Field-Induced Insulator to Semimetal Transition and Field Electron Emission of Nanorods of Semiconductors of Wide Energy Band Gaps

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Significant field emission is found theoretically possible from nanorods of semiconductors of wide energy band gaps. If the nanorod has a thin surface layer containing a large number of localized states, a part of nanorod can exhibit an insulator-to-semimetal transition under high enough fields of direction parallel to its axis, so that field emission occurs at the apex of the metal like tip. The field emission property of silicon carbide nanorods is studied as an example and found to be in qualitative agreement with the experimental findings.

Key words: field emission; nanorod; silicon carbide

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Quasi one-dimensional materials have attracted great interest because of their unusual electronic and mechanical properties. Since the discovery of carbon nanotubes [1], nanorods of many materials have been synthesized, including some wide energy band gap semiconductors, such as GaN [2,3] and SiC [4,5,6,7]. The wide band gap semiconductors offer the potential to develop a new generation of micro- and nano-electronic devices that can operate at high power levels, high temperatures, and in harsh environment [8,9,10,11]. They are attractive also because they usually have large thermal conductivity and high saturation drift velocity. Recently, it is reported that the SiC nanorods exhibit high electron field emission with high stability [4,5,12], in particular, under the lowest turn-on and threshold fields so far reported for nanowires and nanorods [4,5]. However, the physical mechanism responsible for field emission from quasi one-dimensional wide band gap semiconductor materials is not clear, for example, the physical origins of field enhancement at and the continuing supply of electrons to an emission site. In this letter we propose a mechanism for explaining such a phenomenon.

The bulk wide band gap semiconductors without doping are actually insulators at room temperature. When they are made into nanorods, which have high aspect ratios, the densities of localized states induced by the atoms in the surface layer are high. This fact enables that electrons transport via hopping from a metal substrate to the apex of the free tip end of the nanorod when an external field is applied parallel to its axis. In the following, we show several physical processes indicated below will occur: When charges induced by the applied field raise the Fermi level close to the bottom of conduction band (BOCB), an insulator to semimetal transition may occur.

FIG. 1: (a) Set-up for field emission. A nanorod is mounted on the metal cathode vertically. (b) The nanorod has a radius of $r_0$. The surface states are located in the surface layer (the dark line) of thickness $\lambda$.

Then the work function is replaced by the affinity as the vacuum barrier height. The latter is much smaller than the former. At the same time, the degenerate electrons in the metal-like region shield the field and lead to field enhancement at the tip apex.

The set-up for field emission under consideration is schematically illustrated in Fig.1a, the cathode and the anode made of metal is parallel to each other and separated with a large enough distance. A columniform nanorod of radius $r_0$ and with a spherical apex is mounted vertically on the cathode and forms a semiconductor and metal contact (we call it back contact) with the cathode.

When an electric field is initially applied to the nanorod, the BOCB along the nanorod decreases due to field penetration, so negative charges will move to and accumulate in the tip-region of the nanorod and the continuous supply of electrons to an emission site. The Coulomb potential of these negative charges will stop BOCB to decrease farther. The balance between charges and field follows the Poisson equation.

The Fermi level of the nanorod will be continuous at the back contact and keeps constant with that of the metal substrate, but it will vary along the nanorod if...
there is an electric current. For wide band gap bulk materials of no doping, the electric current is negligible. The case for nanorods could be much different since there are many states due to the existence of defects in the surface layer of the nanorods. A recent careful simulation to the Si nanowire has revealed semimetal and metal states originating in the dimer dangling bonds and surface reconstruction [13]. The Shockley model suggests that the number of surface states has the same order of surface atoms [14]. We may assume that this model applies to the case of a surface layer full of defects. It is also known that the surface states and defect states are often inside the band gap and localized. In our model, the area density of localized states due to the surface layer \( g_s(E, E_c) = g_s(E - E_c) \) is nonzero only for \(-E_s < E - E_c < 0\), with \( E_s \) the BOCB. The integral \( \int g_s(E - E_c)dE = \sigma \) is a constant proportional to the number of surface atoms per area. A localization parameter \( \lambda \) is defined to be the average spatial extension of localized states. Then the charges of electrons in localized states distribute in a surface layer of thickness \( \lambda \) (Fig. 1b). The electric current is given by

\[
J = -\pi r^2 n \mu_0 \frac{dE_f}{dz} - 2\pi e r_0 R g_s kT \nu_{ph} \cdot \exp\left(-\frac{2R}{\lambda} - \frac{\Delta W}{kT}\right) \sinh\left(-\frac{R}{kT} \frac{dE_f}{dz}\right) \tag{1}
\]

where the first term is the current of free electrons in the conduction band, while the second term is the contribution of the hopping current [15] that exists only if the Fermi level is inside the band gap, \( n \) and \( \nu_0 \) respectively the density and the mobility of conducting electrons, \( E_f \) the Fermi level, \( g_{sf} = g_s(E_f, E_c) \) the density of localized states with Fermi energy, \( R = \left(\frac{\lambda}{g_{sf} 2\pi kT}\right)^{1/3} \) the mean range of hopping, \( \nu_{ph} \) the frequency of phonons, \( \Delta W = g_{sf} \pi kT \sigma \) the mean energy difference between localized states of electrons before and after hopping.

The electrons occupy the localized states and conduction band states according to the Fermi-Dirac distribution. The charge density inside the nanorod is

\[
\rho (\mathbf{r}) = \rho_s (\mathbf{r}) + \rho_c (\mathbf{r}) \tag{2}
\]

The density of charges in localized states, \( \rho_s (\mathbf{r}) \), is zero outside the surface layer, while inside it is given by

\[
\rho_s = -\frac{e}{\lambda} \int_{E_f}^{E_c} g_s (E - E_s) \frac{2}{\exp(\beta (E - E_f)) + 1} dE \tag{3}
\]

where \( E_f \) is the intrinsic Fermi level of the neutral nanorod. The density of charges in the conduction band is

\[
\rho_c (\mathbf{r}) = -e \int_{E_c}^{\infty} g_c (E - E_c) \frac{2}{\exp(\beta (E - E_f)) + 1} dE \tag{4}
\]

where \( g_c (E - E_c) \) is the density of states of conduction electrons. For simplicity, we will assume that the localized states have a uniform energy distribution in the band gap, i.e., the density of localized states

\[
g_s (E - E_c) = \frac{\sigma}{E_s} \theta (E - E_c + E_s) \theta (E_c - E) \tag{5}
\]

For a given \( \rho (\mathbf{r}) \), the electrostatic potential is the solution of Poisson equation satisfying certain boundary conditions. However, the charge density also depends on the potential through the position of the BOCB and Fermi level. The latter is related to the electric current, which is a constant along the nanorod and equals to the emission current. These entangled quantities are calculated by an iteration process. Firstly, with a given function of Fermi level (initially it is aligned with the Fermi level of substrate), the charge density is given by Eqs.(2)-(4). Secondly the electrostatic potential is calculated by solving the Poisson equation. The third step is to calculate the emission current in the WKB approximation. The forth step is to solve Eq. (1) to obtain a new function of Fermi level. This process is repeated until a satisfactory consistency is reached.

Now we take the wurzite polytype of SiC as an example to demonstrate our calculation. The band gap is 3.0 eV, the work function 4.4 eV, the dielectric constant 10.32, and the mobility of electrons 300. \( \text{cm}^2/\text{Vs} \) [16]. The length of nanorod is assumed to be 2.0 \( \mu \text{m} \). The radius is 10.0 nm if is not stated otherwise. The density of localized states is assumed to be \( 2 \cdot 10^{12}/\text{cm}^2 \), while \( \lambda \) is assumed to be 2.0 nm which resembles to that of Si surface [17]. The work function of substrate (assuming to be tungsten, W) is 4.58 eV. The value of \( \nu_{ph} \) is 2.4 \( \cdot 10^{13} \text{s}^{-1} \). As a step of iteration, the electrostatic potential is obtained by employing finite element method for a given charge distribution. Fig. 2 is an instance of 8.0 V/\( \mu \text{m} \). The vertical axis is also the axis of the nanorod. In the upper region of the nanorod, the field is shielded as that part of the nanorod is metal-like. Due to field enhancement, the potential barrier in front of the tip apex is the thinnest (Fig. 2b). Thus, only field emission from the tip apex is considered below.

The calculated results of the BOCB (solid line) and Fermi level (dotted line) along the nanorod of diameter of 10.0 nm are shown in Fig. 3a. Under the applied field of 3.0 V/\( \mu \text{m} \), the entire nanorod is an insulator. Under 5.0 V/\( \mu \text{m} \), there is a region including the tip where the BOCB is quite close to the Fermi level. Under 10.5 V/\( \mu \text{m} \), the region is wider, where the BOCB almost coincides with the Fermi level. This region is the metal-like region. When the applied field is smaller than 10.5 V/\( \mu \text{m} \), the emission current is tiny, so is the current in the nanorod. Thus the Fermi level is almost unchanged. When the applied field is greater and the electric current cannot be ignored, the Fermi level begins to decrease. The BOCB decreases linearly until the number of electrons in the conduction band is large enough to stop the decrease of BOCB as the BOCB approaches to the Fermi level. In the metal-like region the current is provided by the electrons in the conduction band (the first term of Eq. (1) ). Since the density of electrons in the conduc-
tion band, \( n \), is large in this region, the slope of Fermi level must approach zero in order to keep a constant current. The Fermi level obtained from Eq. (1) is basically horizontal in the metal-like region.

The above typical feature is due to the effect of nano-dimension. Taking \( 8.0 \, V/\mu m \) as an instance, the dependence of band diagram on the radius of nanorod is shown in Fig. 3b, revealing that when the radius is larger than 40.0 \( \mu m \), the metal-like region disappears. This can explain why needle-shaped SiC nanorods [12] and nano protrusions on the tip apex of a ZnO nanorod [18] can improve field emission. The above effect may be understood as follows. When a region becomes metal-like, it then has a high density of electrons in conduction band. Thus, we have to explain how under high fields a section of a nanorod can have a high density of electrons in conduction band. Before the fields are high enough to cause electron emission into vacuum, under the action of applied fields, electrons will move to the tip region through hopping in the surface layer, where the electrons will be trapped in the localized states, which occupy the band gap of the surface layer. As the applied field increases, more and more electrons come to the tip region but cannot yet emit into vacuum. Thus they accumulate in the region so that the localized states will be gradually filled up. Accordingly, the Fermi level gradually approaches the BOCB. Under room temperature, those electrons in the states above Fermi level can hop to conduction band when the energy difference between the Fermi level and the BOCB is small. All of the electrons in conduction band are not localized; i.e., they can move to the core region of the nanorod. This situation remains if field electron emission occurs; it is difficult for electrons in the localized states to be emitted since the surface barrier is too high. But why can this only happen in small nanorods? The density mentioned above can be high only when the density of conduction electrons in the surface layer is very high, and only when the ratio of the volume of the surface layer over that of core region of the nanorod is large enough. The thickness of the surface layer is often fixed, so the second ratio will be low if the core region is too large. In this case, the insulator-semimetal transition will not occur. This explains why a nanorod of large diameter has no metal-like region.

When the tip region becomes metal-like, field enhancement at the apex surface appears, and become more and more obvious while getting more and more metallic (Fig. 2(c)). However, the enhancement factor decreases when the applied field is higher than certain value (it is incidentally the turn-on field). That is because the current is significantly high, leading to a large voltage drop in the section of nanorod of not being metal-like, i.e., the effective voltage across the vacuum gap becomes smaller.

This is more clear from the following analysis. In the insulating region, the hopping current is dominated, while in the metal-like region, the conduction current is dominated. Taking \( 13.5 \, V/\mu m \) as an example, the hopping current (the second term of Eq.(1)) and conduction current (the first term of Eq.(1)) are presented in Fig. 4(a).

The field emission characteristics are obtained by assuming Fowler-Nordheim tunneling [19]. Fig. 4(b) shows the field emission current density versus applied field (the \( J - E \) curve, with current density \( J \) defined by the emission current divided by the cross section area of the nanorod). The inset is the FN plot (\( \ln(J/E^2) \) versus \( 1/E \)). For the fields larger than the turn-on field, the slope of the FN plot decreases, as observed in experiment [4,5,12].
This nonlinear behavior of the FN plot is different from that predicted for a metal surface by the classical theory, i.e., it should be a straight line.

The field emission energy distribution (FEED) is given in Fig. 5(a) for 13.25 V/µm and (b) for 10.0 V/µm. The peak of the FEED shifts toward lower energy while the applied field increases, indicating existence of potential drop in the nanorod. Similar phenomenon was also observed experimentally for non-metallic emission regimes [20,21], but have not yet been reported for nanorods and nanowires. Our calculation shows that the FEED spectrum is sharply cut by the BOCB, only tiny contribution from the localized states is observed in Fig.5(a).

To conclude, a mechanism for field emission from nanorods of wide band gap semiconductors is proposed. As an example, the band diagrams and vacuum barriers of SiC nanorods are calculated. A field-induced insulator to semimetal transition is shown. This transition is responsible to the efficient field emission from the nanorods. It is found that the field enhancement is not a constant with applied fields but varies with the field and has a maximum. The FN plot of the emission current is apparently different from straight line. The field emission energy distribution shows the lowering of Fermi level as applied field increases. We should stress that the appearance of the metal-like region where electrons become degenerate is only possible in the nanoscale.

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