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First-principles Study of Field Emissions from Natrium-Encapsulated Boron-Nitride Nanotube in a Perpendicular Geometry

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(Dated: Received on April 30, 2010; Accepted on June 1, 2010)

The field emission from pure boron-nitride nanotube and boron-nitride nanotube encapsulated with natrium atoms with the electric field perpendicular to the axis of nanotubes is simulated based on a self-consistent method using the density-functional formalism. It has been found that the nearly-free-electron states in boron-nitride nanotube would perform very well in field emissions after natrium atom encapsulation. The characters of total energy distribution curves are analyzed to seek the function of nearly-free-electron states in the field emission, with special attention to response of the emission current to the external electric field. At last, the perpendicular emission geometry is found to possess a very sensitive response degree which is supposed to be related to specific expansion orientation of the nearly-free-electron states in this system.

Key words: Field emission, Boron-nitride nanotube, Nearly-free-electron state, Response

I. INTRODUCTION

The carbon nanotube (CNT) and their geometrical clones have served as the models for studying field emissions for decades due to their outstanding mechanical and electrical properties [1–5]. Boron-nitride nanotube (BNNT) and its derivants, the closely related clones of CNT, have also attracted much researching interests in recent years due to their superior characters [6–8]. For example, BNNT has more stable thermal, chemical, and emission stability than CNT [9–11]. These merits make BNNT family become a more attractive option as the electron-emission source than the CNT.

Theoretical calculations had shown that there are the nearly-free-electron (NFE) states existing in the conduction band of BNNT and these states would be ideal electron transport channels [12, 13] for electron emission. The most prominent character of the NFE states is their disperse distribution in the vacuum region near system surface. And this is apparent from the charge densities of the NFE states. Hu have confirmed that there are the NFE states distributing along the axis of the BNNT with the characteristic of angular momentum, and they originate from a combination of short-range exchange-correlation interaction and long-range image potential [6]. The found that the energies of the NFE states in BNNT would decrease linearly when applied lateral electric fields is enhanced. Also it is easy to make the NFE states fall below the Fermi level by electrons doping or alkali-ornament [6, 7]. Since the NFE states are more active than the bound states and have the distribution feature of dispersion, they may have a pretty performance on field emissions. Yan et al. have simulated the electron emissions originating from the NFE states of BNNT encapsulated with alkali atoms and got some valuable conclusions [7].

In Yan et al.’s study, the direction of electric field (E-field) is along the axis of the nanotubes [7], a conventional geometry of field emission which can make use of high local field near the emission terminal of nanotubes. Recently Hu’s calculation has suggested that the NFE states respond obviously to an E-field perpendicular to the axis of BNNT. This will be very benefit to the field emission [6].

In this work, we will simulate and study the field emission properties of pure BNNT and BNNT encapsulated with Na atoms by the first-principles method. Different from the study by Yan et al. [7], our calculations applied an E-field of which the direction is perpendicular to the axis of nanotubes. From it we found some interesting results about the response of emission current to the E-field, which may be instructive to future design and application of nanotubes and other nano-materials as field emission devices. In this geometry of field emission, the NFE states of the Na-doped BNNT have predominant emission characteristics including very strong emission currents and a good response between the E-field and the emission currents. On the other hand, the field emission from the pure BNNT is also discussed to illuminate the action of the NFE states.

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DOI:10.1088/1674-0068/23/05/553-557 553 ©2010 Chinese Physical Society
II. MODELS AND METHODS

The structures of our computing systems are shown in Fig.1. We calculate the emission currents emitted from a (8, 0) BNNT and the same nanotube with one Na atom encapsulated per unit (Na-BNNT). A super lattice of the nanotubes with infinite length (in y-direction) is chosen as one unit cell in calculation, and the widths of the vacuum layers between the nanotubes in x- and z-directions are 25 Å. We adopted the density functional theory (DFT) implemented in VASP for our electronic calculations [14]. The projector augmented wave (PAW) [15] method is used to describe the electron-ion interaction with a cut-off energy of 400.0 eV. And Perdew-Wang functional known as PW91 is employed for generalized gradient approximation (GGA) [16, 17]. The k-points are sampled on a uniform grid along the axis, i.e. 1×11×1. We apply a perpendicular E-field with the direction along the z-direction (Fig.1) by putting a positive charge sheet on one side and a negative charge sheet on another side of the slab [18]. Several typical directions of E-field perpendicular to the nanotube axis have all been testified, and similar results are obtained. The way of calculating the emission current is some kind of method combining the DFT results and wavefunction matching method, which was already introduced in previous papers [19, 20]. The field emission current density contributed by a state labeled as (n, k/) (band and k point indices) of the emitter under an external E-field F, is

\[
J_{n,k/} = \sum [f_n(k_\perp + G_\perp, z_m) g(\varepsilon_{n,k/} + G_\perp, z_m)]^2
\]

where

\[
f_n(k_\perp + G_\perp, z_m) = \frac{\hbar}{\pi m} \left( \frac{2m\varepsilon_{k/} F}{\hbar^2} \right)^{1/3} \times |Bi\left(\frac{2m\varepsilon_{k/} F}{\hbar^2}\right)^{1/3}(z_a - z_m)|^{-2}
\]

which is interpreted as a tunneling factor related to the Airy function Bi, \(\varepsilon_{n,k/}\) is the eigenenergy, and \(z_a\) is the classical turning point for the linear potential in the vacuum region. We use \(z_m = 7\) Å away from the BNNT surface. The total energy distribution (TED) of the emission current density can be:

\[
J(E) = 2 \sum_{n,k/} \delta(E - \varepsilon_{n,k/}) \eta(\varepsilon_{n,k/}) J_{n,k/}
\]

III. RESULTS AND DISCUSSION

Figures 2 and 3 give band structures and TED curves of the pure (8, 0) BNNT in different E-fields \(F\) (unit: V/Å) perpendicular to nanotube axis. A, B, and C denote A, B, and C states, respectively.

![FIG. 1 Atomic structures containing two unit cells of BNNT and Na-BNNT in y-direction. Light, gray, and black balls denote B, N, and Na atoms, respectively.](image1)

![FIG. 2 Band structures of a pure (8, 0) BNNT in different E-fields \(F\) (unit: V/Å) perpendicular to nanotube axis. A, B, and C denote A, B, and C states, respectively.](image2)
FIG. 3 The simulated TED curves of field emission currents from a pure (8, 0) BNNT in different E-fields $F$ perpendicular to nanotube axis. A, B, and C denote A, B, and C states, respectively.

FIG. 4 Contours of charge densities of the states at Γ point that dominate the electron emissions from a pure (8, 0) BNNT in the perpendicular E-field $F=0.5$ V/Å: (a) state A at the $E_F$, (b) state B at 0.5 eV below the $E_F$, and (c) two states C at 1.0 eV below the $E_F$ (see Fig.2).

peaks and total emission current according to our computing formula.

The band structures and the TED curves of the Na-BNNT in the perpendicular E-field are shown in Fig.5 and Fig.6. Figure 7 gives the related charge densities of some important emission states. A comparison between Fig.2 and Fig.5 shows new characteristics in the band structure of BNNT after Na atom doping: one of the NFE bands shifts down to the bottom of the conduction band and forms a hybridized orbit with the Na atomic orbits [6], while the other bands nearly keep the same. On the other hand, the charge transfer between BNNT and Na atom results in that the $E_F$ shifts up into the conduction band.

Now we check up the TED curves of Na-BNNT (Fig.6) in detail. At 0.1 V/Å, there are two emission peaks with their energy positions at the $E_F$ and 0.5 eV below the $E_F$, respectively. It has been found that the
FIG. 7 (a) and (b) Contours of charge densities of the emission states at Γ point from a (8, 0) Na-BNNT in the perpendicular E-field $F=0.1$ V/Å: (a) the state D contributing main peak at the $E_F$ in the TED curves with $F=0.1$ V/Å, (b) the NFE state E that is related to the left emission peak, (c) the contours of charge densities of the “fake” states F at Γ point from a (8, 0) Na-BNNT in the perpendicular E-field $F=0.4$ V/Å (above) and 0.5 V/Å (below) originating from the periodic potential in the computing model, respectively (see Fig.5 and Fig.6).

The domination of the emission current from the NFE states in a higher E-field is reasonable due to the following reasons: one may be just from the dispersion property of the NFE states, which determines that they are more sensitive to the external E-field than the ordinary states, and will be further discussed in this article; another is the difference between eigenenergies of two states contributing to the emission peaks. According the Fowler-Nordheim (F-N) formula [22], the emission current is

$$J \propto F^2 \exp \left( -\frac{4\sqrt{2m\epsilon_n}}{3\hbar e} \phi^{3/2} F^{-1} \right) \quad (4)$$

For the nano-materials, work function $\phi$ should be replaced as the “effective” work function $\phi_{\text{eff}}$ [19, 21]

$$\phi_{\text{eff}} = \phi + E_F - \epsilon_{n,k//} + \frac{k^2 |\tilde{\epsilon}_{n,k//}|^2}{2m} \quad (5)$$

where $\epsilon_{n,k//}$ and $\tilde{\epsilon}_{n,k//}$ are of the state contributing to the main peak in the TED curve. Since the NFE states contributing to the second peak are at about 0.5 eV below the $E_F$, their “effective” work function for the emission should be larger than the ordinary states at the $E_F$. A higher $\phi_{\text{eff}}$ will bring a quicker increasing of the emission current with the enhanced E-field although it depresses the magnitude of emission current, so the emission peak from the NFE states is possible to exceed the peak from the ordinary states at the $E_F$. The fact that two small peaks become obvious in the TED curve of BNNT in a higher E-field as shown before is ascribed to the same mechanism.

The F-N plots of the field emissions from the BNNT and Na-BNNT in a perpendicular E-field are shown in Fig.8(a). Figure 8(b) presents original emission currents with different E-fields. With the emission currents much lower than that of the Na-BNNT, the BNNT has a linear and reasonable F-N plot. And its emission current increases quicker than the Na-BNNT, which is due to its larger work function [19, 21]. It is unusual that the F-N plot of Na-BNNT began to be anomalous in higher E-field, and that the positions of the emission peaks return to the $E_F$ in the E-field of 0.4 and 0.5 V/Å. We examine the charge densities of the emission states (Fig.7). It is found that these states (such as F labeled in Fig.5) are distributed far away from the nanotubes and lie in the middle between two super lattices. With higher energies, these states originate from the periodic potential between the super lattices due to computing model and are more dispere. When the E-field is large enough, they are also pushed down below the $E_F$ and dominate the field emissions. They should be excluded from our scientific consideration on the field emission.

It may be meaningful to compare our results with Yan et al.’s results [7]. In their calculations, the emission current of Cs-encapsulated BNNT just increases from 0.1 $\mu$A to 10 $\mu$A when the E-field is changed from 0.1 V/Å to 0.3 V/Å, a very small variation range. In
our calculation with a perpendicular E-field, the emission currents would sharply ascend as soon as we enhance the E-field a little and even when the E-field is 0.2 V/Å, the magnitude of the total emission current is 10 orders larger than that at 0.1 V/Å. Considering that both Cs and Na are alkali atoms, so large difference should be attributed to different emission geometry. Hu’s study suggested that the NFE states of BNNT are very sensitive to the lateral E-field due to specific expansion orientation of these NFE states in the real space [6]. The response degree of the NFE state to the lateral E-field is stronger than that to the longitudinal E-field, since in the latter direction the state is bound by one-dimension periodicity. In the case of Na-BNNT, the NFE states should possess similar property although they hybrid with Na atom orbitals. We can expect the response of the NFE states to a perpendicular E-field is much larger than that to an E-field parallel to the nanotube axis. The field emission current with enhanced E-field just reflects this effect. Related to spatial character of the NFE states, this type of rapid response is combined with regular response restricted by the “effective” work function as discussed before, to determine main property of the emission current in different E-fields. In fact, we can fit the data from 0.1 V/Å to 0.3 V/Å in Fig. 8(a) using the F-N formula as shown in Eq.(2), and obtain a nominal work function of Na-BNNT of about 7.43 eV, which is much large even after the terms $\varepsilon_{n,k}^m$ and $\varepsilon_{n,k}^l$ (being zero in this case) are included. So the new response mechanism besides the “effective” work function indeed exists. This property may make us re-examine new field emission geometries and their possible effect [23], and is important to the applications of the NFE states in the fields of field emission and other electronics phenomena, such as electron tunneling which has very low working current.

IV. CONCLUSION

We present a detailed study on the field emission properties of pure BNNT and Na-BNNT in a lateral E-field. The NFE states have pretty field emission properties because of their dispersion character in the real space resulting in a strong sensitivity to the external E-field. After Na atom doping, some of the NFE states in the conduction band fall below the Fermi level and contribute to the electron emissions. Generally, the parameter “effective” work function restricts the response of emission current to the E-field, and determines main character in the TED and F-N curves. However, a much stronger response than previous report is found. It is ascribed to specific expansion orientation of these NFE states, suggesting fundamentality of examining the emission geometry.

V. ACKNOWLEDGMENT

This work was supported by the National Natural Science Foundation of China (No.90921013 and No.10704069).