Field-emission properties of ultrathin 5 nm tungsten nanowire

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We report the field-emission properties of ultrathin tungsten nanowires of 5 nm diameter and several hundred nanometer length. Fowler-Nordheim plots of field-emission current-voltage measurements of such nanowires show marked deviation from linearity. After flashing, cold-field-emission current stability with standard deviation of better than 1% has been observed for periods of at least 30 min at a vacuum level of $10^{-9}$ mbar. Beyond this, field-emission current noise was found to mainly comprise current step jumps and current spikes. At high emission current densities in the order of $10^6$ A cm$^{-2}$, the noise changes into flicker noise. Field emission at high current density induced surface diffusion and crystallization of the disordered nanowire tip due to temperature rise at the field-emitting tip. Further increase in the emission current density initiated local arc destruction which caused shortening of the nanowire length. © 2006 American Institute of Physics. DOI: 10.1063/1.2400722

I. INTRODUCTION

Cold-field emitters are traditionally based on micrometer-sized cathodes, albeit with very sharp tips. Studies have suggested that a further reduction in emission area would change the field-emission properties significantly. In 1995, Rinzler et al. and de Heer et al. studied the field-emission properties of individual carbon nanotubes and carbon nanotube films, respectively, and observed high emission current capability from carbon nanotubes. This observation sparked widespread interest in studying the field-emission properties of carbon nanotubes and other one-dimensional (1D) nanostructures, but mainly as areal electron sources. Much less effort has been expended in the study of single 1D nanostructures probably due to the difficulties in assembling a nanowire or a nanotube as an individual electron emitter. Nonetheless, de Jonge managed to demonstrate a single carbon nanotube electron source which showed good emission current stability, long lifetime, low electron-energy spread, and high brightness. Such desirable results encourage the exploration of other 1D nanostructures as point electron emitters.

In this paper, we report the field-emission properties of ultrathin tungsten nanowires grown by the field-emission-induced growth (FEIG) technique. The tungsten nanowires have diameters of only $\sim5$ nm and are typically a few hundred nanometers in length. The emission current-voltage relationship, emission current stability, and field-emission-microscopy (FEM) patterns are obtained and discussed. Due to the small emission area and high aspect ratio of a nanowire, which are markedly different from those of a conventional tungsten cold-field emitter, the FEIG tungsten nanowire demonstrates unique field-emission properties. A study of such emitters also provides further insight into physical mechanisms that influence the emission properties of metallic nanowires in general.

II. EXPERIMENT

The nanowire was grown on an etched tungsten cathode tip that has been spot welded on a filament loop on a standard filament base. In the FEIG method, constant low-current field emission in the presence of an organometallic precursor vapor results in the growth of a single nanowire at the cathode tip, as described elsewhere. Figure 1 shows a typical tungsten nanowire grown at an emission current of 100 nA for 2 s in the presence of tungsten hexacarbonyl vapor at a local pressure of $\sim10^{-2}$ mbar. Under such growth conditions, the nanowire has a disordered/amorphous tungsten core of about 4 nm in diameter that is overcoated by 1 nm thickness of carbon along its length. The growth characteristics and material properties of FEIG tungsten nano-
wires have been reported elsewhere. Typically, the nanowire is grown 400–800 nm long, which yields a very high aspect ratio freestanding wire on a sharp metallic tip.

After growth, the nanowire was transferred immediately to an UHV field-emission characterization chamber. Current-voltage (I-V) measurements and current-stability (I-t) measurements with concurrent FEM imaging, were carried out. FEM images were recorded using a digital video camera at 30 fps (frames per second).

Since the field-emission characteristics vary between nanowires due to differences in tip structure and morphology, we studied numerous nanowires and extracted generic emission characteristics that represent this class of emitters.

III. RESULTS AND DISCUSSIONS

A. Fowler-Nordheim plot

Prior to I-V measurements, each tungsten nanowire was flash cleaned for a few seconds at a temperature of around 600 °C to desorb loosely bound adsorbate molecules. The flashing temperature was kept below 800 °C to prevent detachment of the nanowire from its pedestal tip. While some of the I-V characteristics followed the Fowler-Nordheim (FN) equation and showed a linear FN plot, most of the FEIG tungsten nanowires exhibited different degrees of deviation from linearity towards lower currents, as shown in the inset of Fig. 2. The deviation is not due to leakage current or the measurement noise floor since the series of data points for the FN plot is taken for emission currents of 10 nA and higher to avoid the effect of system noise which is about 5 pA. In any case, leakage current will only cause the FN plot to flatten in low emission current region.

Nonlinearity of FN plot has been reported in the single atom emitter of Binh et al. The deviation was attributed to the presence of localized bands at the single atom emitter tip. The localized bands shift with the applied voltage which induces the change of the electron-supplying function towards emitting surface and thus causes the respective FN plot to curve downwards at high emission currents.

On the other hand, the deviation from the ideal FN plot observed for our nanowires is at low rather than at high currents. Moreover, the emission area of a 5 nm diameter nanowire is unlikely to be confined to a single protruding atom as in the case of Binh et al. Other mechanisms that could result in a deviation from the FN equation are the space-charge effect and resistive-heating effect. Both effects can be discounted as the cause of the observed deviation since they are expected to cause deviations at higher rather than at lower currents.

Recently, Edgcombe and de Jonge also observed a FN plot that is similarly curved for single carbon nanotube field emitters of 1–4.4 nm diameter. They attributed the curved FN plot to the highly nonuniform electric field/surface potential at the high curvature emission tip. This phenomenon has been studied theoretically by Fursey and Glazanov and Cutler et al. who noted the variation in the electric field strength in the vicinity of an emitter tip especially when the emitter diameter is comparable to the electron tunneling distance (of around 1.5 nm) across the surface barrier. For a 5-nm-diameter tungsten nanowire, electrostatic modeling shows that the electric field at 1.5 nm from the apex falls by 78% from that at 0.5 nm. Such changes in the electric field give rise to an electron transmission function that is different from that used to derive the ideal FN equation which assumes a constant electric field across a planar anode-cathode gap. The degree of deviation depends on the ratio of electron tunneling distance to the emitter size. The ratio is expected to be higher in the low-current (low-field) regime due to the larger tunneling distance and exaggerates the deviation from the classical FN plot at lower currents.

An ideal FN plot is shown in Fig. 2 as a comparison against the experimental data based on the simplified Fowler-Nordheim field-emission equation in S.I. units,

$$I = \frac{A \times 10^{-6} (\beta V d)^2}{\phi} \exp \left( \frac{10.4}{\sqrt{\phi}} \right) \exp \left( -\frac{6.44 \times 10^9 \phi^{3/2}}{\beta V d} \right),$$  

where $I$ is the emission current in amperes. Since the work function ($\phi$) of amorphous tungsten has not been reported yet, $\phi$ of the disordered tungsten nanowire is assumed to be 4.3 eV, same as $\phi$ of the (116) tungsten crystal plane which has the lowest work function among the tungsten crystal planes exposed by the nanowire’s rough surface. $A$ is the emission area taken to be $\pi r^2$, where $r$ is the tip radius of the nanowire which is 2.5 nm. $\beta V/d$ is the local electric field at the nanowire tip in V/m, where $\beta$ is the unitless field-enhancement factor chosen to be 240 000 to give the best fit to the experimental data in the high current region, $V$ is the anode bias voltage, and $d$ is the nanowire tip to anode distance. The high $\beta$ value is expected due to the high aspect ratio of the nanowire growing on a sharp tungsten microtip.

A simulation carried out using the charge particle optics (CPO) program with cylindrical symmetry to resemble the actual field-emission setup was performed to model the electric field and electron trajectories. The $\beta$ value obtained from
the simulation for a hemispherical-cap nanowire of 500 nm length and 5 nm diameter is 130 000. The actual $\beta$ value of the tungsten nanowire is expected to be one to two times higher than the simulated value due to nanowire tip edge and nanoprotrusion roughness on the nanowire tip which would induce a higher local electric field compared to the smooth hemispherical cap assumed in the simulation.\textsuperscript{17}

**B. Emission current stability**

The emission current from a fresh FEIG nanowire emitter is very unstable due to the dynamics of adsorbate molecules on the nanowire tip surface. These adsorbate molecules would have accumulated on the nanowire during the growth and transfer processes during which the nanowire was exposed to tungsten carbonyl and air, respectively. Figure 3 shows a typical current profile of a fresh tungsten nanowire during a stability test with constant voltage bias. Irregular current spikes that could be up to two orders of magnitude greater than the base emission current occur randomly. One interesting feature of the current spike is its sudden increase of current followed by a gradual decay. This type of emission noise was eliminated immediately upon flash cleaning at 600–800 °C for 5 s. Thus, we believe that the noise is related to the loosely bound adsorbate molecules on the nanowire surface which will change the work function of emission tip and lead to drastic changes in the emission current. The actual mechanism that causes such irregular current spikes is not clear, but we suspect that it involves cycles of adsorbate-nanotip buildup induced by the electric field gradient and subsequent destruction of the ultrasharp adsorbate nanotip by the increasing emission current; a similar mechanism is thought to trigger the arc destruction of tungsten microtips.\textsuperscript{18}

After flash cleaning, the emission current stability of a tungsten nanowire (at $3 \times 10^{-9}$ mbar) improved significantly, as the current fluctuation (standard deviation) reduced from 72% to 0.25%. The emission current of about 700 nA remained stable over the 20 min stability test span. Emission current stability was measured at a sampling rate of 10 Hz for a short-term stability test. At the typical operation current of $\sim 100$ nA and anode bias of the nanowire emitter (500 V) the rms noise ($<50$ mV) of the system amplifier (Trek 609A-3) would translate into an emission current fluctuation noise of not more than 0.15%. In a worst-case scenario, which we have not observed, spontaneous voltage spikes of $\sim 1$ V from the amplifier would only induce current spikes of less than 3% of the total emission current. Thus, system noise would not be expected to contribute significantly to the observed emission current fluctuation. We attribute the good emission stability to the nanoscale emission area and the long supporting shank. The small emission area reduces significantly the probability of residual gas molecules or ions arriving at the emission surface. On the other hand, the long nanowire shank distances the emission tip away from the large microtip pedestal surface that acts like an adsorbate molecule reservoir. The rough surface of the long and thin nanowire shank reduces the diffusion of adsorbates from the reservoir and nanowire surface toward the emission tip, thus prolonging the duration before adsorbate molecules migrate to the tip. Stable emission current densities in the range of $10^5$–$10^6$ A/cm$^2$ at 10$^{-9}$ mbar with standard deviation of less than 1% can last for at least 30 min before the first steplike current jump appears which is comparable to the characteristics of a carbon nanotube electron source.\textsuperscript{19} Such stability is much better compared to that of tungsten microtip cold-field emitters. Crewe\textit{ et al.} reported that cold field emission from a tungsten microtip with about 50 nm tip radius operating at about 100 nA exhibits short-term current fluctuations ($\sim 1$–100 ms duration) of between 1.5% and 5% of the total probe current at comparable vacuum levels.\textsuperscript{20,21}

Between current jumps, the current remained stable nevertheless. As emission continued, the period between current jumps progressively shortened from tens of minutes until finally the jump frequency exceeded the current measurement sampling rate (0.5 Hz for a 24 h stability test run). After several hours, the emission current exhibited high frequency and high-magnitude current jumps around an average value. Such behavior would be expected if adsorbates slowly accumulate on the emission tip, thereby causing fluctuations in the emission. Compared to microtip emitters that need extraction voltages of a few kilovolts, the nanowire field emitter operates with a bias of a few hundred volts. The low anode biases involved reduce significantly the ion sputter roughening of the emitter surface and thus reduces the buildup of local protrusions that can lead to emitter arc destruction as observed for microtip emitters.\textsuperscript{22} Structural damage of the emission tip of a microtip changes the tip radius significantly, which leads to a severe change of the field-enhancement factor or equivalent emission current. On the other hand, damage to the emission tip of a tungsten nanowire will not change the tip radius significantly since the radius is constrained by the wire diameter. Thus, a tungsten nanowire may be expected to continue emitting without much loss in emission current even if it sustains structural (but not catastrophic) damage along the way.

One surprising feature of the tungsten nanowire emitter is its ability to support high emission current densities, considering its small diameter and disordered structure. Figure 4 shows stable and continuous emission current of greater than 500 nA for at least 20 min. For a nanowire with tip diameter of between 4 and 5 nm, the corresponding current density is $(2.5–4.0) \times 10^6$ A/cm$^2$.\textsuperscript{23}

**FIG. 3.** Emission current from fresh FEIG tungsten nanowire. The anode is biased at 450 V. Current sampling interval=100 ms.
The nature of the emission current noise changes with emission current density (Fig. 5). Step jumps and spikes were typically encountered at low and moderate emission current densities ($<10^6$ A/cm$^2$). The magnitude of step jumps and spikes could be up to a few times higher than the preceding current. Such fluctuations are characteristic of emitters with nanoscale emission area such as single atom emitters. Any discrete event such as adsorption, desorption, or flip-flop of an adsorbate molecule will induce an immediate and observable effect in the total emission current. At high emission current densities greater than $10^6$ A/cm$^2$, the emission noise changed to flicker noise that is indicative of surface diffusion of adsorbate molecules or surface atoms. The flicker noise was accompanied by emission-spot dynamics. It is thought that the surface-diffusion dynamics was induced by a temperature rise at the nanowire tip at such current densities. Compared to tungsten micrometer-sized cold-field emitters which exhibit rapid emission current deterioration right after a flash clean, and flicker noise and spikes as the main components of emission noise, the tungsten nanowire emitter is characterized mainly by step jumps while exhibiting little drift in the current baseline.

C. Initiation of flicker noise and surface dynamics

Typical FEM images are shown in Fig. 6. The images show no symmetrical patterns as would be observed for clean tungsten microtip surface since the disordered nanowire surface is neither clean nor symmetric. The FEM pattern consists of irregular emission spots which might have originated from the disordered tungsten, overcoated carbon, or even adsorbates. The FEM resolution $\delta$ can be estimated from

$$\delta = \left( \frac{2hT}{mM} \right)^{1/2} \left[ 1 + \frac{2mv_0^2}{hM} \right]^{1/2},$$

where $M$ is the magnification factor, $T$ is the electron transit time from emission tip to screen, $v_0$ is average transverse velocity of Fermi electron, and $m$ is the electron mass. As stated by Rose, the FEM resolution will improve to just a few angstroms on a nanoprotrusion due to a greater local $M$. Brodie presented evidence that the atomic resolution of FEM is possible for a whisker emitter with a radius of about 5 nm. The small radius of our FEIG nanowire field emitter ($\sim 2.5$ nm) suggests that they would have a better FEM resolution than clean tungsten microtip. Emission spots in the FEM image (Fig. 6) are likely to arise from subnanometer emission sites on the nanowire edge or nanoprotrusions on the nanowire tip. At high emission current density ($>2 \times 10^6$ A cm$^{-2}$), the emission spots are seen to move around as discrete entities in the emission pattern area and this phenomenon is coincident with the appearance of flicker noise. The movement of emission spots at high emission current appears to follow a circular path, around the rim of the circular FEM pattern (refer to supplementary data). These observations at high emission current density suggest that (i) diffusion of entities takes place along the edge of the nanowire tip, in a manner similar to the diffusion of surface atom/adsorbates along edges between crystal planes of thermal-
field-emission tungsten tips, and (ii) each emission spot is likely to have originated from an individual adsorbate molecule or atom.17

The simultaneous appearance of emission-spot dynamics with the occurrence of flicker noise at high emission current density shows the close relationship between the two. Indeed, previous studies have proposed that flicker noise observed during field emission is mainly due to the surface diffusion of adsorbates or surface atoms on the emission surface.23-25 The activation energy for surface diffusion is supplied by thermal energy as the tungsten nanowire tip heated up considerably at high emission current density due to the Nottingham effect27,28 and Joule heating.10,11

D. Crystallization of nanowire tip

A most striking observation is the crystallization of the disordered tungsten nanowire at the tip after a long period of field emission at high emission current density. Figure 7 shows a high-resolution transmission electron microscopy (TEM) image of a nanowire tip after emission at 1 μA for a period of 1 h. The nanowire has been transformed into a crystalline structure up to at least 20 nm from the tip, while the rest of the shank showed smaller crystalline grains in otherwise disordered material towards the nanowire base. Since the nanowire is freestanding from the substrate tip, it was susceptible to vibration during TEM viewing. We were only able to obtain high-resolution TEM images after coating the nanowire tip with electron-beam induced carbon contamination to stiffen the nanowire. Diffraction data could not be obtained due to residual vibration and the small amount of crystalline material embedded in the amorphous carbon contamination.

Thermal annealing is well known to induce crystallization of amorphous structures. For example, Hofmeister et al. showed that thermal annealing of 8–24 nm diameter amorphous Si particles (Si mp, 1414 °C) at just 900 °C for 1 h produced almost completely crystalline Si particles.29 It was reported that the thermal-annealing-induced nanocrystallization of amorphous alloys starts with the formation of minimum grain sizes of a few nanometer diameter at temperatures close to half the melting point of the bulk alloy, with increasing grain size as the annealing temperature increases.30 Likewise, the melting point of the disordered 5 nm tungsten nanowire is expected to be much lower than that of bulk tungsten (mp, 3422 °C), due to the size dependence of melting temperature.31,32 It has also been reported that the temperature of a carbon nanotube tip (30 nm diameter, 40 μm long) field emitting at 1 μA can be up to 2000 K due to resistive heating.10,33 Evidence from the crystallization of our nominally disordered nanowire tip is commensurate with a considerable temperature rise at the tip, being furthest away from the substrate thermal sink. The polymorphous crystallization process converts the nanowire tip from a metastable amorphous phase to a more stable crystalline phase. At the initiation of high emission current density, resistive-heating-induced temperature rise along nanowire shank establishes the highest temperature at the nanowire tip region but temperature drops towards the nanowire base/thermal sink. With subsequent thermal diffusion, the temperature profile will increase overall until the steady-state temperature profile is achieved, balancing resistive heating, thermal diffusion, and radiation loss. Nucleation is expected to originate at the tip/hottest region following which crystal growth progresses down the shank, reflecting the temperature profile along the nanowire. Modeling of the temperature rise requires knowledge of the electrical conductivity, the thermal conductivity, and the precise physical dimensions of the 5 nm disordered nanowire, which we are currently investigating. Studies will then be performed by in situ TEM to obtain the current at the onset of crystallization.

E. Nanowire shortening at high current densities

Further voltage ramps to current densities greater than 10⁷ A cm⁻² often led to sudden drops in emission current, followed by an increase in the turn-on voltage. We examined this phenomenon in situ within the scanning electron microscope (SEM) chamber, where an as-grown FEIG tungsten nanowire was forced to emit at high currents. A tungsten nanowire was first grown on a tungsten cathode tip as shown in Fig. 8(a), pointing towards a tungsten anode tip positioned 10 μm ahead of the cathode tip. Up/down voltage ramps were then performed step by step with increasing maximum emission currents of 2, 3, 5, and 10 μA from the nanowire cathode. Figures 8(b) and 8(f) show SEM images of the nanowire taken after consecutive voltage ramps at 1, 2, 3, 5, and 10 μA current-compliance settings. The respective nanowire length (L), current compliance, and turn-on voltage for 10 nA field-emission current (V_on) are also indicated. The experiment showed that the nanowire length was shortened after a catastrophic event triggered at high emission current density which appears as a sudden drop of emission current during voltage ramp. The shortened nanowire will then need higher emission current to further reduce the nanowire length. This suggests that a shorter nanowire is able to deliver higher emission current before tip destruction. In fact, such FEIG W nanowires are able to deliver stable emission current densities of up to 10⁹ A cm⁻². A higher voltage is then required for turn on due to the reduction of the field-enhancement factor at the nanowire tip after the nanowire length has been reduced.8
For shorter nanowires, higher emission currents were needed to trigger nanowire shortening, which suggests that resistive heating is the main culprit since the temperature rise at the nanowire tip due to resistive heating depends on \( F^2 L^2 \), where \( I \) is the emission current and \( L \) is the nanowire length.\(^{34}\) Joule heating at high emission current densities can lead to uncontrolled positive feedback of temperature/emission current rise. The excessive temperature rise under strong electric field will eventually lead to localized field evaporation/arc destruction of the nanowire tip thereby shortening the nanowire.

IV. CONCLUSIONS

In conclusion, we have studied the field-emission properties of 5 nm diameter tungsten nanowires grown by the FEIG method. Fowler-Nordheim plots of field-emission current-voltage measurements of such nanowires show marked deviation from linearity at low currents, due to the change of electron-potential profile at cathode tip of highly curvature nanowire tip as compared to the classical field-emission model. After flashing, good cold-field-emission current stability with a standard deviation of better than 1% has been observed for a period of at least 30 min at a vacuum level of 10\(^{-9}\) mbar. Field-emission current noise comprising current step jumps and current spikes was observed after the period of stable emission. At higher current densities in the order of \( 10^8 \) A cm\(^{-2}\), the noise changed into flicker noise as a result of surface-diffusion effects induced by elevated temperatures at the tip. Field emission at high current density also caused thermally induced crystallization of the disordered nanowire tip. Further increase in the emission current density initiated local arc destruction which shortened the nanowire. A reduction in nanowire length increased the turn-on voltage, reduced the total current, and at the same time increased the current-carrying capability of the nanowire field emitter.

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