Schottky barrier formation at a carbon nanotube—metal junction

Wenguang Zhu[a)]
Department of Physics, Harvard University, Cambridge, Massachusetts 02138
and Center for Computational Materials, Institute for Computational Engineering and Sciences, University of Texas, Austin, Texas 78712

Efthimios Kaxiras
Department of Physics, Harvard University, Cambridge, Massachusetts 02138
and Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138

(Received 6 October 2006; accepted 8 November 2006; published online 12 December 2006)

The issue of Schottky barrier formation at carbon nanotube (CNT) contacts with metal leads is of crucial importance for nanotube-based electronic devices. The authors examine the electronic properties of a particular structure containing a metal/CNT contact that resembles experimental setups for CNT field-effect transistors. The model consists of a single-wall (8,0) CNT with its central section fully covered by a Pd ring, representing the metal electrode. Through first-principles total energy and electronic structure calculations within density functional theory, the authors establish that the junction between the metal-covered part and the bare part of the CNT is responsible for the experimentally measured Schottky barrier of ~0.4 eV in CNT field-effect transistors. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2405393]

The hope of using carbon nanotubes as elements of electronic devices has advanced considerably toward becoming reality with recent demonstrations of carbon nanotube (CNT) field-effect transistors (CNT-FETs).[1–8] In these experimental devices, the contacts between the semiconducting carbon nanotube and the metal electrodes are found to be crucial for the performance of the CNT-FET.[9,10] Previous theoretical studies have addressed certain aspects of the structure and electronic properties of model systems involving metal and semiconducting CNT contacts. In these studies, however, the metal/CNT contacts are modeled by simply placing the nanotubes either on top of one or between two parallel, flat, ideal metal surfaces.[11–13] A more recent study considered a geometry in which a single-wall CNT is fully covered by a Pd metal electrode with periodic boundary conditions, representing a homogeneous, infinitely long system along the nanotube axis.[14] These calculations have demonstrated that there exists no electrostatic-type or Schottky-type barrier to electron transfer between the metal and the nanotube at the interface. Interface states due to the charge transfer at the Pd/CNT contact fill the band gap of the semiconducting CNT, resulting in a contact of metallic nature.[14] Experimental measurements, on the other hand, indicate clearly the existence of Schottky-type barriers at the metal/CNT contact, at least for nanotubes of small diameter which have significant band gaps.[15] This discrepancy suggests that a more detailed analysis of the CNT/metal contact is necessary to establish the origin of the barrier to electron transport. Inspired by these observations, we considered a structure in which only one section of the nanotube is fully covered by the metal lead and the rest of the nanotube is bare. This geometry contains the essential feature of having a portion of the nanotube in contact with the metal while another portion is exposed and acts as the semiconducting element, in close analogy to experimental setups.[15]

In experiments, the best performance of CNT-FETs is achieved with Pd electrodes.[15,16] Accordingly, our model system involves a ring of Pd atoms covering the central section of the (8,0) single-wall CNT, which is normally semiconducting. We analyzed the properties of two possible structures that are comparable in energy but involve different arrangements of the Pd atoms around the CNT. As in the case of CNTs that are fully immersed in a bulk Pd structure,[14] we find that for both structures there exists no electrostatic barrier to electron transfer between the metal and the CNT. By comparing the energy levels of these structures to those of the ideal, bare (8,0) CNT, we demonstrate that the junction between the metal-covered and bare parts of the CNT gives rise to *p*-type Schottky barriers of ~0.4 eV.

Our first-principles calculations are based on density functional theory and the Perdew-Wang 1991 version of the generalized gradient approximation (PW91-GGA),[17] as implemented in VASP.[18] Default plane-wave cutoffs from the GGA ultrasoft-pseudopotential database[19] are used for both Pd and C in the calculations. The Monkhorst-Pack scheme[20] is employed for Brillouin zone sampling. Optimized atomic geometries are achieved when the magnitude of the forces on all unconstrained atoms is smaller than 0.03 eV/Å. These choices of computational parameters produce a diameter of the freestanding (8,0) single-wall carbon nanotube (SWCNT) of 6.37 Å.

To model a partially Pd-covered CNT in a periodic supercell, we construct a long (8,0) CNT segment consisting of 160 C atoms, equivalent to five repeat units along the ideal nanotube axis. The central portion of the CNT is covered by a ring consisting of 32 Pd atoms. The entire structure is repeated periodically in the directions perpendicular to the CNT axis, with a vacuum region of 15 Å separating adjacent CNTs in each direction. By placing the Pd atoms at different initial positions, we obtained two stable structures after relaxation, referred to as structures A and B in the following, shown in Fig. 1. In structure A, all Pd atoms are roughly on the surface of a cylinder coaxial with the nanotube, forming a uniform single-layer coating on the nanotube which ex-

[a)]Electronic mail: zhu@fas.harvard.edu

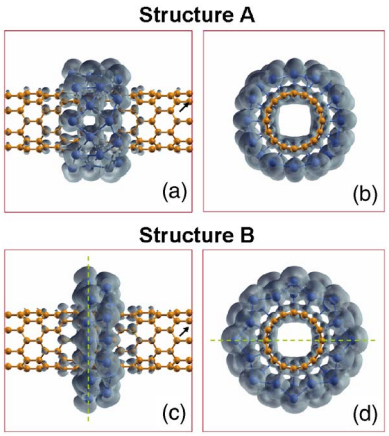

FIG. 1. (Color online) Fully relaxed atomic structures of the two partially coated (8,0) CNT structures. In (a) and (b), we show two views of structure A along and perpendicular to the nanotube axis, respectively; (c) and (d) are the corresponding views of structure B. The black arrows in (a) and (c) indicate the C atom we chose as a reference for aligning the energy levels of the Pd-covered (8,0) CNT and the ideal (8,0) CNT in the density of states plots in Fig. 3. C atoms are shown in orange and Pd atoms in blue. The isosurfaces (at the value 0.01 $e/Å^3$) represent the partial charge densities of all states with energies within the band gap of the ideal (8,0) CNT.

tends over approximately two repeat units along the CNT axis. In contrast, the Pd atoms form a more compact double-layer coating on the surface of the nanotube in structure B. The stability of the two structures is comparable, with the total energy of structure B slightly lower than that of A by only 0.014 eV per Pd atom. Neither structure is close to the bulk Pd structure. Rather, their stability derives from optimizing interactions between the Pd atoms and the C atoms on the nanotube, as well as interactions among the Pd atoms. Thus, while not unique, these structures should incorporate the salient features of actual structures formed during deposition of Pd on the CNT to form the metal contacts. We analyzed in detail and compared the electronic structure features of both structures, especially the electronic energy level alignments and corresponding barriers to electron transport from one side to the other.

In Figs. 2(a) and 2(b), we show the calculated self-consistent electrostatic potential of structure B. The two representative contour plots of the electrostatic potential are taken in the plane perpendicular and parallel to the nanotube axis, respectively, indicated by the dashed lines shown in Figs. 1(c) and 1(d). Blue and red areas in these contour plots represent regions where the electrostatic potential is lower

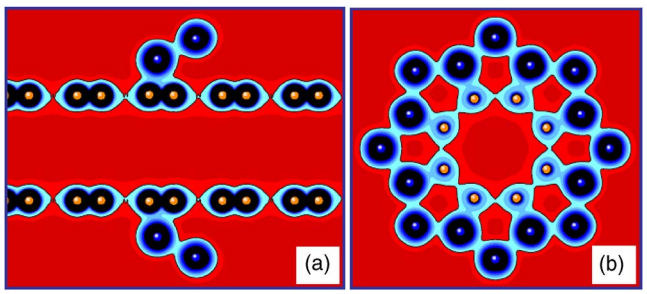

FIG. 2. (Color online) Self-consistent electrostatic potential for structure B along two representative cross sections, indicated by the dashed lines in Figs. 1(c) and 1(d). Contours shaded blue represent negative and red represent positive values of the electrostatic potential, relative to the Fermi level; C and Pd atom positions are indicated in the same convention as in Fig. 1.

and higher than the Fermi level of the system. The existence of contiguous blue areas extending from the nanotube to the metal Pd through the interface indicates that there is no electrostatic potential barrier between the nanotube and the metal electrode for conduction electrons near the Fermi level in the region of contact. The corresponding electrostatic potential plots for structure A show similar features, that is, no barrier. This is very similar to the features of the electrostatic potential plots for the (8,0) CNT when it is fully immersed in bulk Pd.[14] We have also examined the nature of charge redistribution at the interface between the metal ring and the CNT, which is again very similar to what transpires in the case of the nanotube fully immersed in bulk Pd. Specifically, electronic charge is transferred to the interface region between the two components from both sides,[14] which generally helps reduce any barrier to electron transport.

Next, we investigate the possible formation of a Schottky barrier in the partially Pd-covered (8,0) CNT along the nanotube axis. Figure 3(a) shows a schematic plot of the energy diagram at a typical metal/*p*-type semiconductor interface. A *p*-type Schottky barrier is defined as the energy difference between the Fermi level of the metal and the top of the valence band of the semiconductor, which can be determined by comparing features of the metal/semiconductor combined system to those of the pure semiconductor system. In order to align the energy levels obtained for the two systems, we follow the method of potential profile lineup, as in. Refs. 12 and 21. In this approach, the average electrostatic potential at the core of a C atom far away from the metal is chosen as the reference for aligning the energy levels of the Pd-covered (8,0) CNT and the ideal, bare (8,0) CNT. Figure 3(b) shows the average core potential for all C atoms in a period of the structures A and B along the nanotube axis direction. The data points at the two ends of the curves correspond to the C atoms used as the reference, indicated by arrows in Figs. 1(a) and 1(c), while the middle portions of the curves correspond to the CNT region covered by the Pd metal. The essentially constant values of the average core potential for the C atoms far away from the Pd-covered region demonstrate that the length of the nanotube used in our calculations is sufficiently long to ensure that the far-away C atoms are unaffected by the presence of the Pd ring. Thus, aligning the core levels of the far-away C atoms to those of the bare CNT provides a reliable means of estimating the Schottky barrier.

Figures 3(d) and 3(e) show the local density of states of the reference C atoms for structures A and B, respectively, in which the energy levels are aligned with those of the free-standing (8,0) CNT, shown in Fig. 3(c), by the average core potential of the reference C atoms. In these figures, the vertical dotted red lines denote the position of the Fermi level in structures A and B. The shaded region represents the band gap of the free standing (8,0) CNT. From these plots, *p*-type Schottky barriers of 0.39 and 0.45 eV are obtained for structures A and B, respectively. These values are remarkably close to experimental measurements of around 0.4 eV.[15] The excellent agreement may be somewhat fortuitous, given the well-documented limitations of density functional theory to reproduce accurately band gaps of semiconductors.[22] A slightly higher Schottky barrier for structure B than A is qualitatively consistent with the geometric features of these structures, since the Pd atoms in structure B have a smaller contact area with the nanotube surface.

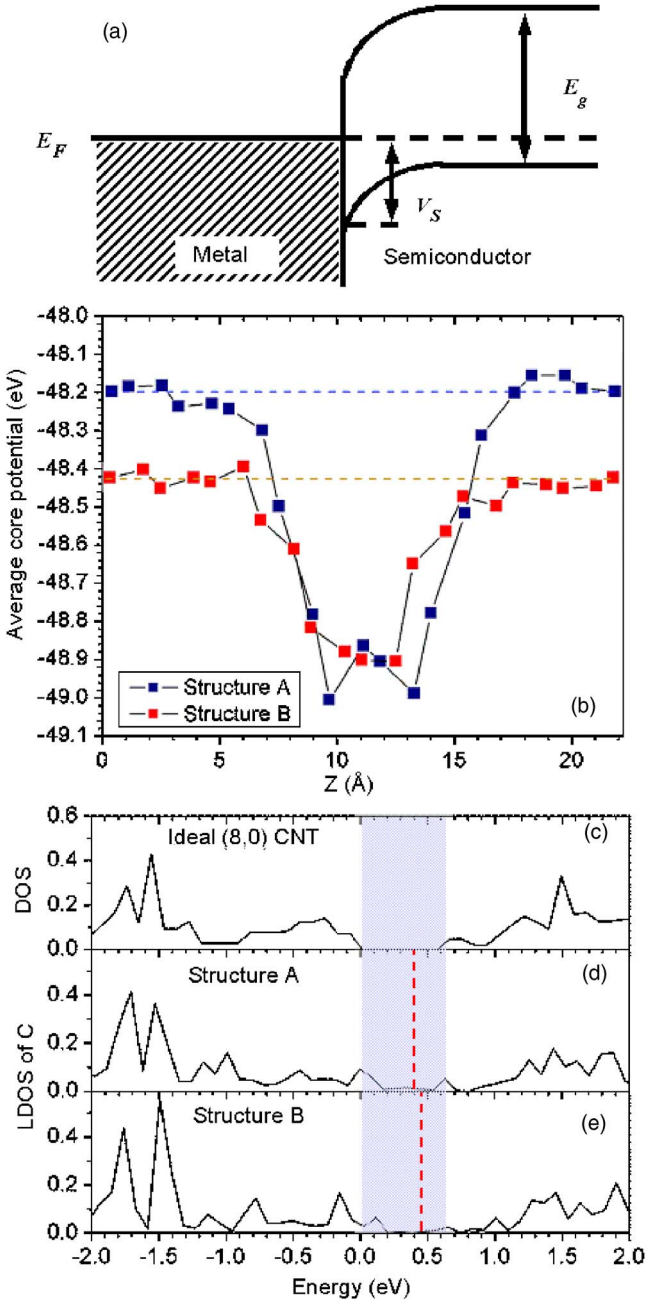

FIG. 3. (Color online) (a) Schematic plot of p-type Schottky barrier (V_S) at metal/semiconductor interface; E_g is the band gap of the semiconductor and E_F is the Fermi level. (b) The average electrostatic potential at the core of a C atoms as a function of their position along the nanotube axis in the periodic supercells of structures A (blue squares) and B (red squares). The points at the two ends of the curves correspond to the reference C atoms indicated by arrows in Figs. 1(a) and 1(c). (c) The density of states of the ideal (8,0) CNT. [(d) and (e)] The local density of states of the reference C atoms. The vertical dotted red lines denote the Fermi level of the systems. The shaded region represents the energy gap of the ideal (8,0) CNT.

To illustrate the nature of electronic states near the junction region, we plot in Fig. 1 the partial charge density which includes all states whose energies fall within the band gap of the ideal (8,0) CNT, for the two structures. The value of the isosurface shown to describe the partial charge density is set to 0.01 e/Å^3. The plots in Figs. 1(a) and 1(c) clearly indicate that these electronic states decay very quickly when passing from the metal coating region to the bare nanotube region along the nanotube axis. These can be described as typical metal-induced gaps states.

In summary, we studied the electronic structure of two different model structures involving a (8,0) semiconducting SWCNT which is partially covered by a ring of Pd atoms; this geometry captures some of the essential features of experimental setups for CNT-FETs and, in particular, the presence of both metal-covered and freestanding sections of the CNT. The features of the electrostatic potentials and the charge redistributions at the interface between the metal and the CNT are similar those for CNTs fully immersed in bulk Pd. By comparing the energy levels of these structures to those of an ideal (8,0) CNT, we found that the junctions between the metal-covered part and the bare part of the semiconducting CNT give rise to p-type Schottky barriers in the range of ~0.4 eV, a value remarkably close to experimental measurements.

This work was sponsored by the Institute for the Theory of Advanced Materials in Information Technology (ITAMIT), University of Texas, Austin, which is funded by NSF Grant No. DMR-0325218.

[1] *Carbon Nanotubes: Synthesis, Structure, Properties, and Applications*, edited by M. S. Dresselhaus, G. Dresselhaus, and Ph. Avouris (Springer, Berlin, 2001), p. 147.
[2] M. P. Anantram and F. Léonard, Rep. Prog. Phys. **69**, 507 (2006).
[3] S. J. Tans, A. R. M. Verschueren, and C. Dekker, Nature (London) **393**, 49 (1998).
[4] A. Bachtold, P. Hadley, T. Nakanishi, and C. Dekker, Science **294**, 1317 (2001).
[5] R. Martel, T. Schmidt, H. R. Shea, T. Hertel, and Ph. Avouris, Appl. Phys. Lett. **73**, 2447 (1998).
[6] R. Martel, V. Derycke, C. Lavoie, J. Appenzeller, K. K. Chan, J. Tersoff, and Ph. Avouris, Phys. Rev. Lett. **87**, 256805 (2001).
[7] A. Javey, J. Guo, Q. Wang, M. Lundstrom, and H. Dai, Nature (London) **424**, 654 (2003).
[8] D. Mann, A. Javey, J. Kong, Q. Wang, and H. Dai, Nano Lett. **3**, 1541 (2003).
[9] S. Heinze, J. Tersoff, R. Martel, V. Derycke, J. Appenzeller, and Ph. Avouris, Phys. Rev. Lett. **89**, 106801 (2002).
[10] F. Léonard and J. Tersoff, Phys. Rev. Lett. **84**, 4693 (2000).
[11] S. Dag, O. Gülseren, S. Ciraci, and T. Yildirim, Appl. Phys. Lett. **83**, 3180 (2003).
[12] B. Shan and K. Cho, Phys. Rev. B **70**, 233405 (2004).
[13] S. Okada and A. Oshiyama, Phys. Rev. Lett. **95**, 206804 (2005).
[14] W. Zhu and E. Kaxiras, Nano Lett. **6**, 1415 (2006).
[15] Z. Chen, J. Appenzeller, J. Knoch, Y.-M. Lin, and Ph. Avouris, Nano Lett. **5**, 1497 (2005).
[16] W. Kim, A. Javey, R. Tu, J. Cao, Q. Wang, and H. Dai, Appl. Phys. Lett. **87**, 173101 (2005).
[17] J. P. Perdew, in *Electronic Structure of Solids'91*, edited by P. Ziesche and H. Eschrig (Akademie, Berlin, 1991), p. 11; J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).
[18] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).
[19] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990); G. Kresse and J. Hafner, J. Phys.: Condens. Matter **6**, 8245 (1994).
[20] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
[21] R. G. Dandrea and C. B. Duke, J. Vac. Sci. Technol. A **11**, 848 (1993).
[22] D. R. Hamann, Phys. Rev. Lett. **42**, 662 (1979); G. B. Bachelet and N. E. Christensen, Phys. Rev. B **31**, 879 (1985); R. O. Jones and O. Gunnarson, Rev. Mod. Phys. **61**, 689 (1989); F. Aryasetiawan and O. Gunnarsson, Rep. Prog. Phys. **61**, 237 (1998).