Our x-ray photoemission spectroscopy spectrum shows that the surfaces of nanorods were oxidized in the atmosphere. The oxidized (110) plane has high work functions (6.4 eV) and were relatively nonemitting. The pyramidal geometry provides a better angular confinement with out thermal build-up. This is in analogy to a three-facet structure observed on W(111) substrate having a threefold symmetry by Yu et al.

The FE measurements on these pyramidal nanorods and a conventional film were performed in a vacuum chamber with a pressure better than 1×10^-8 Torr. The procedure for obtaining the FE characteristics was as follows: First, the nanorods surface was imaged by STM and the tip was centered above the selected individual nanorod. Then, the tip was withdrawn from the nanorod apex and the feedback was disconnected so that current–voltage (I–V) curves can be obtained at fixed separation of about 280 nm. The electrical connection from the W nanorods cathode to the STM tip anode was made by a copper wire attached to the top surface of W film and by-passed the metal/semiconductor diode that

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**Fig. 1.** SEM images showing the top (a) and side (b) views of pyramidal W nanorods and the top (c) and side views (d) of a conventional W film.

**Fig. 2.** XRD spectrum of W nanorods showing β-phase structure with (100) texture.

**Fig. 3.** (a) STM image of pyramidal W nanorods. The facet boundaries on a pyramidal apex in (a) are guided by the dotted lines. (b) A schematic diagram of a W nanorod showing the square-based pyramidal apex oriented in the (100) direction with (110) facets. Electric field lines are also depicted in the figure.
minimizes the voltage drop across the interface. The voltage was increased up to a burn-out voltage value until the emission current drops to zero due to the emitter-tip failure. After FE measurements, the feedback was connected again and the tip was brought back into the tunneling range for measuring morphology changes occurred in the emitting surface of nanorods. The plots of typical electron emission current $I$ versus applied dc voltage $V$ characteristics measured by STM for a W nanorod having a pyramidal apex (open triangles $\triangle$) and conventional W film (open circles $\bigcirc$) are shown in Fig. 4. The turn-on voltage was observed to decrease from $\sim$510 V for the conventional film surface to $\sim$145 V for the pyramidal apex geometry. A higher emission current of $\sim$23 μA at the burn-out voltage of $\sim$260 V was obtained for a pyramidal nanorod which was stable within ±0.5 μA for an observation time over $\sim$2 h. The conventional film gives the maximum emission current of $\sim$0.7 μA having <5% fluctuations at the burn-out voltage of $\sim$720 V.

In a standard one-dimensional Fowler–Nordheim (F-N) theory using planar electrodes configuration the emission current $I$ (A) is a function of the work function $\phi$ (eV), extraction voltage $V$ (volts), field enhancement factor $\gamma$ (cm$^{-1}$), and emission area $A$ (cm$^2$) and is given by $I = aV^2 \exp[-b/V]$, where $a = 1.54 \times 10^{-6} A\gamma^2(\phi)^{-1}$ and $b = 6.83 \times 10^7 (\phi)^{3/2}(\gamma)^{-1}$. A plot of experimental ln($I/V^2$) versus $1/V$ is thus expected to yield a straight line with the intercept and slope to be $\ln(a)$ and $-b$, respectively. The $\gamma$ is a proportionality factor between the applied voltage $V$ and the electric field $E (= \gamma V)$ at the cathode apex. The $\gamma$ can be split into components $\gamma = g/d$, in order to separate the geometric enhancement factor $g$ from the cathode-anode separation $d$. For nanorods, $g$ deviates from 1 (for a flat surface) because of the compression of the equipotential surfaces around a protrusion on the cathode that leads to the maximum electric field being at the apex. The F-N plots for pyramidal nanorods and the conventional film are given as the inset in Fig. 4. The curve from the conventional film surface exhibits a straight-line behavior, whereas the F-N curve for a pyramidal W nanorod is nonlinear. The nonlinear behavior of the F-N curve from the pyramidal nanorod pointed out the failure of F-N theory for very sharp tips, which was experimentally observed by previous researchers. By using the bulk W work function of 4.5 eV, the FE properties of the conventional film and nanorod were calculated. The values of $g$ calculated from the above equation were 1.89 and 4.62 for a conventional film and a nanorod, respectively. The emission areas determined from the F-N equation for a film and a nanorod were 0.03 and 27.67 μm$^2$, respectively. The large emission area in the case of nanorods may suggest that emission occurred from a few nanorods when an anode tip was positioned 280 nm above the surface during FE. This is because the field from the tip at 280 nm height can reach several nanorods compared with one nanorod if the tip is positioned much closer to the surface. This was confirmed by the STM topography of pyramidal nanorods after obtaining FE curves at the cathode-anode separation of about 280 nm and is shown in Fig. 5. The facet boundaries on the pyramids were washed out after the FE [see Fig. 5(a)] and nanolip structures shaped like the lips of an open mouse on the pyramidal apexes were observed. A high resolution STM image of a nanolip structure is shown as the inset in Fig. 5(b). The nanolip has a width of about 50 nm with ridges having a radius of curvature of $\sim$5 nm. A height profile of a nanolip...

![Image](https://example.com/image1.png)

**Fig. 4.** Field emission $I-V$ characteristics obtained from pyramidal apex W nanorods ($\triangle$) and the surface of a conventional W film ($\bigcirc$) at the anode-cathode separation of $\sim$280 nm. In the inset, F-N plots for pyramidal apex W nanorods ($\Delta$) and conventional W film ($\bigcirc$) are shown. The conventional film surface shows a linear FE behavior while the pyramidal W nanorod shows a nonlinear FE behavior.

![Image](https://example.com/image2.png)

**Fig. 5.** STM surface morphology of pyramidal W nanorods after the field emission. (a) The formation of nanolips on the nanorod apexes is visible. (b) A line profile along the dashed line through the nanolips structure shown as an inset in (b).
obtained from the dotted line that cuts across the center of a nanolip [inset of Fig. 5(b) is shown in Fig. 5(b)].

The formation of nanolips structures over the nanorods apexes is due to the field-assisted surface diffusion under high electric field ($\sim 10^7$ V/cm) during the FE process. The millisecond time scale associated with the formation of a sharp W tip through a field assisted surface diffusion is much shorter than our data acquisition time ($\sim 5$ s per data point). The role of field assisted surface diffusion over the low-index crystal planes to minimize the surface free energy of W field emitter tip has been noticed previously. The asymmetrical orientation of the pyramidal nanorods with respect to the anode tip produces deformation of the nanolips shape from circular to elliptical.

We were not equipped to measure the temperature of emitting nanorods during FE. Both ohmic heating and the Nottingham effect could change the tip temperature from the ambient. In our case, all the W nanorods are connected to each other through the Si substrate that has sufficient thermal conductivity. Therefore, the local rise of the temperature near W melting point is probably unlikely.

Rinzler et al. reported that the FE emission from an individual carbon nanotube was dramatically enhanced when the tube end was opened by the laser evaporation or oxidation etching. Apart from carbon nanotubes other nanostructures such as AlN nanotubes and MoS$_2$ nanoflowers were shown to have excellent emission properties when their ends were opened. Similarly, we suggest that the open edges of the nanolips created on the pyramidal W nanorods apexes give better FE performance in terms of high emission current and stability. Another possibility is the field-induced evaporation of oxide layer from the W nanorod apex and a fresh tungsten surface was exposed. This can increase the FE because the work function of clean tungsten surface is lower than that of oxidized tungsten surface.

**IV. CONCLUSION**

In summary, we have fabricated square-base pyramidal W nanorods using a GLAD technique and characterized their FE using a STM tip as an extraction anode. A higher emission current was observed from the pyramidal $\beta$–W nanorods compared to the conventional W film. The nanolips structure formed on the nanorod apex during FE gives enhancement and stability in the maximum emission current.

**ACKNOWLEDGMENTS**

The work was supported by NSF DMR. The authors thank Dexian Ye for taking SEM images.

20. To determine the field emission parameters for pyramidal nanorod, we did a linear fit to the higher voltage region of the F-N plot.