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Physical properties of the junction of scandium and carbon nanotubes*

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Abstract: Using first-principles calculations, the contact between the scandium (Sc) and semiconducting carbon nanotube (CNT) is investigated. This is one of the best quality of n-type contacts. Two junction models with (8,0) CNT on low-index Sc surfaces are constructed to elucidate the structural and electronic properties of Sc/CNT junctions. Analyses based on density of states and charge difference reveal that strong chemical bonds are formed between Sc and C atoms due to hybrid states of Sc 3d state and C 2π state. With respect to Ti(0001)/CNT junction, we find the dipole layer formed at the interface of Sc(0001)/CNT is comparable with that of Ti(0001)/CNT but gives a negative barrier at the interface. This indicates that the excellent contact properties of Sc metal electrode are caused by its low work function and excellent binding with CNT.

Key words: Carbon nanotubes (CNTs), Metal-semiconductor junction, First-principle calculations
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1 Introduction

Carbon nanotubes field-effect transistors (CNT-FETs) are one of the most promising devices in post-Moore era because of their reliable mechanical strength, excellent thermal conductivity, and high carrier mobility (Dai *et al.*, 2006; Avouris *et al.*, 2007; Charlier *et al.*, 2007). Great effort has been made to improve the performance of CNT-FETs over the last decade, and several advantages over conventional metal-oxide semiconductor FETs have been demonstrated, such as room-temperature ballistic transports, lower operating voltage, higher packing density, etc. (Dai *et al.*, 2006; Avouris *et al.*, 2007). It is evident that the nature of contact between semiconducting CNT and metallic electrode determines CNT-FETs' operating mechanism.

To achieve high device performance and explore the intrinsic electron transport of CNTs, Ohmic contacts are always pursued and many experimental and theoretical works have explored this issue (Heinze *et al.*, 2002; Javey *et al.*, 2003; Dai *et al.*, 2006; Avouris *et al.*, 2007; Charlier *et al.*, 2007; Zhang *et al.*, 2007). The electrodes of high work function metals, such as Pd, Au, and Pt, have been recorded for fabricating CNT-FETs, and Pd achieves almost transparent contact to holes for CNTs with diameters larger than 1 nm (Javey *et al.*, 2003; Dai *et al.*, 2006; Avouris *et al.*, 2007). Theoretical works suggest that the proper work function of the electrode and the specific character of the chemical bonding at the contact should account for the nearly zero Schottky barrier height of Pd/CNT hybrid system (Shan and Cho, 2004; Nemec *et al.*, 2006; Zhu and Kaxiras, 2006; Vitale *et al.*, 2008). Besides p-type CNT-FETs of high performance, the complementary parts n-type devices are also essential for further logic circuits fabrications. Recent experiments show that nearly perfect n-type CNT-FETs can be obtained by contacting semiconducting CNTs with scandium (Sc) (Zhang *et al.*, 2007; 2008).

To optimize the n-type devices, the device

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characteristics require a better understanding of metal/CNT junction. Although there are some studies on the binding properties between Sc clusters and nanocarbons (Krasnov *et al.*, 2007; Kuzubov *et al.*, 2009), the stability and properties of Sc/CNT interface have rarely been addressed before. In this study, we perform a series of simulations on Sc/CNT contact in the atomic scale to explore its structural stability and electronic properties.

2 Calculations and results

2.1 Model and its structure

A semiconducting (8,0) CNT adsorbed on Sc surface is employed as a structural model of the contact between semiconducting nanotubes and metallic electrodes. This contact model corresponds to a side-contact situation (though end-contact geometry is also possible in realistic fabrications, we do not extend our study to this situation due to the complicated Fermi-level pinning effect at the interface). This contact model is one of the most probable geometries for metal/CNT contact since devices are fabricated by placing the nanotubes on the top of predefined metallic electrodes or by depositing metallic electrodes onto CNTs laid on the substrate. Meanwhile, such a structural model has been successfully used to study other metals/CNT contacts (Shan and Cho, 2004; Okada and Oshiyama, 2005). Therefore, the periodic boundary condition is used in the simulation setup and we carefully set up the contact model as follows. The periodic lengths of Sc surfaces along [1000] and [0100] directions are both 0.332 nm (0.331 nm for experimental data) in our *ab initio* calculations, compared with 0.426 nm for the periodic axis of a zigzag CNT. Thus, we can construct supercells with 4 periods along [1000] or [0100] for surface slabs to contact with 3 periods of nanotube. To make this commensurate with the nanotube axis, we compress Sc surface slabs along [1000] or [0100] by 3.6%. Our calculations find that the introduced strain, moving up the Fermi level of Sc surface about 0.01 eV, has been made commensurate between nanotube axis and surface slabs so that it should not prevent us reaching our final conclusion.

For Sc surfaces, we consider two of the most stable low-index surfaces (0001) and (1000) with at least four atomic layers to elucidate the properties of Sc/CNT junction. As shown in Figs. 1a and 1b, at least 1.00 nm vacuum region is set up to minimize the images' interaction and each nanotube is separated by more than 0.80 nm in the lateral direction to simulate an individual Sc/CNT junction. We place CNT on the metal surfaces with the axis along [1000] and [0100] directions, respectively. To achieve a commensurate lattice between nanotube axis and Sc surface slabs with smallest strains, we adopt 1×1×3 supercells of (8,0) nanotube (totally 96 C atoms) to match two metal slabs with 96 Sc atoms both in the supercells. A model with about 200 atoms (about 800 electrons) already demands a great deal of computing resource. We should stress that many degrees of freedom can be chosen for determining correct initial configurations of geometric optimizations as shown in Fig. 1a, and it should be a reference for potential alignment for additional different calculations.

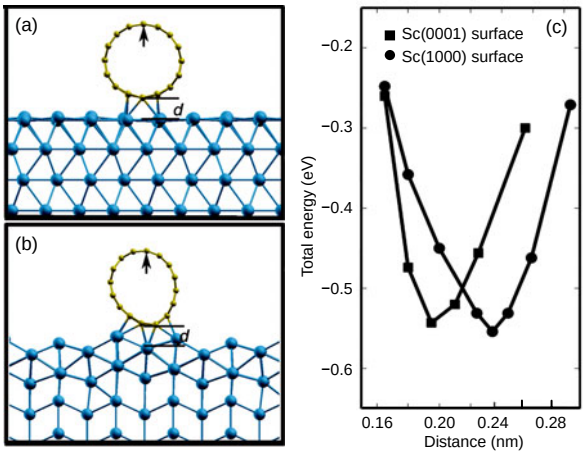

Fig. 1 Atomic structures of Sc/CNT junctions after relaxation

(a) Side view of (8,0) CNT on Sc(0001) surface; (b) Side view of (8,0) CNT on Sc(1000) surface; (c) Total energy of Sc/CNT junctions as a function of the spacing (denoted as *d*) between Sc surface and CNT wall as shown in (a) and (b). Arrows indicate the C atom as a reference for the potential lineup

All calculations reported here are performed using vienna *ab initio* simulation package (VASP) (Kresse and Furthmuller, 1996) based on the density functional theory with the generalized gradient approximation (Perdew and Wang, 1992). Ultrasoft pseudopotentials are employed to describe the core-valence interactions (Vanderbilt, 1990), and 1×1×6 Monkhorst-Pack grids (Monkhorst and Pack,

1976) are used to sample the Brillouin zone for both two junctions within the periodic condition. The valence wavefunctions are expanded in terms of a plane-wave basis set with an energy-cutoff of 300.0 eV and the charge density cutoff is 1200.0 eV. We carry out geometrical optimization on Sc/CNT junctions following previous studies (Shan and Cho, 2004; Okada and Oshiyama, 2005). We first test various possible configurations of Sc/CNT junctions considering the Sc/CNT distance, helical angle of CNT, and relative Sc/CNT translation, and then choose the most energy favorable one to relax the entire junction with the bottom metal layers fixed. The optimized geometries are achieved when the forces on all unconstrained atoms are smaller than 0.4 eV/nm.

Fig. 1c shows binding energies of (8,0) nanotube on Sc(0001) and Sc(1000) surfaces as a function of the distance between a wall of nanotube and the top surface atoms, respectively. We find that the optimum spacings for Sc(0001) and Sc(1000) surfaces are 0.192 and 0.230 nm, respectively. An obvious distortion of CNT is exhibited on Sc(1000) surface after structural relaxation (Fig. 1b). Chemical bonds between Sc atom and C atom with the shortest Sc-C distance for Sc(0001) and Sc(1000) surfaces are 0.229 and 0.233 nm, respectively. These values are consistent with a previous study on a single Sc atom adsorbed on CNTs (Krasnov *et al.*, 2007). The binding energies calculated for these two surfaces are 5.6 and 5.8 eV/nm, respectively. The binding energies are comparable with that of Pd surfaces (Shan and Cho, 2004). A small difference of binding energies between two surfaces also suggests that Sc metal wet CNT wall easily, which agrees with the experiment that Sc atoms have uniform coatings on CNT (Zhang *et al.*, 2007).

2.2 Electronic structures and analysis for the Schottky barrier

We then examine the electronic structures of Sc/CNT junctions. Fig. 2 shows the density of states (DOSs) for both two contacts, together with DOS for an isolated CNT, respectively. We align the energy levels of different calculations with the average potential at the atomic core of a carbon atom, denoted by the arrow in Fig. 1. With respect to Sc(0001)/CNT contact, we find that the Fermi level is located by 0.23 eV above the conduction bands minimum (CBM) of (8,0) nanotube and across the unoccupied 2π bands. While for Sc(1000)/CNT, the Fermi level is only at 0.10 eV above CBM. Thus, charges will transfer from Sc surfaces to nanotube. DOS of the isolated CNT indicates that the distortion evidently affects its electronic structure after binding with Sc surface. The bandgap of CNT(8,0) is narrowed by approximately 0.10 eV for Sc(0001)/CNT, and a value of 0.20 eV is found for that of Sc(1000)/CNT. While for two Sc/CNT junctions, the local DOS of carbon atoms displayed in Figs. 2b and 2c clearly show that the bandgap region of the isolated nanotube is populated by states hybridization between Sc 3d states and C 2π states as shown in Figs. 2c and 2f, respectively.

We then display the difference between the charge density of Sc/CNT junction and the sum of charge densities of the isolated nanotube and the tube-free Sc surface ($\Delta\rho=\rho_{Sc/CNT}-\rho_{Sc}-\rho_{CNT}$) in Figs. 3a and 3b. Evidently, both depleted and accumulated charges are distributed around the interface region. The accumulated electrons are pronounced around Sc-C bonds while the depleted charges are mostly located at the Sc atoms closest to the interface. It is clear that electrons are transferred mainly from 3d state of Sc surface to 2π state of nanotube (Shan and Cho, 2004).

The Schottky barrier between metal and semiconducting nanotube interface can be determined through the potential profile lineup (Shan and Cho, 2004). The limitation of current density functional theory (DFT) framework prevents us obtaining accurate bandgaps of semiconductors, therefore, we cannot give the exact value for n-type Schottky barrier at Sc/CNT interface. To make sense, since Ti is another popular metallic electrode in realistic fabrications for n-type devices and gives a relatively large contact resistance with respect to that of Sc electrodes (Chen *et al.*, 2005; Zhang *et al.*, 2007), we compare Sc/CNT junctions with Ti/CNT junction in the same calculation framework (Ti(0001) can match well with 1×1×2 supercell of (8,0) CNT along [1000]). Thus, we construct Ti(0001)/CNT junction following that of Sc/CNT with four Ti atom layers. The optimizing procedure is the same as that for Sc/CNT junctions.

The n-type Schottky barrier ΔE_n can be expressed as the difference between CBM of semiconductor E_c and the Fermi level of junction E_F (Shan and Cho, 2004; Sze and Ng, 2007):

$$\Delta E_n=E_c-E_F=\{E_c-<V>_{CNT}\}-\{E_F-<V>_{CNT}\}. \quad (1)$$

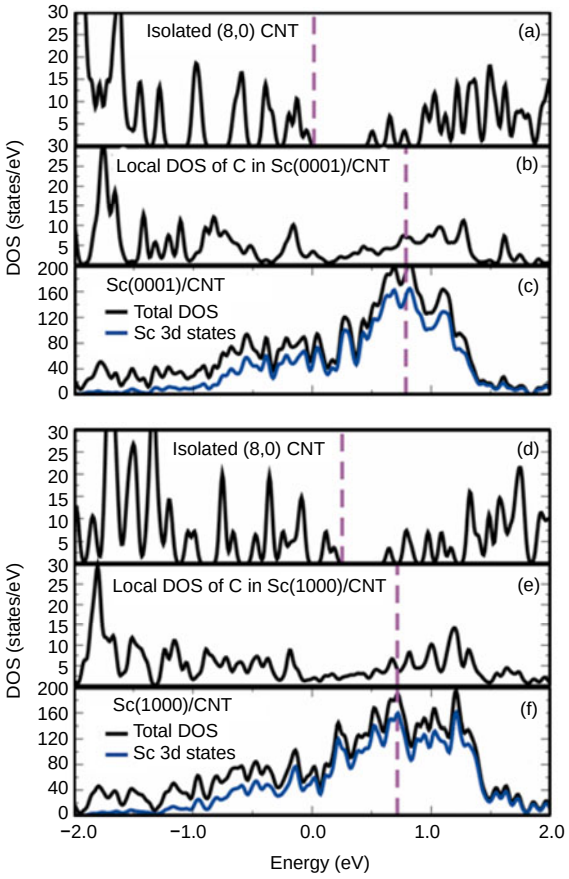

Fig. 2 Density of state (DOS) of CNT-Sc contact

(a) and (d) DOS of an isolated (8,0) CNT with the atomic structure of that adsorbed at Sc(0001) and Sc(1000) surfaces, respectively; (b) and (e) Local DOS of C atoms in Sc(0001)/CNT and Sc(1000)/CNT junctions, respectively; (c) and (f) Total DOS and Sc 3d states of Sc(0001)/CNT and Sc(1000)/CNT junctions, respectively. The dashed lines denote the Fermi level of systems. A width of 0.03 eV is used for the Gaussian broadening, and all levels are aligned with the average core potential of the C atom indicated by arrows in Figs. 1a and 1b

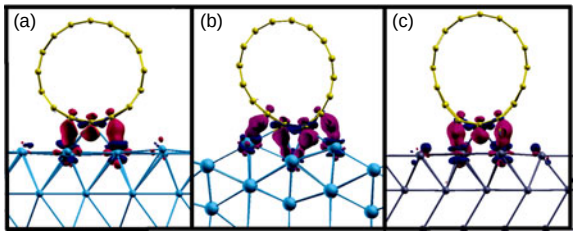

Fig. 3 Isovalue plots of charge difference $\Delta\rho$ for three junctions

(a) Sc(0001)/CNT junction; (b) Sc(1000)/CNT junction; (c) Ti(0001)/CNT junction. An isovalue of 50 e/nm^3 is used for all plots, and the accumulated charge density is plotted in magenta and the depleted charge density in blue

We should make an alignment for E_c and E_F by two separate calculations for nanotube and metal/CNT junctions (Shan and Cho, 2004). Here we choose alignment with the average potential $<V>$ at atomic core of a carbon atom further away from the interface as shown in Figs. 1a and 1b. Therefore, we find negative barriers for Sc(0001)/CNT and Sc(1000)/CNT junctions with –0.18 and –0.08 eV, respectively. These negative values suggest that electrons should be injected freely into the nanotube's conduction bands.

Then we perform the same calculation on Ti(0001)/CNT junction and find a 0.06 eV barrier existing at the interface. These results suggest that Sc should be superior to Ti for electrons injecting as contact metals, which is also consistent with experimental measurements (Zhang *et al.*, 2007). Further calculation on charge difference of Ti(0001)/CNT junction shown in Fig. 3c clearly indicates strong interactions between Ti and C atoms. The redistributed charge has almost the same characteristics as that of Sc(0001)/CNT junction as shown in Fig. 3a. These same bonding characteristics are due to the partially filled 3d states of Ti and Sc metals which dominate around the Fermi level. The redistributed charge around the interface counteracts with the dipole moment at the interface, $\Delta\mu=-e\int_{\text{cell}}\Delta\rho(r)z\mathrm{d}r$, where e is the electron charge, z denotes the distance between charges and r is the spatial coordinate. The change is intuitive to understand barrier height at the interface (Shan and Cho, 2004; Okada and Oshiyama, 2005). We find that Sc(0001)/CNT and Ti(0001)/CNT junctions give comparable dipole moments with 0.023 and 0.019 e·nm per cell perpendicular to the interface, respectively. Since the n-type Schottky barrier height at interface is mainly determined by the work function of metal electrode, affinity of nanotube, and strength of dipole layer at the interface (Shan and Cho, 2004; Sze and Ng, 2007), the relatively low work function of Sc metal should account for the negative barrier at the interface when comparing with Ti metal. Our *ab initio* calculations on work functions for Sc(0001), Sc(1000), and Ti(0001) surface slabs give 3.59, 3.55 and 4.42 eV, respectively, which are consistent with the experimental values of 3.50 and 4.33 eV respectively for Sc and Ti (Sze and Ng, 2007). Therefore, we can ascribe the good n-type contact properties of Sc metal (Zhang *et al.*, 2007; 2008) to its low work function and excellent binding properties with CNTs.

3 Conclusions

We studied the structure and properties of a semiconducting (8,0) CNT on Sc low-index surfaces. Firstly, we find the nanotube adsorbed on Sc surfaces result of large binding energies both for Sc(0001) and Sc(1000) surfaces with 5.6 and 5.8 eV/nm, respectively. The equilibrium spacings between Sc surface and CNT are around 0.230 and 0.192 nm, respectively. Cross-section of CNT is distorted due to the large binding interaction that leads to the narrowing band-gap of CNT. The analyses on the DOS and charge difference suggest Sc-C bonds are formed due to 3d state of Sc surface hybrid with C 2π states. Secondly, we find the negative n-type Schottky barriers for two junction models at the interface by the potential profile lineup (Shan and Cho, 2004), which suggests that electrons of Sc electrode can be freely injected into CNTs, and it is in agreement with transport measurements on Sc contacted CNT-FETs (Zhang *et al.*, 2007; 2008). Lastly, comparing with Ti(0001)/CNT junction, we find Sc and Ti give almost the same binding characteristics with CNT due to the partially filled 3d states around the Fermi level. Furthermore, the dipole layer building up at the interface of Sc(0001)/CNT junction is comparable with that of Ti(0001)/CNT.

In summary, we ascribe the excellent contact properties of Sc electrode (Zhang *et al.*, 2007; 2008) to its relative low work function and excellent binding with CNT. Our results may be useful for a better understanding of the metal/CNT contact, which is critical to the performance of CNT electronic devices.

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