

First-Principles Calculations of Carbon Nanotubes Adsorbed on Si(001)

W. Orellana,¹ R. H. Miwa,² and A. Fazzio¹

¹*Instituto de Física, Universidade de São Paulo, CP 66318, 05315-970, São Paulo, SP, Brazil*

²*Faculdade de Física, Universidade Federal de Uberlândia, CP 593, 38400-902, Uberlândia, MG, Brazil*

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We report first-principles calculations on the adsorption of a metallic (6,6) single-walled carbon nanotube (SWCN) on the Si(001) surface. We find stable geometries for the nanotube between two consecutive dimer rows where C-Si chemical bonds are formed. The binding energy in the most stable geometry is found to be 0.2 eV/Å. Concerning the electronic properties, the most stable structure shows an increase in the density of states near the Fermi level due to the formation of C-Si bonds enhancing the metallic character of the nanotube by the contact with the surface. These properties may lead one to consider metallic SWCNs adsorbed on Si substrates for interconnections and contacts on future nanoscale devices. Finally, the nature of the nanotube-surface interaction for nanotubes of larger diameters is also discussed.

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The remarkable mechanical and electrical properties of carbon nanotubes (CNTs) [1] have started a fascinating field of research addressing their practical applications for future nanoelectronic devices. CNTs may also be promising for applications as wiring materials for interconnections of either conventional or molecular electronic devices as recently proposed [2]. The above suggestion is supported by the convenient structural characteristics of CNTs such as nanometer diameter, micrometer lengths, and excellent mechanical strength [3].

However, the major challenge for the use of CNT as nanodevices is the formation of organized arrangements at specific orientation on technologically important substrates. Recent advances in this way have been attained by using the tip of an atomic force microscope in controlling the shape and organization of CNTs on silicon surfaces [4,5]. Such manipulation offers the possibility to design and construct a wide range of nanoelectronic devices. Concerning the electrical properties, CNTs can be either metallic or semiconducting depending on their diameter and helicity. Metallic CNTs provide a nearly perfect model system for one-dimensional (1D) conductors, which are able to carry a high current density by only two 1D subbands [3]. However, the electronic and structural properties of CNTs on realistic arrangement, i.e., considering the interaction with solid substrates on which they are supported, are not yet clarified. In fact, recent experiments have shown a strong interaction between CNTs and the H-passivated silicon surface inducing important deformation on the adsorbed nanotube [4].

In this Letter we investigate, from first-principles calculations, adsorption processes of a metallic CNT on a clean Si(001) surface. We find stable geometries for the CNT on the surface trench where C-Si chemical bonds are formed. The subbands associated with these bonds increase the density of states near the Fermi level forming an electronic channel throughout the CNT-

surface contact. This suggests the possibility to use CNTs as interconnections and contacts on future nanoscale devices.

The calculations were performed in the framework of the density functional theory [6] using a basis set of numerical atomic orbitals as implemented in the SIESTA code [7]. For the exchange-correlation potential, we adopt the generalized gradient approximation [8], as well as standard norm-conserving pseudopotentials [9]. We use a split-valence double- ζ basis set plus the polarization functions [10]. The single-walled carbon nanotube (SWCN) on the silicon surface is simulated by a 152-atom supercell within the repeated slab method. Our surface model consists of eight silicon monolayers (ML) in a 2×4 surface unit cell, describing a (2×2) reconstructed Si(001) surface. The dangling bonds of the bottom silicon layer are passivated by H atoms. We also consider a vacuum region of 18 Å separating the image surface. Our calculations were performed for a (6,6) metallic CNT with a diameter of 8.2 Å containing 72 atoms. For the Brillouin zone sampling, we use three k points along the CNT axis [11]. The positions of the topmost 6 ML surface atoms plus the CNT atoms were relaxed until all the force components were smaller than 0.05 eV/Å.

Initially, we search for equilibrium geometries of the CNT on the Si(001) surface considering two adsorption positions: (i) between two consecutive dimer rows (on the surface "trench"), and (ii) on the top of the Si-dimer rows. Furthermore, for each adsorption position, we also consider the rotation of the CNT around its axis. Our (6,6) nanotube adsorbed on the Si surface has a periodic geometry by a CNT rotation of 30°, where two different symmetric configurations are found by a CNT rotation of 15°, favoring the formation of the C-Si bonds. These CNT adsorption configurations are, first, with the bottommost C-C bonds forming a zigzag line parallel to the tube axis

(T0) and, second, with the bottommost C-C bonds oriented perpendicular to the tube axis (T15).

Our results show that the most stable configuration for the adsorbed CNT is the T0 geometry on the surface trench, as shown in Fig. 1; the binding energy per unit length of the CNT is calculated to be $0.21 \text{ eV}/\text{\AA}$, which is in close agreement with recent empirical calculations [12]. In the equilibrium geometry, the vertical buckling of the Si-dimer rows is in phase. We observe distortions at alternate dimers reducing the buckling angle up to 9° . Before the CNT adsorption, the Si dimers were buckled by 19° . The CNT also shows distortions at the C atom nearest neighbors to these dimers relaxing outward from the tube. These distortions suggest the formation of CNT-surface chemical bonds, where C-Si bond length is found to be 2.11 \AA . Indeed, we observe the formation of 2 C-Si bonds per unit cell where the corresponding Si atoms belong to alternate dimer rows. We also find a second equilibrium structure for the CNT on the surface trench in the T15 geometry. For this structure, the CNT binding energy is calculated to be $0.15 \text{ eV}/\text{\AA}$. The shortest C-Si distance is found to be 3.0 \AA , approximately 30% larger than those found in the T0 geometry. However, no significant distortions on the surface and on the CNT are observed, suggesting a weaker CNT-surface interaction as compared with the T0 geometry.

We also calculate the adsorption of the CNT on the top of the dimer rows, for both T0 and T15 geometries. Our results show that these adsorption processes are endothermic, i.e., the CNTs do not form equilibrium geometries on

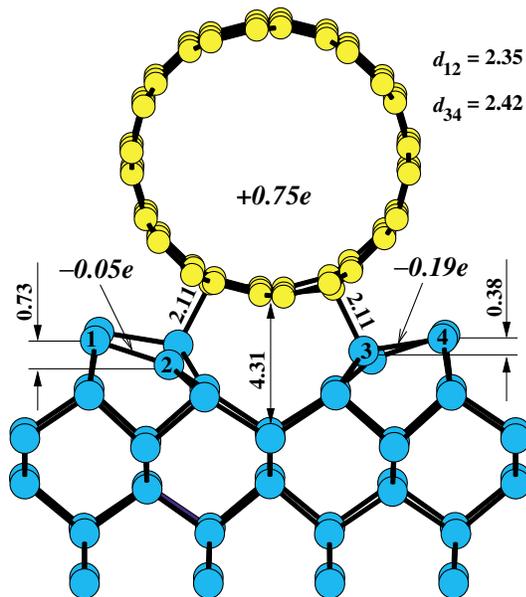


FIG. 1 (color online). Equilibrium geometry for the adsorbed CNT on the Si(001) surface for the most stable structure (T0 geometry). The distances are in \AA and the charge transfers from the CNT (positive) to the surface (negative) are indicated in units of electrons per unit cell. Small spheres are C atoms and the larger spheres are Si atoms.

the top of the dimer rows. Hereafter, the two equilibrium geometries previously found at the surface trench will be called T0 and T15. It is worthy to point out that, similarly to our results of nanotube on Si(001), the formation of organized arrangement of C_{60} molecules on the Si(001) surface trench has been experimentally observed [13]. Moreover, evidences of chemical bonds between the C_{60} molecule and the clean Si(001) surface have been recently reported [14,15].

Since CNTs are much harder than crystalline silicon [3], we compress the silicon lattice by about 3% with respect to experimental values in order to match the surface width with the equilibrium CNT length for our supercell approach. In the compressed clean surface, the angle of vertical buckling increases by about 2° with respect to the equilibrium (uncompressed) surface, increasing the vertical buckling by about 0.1 \AA , whereas the Si-dimer bond length is the same in both structures (2.39 \AA). The electronic band structure of the compressed surface preserves the main features as compared with the equilibrium one, where the calculated band gap is quite similar in both structures ($\sim 0.2 \text{ eV}$).

The surface compression results in a quite artificial alignment of C and Si atoms along the CNT-surface contact in our calculation. This alignment must occur at some point of a realistic contact; however, a mismatch between C and Si atoms must also be present. In order to estimate the alignment effect in the C-Si bond formation, we calculate the adsorption of the CNT at the surface trench shifting the nanotube by about 0.62 \AA , which corresponds to the largest mismatch between C and Si atoms. Our results show the formation of C-Si bonds with essentially the same bond lengths of the aligned structure. However, we note a relaxation of the Si-dimer atoms which now bind with different C atoms than those previously found in the aligned structure. The difference in total energy between the fully relaxed mismatched and the aligned structures is calculated to be 83 meV per unit cell, implying a decrease in the binding energy for the T0 geometry by about $0.01 \text{ eV}/\text{\AA}$. Because of this small energy difference, we conclude that the shift between the CNT and the surface has a minor influence in the structural properties of the CNT-surface contact where the formation of C-Si chemical bonds are independent of the alignment of the C and Si atoms.

We can estimate the shear force (F_s) and shear stress (σ_s) for the CNT in the T0 geometry using $F_s = \Delta E_t / \Delta x$ and $\sigma_s = F_s / A$, where ΔE_t is the difference in energy between the unrelaxed mismatched structure and the equilibrium aligned one, Δx is the CNT displacement, and A the area of the CNT-surface contact. For $\Delta E_t = 0.69 \text{ eV}$, $\Delta x = 0.62 \text{ \AA}$, and $A = 45 \text{ \AA}^2$ (the contact area in the supercell), we find $F_s \sim 1.8 \text{ nN}$ and $\sigma_s \sim 4 \times 10^9 \text{ N/m}^2$.

From the Mulliken population analysis, we estimate the electronic charge transfer between the CNT and the Si surface for the T0 equilibrium geometry. We find that

$0.75e$ per unit cell are transferred from the nanotube to the surface, mostly to the Si dimers where C atoms form chemical bonds (see Fig. 1). Consequently, these dimers increase their charge by about $0.19e$ per unit cell. The dimers that do not form bonds with the CNT increase their charge in $0.05e$ per unit cell. The rest of the charge is distributed throughout the surface. Such charge transfer is expected to occur because the dimers at the clean surface exhibit empty states localized at the lower Si atoms. Meanwhile, the carbon nanotube exhibits an excess of electrons at the molecular π states. Therefore, the formation of C-Si chemical bonds in the T0 geometry would be originated from a rehybridization of the empty $3p$ states of the lower Si atoms of the dimer and the occupied $2p$ states of the nearest C atoms of the CNT forming a sp^3 -like hybridization.

Figure 2 shows the electronic band structure and density of states (DOS) for the isolated CNT [Fig. 2(a)], for the Si surface plus the CNT at a height of 5 \AA from the dimers [Fig. 2(b)], and for the adsorbed CNT in the T0 geometry [Fig. 2(c)]. Here, Γ - J (Γ - J') represents the direction of the wave vectors perpendicular (parallel) to the dimer trench or the tube axis. In Fig. 2(b), we see that the band structure of the surface plus the CNT separated by 5 \AA is a superposition of the isolated systems suggesting that at this distance there is no interaction between them. In Fig. 2(c), we see that the band structure for the T0 geometry, along the Γ - J direction, preserves the semiconducting character of the clean surface. The states labeled as ν_1 , ν_5 , c_1 , and c_4 can be associated with CNT states since they do not exhibit any dispersion along Γ - J , which characterizes CNT states [see Fig. 2(a)]. Additionally, they show an important charge concentration at the C atoms. Thus, the ν_1 and ν_5 (c_1 and c_4) states would be originated by the splitting of the HOMO (LUMO) states of the isolated CNT [Fig. 2(a)], which is found to be 0.23 eV (0.43 eV). These splittings are partially associated to the local CNT distortion and the rehybridization involved in the formation of the C-Si chemical bond. Along Γ - J' , we observe a strong perturbation of the lowest unoccupied surface states for the T0 geometry [Fig. 2(c)], as compared with the noninteracting CNT-surface system [Fig. 2(b)]. These states (c_2 and c_3) are associated with surface dangling bonds of the clean surface which move downward induced by the formation of the C-Si bonds. In addition, ν_1 and c_1 hybridize with surface states along Γ - J' , giving rise to mixed states. The partially occupied ν_1 , c_1 , and c_2 states cross the Fermi level at $\sim 0.18\Gamma J'$ increasing the density of states at the Fermi energy. This suggests an enhancement of the metallic character of the CNT throughout the contact with the Si surface, as induced by the formation of C-Si bonds.

The total charge density plot for the T0 geometry is shown in Fig. 3(a). Here we clearly see the formation of one C-Si bond per dimer plane, where the bonds always involve the lower Si atom of the dimer with the nearest C

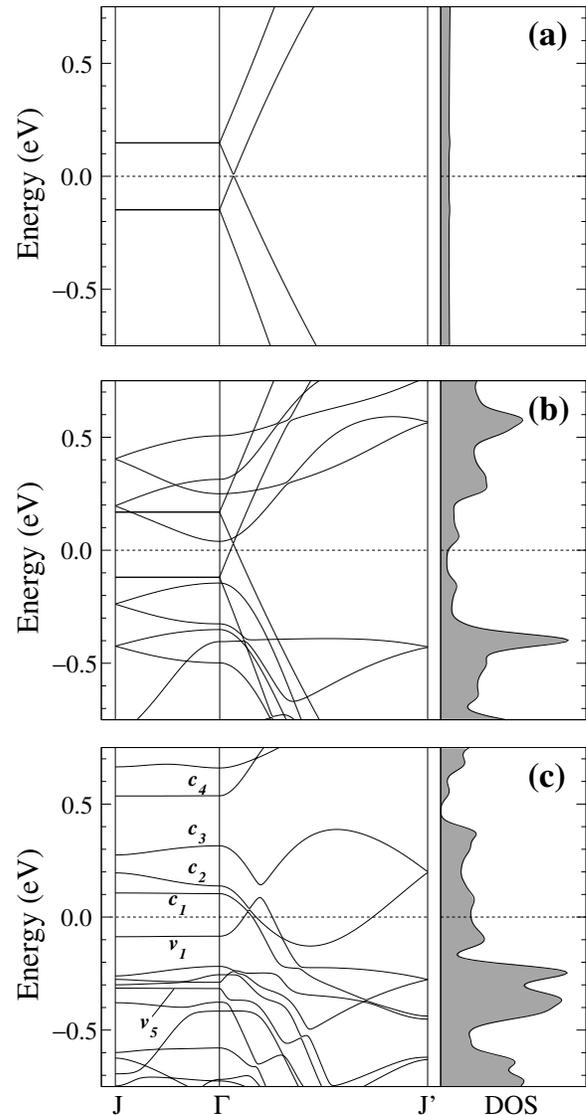


FIG. 2. Electronic band structure for the CNT and the Si(001) surface along directions parallel (Γ - J') and perpendicular (Γ - J) to the dimer trench or the tube axis. (a) The isolated CNT. (b) The Si surface plus the CNT at 5 \AA from the dimers. (c) The adsorbed CNT on the most stable structure (T0 geometry). The DOS along Γ - J' is also shown. The zero of energy is taken as the Fermi level, indicated by dashed lines.

atom of the CNT. Figure 3(b) shows the charge density plot of the subbands that cross the Fermi level [ν_1 , c_1 , and c_2 in Fig. 2(c)]. Here we observe a strong concentration of charge localized at the CNT-surface contact, mainly at the C-Si bond and at the bottommost C atom, which belong to the zigzag C-C bonds. However, along the zigzag C-C bonds (normal to the plane of Fig. 3), the charge distribution is delocalized due to the overlap of the wave functions. This result shows the formation of a nearly 1D electronic channel along the CNT-surface contact.

In an interesting work, Hertel *et al.* [16] found strong structural deformations on adsorbed SWCNs attributed to

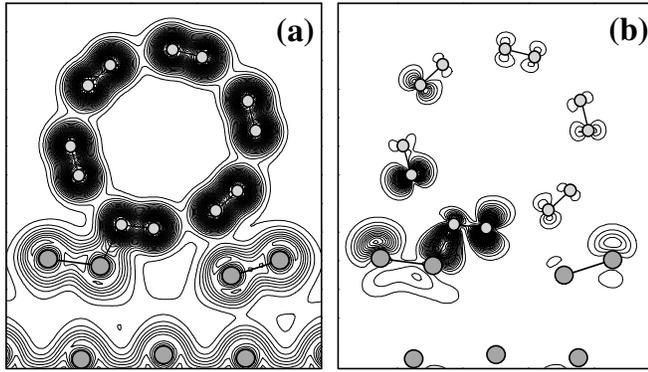


FIG. 3. Charge density contour plots for the adsorbed nanotube on Si(001) in the T0 geometry on a plane passes through a C-Si bond. (a) Total charge density. (b) Charge density of the subbands that cross the Fermi level. The contour spacings are 10^{-2} and $4 \times 10^{-5} e/\text{\AA}^3$, respectively.

surprisingly high van der Waals interactions. Additionally, they found a large binding energy of $0.8 \pm 0.3 \text{ eV/\AA}$ for multiwalled (undistorted) CNTs with diameters of about 100 \AA , adsorbed on H-passivated Si(001) surfaces. Assuming that the CNT binding energy is proportional to the number of C-Si bonds at the contact region, we can estimate the binding energy of undistorted CNTs of large diameters, adsorbed on the clean Si surface. Based on our results for the most stable T0 geometry, we determine the distance between the adsorbed CNT and the Si surface where C-Si bonds are formed, in $h = 0.5 \text{ \AA}$, as illustrated in Fig. 4. In the same figure, we also depict the corresponding contact region for a 100 \AA diameter CNT (shaded area) using the same distance h . From geometrical arguments, the binding energy of the larger CNT may be written approximately as a function of the smaller one as $E_b \approx \epsilon_b \sqrt{D/d}$, where D is the diameter of the large CNT; d and ϵ_b are the diameter and binding energy, respectively, for our CNT in the T0 geometry. For $D = 100 \text{ \AA}$, $d = 8.2 \text{ \AA}$, and $\epsilon_b = 0.2 \text{ eV/\AA}$, we find $E_b \approx 0.7 \text{ eV/\AA}$, which is very close to the experimental value reported by Hertel *et al.* [16]. Since our results show the formation of chemical bonds, we suggest that the interactions between the CNT and the H-passivated Si surface reported above would be mainly chemical, where the H atoms may have been removed from the CNT-surface junction during the adsorption process.

In summary, we have shown from first-principles calculations that metallic CNTs can be chemisorbed on clean Si(001) surfaces. The electronic structure of the adsorbed nanotube shows an enhancement in its metallic character due to the formation of bonds with the surface, inducing to the creation of an electronic channel along the CNT-surface contact. These results suggest the possibility to use CNTs as contact and wiring materials for a new silicon-based nanoelectronic technology.

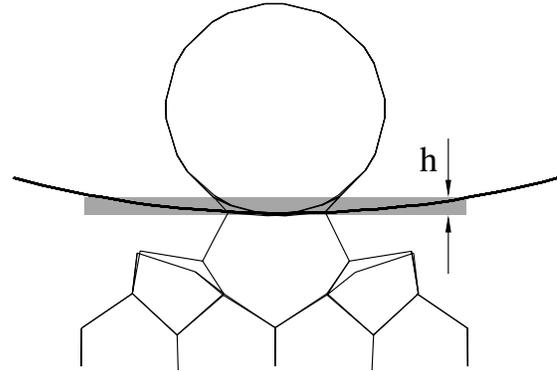


FIG. 4. Schematic representation of the contact region for the CNT in the T0 geometry. The arc represents the contact region for a 100 \AA diameter CNT at the same configuration. The shaded area is our estimation for the region where C-Si bonds are formed for the larger CNT, using the same distance h calculated for the small CNT.

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