Electron Field Emission Properties of Closed Carbon Nanotubes

Alper Buldum[1] and Jian Ping Lu[2]

[1]*Department of Physics, The University of Akron, Akron, Ohio 44325, USA*

[2]*Department of Physics and Astronomy, The University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599, USA*

(Received 28 June 2002; published 1 December 2003)

Recent experiments have shown that carbon nanotubes exhibit excellent electron field emisson properties with high current densities at low electric fields. Here we present theoretical investigations that incorporate geometrical effects and the electronic structure of nanotubes. The electric field is dramatically enhanced near the cap of a nanotube with a large variation of local field distribution. It is found that deviation from linear Fowler-Nordheim behavior occurs due to the variation of the local field in the electron tunneling region. The maximum current per tube is of the order of 10 μA. Local and microscopic aspects of field emission from nanotubes are also presented.

DOI: 10.1103/PhysRevLett.91.236801 PACS numbers: 73.63.Fg, 73.22.Dj, 79.70.+q, 85.35.Kt

Carbon nanotubes have novel physical properties and have great potential for future technological applications. One of the most promising applications is employing carbon nanotubes as electron emitters in field emisson devices. Recent experiments have shown that nanotubes have excellent field emisson properties with high current density at low electric fields [1–9]. Their emission characteristics and durability are found to be far better than other electron emitters [10]. Nanotubes offer promising device applications such as flat panel displays and microwave power amplifiers; however, an understanding of the fundamental physics of electron field emission from nanotubes is crucial. We have performed theoretical investigations on the electron field emisson properties of closed carbon nanotubes and included geometrical effects and the electronic structure of nanotubes in our calculations. These investigations enhance the understanding of the important physics taking place during field emission from nanoscale materials. In addition, they provide a theoretical basis for the development of new field emisson devices.

Field emission can be described as emission of electrons from surfaces by high electric fields and/or at high temperature. It has been extensively studied since the late 1920's. Fowler and Nordheim developed a general model for electron emission from planar surfaces and their model has been widely used for electron emission from large objects. According to the Fowler-Nordheim model, emission from planar or large surfaces produces straight lines in so-called Fowler-Nordheim (FN) plots [i.e., a $\log(I/V^2)$ vs $1/V$]. However, almost all experimental FN plots for nanotube field emitters deviate from straight lines [10]. This behavior has been related to localized states at the nanotube cap, space-charge effects, and adsorbates, but the reasons for this behavior are still unclear. Thus, field emission from nanotubes requires further modeling in order to understand their field emisson mechanisms.

In order to investigate electron field emission from closed carbon nanotubes, we employed a model which incorporates the geometry and electronic structure of nanotubes. By solving Laplace's equation numerically and calculating the effective electronic potential using self-consistent field (SCF)-pseudopotential electronic structure calculation method, the variation of the local potential energy is obtained. We use complete pseudopotentials given in the Kleinman-Bylander form [11] and the Ceperley-Adler [12] exchange-correlation potential. Localized electronic states at the nanotube cap and at the apex of nanotips are found to be very important for field emission [13–16]. The electronic structure of a nanotube is derived using a π-orbital tight-binding Hamiltonian [17]. Although only a finite region of the nanotube is under a high electric field, its electronic structure is similar to a very long or a semi-infinite nanotube. In order to have a more accurate description of the electronic structure of the nanotube, the surface Green's function matching method [18] is used on one end. Thus, nanotubes are considered to be semi-infinitely long for their electronic structure and the effects of finite lengths on the nanotubes electronic structure are avoided. On the other hand, a finite portion of a nanotube including its cap is considered in the applied electric field region. In the remaining part of this Letter, the finite portion of a nanotube in the applied electric field region is referred to as the nanotube length. Furthermore, current-voltage characteristics for different tube sizes and lengths were calculated using the WKB approximation [19]. Using these methods, effects of geometry and electronic structure on the field emisson current are investigated.

An important advantage of using nanotubes for electron field emission is their high aspect ratio that enables enhancement of electric field close to the nanotube cap. In Figs. 1(a) and 1(b) calculated electric field lines and spatial variation of electric field magnitude near the nanotube's cap are presented. In these calculations carbon nanotubes are considered to be metallic and Laplace's equation is solved numerically to obtain the variation in electrostatic potential and electric field. Similar numerical calculations were performed for nanoscale emitting

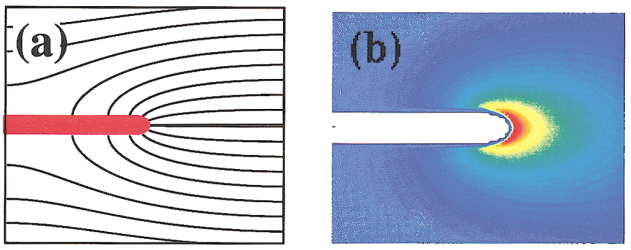

FIG. 1 (color). Electric field lines and spatial distribution of field intensity near the nanotube's cap. (a) Calculated electric field lines near a closed (5, 5) tube's cap. (b) Spatial distribution of field intensity near a (10, 10) tube's cap. The field is dramatically enhanced near the cap.

structures [20,21]. The calculations reported here on (5, 5) and (10, 10) nanotubes show that the electric field is found to be dramatically enhanced near the cap with a large variation of the local field distribution. In Fig. 1(b) the color change from blue to red represents increase in the magnitude of the field. Recently, Cummings *et al.* [22] used electron holography to determine the magnitude and spatial distribution of the electric field surrounding individual nanotubes experimentally. The electric field was concentrated at the cap and was stable in time. Moreover, the holography showed no potential drop along the length of the nanotube, even in the strongly field-emitting regime. The calculated spatial distribution of the electric field here agrees well with these experimental results.

An important factor in field emission is the relationship between the applied and the local electric field where electron tunneling occurs. The field enhancement factor β is defined as $\beta = E_{\mathrm{loc}}/E_{\mathrm{app}}$, where E_{loc} is the local and E_{app} is the applied (or macroscopic) electric field. In our calculations, E_{app} is considered as the electric field very far away from the nanotube and E_{loc} is considered as the electric field at the position where the electron leaves the tunneling barrier. In order to estimate β of a protrusion, simple models were proposed [23]. One of these is the "hemisphere on a post" which fits well with a closed nanotube's geometry. A simple generalized expression in the form $\beta = m + h/\rho$, where $m = 2$, h is the tube height, and ρ is the hemisphere's radius [23,24] was expected to express the field emisson factor; however, recent numerical calculations showed that this expression overestimates β and precise numerical calculations are necessary [20,21,23]. In Fig. 2(a), calculated β values (for the on-axis field) as a function of E_{app} are presented for different tube lengths. As expected for sharp tips and protrusions on a flat planar surface, β depends on E_{app} and it is very important in the deviation of Fowler-Nordheim plots from straight lines.

The current density from individual nanotubes is due to tunneling of electrons through a potential barrier. The variation of electronic potential energy (and thus the barrier for tunneling electrons) strongly depends on

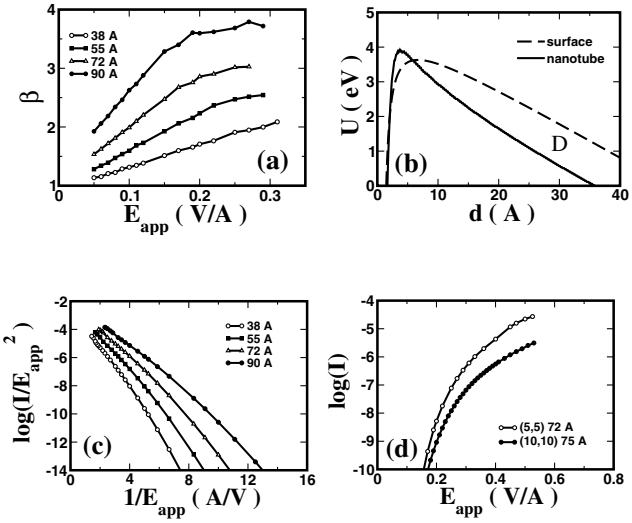

FIG. 2. (a) Field enhancement factors β of (5, 5) tubes of different lengths as functions of the applied electric field. Hollow circles, filled squares, hollow triangles, and filled circles represent tubes with 38, 55, 72, and 90 Å lengths, respectively. (b) Potential energy barriers for tunneling electrons. Solid and dashed lines represent the barriers of a (5, 5) nanotube and a flat metallic surface. Both systems have the same work function [25], $\Phi = 4.8$ eV, and the same local electric field, $E_{\mathrm{loc}} = 0.1$ V/A, in the tunneling region. (c) Fowler-Nordheim plots of electron emission from closed (5, 5) tubes of different lengths. Hollow circles, filled squares, hollow triangles, and filled circles are for tubes with 38, 55, 72, and 90 Å lengths, respectively. (d) Current vs applied electric field characteristics of a closed (5, 5) and a (10, 10) tube of similar length. Hollow circles are for a (5, 5) tube with 72 Å length and dark circles are for a (10, 10) tube with 75 Å length.

the variation of local electrostatic potential. By incorporating the electrostatic potential and the effective potential of electrons from SCF-pseudopotential electronic structure calculations, the variation of potential energy of electrons and thus the potential barrier for tunneling are calculated. Because of the large variation of the local electric field in close proximity to the nanotube cap, the potential energy and the barrier for tunneling electrons are quite different from planar surfaces. In Fig. 2(b) the tunneling barriers of a flat surface and a nanotube are presented. The difference in the area under the potential curves (region D in the figure) changes with applied electric field and is due to the dependence of β on E_{app}.

The current density due to the emission of electrons from nanotubes depends on many important factors such as the work function, tunneling barrier, nanotube length, diameter, and the electronic structure at the nanotube cap. In order to understand the field emisson mechanism and determine the dependence of emission current on these factors, current vs applied field characteristics are calculated using the WKB approximation. The effective electronic potentials from SCF-pseudopotential calculations

that contain the image potential and local density of electronic states from tight-binding calculations are also considered.

An important result of recent experiments using nanotubes as field emitters is the deviation of the Fowler-Nordheim plot from linear behavior; however, the reasons for this deviation are still unclear [10]. This behavior has been related to localized states at the nanotube cap, space-charge effects, and adsorbates. The theoretical investigations presented here produce similar nonlinear FN plots as shown in Fig. 2(c). In this figure, FN plots are presented for different nanotube lengths. As seen from the figure, longer nanotubes emit first and they have low turn-on (for an emission current of 1 nA) and threshold (for an emission current of 1 μA) field values. The same behavior with very similar FN plots was observed in recent experiments [26]. In our investigations, the deviation from linear FN behavior is not due to the localized states but due to changes in the tunneling barriers as a result of the spatial variation of the electric field. A decrease in magnitude of the electric field over a short distance to the nanotube cap results in different tunneling barriers as compared to those from a flat surface or a large tip [see Fig. 2(b)]. A flat surface's tunneling barrier produces a linear FN plot. On the other hand, the difference between nanotube and flat surface tunneling barriers changes with the applied electric field. This difference and its dependence on E_{app} appear to be the most important factor that causes the deviation from linear FN behavior in our investigations.

As can be seen in the figures, the applied electric field values in these calculations are higher then the experimental values. Considering the almost linear increase of β with nanotube length, lower experimental turn-on field values can be explained. In the calculations reported here, a nanotube of $\sim$10 nm length has 2 V/nm as a turn-on field, but in experiments a long nanotube of 10 μm length has a high β and needs only 1 V/μm as a turn-on field [26]. An important result of our calculations is that the maximum current per tube is found to be of the order of 10 μA, which may produce high current density values for technological applications.

Another important geometrical factor is the nanotube diameter. Both field enhancement and electronic structure of nanotubes differ for nanotubes of different diameters. The current vs applied field calculations for (5, 5) and (10, 10) nanotubes are presented in Fig. 2(d). A (5, 5) nanotube with a small diameter and larger local density of electronic states at the tube's cap emits more current. On the other hand, the local electric field in close proximity to a (10, 10) tube's cap has smaller magnitude but decreases more slowly than a (5, 5) tube's local field and has higher local field values relatively far from the apex of the cap. In this respect, both the local geometry and the electronic structure have important roles on the field emisson properties of nanotubes.

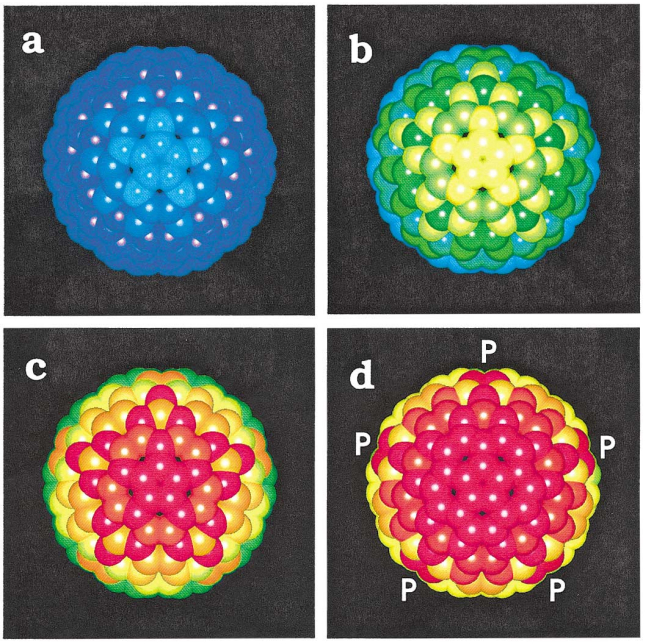

FIG. 3 (color). Top views of a closed (10, 10) tube's cap during field emission. Different colors of atoms denote their electron emission intensity (violet = low, red = high). The panels are ordered with respect to increases in the applied field with values of 0.20, 0.30, 0.40, and 0.45 V/A with total current values of 0.9 nA, 65 nA, 0.6 μA, and 1.2 μA, respectively. At low voltage values, only the atoms at the apex of the cap start to emit; then more atoms begin to emit as the applied field increases.

The model employed to investigate field mission enables us to study field emission locally and determine the emission current from individual atomic sites. Thus, the net current from the nanotube is the superposition of the current from each site. Using this approach a microscopic picture of field emission is obtained and contributions from atomic sites at the apex of the cap and pentagonal rings to the emission current are found. In Fig. 3, the atoms on the nanotube's cab are represented and labeled by colors with respect to their contributions to the emission current. The panels are ordered with respect to increased applied field. At low applied field only (panel a) the atoms at the apex of the cap are emitting. There is a pentagonal ring at the apex and the atoms of the pentagonal ring are the first to start emitting electrons. By increasing the applied field, more atoms begin to emit, as indicated by the color change representing the emission from the other atoms. There are five other pentagonal rings in the cap, shown in Fig. 3(d), and they have a high local density of states for field emission. However, not only these atoms emit a significant amount of current; the other cap atoms bonded to the pentagons also make significant contributions to the total current.

In conclusion, theoretical investigations on the field emisson properties of closed nanotubes are performed. Microscopic aspects of electron field emission

from nanotubes are presented. These aspects are important for both understanding the fundamental physics of field emission from nanotubes and future field emisson device applications. The electric field is dramatically enhanced near the cap of a nanotube with a large variation of the local field distribution. It is found that deviation from linear Fowler-Nordheim behavior occurs due to the variation of the local field in the electron tunneling region. The maximum current per tube is of the order of 10 μA. A local microscopic physical picture of field emission from nanotubes is also obtained.

[1] A. G. Rinzler *et al.*, Science **269**, 1550 (1995).
[2] W. A. de Heer, A. Chatelain, and D. Ugarte, Science **270**, 1179 (1995).
[3] P. G. Collins and A. Zettl, Appl. Phys. Lett. **69**, 1969 (1996).
[4] Q. H. Wang, T. D. Corrigan, J. Y. Dai, R. P. H. Chang, and A. R. Krauss, Appl. Phys. Lett. **70**, 3308 (1997).
[5] Y. Saito, S. Uemura, and K. Hamaguchi, Jpn. J. Appl. Phys., Pt. 2 **37**, L346 (1998).
[6] J. M. Bonard, J. P. Salvetat, T. Stockli, W. A. de Heer, L. Forro, and A. Chatelain, Appl. Phys. Lett. **73**, 918 (1998).
[7] W. Zhu, C. Bower, O. Zhou, G. Kochanski, and S. Jin, Appl. Phys. Lett. **75**, 873 (1999).
[8] A. M. Rao, D. Jacques, R. C. Haddon, W. Zhu, C. Bower, and S. Jin, Appl. Phys. Lett. **76**, 3813 (2000).
[9] H. Murakami, M. Hirakawa, C. Tanaka, and H. Yamakawa, Appl. Phys. Lett. **76**, 1776 (2000).
[10] For a general review of experimental results and comparison, please see J. M. Bonard *et al.*, Solid-State Electron. **45**, 893 (2001).
[11] D. R. Hamann, Phys. Rev. B **40**, 2980 (1989); L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).
[12] D. M. Ceperley and B. J. Adler, Phys. Rev. Lett. **45**, 566 (1980).
[13] S. Han and J. Ihm, Phys. Rev. B **61**, 9986 (2000).
[14] G. Zhou, W. Duan, V. Gu, and Y. Kawazoe, Appl. Phys. Lett. **80**, 1999 (2002).
[15] Ch. Adessi and M. Devel, Phys. Rev. B **62**, R13 314 (2000).
[16] A. Mayer and J. P. Vigneron, J. Vac. Sci. Technol. B **17**, 506 (1999).
[17] A. Buldum and J. P. Lu, Phys. Rev. B **63**, 161403(R) (2001).
[18] F. Garcia-Moliner and V. R. Velasco, Phys. Rep. **200**, 83 (1991); M. B. Nardelli, Phys. Rev. B **60**, 7878 (1999).
[19] P. M. Morse and H. Feshbach, *Methods of Mathematical Physics* (McGraw-Hill, New York, 1953); A. Modinos, *Field, Thermoionic and Secondary Electron Spectroscopy* (Plenum, New York, 1984).
[20] C. J. Edgcombe and U. Valdre, J. Microsc. **203**, 188 (2001).
[21] G. C. Kokkorakis, A. Modinos, and J. P. Xanthakis, J. Appl. Phys. **91**, 4580 (2002).
[22] J. Cummings, A. Zettl, M. R. McCartney, and J. C. H. Spence, Phys. Rev. Lett. **88**, 056804 (2002).
[23] R. G. Forbes, C. J. Edgcombe, and U. Valdre, Ultramicroscopy **95**, 57 (2003).
[24] R. V. Latham, *High Voltage Vacuum Insulation: The Physical Basis* (Academic, London, 1981).
[25] S. Suzuki, C. Bower, Y. Watanabe, and O. Zhou, Appl. Phys. Lett. **76**, 4007 (2000).
[26] O. Zhou (private communication).