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The screening effect on field enhancement factor of the finite-length small radius single-walled carbon nanotubes

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The screening effects on the field enhancement factors of (3,3) and (5,0) finite length single-walled carbon nanotubes (SWCNTs) with respect to different kinds of tube terminations, either capped or H-terminated, are examined using first-principles calculations. Results show that for capped SWCNTs, the field enhancement factors of the (3,3) tube are slightly greater than those of (5,0) ones, while for H-terminated tubes exhibit the opposite effect. The effects of different endings on the SWCNT work functions are also investigated. Calculations show that for the capped SWCNTs, the work functions of (3,3) tubes are larger than those of (5,0) tubes, whereas for the H-terminated cases, the work functions of (3,3) tubes are smaller than those of the (5,0) tubes. Moreover, a saturated behavior of enhancement factors β versus the length of tubes is observed. Finally, the field enhancement factors of fixed length tubes can be enhanced to eventually achieve a convergent tendency as their tube-tube distance increases. © *2009 American Institute of Physics*.
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I. INTRODUCTION

Since their discovery in 1991,[1] carbon nanotubes (CNTs) attracted significant attention from scientists and researchers. Due to their hollow cylindrical symmetry and nanoscale size, CNTs exhibit valuable physical properties and have great potential in applications involving nanodevices and nanotechnoloy. Using CNTs as field emitters in flat panel displays[2] is one of the most promising applications of CNTs. Compared to conventional field emitters, CNTs have the advantage of a far superior field enhancement factor (β). A simple classical field-emission model shows that their high β (Refs. 3 and 4) is attributable to the high aspect ratios of CNTs, usually on the order of 10^3. However, as CNTs decrease in size to the nanometer scale, they may create a unique field-emission mechanism. The values of the enhancement factor β are not accessible directly due to experimental difficulty. However, the theoretical values of the enhancement factors for nanosized single-walled CNTs (SWCNTs) can be calculated. Therefore, this study considers more than the ratio aspect model and we perform extensive first-principles calculations to examine the quantum effect on the field emission characteristics of CNTs.

Similar to other conventional emitters, the work functions (Φ) of SWCNTs are related to the field emission process. The work function represents the energy needed to remove one electron from the inside of a bulk solid to the outside. Many researchers attempted to measure the values of CNT work functions.[5–8] For instance, Shiraishi and Ata[7] measured the SWCNT work function Φ to be 5.05 eV using the photoelectron emission method. Recent first-principles calculations show that the work functions of finite size SWCNTs depend on the atomic structures of their ends.[9–11] A systematic study by Su *et al.*[12] reports on the theoretical calculations of work functions Φ of an infinite length armchair and zigzag SWCNTs as well as infinite length multiwalled CNTs. They found that for armchair SWCNTs the work function Φ is not only close to that of a graphene ($\sim$4.48 eV), but also independent of the diameter of the tube. They also found that the work function Φ of the zigzag SWCNTs with a diameter greater than 10 Å is close to that of a graphene; on the other hand, for zigzag SWCNTs with a diameter smaller than 10 Å, the work function Φ will increase dramatically as the diameter decreases. Nevertheless, the work function Φ is a basic electronic property of the material. The main choice of field emission sources depend on the role of field enhancement factor β. An emission source with a greater factor β can produce higher field emission and alleviate the effective emission threshold voltage.

Researchers conducted numerous studies on the field enhancement of nanotubes. The field enhancement factors revealed by experiments are usually estimated using the conventional Fowler–Nordheim theory,[13,14] though this theory is basically a simplified model of a free-electron metal. Previous studies[15,16] report that the inconsistency in field enhancement factors between the experiments and the simplified theory can be ascribed to the field screening effect due to the proximity of neighboring nanostructures. The study by Nilsson *et al.*[15] showed that the screening effect is negligible (i.e., β is independent of the tube-tube distance) when the separations is at least greater than two times of the height of the CNT. Several other theoretical studies[17–20] discuss the field enhancement properties of finite length SWCNTs and two of these studies[17,18] are inconsistent. The *ab initio* study by Han and Ihm[17] shows that the evolution of the field enhancement factor with the length of various SWCNTs is lin-

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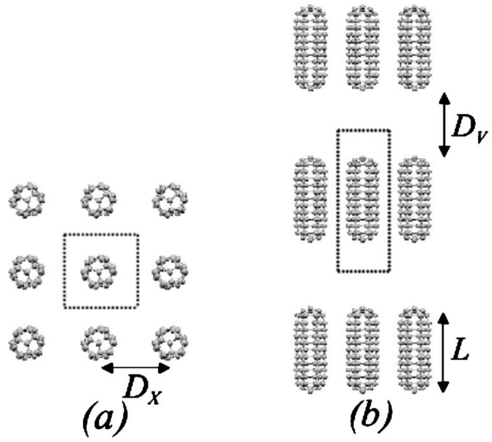

FIG. 1. (a) and (b) are the top and side view for tubes arranged in an artificial square array.

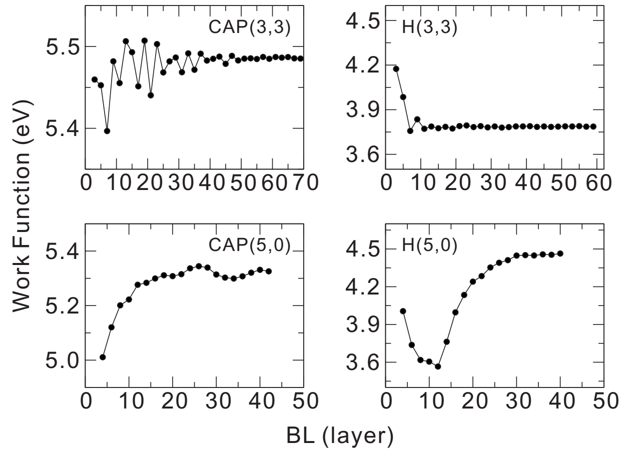

FIG. 2. Work functions of capped and H-terminated (3,3) and (5,0) tubes with D_x=15 Å vs the length of tube body (BL). The lines serve as visual guides.

ear for lengths up to 10 nm. Adessi and Devel[18] reported contrasting results and stated that this evolution exhibits a saturation phenomenon of factor β versus the lengths of CNTs according to Possion's equation. On the other hand, the results of β for simulation and analytical calculations are based primarily on a planar model of the tube within a variety of approximations. As a result, it is necessary to examine the discrepancies between previous studies and more effort should be devoted to understanding the role of β during the field emission process in the absence of a parallel planar anode-cathode.

This work utilizes first-principles calculations to investigate the field emission properties of finite length (3,3) and (5,0) SWCNTs with either capped ends or with H-terminations. Section III illustrates that the tube length depends on work functions Φ. It also presents the effects of tube-tube distance on enhancement factor β with different lengths under an external electric field.

II. METHOD OF CALCULATION

Calculations performed within the local density approximation framework[21] utilized the Ceperley–Alder form of exchange-correction functional and ultrasoft pseudopotentials[22] with a plane-wave cutoff of 358 eV. A supercell geometry is adopted to calculate work function Φ. For a large enough unit cell, the Fermi energy can be determined by the degree of the vacuum level, which in turn makes it possible to find Φ. For finite-length SWCNTs, the nanotubes are put into a supercell geometry so that the tubes are aligned in a square array with a distance D_x between both centers of the adjacent tubes, as Fig. 1 shows. The lattice constant of the supercell along the z-axis is given by $L+D_v$, where L is the length of the tube (including H-terminated or capped ends) and D_v is the vacuum thickness along the tube axis, which is set to 20 Å for all calculations. The k-point sampling is $1\times1\times1$ for finite-length SWCNTs. All atoms are fully relaxed until the residual force on each atom is less than 0.02 eV/Å. The vacuum level is defined as the average potential outside the material in which the potential approaches a constant. Accordingly, the Fermi level and the vacuum level must be determined by the same calculation for a meaningful result and the difference between them is defined as the work function. To study the enhancement factor β, we impose an E-field by applying a classical dipole sheet at the middle of the vacuum region in the z-direction.[23] Dipole correction is included in the calculations and the distortions in atomic structures induced by the external field are neglected. The values of β can be calculated directly from the ratio of the maximum value of E_{loc}, on the tube axis near its end, to E_{app}, where E_{loc} and E_{app} are, respectively, called the local electric field and the applied electric field, and β is dimensionless. The magnitude of E_{loc} is the derivative of the Coulomb potential energy difference caused by the presence of an applied field with respect to the position.

III. RESULTS AND DISCUSSION

Initially, we calculated work function Φ versus the different body lengths (BLs) for (3,3) and (5,0) tubes with either capped end or H-termination. The separation D_x between two adjacent tubes is set to 15 Å. Figure 2 plots Φ as a function of the BLs. The values of Φ vary with the BLs of nanotubes and approximate to limits as the BL increases to certain values. The limits of Φ for capped and H-terminated (3,3) long tubes are about 5.5 and 3.8 eV, respectively. For capped and H-terminated (5,0) long tubes, the limits of Φ are about 5.3 and 4.3 eV, respectively. Note that the work functions obtained directly from calculations for isolated infinite-length (3,3) and (5,0) tubes are around 4.5 and 5.4 eV, respectively. Pristine capped tubes generally have a higher Φ than H-terminated tubes, which is consistent with our previous report.[11] The physical origin of this phenomena can be attributed to the direction of the dipoles at the tips of the tubes. The dipoles at the tips are positive and negative for H-terminated nanotubes and capped pristine nanotubes, respectively.[11] Moreover, the oscillation of work function Φ for shorter tubes as shown in Fig. 2 is ascribed to the quantum size effect.[24]

Then, we applied an external electric field with a magnitude of 0.1 V/Å to the nanotubes and calculated the corresponding enhancement factors β for both (3,3) and (5,0) tubes with either capped end or H-termination by varying

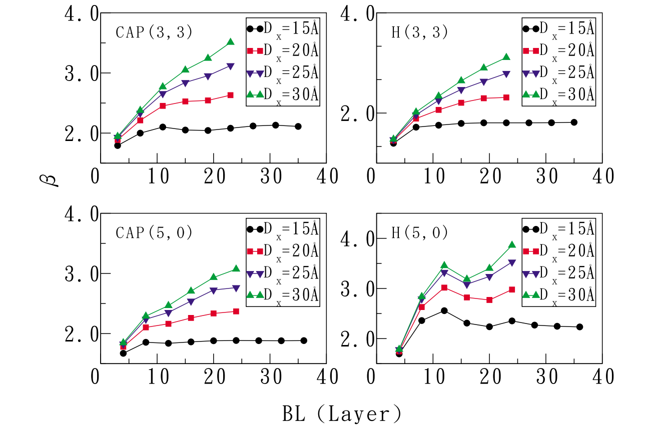

FIG. 3. (Color online) Field enhancement factors β of capped and H-terminated (3,3) and (5,0) tubes of different D_x as functions of the length of BL under an electric field of 0.1 V/Å.

both tube lengths and tube-tube distances. Figure 3 plots the calculated β for various D_x as a function of BL. For a short tube-tube distance, D_x=15 Å, the saturated values of β for either capped or H-terminated (3,3) and (5,0) tubes reach a limit value of 2 as BL approaches infinity. This saturated behavior agrees with the study by Adessi and Devel.[18] Moreover, the values of β for each type of tube are enhanced as the tube-tube distance D_x increases. These results can be attributed to the fact that the greater the tube-tube distance D_x is, the less the screening effect becomes. Nevertheless, a convergent tendency for β can be observed as D_x increases for a fixed length tube. The results are similar to the previous report.[15] Figure 4 shows the plot of β against D_x for H-terminated (3,3) tube with different BLs under an electric field of 0.1 V/Å. For the case of BL=3, the screening is negligible when D_x was increased to 25 Å and beyond. In such a case, the intertube distance is about 9.85 times half the length of the tube. For BL=7, 11, and 15, the ratios of the relative intertube distance to half the length of the tube are, respectively, about 7.00, 7.26, and 6.98, which are all greater than the suggested lower bound of 2 by Nilsson *et al.*[15] We note that the suggested lower bound of 2 is derived in the

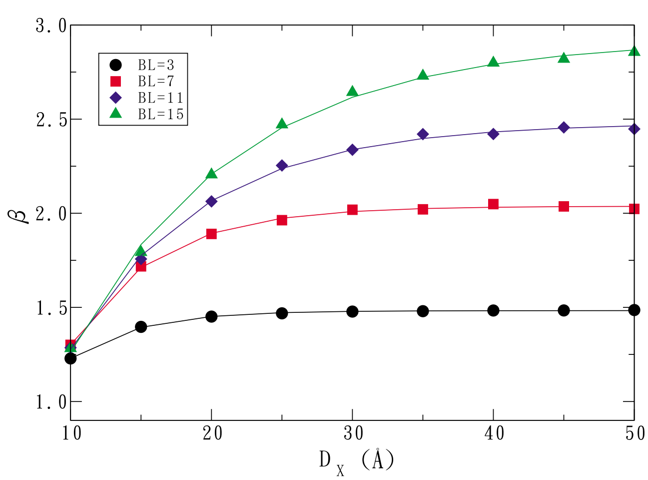

FIG. 4. (Color online) Field enhancement factors β of H-terminated (3,3) tube of different BLs as functions of D_x under an electric field of 0.1 V/Å. The solid curve lines are fitted lines.

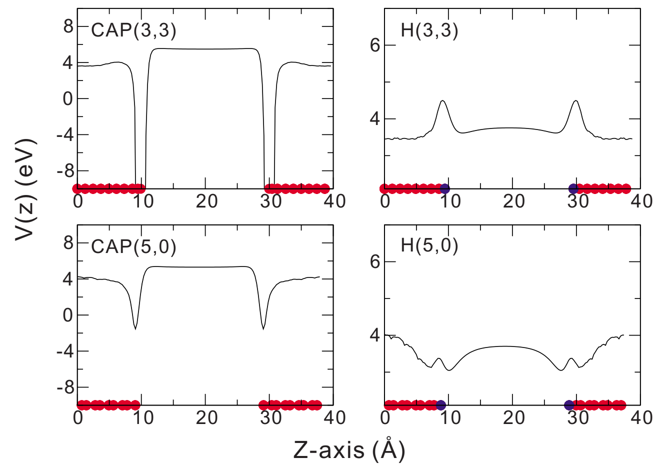

FIG. 5. (Color online) Local Coulombic potential (without the applied electric field) observed at the center along tube axis (x=0 and y=0) for either capped or H-terminated (3,3) and (5,0) tubes with D_x=15 Å. The length of tube body of (3,3) and (5,0) tubes is 15 and 16 layers, respectively. Solid circles are the position of a tube and red (grey) as well as blue (dark grey) denote carbon and hydrogen atoms, respectively. Fermi level is set to zero.

micrometer scale, while our calculations were performed in the nanometer range. Finally, for tubes with the same BL and tube-tube separation, the enhancement factor β of capped (3,3) tubes is slightly higher than that of capped (5,0) tubes. The factor β of H-terminated (3,3) tubes is slightly lower than that of H-terminated (5,0) tubes. For capped tubes, the atomic structure at the two ends of the capped (3,3) tube is sharper (the length of the tip divided by the diameter) than that of the capped (5,0) tube. Hence, the β factors of capped (3,3) tubes should be larger than those of capped (5,0) tubes. On the other hand, it is difficult to clearly define sharpness for H-terminated tubes, which prevents it from being compared with the classical emission theory. Thus, explaining this enhancement requires more than simply electrostatics theory based on the geometrical aspect ratio.[25] Therefore, we further calculate the local Coulomb potential $V(z)$ along tube axis without the applied electric field for both capped and H-terminated (3,3) and (5,0) tubes. Figure 5 plots the local Coulomb potential as a function of position. For capped tubes, the accumulation of electrons at the tip of the tube results in a negative dipole. For H-terminated tubes, however, electrons are likely to accumulate on the tube body and at the mouth (tip-body interface) of (3,3) and (5,0) tubes, respectively, which leaves the tip as a positive dipole. Consequently, under an applied electric field, capped (3,3) tubes emit electrons more easily emitted than capped (5,0) tubes. This is because more electrons accumulate at the tip of capped (3,3) tubes than capped (5,0) tubes, which may result in a higher enhancement factor compared with the (5,0) tube. For H-terminated tubes, on the other hand, electrons are more easily pulled out of the tip for (5,0) tubes under an applied electric field than (3,3) tubes. Since the local Coulomb potential barrier for (5,0) tubes is lower than that for (3,3) tubes, the (5,0) tubes should have a higher enhancement factor than the (3,3) tubes. This local Coulomb potential profile provides a qualitative explanation as to why the enhancement factor β of a capped (3,3) tube is greater than that of a capped (5,0) tube, whereas an opposite result appears for H-terminated (3,3) and (5,0) tubes.

IV. CONCLUSIONS

SWCNT work functions Φ are influenced by chirality and tip structures. Capped and H-terminated tubes generate different dipole directions at the tips. This dipole effect plays an important role in affecting the field emission enhancement factor β. It can also be used to qualitatively explain why capped (3,3) tubes and H-terminated (5,0) tubes have greater factors β than capped (5,0) tubes and H-terminated (3,3) tubes, respectively. Results show a saturated behavior of β factor versus BL for smaller tube separation. Due to the decreasing screening effect caused by neighboring tubes, the values of β are further enhanced as the tube-tube distances D_x increase. Fixed length tubes exhibit a convergent tendency for β as D_x increases. Compared to short tubes, the β of long tubes converges slowly as D_x increases. A larger converged enhancement factor appears for longer tubes. Our calculated results of Φ and β not only provide an insight into understanding the field emission characteristics of finite-length SWCNTs, but also provide a guideline for the growth procedure and applying efficient SWCNTs as field emitters.

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