Coverage and strain dependent magnetization of titanium-coated carbon nanotubes

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First-principles, spin-relaxed pseudopotential plane wave calculations show that Ti atoms can form a continuous coating of carbon nanotubes at different amounts of coverage. Fully relaxed geometry has a complex but regular atomic structure. The semiconducting tube becomes ferromagnetic metal with high quantum conductance. However, the magnetic properties of Ti-coated tubes depend strongly on the geometry, amount of Ti coverage and also on the elastic deformation of the tube. While the magnetic moment can be pronounced significantly by the positive axial strain, it can decrease dramatically upon the adsorption of additional Ti atoms to those already covering the nanotube. Besides, the electronic structure and the spin-polarization near the Fermi level can also be modified by radial strain.

I. INTRODUCTION

Continuous Ti coating of varying thickness, and quasicontinuous Ni and Pd coating of single-wall carbon nanotubes (SWNT) have been obtained by using electron beam evaporation techniques.1 Calculations have provided theoretical support for those experimental findings showing that SWNTs can be covered continuously by Ti atoms2,3 and form a complex but regular atomic structure with a squarelike cross section.4 Upon Ti coating, a semiconducting SWNT (s-SWNT) becomes metallic with high density of states (DOS) at the Fermi level, $D(E_F)$, and high quantum conductance. More importantly, Ti-coated SWNTs have ferromagnetic ground states with large magnetic moments $\mu$.4 While metal-coated SWNTs with a controllable size and high conductance have been considered very promising as interconnects in future nanoelectronics, nanostructures, or nanowires having ferromagnetic ground states and large spin polarizations at the Fermi energy $E_F$ have been a subject of interest in spintronics.5,6

Spintronics aims to increase the information transport capacity and versatility of electronic devices by using the spin degrees of freedom of conduction electrons.5–10 Owing to the broken spin degeneracy in a magnetic ground state, energy bands $E_s(k\uparrow)$ and $E_a(k\downarrow)$ split, and may lead to different density of states for different spin orientations. In this paper, we elucidate our findings reported earlier as a short communication4 by placing emphasis on the electronic structure of a Ti-coated SWNT corresponding to its ferromagnetic ground state, and by further investigating its spin-dependent properties. We, in particular, are concerned with the spin polarization at $E_F$,

$$P(E_F) = \frac{|D^\uparrow(E_F) - D^\downarrow(E_F)|}{D^\uparrow(E_F) + D^\downarrow(E_F)}, \quad (1)$$

in terms of majority (minority) spin density of states $D^\uparrow(E_F)$ [$D^\downarrow(E_F)$]. We investigate how the magnetic moment $\mu$, and $P(E_F)$ can be modified with the applied strain and amount of Ti coverage. We found that $\mu$, as well as $P(E_F)$, depends strongly on the applied strain and on the Ti coverage. While a strain of $\varepsilon_x = 0.1$ along the axis of the tube induces a 25% increase of $\mu$, the adsorption of four additional Ti atoms on the Ti-coated (8,0) SWNT causes a 44% reduction of the magnetic moment. The radial strain leading to the elliptical deformation of the circular cross section modifies the spin-dependent electronic structure near $E_F$. The manipulation of the spin-dependent properties of a Ti-coated SWNT with applied strain and with Ti coverage suggest interesting technological applications such as spin filters, spin-resonant tunneling diodes, unipolar spin transistors, and nanoscale magnetism, etc.

II. METHOD

We performed spin-relaxed, first-principles pseudopotential plane wave calculations11,12 within the density functional theory.13 We used a spin-polarized generalized gradient approximation14 (GGSA) and ultrasoft pseudopotential12,15 with a uniform energy cutoff of 300 eV. Calculations have been performed in momentum space by using periodically repeating tetragonal supercells with lattice constants, $a_t=b_t \approx 20$ Å and $c_t=c$ [ $c$ being the one-dimensional (1D) lattice constant of SWNT]. The Brillouin zone of the supercell is sampled by using the Monkhorst-Pack16 special $k$-point scheme. All atomic positions (i.e., all adsorbed Ti atoms and carbon atoms of a SWNT), as well as $c$, have been optimized. In order to further test that the structures of Ti-adsorbed or Ti-coated SWNTs obtained through geometry optimization are stable, we carried out ab-initio molecular dynamics calculations at $T=500$ K using the Nosé thermostat. All structures reported in this paper are maintained stable at $T=500$ K for a sufficient number of time steps.

III. RESULTS AND DISCUSSION

Adsorption of an individual Ti atom above the center of hexagon (i.e., $H$ site) is found to be energetically most favorable; it has a binding energy of $E_b=2.2$ eV and a magnetic moment of $\mu=2.2 \mu_B$ (Bohr magneton) in the magnetic ground state.2 Ti 3d orbitals play a crucial role in the bonding, and electrons are transferred from Ti to SWNT.2,3 Significant adsorption energy of $E_b=2.2$ eV indicates a rather strong Ti-SWNT chemisorption bond formed by charge rearrangement between Ti and C atoms. This way, one of the
a uniform coating, the Ti-C interaction has to overcome the Ti-Ti interaction. Otherwise, adsorbed Ti atoms would be clustered to form small Ti particles on the surface of the SWNT so that continuous coating would be hampered as one experienced for other adsorbed transition metal atoms. A significant C-Ti interaction occurs through Ti-3d and C-2p hybridization; it is comparable to Ti-Ti coupling and is almost unique to Ti among transition metal elements. This makes Ti an important element in the coating of SWNTs.\textsuperscript{1} Depending on the radius and chirality, the circular cross section changes to either a squarelike or polygonal form as described in Fig. 1.\textsuperscript{4} The magnetic moments were calculated at 15.3, 13.7, and 9.5 $\mu_B$ for Ti-coated (8,0) (i.e., C$_{32}$Ti$_{16}$), (9,0) (i.e., C$_{36}$Ti$_{18}$), and (6,6) (C$_{24}$Ti$_{12}$) SWNTs, respectively. While spin-unpolarized band structure calculations\textsuperscript{4} have indicated that these systems are quasi-one-dimensional metals\textsuperscript{17} with high DOS at $E_F$, spin-polarized bands corresponding to the ferromagnetic ground state have been studied in the present paper.

We investigate now the effect of the adsorption of additional Ti atoms on the C$_{32}$Ti$_{16}$ surface. Whether the regular atomic structure and the electronic properties of C$_{32}$Ti$_{16}$ are affected will be the issue we shall clarify. To this end, we consider that four additional Ti atoms are attached at the corners of the squarelike cross section of C$_{32}$Ti$_{16}$ to make C$_{36}$Ti$_{20}$. The fully optimized, stable atomic structure of C$_{32}$Ti$_{20}$ is shown in Fig. 2(d). The adsorption of four additional Ti atoms corresponds to the initial stage of a second Ti atomic layer to cover the SWNT surface. The average binding energy of these additional Ti atoms was found to be ~4.6 eV/atom. It is larger than that of C$_{32}$Ti$_{16}$ owing to the onset of the Ti-Ti coupling in three dimensions. The effect of these four Ti atoms on the structure of C$_{32}$Ti$_{16}$ is minute. However, the calculated magnetic moment undergoes a dramatic change upon the chemisorption; $\mu$ of C$_{32}$Ti$_{16}$ decreases from 15.3 to 6.8 $\mu_B$/cell in C$_{32}$Ti$_{20}$. This important result implies that the net magnetic moment of a Ti-covered SWNT is strongly dependent on the amount, as well as geometry, of Ti coverage. The magnetization of the nanostructure C$_{40}$Ti$_{14}$ can be engineered by varying the number $N$, and the decoration of adsorbed Ti atoms.

Next, we examine the effect of Ti coverage on the spin-dependent electronic properties. The spin-polarized energy band structure and densities of states for majority and minority spin states of the Ti-coated (8,0) SWNT are presented in Fig. 2. The band structure of the bare (8,0) sSWNT has changed dramatically; the band gap between conduction and valence band diminished because of several bands crossing the Fermi level. The total current in magnetic systems can be obtained as $I=I^+ + I^-$, where $I^+$ ($I^-$) is the contribution to the current from majority (minority) spin-current-carrying states. The current for a given spin orientation is obtained using the Landauer formula\textsuperscript{17-19}

$$
\bar{E}_b = \{16E_T[\text{Ti}] + E_T[\text{SWNT}] - E_T[\text{Ti + SWNT}]\}/16, \quad (2)
$$

has been found (in terms of the total energies of individual Ti atoms, optimized bare SWNTs, and Ti-covered SWNTs) to be 4.3 eV for the equilibrium lattice parameter $c=c_0$. Because of the attractive interaction among nearest-neighbor Ti atoms, $\bar{E}_b$ comes out much higher than the binding energy of the adsorbed single Ti atom. The charge transferred from Ti to C is approximately 0.4 electrons in the case of continuous coating, C$_{32}$Ti$_{16}$. This value is about 0.6 electrons smaller than the charge transferred from a single Ti atom adsorbed on an (8,0) SWNT. It appears that the interaction between individual Ti and a SWNT is decreased by the Ti-Ti coupling, causing a back transfer of the charge. Nevertheless, for

FIG. 1. Optimized atomic structures of Ti-covered (a) (8,0) SWNT (C$_{32}$Ti$_{16}$); (b) (9,0) SWNT (C$_{36}$Ti$_{18}$); (c) (6,6) SWNT (C$_{24}$Ti$_{12}$).
consistent treatment, the contact potential also causes electron-phonon interaction in the tube by itself. In a self-reduced due to the scattering of carriers from the abrupt decrease. Therefore, a rigorous treatment of the conductance circumstances, the mean free path of electrons $l_n$ becomes infinite at $T=0$, and the electronic transport occurs ballistically and coherently. This situation has been treated as an ideal 1D

constriction, where the electrons are confined in the transversal direction, but propagate freely along the axis of the wire. Then the current, for example, for majority spin states can be expressed as $I_{\uparrow}=\Sigma_i \eta_i e_v [D_{\uparrow}(E_F+eV_b)-D_{\downarrow}(E_F)]$, where degeneracy, group velocity, and density of states of each subband crossing $E_F$ for spin-up electrons are given by $\eta_i$, $v_i$, $D_i$, respectively. Since $D_i(E_F+eV_b)-D_i(E_F)\sim (eV_b) \partial D_i(E) / \partial E |_{E_F}$ and $1/e\partial eV_b / \partial E |_{E_F}$ then $G_{\uparrow}=I_{\uparrow}/V_b=\Sigma_i \eta_i e^2/h$. Accordingly each subband crossing the Fermi level is counted as $\eta_i$ current-carrying state for a given spin direction with channel transmission $T_{\uparrow}=1$. Then the maximum “ideal” conductance of a defect-free Ti-covered ideal tube becomes $G^{\uparrow}=e^2N_{\uparrow}^2/h$, where $N_{\uparrow}=\Sigma \eta_i$. We found $G^{\uparrow}=4e^2/h, G^{\uparrow} = 5e^2/h$ for C$_{32}$Ti$_{16}$ and $G^{\uparrow} = 6e^2/h, G^{\uparrow} = 8e^2/h$ for C$_{32}$Ti$_{20}$. Apparently, more bands that cross the Fermi level increase $D^{\uparrow}(E_F)$ and $D^{\uparrow}(E_F)$ upon the adsorption of the additional four Ti atoms. We note that the regular structure shown in Fig. 2 may occur under idealized conditions; normally irregularities are unavoidable, in particular for a thick Ti coating. While the transmission coefficient can decrease in the thick but inhomogeneous Ti coating, $G$ is expected to be still high owing to the new conductance channels opened at $E_F$.

Densities of states corresponding to majority and minority spin states in Fig. 2 indicate that $P(E_F)$ is low and hence C$_{32}$Ti$_{16}$ and C$_{32}$Ti$_{20}$ structures, apart from being high conducting, may not be of interest for spintronics applications. Present results indicate that the spin-dependent electronic structure and the magnetic moment of these nanostructures can be modified also by applied axial and radial strain, $\epsilon_{zz}$. In Fig. 3(a) the magnetization of a Ti-covered (8,0) SWNT is plotted as a function of $c$. Each theoretical data point corresponds to the magnetic moment of C$_{32}$Ti$_{16}$ system relaxed under the constraint of a fixed $c$, hence under a given axial strain $\epsilon_{zz}$. Figures 3(b) and 3(c) also show the change of stress and total energy as a function of $c$. The equilibrium lattice parameter occurs at $c_0=4.17$ Å. The axial strain is defined as $\epsilon_{zz}=(c-c_0)/c_0$. Starting from a compressive range with $\epsilon_{zz}<0$, the net magnetic moment $\mu$ of C$_{32}$Ti$_{16}$ increases with increasing $c$, and continues to increase by stretching the system along the tube axis in the tensile range with $\epsilon_{zz}>0$.

Ferromagnetism in magnetic structures is generally explained in terms of the Heisenberg model, which considers spin-spin coupling between magnetic atoms at different lattice sites through exchange interaction. First-principles calculations based on the discrete Fourier transform (DFT), which treat the magnetism of metallic structures from the viewpoint of itinerant electrons, reveal that a ferromagnetic state is energetically favorable. In fact, when $c$ increases, the average Ti-Ti distance will increase (see inset in Fig. 3). Here parallel spin alignment is promoted by a $p-d$ hybridization, hence by electron transfer between the localized $d$ orbitals of Ti atoms and extended $2p$ orbitals of C atoms. The important role of C atoms is also pointed out in recent DFT calculations, where $p$ orbitals of C are found to interact strongly with the $d$ orbitals of adsorbed Ti. The stronger the $p-d$ hybridization, the lower the $d$-$d$ exchange interaction and so as the resulting magnetic moment. Here, increasing

FIG. 2. (Color online) (a) Fully optimized atomic structure and squarelike cross section of Ti-coated (8,0) zigzag SWNT including 16 Ti atoms per unit cell (C$_{32}$Ti$_{16}$). Ti and C atoms are indicated by large-light and small-dark circles. (b) The spin-polarized band structure of C$_{32}$Ti$_{16}$ at $\epsilon_{zz}=0$ with the Fermi level set to zero of energy. Majority spin, $E_{\uparrow}(k \uparrow)$ and minority spin, $E_{\downarrow}(k \downarrow)$ bands are shown by continuous and dotted lines, respectively. The spin-polarized density of states for the majority $D^{\uparrow}(E)$ and minority $D^{\downarrow}(E)$ spin states. (d) The fully optimized atomic structure of a Ti-covered (8,0) SWNT including four additional Ti atoms adsorbed at the corners of the squarelike tube (i.e., C$_{32}$Ti$_{32}$). (e) and (d) show the corresponding spin-polarized band structure and DOS, respectively. The nearest Ti atoms to the four additional adsorbed Ti atoms are indicated by nnTi.
the Ti-Ti distance decreases the d-d coupling between Ti-Ti atoms, but increases the p-d hybridization. The fact that in the absence of Ti-Ti coupling the magnetic moment of C32 Ti16 could be 16 times the magnetic moment of C32 Ti, i.e., 16 × 2.2 μB instead of 15.3 μB, corroborates our arguments.

The decrease of the magnetic moment of C32 Ti16 from 15.3 to 6.8 μB owing to the adsorption of four additional Ti atoms can be explained also by using similar arguments. In Fig. 2(d), additional Ti atoms adsorbed at the high curvature sites of squarelike cross sections of C32 Ti16 affect the inter-

action between existing Ti atoms at their close proximity with the nearest C atoms of the SWNT. These Ti atoms are specified as nTi atoms in Fig. 2. Increasing coupling among Ti atoms by forming three-dimensional-like Ti particles at the corners causes an electronic charge that was donated to nearby C atoms to be back donated to nTi atoms and hence to decrease the p-d hybridization. A detailed charge density analysis show that the excess charge of 0.3 electrons at each carbon atom interacting with nTi atoms of C32 Ti20 decreases to 0.2 electrons upon the adsorption of four additional Ti atoms. At the end, nTi atoms, which initially carry majority spin as others, have their spin flipped upon the adsorption of additional Ti atoms. This situation implies that the magnetic moment of the Ti-coated SWNT will decrease further as Ti coverage increases.

Half-metals8–10 are another class of materials that exhibit spin-dependent electronic properties relevant for spintronics. Half-metals, where the bands exhibit metallic behavior for one spin direction but become semiconducting for the opposite spin direction, provide the ultimate spin polarization of \( P = 1 \) at \( E_F \). Accordingly, the difference between the majority and minority spin electrons per unit cell should be an integer number. Interestingly, as seen in Fig. 3(a) the magnetic moment of C32 Ti16 becomes equal to 17 μB under the strain \( \varepsilon_{zz} \simeq -0.04 \) corresponding to \( c = 4.34 \text{ Å} \). An integer \( \mu \) per unit cell reminds of the possibility of a half-metallic behavior. In Fig. 4 the band structure and DOS of C32 Ti16 corresponding to \( \varepsilon_{zz} \simeq -0.04 \) are illustrated. Here, since both \( E_d(k\uparrow) \) and \( E_d(k\downarrow) \) cross the Fermi level, the system is a ferromagnetic metal, but \( P(E_F) \) is significantly increased as compared to the case of \( \varepsilon_{zz} = 0 \) [shown in Fig. 2(b)]. Hence, whereas the half-metallic behavior did not occur, the spin polarization has
been enhanced significantly and becomes suitable for spintronic applications. The analysis of spin-polarized bands of C_{32}Ti_{8} for $c_{0}$=4.17 Å and $\epsilon$=4.34 Å shows that in the latter 64% (36%) of the current is carried by majority (minority) spin states. Whereas, in the case of $c_{0}$=4.17 Å (i.e., $\epsilon_{zz}$=0) the shares of majority and minority spins are almost equal. This is clearly another interesting effect of applied strain.

Finally, we explore the effect of radial strain $\epsilon_{yy}= (b-R)/R$, which is defined in terms of the minor, $b$, and major, $a$, axes of the elliptically deformed cross section and the radius $R$ of the bare tube. Earlier studies have revealed important effects of the radial deformation of SWNTs on their electronic and chemical properties. For example, a $s$-SWNT has become metallic, and the electronic charge distribution on its surface has undergone a significant change. It has been also found that the chemical activity of SWNT at the high curvature site has increased to lead to a stronger bonding with foreign atoms such as H, Al. Here we expect that the spin-dependent electronic structure of Ti adsorbed on the SWNT is affected by radial deformation. In Fig. 5, we show the calculated $D^{\uparrow}(E)$ and $D^{\downarrow}(E)$ of the C_{32}Ti, where Ti is adsorbed on the bare, as well as at the high curvature site of a radially deformed ($\epsilon_{yy}$=0.3) (8,0) SWNT. Radial deformation had a minute effect on the value of the net magnetic moment. However, the dispersion of bands and $P(E)$ near $E_{F}$ have been affected by radial deformation. The forms of $D^{\uparrow}(E)$ and $D^{\downarrow}(E)$ near $E_{F}$ suggest that the spin-dependent transport under bias voltage $V_{b}$ can be monitored by $\epsilon_{yy}$.

**IV. CONCLUSION**

First-principles spin-relaxed calculations showed that the chemical interaction between SWNTs and the Ti atom adsorbed to the hollow site is significant and favors the continuous coating of the tube surface. A semiconducting SWNT is metallized upon the adsorption of Ti atoms. Zigzag, as well as armchair, SWNTs are metallic and have a ferromagnetic ground state when they are continuously covered with Ti atoms. Spin-relaxed calculations predict interesting spin-dependent electronic and magnetic properties. The magnetic moment of the (8,0) SWNT can increase with the increasing number of adsorbed Ti atoms to a value as large as 15.3 $\mu_{B}$; it, however, decreases if additional Ti atoms are adsorbed on the Ti coating on SWNT surface. On the other hand, electronic conduction channels for each spin direction undergo a change; while $G^{\uparrow}$=4$e^{2}/h$ ($G^{\downarrow}$=5$e^{2}/h$) for C_{32}Ti_{16}, it changes to $G^{\uparrow}$=6$e^{2}/h$ ($G^{\downarrow}$=8$e^{2}/h$) for C_{32}Ti_{30}. We showed that the magnetic properties of the Ti-covered SWNT can be modified also by applied axial strain; the magnetic moment increases with increasing $\epsilon_{zz}$ (namely by stretching the tube). Not only the net magnetic moment, but also the spin polarization at the Fermi level can be increased by increasing axial strain. Finally, we studied the effect of the radial strain on the spin-dependent electronic and magnetic properties.

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Numerical calculations have been performed by using the VASP package: G. Kresse and J. Hafner, Phys. Rev. B 47, 558 (1993); G. Kresse and J. Furthmüller, ibid. 54, 11 169 (1996).


