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Local field emission of electrons from an individual boron nanowire at nanometer electrode separation

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ABSTRACT

The field electron emission properties of an individual β-rhombohedral boron nanowire (β-*r* BNW) with electrode separation at nanoscale have been studied by ultrahigh vacuum four-probe scanning tunneling microscope (STM) system. A reproducible and stable emission current can be obtained. The maximal emission current density of individual boron nanowire is about 5×10^4 A/cm^2 at a low bias voltage (80 V). An obvious deviation from the Fowler–Nordheim (FN) theory appears, when the electrode separation reduced below 120 nm. This deviation is tentatively assumed to due to the invalidation of free electron cloud approximation in FN theory.

1. Introduction

One-dimensional (1D) nano-materials have exhibited the superior field emission properties than those used traditionally due to their high aspect ratios, small radius of curvature at the tip, low turn-on field and physical and chemical stable properties. Among them, the carbon nanotubes (CNTs) were considered as the most promising cold field emission cathode material. However, due to uncontrollable preparation and complicated electronic structures, it is very difficult to put CNTs into practical applications. In our previous studies, some nano-structures based on boron, such as single crystalline boron nanocones and nanowires array with α-tetragonal structure, have been synthesized repeatedly and showed a great potential to be an ideal cold field emission (FE) cathode material [1,2]. Furthermore, the field emission measurements of 1D nanostructures were carried out with micron-scale electrode separation so far, and the required bias voltages are mostly around hundreds of volts, even higher than one thousand volts in some experiments [3]. For the application of field emission source of nanowires, the high voltage requirement is one of the remarkable obstructors, especially for the portable devices. The most feasible solution is to get the anode closer with emitter, which could obtain higher applied electric field with the same bias voltage.

In this paper, we report a field emission electron source of an individual β-rhombohedral boron nanowire (β-*r* BNW) with varying electrode separation *d* at nanoscale. Using only 80 V anode voltage, we can easily obtain 5×10^4 A/cm^2 emission current density with an inter-electrode distance of 250 nm, which is comparable to the multi-wall carbon nanotubes [4,5]. The measurements show an obvious deviation from the FN theory when the electrode separation is reduced below a threshold (here is 120 nm). This result illuminates the limitation of inter-electrode distance for FN theory. Considering a good flexibility with the stable resistance to mechanical fracture even under a strain of 3% [6], our studies proved that the β-*r* BNW could be applied in the future portable flexible display devices.

2. Experiments

The β-*r* BNWs were synthesized through a developed chemical vapor deposition (CVD) method in a high temperature tube furnace [6]. A chemical etched tungsten probe was used as the substrate to grow boron nanowires. The field emission measurements were performed in a four-probe scanning tunneling microscopy (STM) system, which has four independent STM set-ups and a scanning electron microscopy (SEM) [7]. The whole system is assembled in ultra high vacuum (UHV) chamber with basic pressure around 2×10^{-10} mbar. The anode was another clean tungsten probe whose diameter at its apex is around hundreds of nanometers. Taking advantage of the scanning piezo tube of STM, we could easily manipulate the probes and control the anode–cathode separation very precisely at nanometer scale. Fig. 1a shows the SEM image of prepared boron nanowire used as cathode and another W probe as anode, where the anode diameter and anode-nanowire separation are about 200 and 350 nm, respectively. The field emission of electrons from selected single B nanowire (grounded) can be realized with a positive bias voltage applied on the anode probe (shown in the sketch Fig. 1b), A Keithley 6430 source-meter was used for supplying the voltage (varying from 0 V to a maximum of 80 V) and measuring the current (with sub-fA sensitivity) simultaneously.

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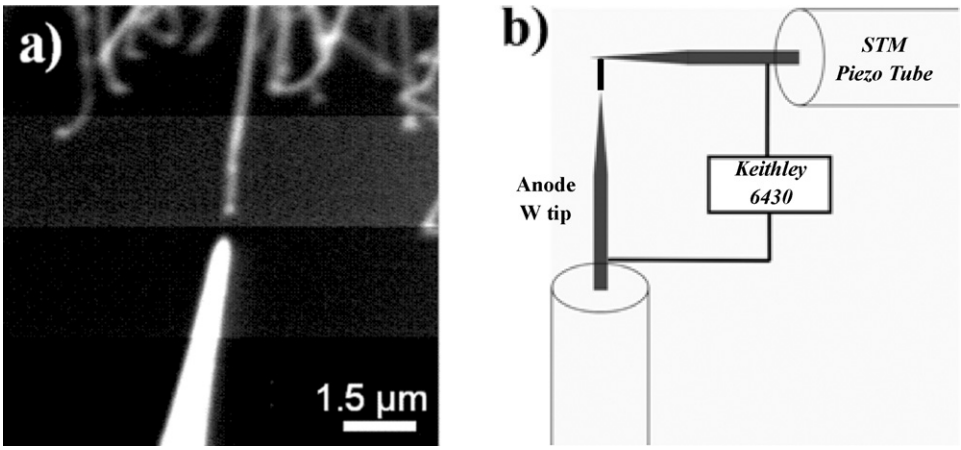

Fig. 1. (a) SEM image of an individual boron nanowire cathode and a tungsten probe anode for field emission measurement in a four-probe STM system. The diameter of the nanowire is 50 nm, and the electrodes separation d is 250 nm; (b) schematic illustration of the measuring installation. The black thicker line indicates a B nanowire prepared on a W probe. Both probes can be manipulated with the STM piezo fine movement so that the anode–cathode separation is controlled very precisely at nanometer scale.

3. Results and discussion

The field emission of electrons is usually analyzed in the framework of Fowler–Nordheim (FN) theory [8]. The emission current I can be written as

$$I = \left(\frac{E_{local}^2}{\Phi}\right) \exp\left(\frac{-B\Phi^{3/2}}{E_{local}}\right)$$

where the local electric field E_{local} is connected with the applied electric field $E_{applied}$ as $E_{local} = \gamma E_{applied}$, Φ is the work function and γ is the field enhancement factor; $B = 6.83 \times 10^7$ (V eV$^{-3/2}$ cm^{-1}) is a universal constant. The experimental data is usually treated as follows. As the $E_{applied} = V/d$, where V and d are the applied voltage and anode–cathode separation, the slope of Ln(I/V^2) plotted *vs.* $1/V$ (F–N plot) gives the value of $\Phi^{3/2}d/\gamma$. According to this formula, the Ln(I/V^2) should have a linear relation with $1/V$ in emission range.Fig. 2a shows the emission current–voltage (I–V) curve of an individual B nanowire with inter-electrode distance as 200 nm. The measured boron nanowire is about 50 nm in diameter and more than several μm in length. The separation between the tip of the nanowire and anode probe is much smaller than the length of the nanowire itself, which promises the concentration of the field between the tip of nanowire and the anode probe. So it is reasonable to take the nanowire and its substrate probe as an equipotential surface, what means we could take the distance between the tip of the nanowire and the anode probe as the anode–cathode separation d approximately. The emission current reaches 1 μA at only 80 V bias voltage and does not show any sign of saturation. The corresponding emission current density reaches 5×10^4 A/cm^2, which is a little smaller than the reported α-tetragonal nanowire [2]. This value could become higher if we consider the voltage limit of the system and the UHV circumstances. Our experiment is essentially different from all previous field emission studies, for the reason that we have the capability to operate at low voltage in order to get such high current density (here is 80 V to get 10^4 A/cm^2). The emission threshold field, defined here as the applied field required for a current of 1 pA [9], can be evaluated as $E_{applied}^T = V/d = 140$ V/μm. The F–N plot in the inset of Fig. 2a shows a good linearity. If we assume the work function Φ of β-r BNWs is the same as α-t BNWs, which is equal to 4.4 eV [2], the enhancement factor $\gamma = -B\Phi^{3/2}d/k = 20$ (k is the slope of F–N plot). The small γ value and ultra low operating voltage are no other than the characteristics of nanoscale field emission electron source.

Fig. 2b shows the current stability curve with time at bias voltage $V = 60$ V, when the current density maintains around 2000 A/cm^2 for 1 h. A drastic drop of emission current appears in the initial few minutes for the first measurement almost on each boron nanowire. This may be induced by the desorption of contaminant on surface or the reshaping of emitting surface resulted from the emission current [10–12]. Moreover, after the stable value achieved, the

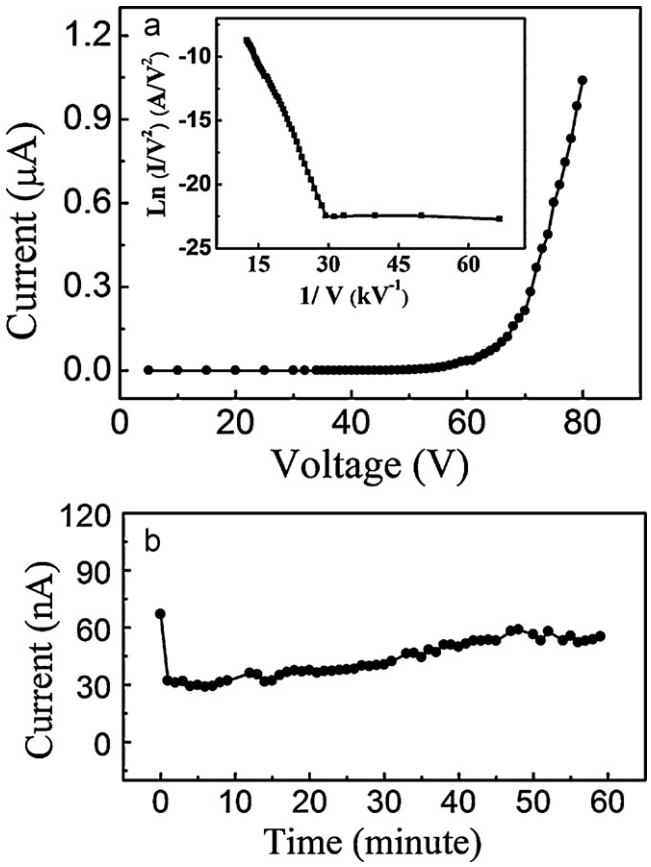

Fig. 2. (a) Field emission current against electric field (I–V) curve measured on the single boron nanowire with an interelectrode distance of 250 nm. The inset straight F–N plot indicates that the emission follows F–N behavior; (b) field emission current as a function of time at a bias of 60 V, which shows a good stability of emission current form an individual B nanowire.

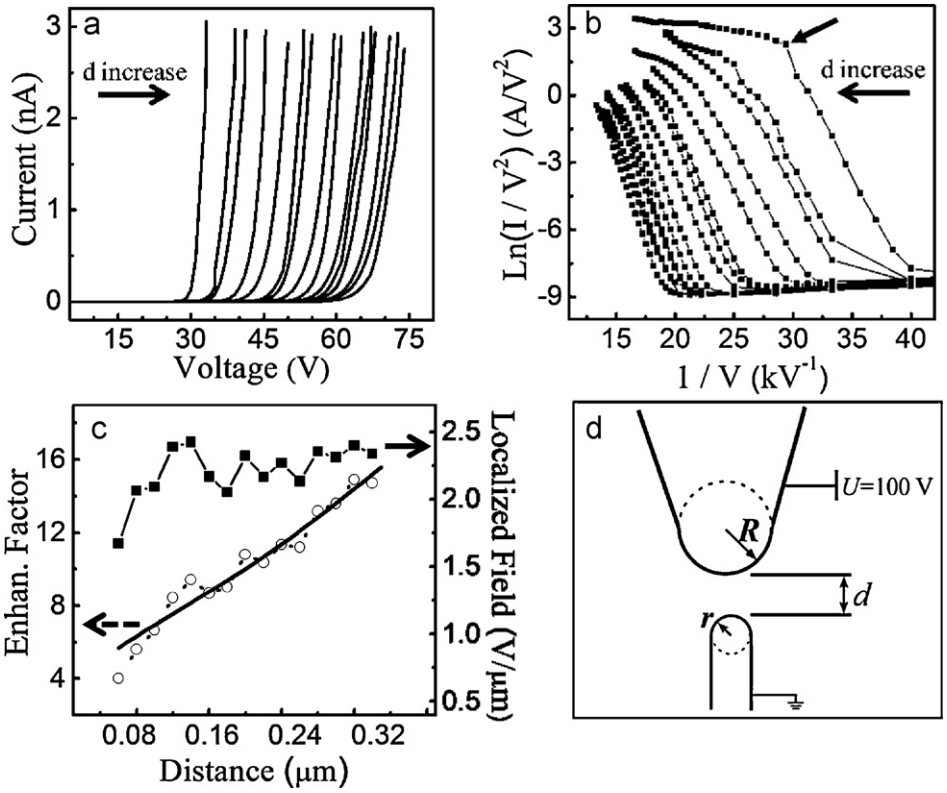

Fig. 3. (a) The field emission curves with different electrode separation *d*, which increases gradually from 60 nm to 340 nm with the increment of 20 nm; (b) the corresponding F–N plots of (a); (c) The solid square spots show turn-on field against anode–cathode separation *d*. The circle spots and solid line give the experimental and calculated data of dependences of enhancement factor γ on separation d, respectively; (d) scheme of boundary condition in numeric simulation for electric field at the apex of the nanowire.

current starts rising up with time very slowly. We tentatively assume that this current increasing is just caused by the local Joule heating, which causes the decrease of work function or even the thermal electron [9,13].

Thanks to the ability of accurate distance control, we could decrease the separation between anode and cathode down to dozens of nanometers, which is only limited by the resolution of SEM. Fig. 3a shows the *I–V* plots of another one dimensional boron nanowires at the electrode separation varying from 60 to 340 nm, with each step of 20 nm. Because the emission currents decay very fast with electrode separation increasing, in order to exhibit all plots clearly, Fig. 3a is only a close-up part in the range of 0–3.2 nA. From the corresponding curves of $1/V$ against $\mathrm{Ln}(I/V^2)$ shown in Fig. 3b, we can find that the F–N plots are straight only if the separation d is larger than 120 nm. This indicates that when d is larger than 120 nm, the electron emission from boron nanowires is in accordance with the Fowler–Nordheim theory very well. However, $\mathrm{Ln}(I/V^2)$ *vs.* $1/V$ curves show obvious deviation from linearity with the diminishing of d from about 120 nm. For the plot at $d = 60$ nm, the knee point (indicated by an arrow) is at the bias voltage of 33 V and emission current of 2.5 nA, respectively. In previous studies, these deviations from linearity were attributed to the thermal effect of high current density [14,15] or the semiconductor behavior of emitter [16,17]. However, in our experiment, this deviation becomes more seriously when the separation is getting smaller, even though the emission current density at knee point decreases. This indicates that this kind of deviation is totally unrelated with Joule heating caused by the emission current.

The plot of the enhancement factor γ with separation d is shown in Fig. 3c (circle spots). All the γ are extrapolated from the Fowler–Nordheim equation here, even for $d < 120$ nm where we use the low field range (the F–N plot is still linear) to extrapolate γ. Furthermore, the theoretical calculation is carried out using a tip–tip model, which is different with the previous studies [18–20]. The elementary method is to solve the Poisson equation:

$$\nabla^2\varphi = \frac{\rho}{\varepsilon_0}$$

Fig. 3d shows the definition of boundary conditions. Two hemispheres are used to imitate the tungsten probe and boron nanowire. Both electrodes are considered as metal and treated as equipotential bodies with periodic boundary conditions. The electric potential at nanowire is set to 0 V while the counter electrode is 100 V. The diameters of the probe and the nanowire are assumed as 300 nm and 50 nm, respectively, which are similar with the real case. The black solid curve in Fig. 3c is the theoretical simulation result, which shows a linear relationship between γ and d in the whole range. In the range of $d > 120$ nm, this is in agreement with our experimental results and also Xu's work [19] very well. However, when d becomes less than 120 nm, the enhancement factor γ decline more rapidly than the simulating prediction. This disagreement indicates that, when the separation goes down to 120 nm, even at the relative low electric field where the F–N curve still could keep its linearity, the electron emission mechanism already changed somehow.

To understand such disagreement, we need to exclude the haphazard change of topography or composition at the tip of nanowire during measurement above all. In accordance with the FN theory, the enhancement factor is determined by the geometric configuration of emitting setup and completely independent with the other properties of emission source. In fact, to get the same emission current, the local electric field $E_{local} = \gamma E_{applied}$ at the tip of nanowire should be unrelated with the separation d. Defining the turn-on applied field as mentioned before, the turn-on local field can be expressed as $E^T_{local} = \gamma V^T/d$. The solid square spots in Fig. 3c shows the turn-on local electric field varied with d.

It basically keeps constant around 2300 V/μm when $d > 120$ nm. However, if $d < 120$ nm, the required local field becomes smaller continuously with the decreasing of d. This kind of continuous decline could not be considered as a consequence of haphazard changes of the nanowire emitter since this feature is repeatable among many measuring circles. Moreover, it is scarcely possible to cause some changes of emitter only by such low emission current. Therefore, it would be reasonable to attribute all these deviations from classical field emission theory to the reduction of separation d.

This phenomenon could be understood if considering the basic assumption of the Fowler–Nordheirmes theory. The F–N theory assumes that the electrons in cathode material form a free electron cloud, which obeys the Fermi-Dirac distribution. Then, the electrons tunnel through a one-dimensional potential barrier when a bias voltage is applied. This assumption of free electron cloud approximation is accurate enough at the macroscopic or even mesoscopic scale. However, size effects become dominant when the electrode separation reaches nanoscale range. It is very possible that the electron in emitting source cannot be considered as the free electron any more. The particular electronic structures, surface states, even the image potential might need to be taken into account. So our study shows the transition from classic F–N field emission to the quantum behavior. The critical transition distance here is around 120 nm. Our experiment could be considered as the exploration of the size limitation of F–N tunneling.

4. Conclusions

In conclusion, four-probe STM has been used to study the field electron emission properties of an individual boron nanowire with β-rhombohedral structure. The maximal emission current density reached 5×10^4 A/cm^2. The precise controlling of separation d between anode and nanowire at nanoscale was achieved by manipulating the probes via the scanning piezo tube of STM. We observed that as the separation decreasing from 340 nm to 60 nm, the deviation from F–N theory becomes more remarkable, especially when the separation is less than 120 nm. We tentatively attributed this deviation to the invalidation of free electron cloud approximation when the size effect shows up. Our results reveal the size limitation of the classic FN theory, showing significant exploration of the design and fabrication of nanoscale electron sources.

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