

# Stability and electronic properties of carbon nanotubes adsorbed on Si(001)

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## Abstract

We report first-principles calculations on the adsorption of an armchair (6,6) single-walled carbon nanotube (CNT) on the Si(001) surface. We study several well-ordered adsorption configurations for the nanotube on the Si surface. Our results show stable geometries between two consecutive Si-dimer rows (the surface trench). The binding energy per tube length for the CNT in the most stable geometry is calculated to be 0.2 eV/Å. In this geometry, we observe the formation of C–Si chemical bonds. The density of states along the dimer rows for the lowest-energy adsorbed configuration shows an increase in the number of states at the Fermi level. This suggests an enhancement of the nanotube metallic character throughout the contact with the Si surface due to the formation of the C–Si bonds. These properties may lead to consider metallic CNTs as one-dimensional wires on the silicon surface with promising applications for contact and interconnections of future nanoscale electronic devices.

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## 1. Introduction

Since their discovery more than 10 years ago [1], carbon nanotubes (CNTs) have attracted a growing interest due to their exceptional mechanical properties such as nanometer diameter, micrometer lengths and excellent mechanical strength. Concerning their electrical properties, CNTs can be ei-

ther metallic or semiconducting depending on their diameter and chirality. Metallic CNTs provide atomic-uniform nearly one-dimensional conductors which are able to carry a remarkably high current density [2]. These properties make them ideal for applications in future nanoscale electronic devices. Recently, much attention has been focused on the application of CNTs as wiring material for self-assemble nano-interconnections of either conventional or molecular electronic devices [3]. However, the formation of organized arrangements of CNTs at specific locations on technologically important substrates and the characterization of nanotube-substrate contact remains major challenges. Recent successful attempts to manipulate CNTs on Si

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surfaces have been performed by using the tips of an atomic force microscope [4,5]. In this work, we study from first-principles calculations the structural and electronic properties of a metallic (6,6) CNTs adsorbed on a clean Si(001) surface. We investigate the stability and contact properties of the most probably CNT adsorption configurations.

## 2. Computational details

The calculations were performed in the framework of the density functional theory [6], within the generalized gradient approximation (GGA) [7]. We use numerical atomic orbitals as basis set (double-zeta plus polarization) as implemented in the SIESTA code [8], as well as standard norm-conserving pseudopotentials [9]. Our surface model consists of eight silicon monolayers (ML) in a  $2 \times 4$  surface unit cell, describing a  $(2 \times 2)$  reconstructed Si(001) surface. We consider a vacuum region of 18 Å separating the image surfaces and an H-pas-

sivated bottom layer. Our calculations were performed for a (6,6) metallic single-walled CNT with a diameter of 8.2 Å containing 72 carbon atoms. The sampling of the Brillouin zone was performed with 3  $k$  points [10] along the CNT axis. The position of the topmost 6 ML surface atoms plus the nanotube atoms were relaxed until all force components were smaller than 0.05 eV/Å. In order to use periodic boundary conditions for our supercell calculation, we had to fit the surface width with the tube length compressing the Si-surface lattice by about 3% with respect to its experimental value. After exhaustive investigation of the effect of this artificial strain on our results, we find minor influence in the structural and electronic properties of the CNT adsorption processes.

## 3. Results and discussion

We consider two adsorption positions for the CNT on the Si(001) surface: (i) between two

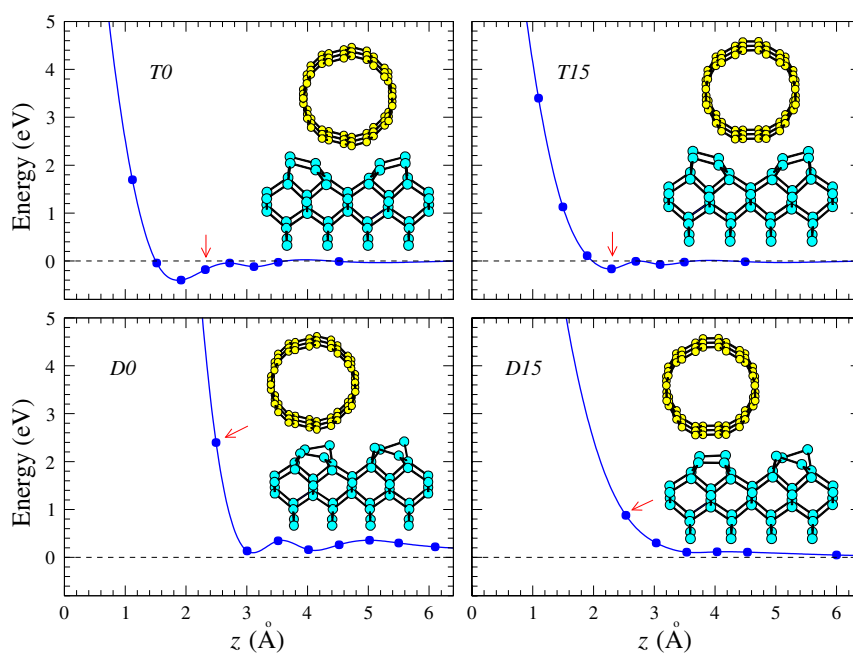


Fig. 1. Total energy as a function of the CNT height from the Si dimer rows. (*T0*) The CNT approaching to the surface trench. (*T15*) The CNT approaching to the surface trench rotated 15° with respect to the *T0* geometry. (*D0*) The CNT approaching to the dimer row. (*D15*) The CNT approaching to the dimer row rotated 15° with respect to the *D0* geometry. The inset figures are the geometries of the system at the CNT height indicated by the arrows.

consecutive Si-dimer rows (on the surface “trench”) and (ii) on the top of the Si-dimer rows. Additionally, for each adsorption positions we consider two configurations for the nanotube by a rotation of  $15^\circ$  around its axis. The four configurations (named  $T0$ ,  $T15$ ,  $D0$ , and  $D15$ ) are shown in the inset of Fig. 1. Configurations  $T0$  and  $D0$  represent the CNT being adsorbed on the trench and on the dimer row, respectively, approaching to the

surface with the bottom most C–C bonds forming a zigzag line parallel to the tube axis. Configurations  $T15$  and  $D15$  represent the CNT being adsorbed on the trench and on the dimer row, respectively, approaching to the surface with the bottom most C–C bonds oriented perpendicular to the tube axis. Both CNT configurations are periodic under a CNT rotation of  $30^\circ$  and were chosen because they optimize the C–Si distance which may favor the

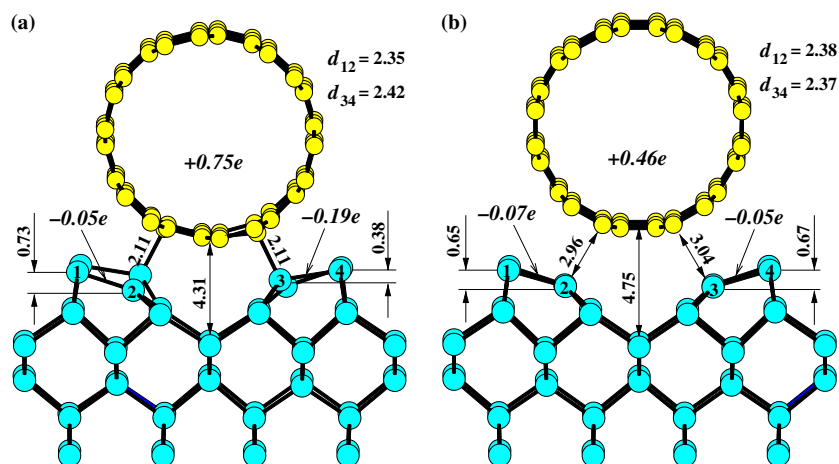


Fig. 2. Equilibrium geometries for the adsorbed nanotubes on the Si(001) surface. (a) The most stable geometry ( $T0$ ). (b) The second stable geometry ( $T15$ ). The charge transfer from the CNT (positive) to the surface (negative) are indicated in units of electrons per unit cell and distances are in Å. Small circles are C atoms and the larger circles are Si atoms.

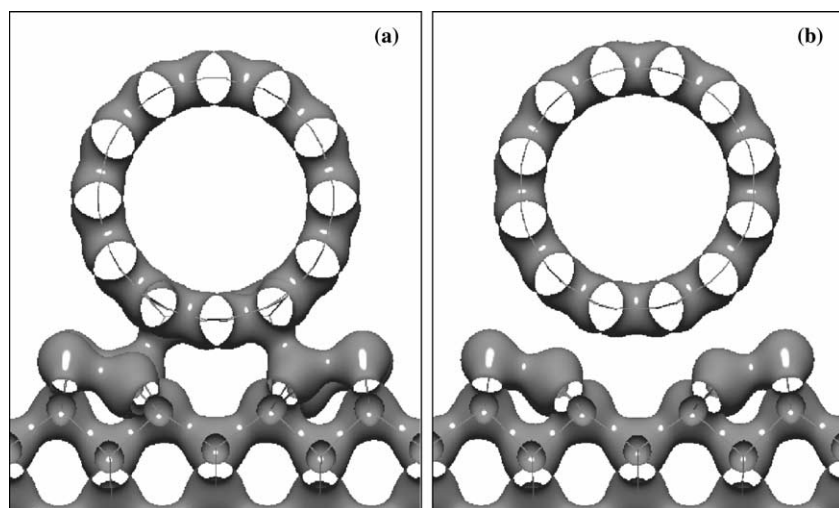


Fig. 3. Total charge density isosurfaces for the adsorbed CNT on the surface trench. (a) For the lowest-energy  $T0$  geometry. (b) For the second lower-energy  $T15$  geometry.

formation of bonds. Fig. 1 shows the total energy as a function of the CNT height from the dimers, for the four adsorption configurations. For these calculations we consider a 6 ML surface structure where the CNT atoms were not allowed to relax. We observe that the CNT is adsorbed on the trench ( $T0$  and  $T15$  geometries) exhibiting both physisorption and chemisorption. However, on the dimer rows the adsorption processes are endothermic ( $D0$  and  $D15$  geometries). In order to investigate in more detail the adsorbed geometries, we consider a larger 8 ML surface structure allowing all the CNT atoms to relax. Our results show that the most stable structure is found on the surface trench with the CNT in the  $T0$  geometry, as shown in Fig. 2(a). The binding energy per unit length of the CNT is calculated to be  $0.21 \text{ eV/\AA}$ , in close agreement with recent empirical calculations [11]. A local distortion observed at the CNT–dimer junction suggests the formation of one C–Si chemical bond per dimer plane, with bond length of  $2.11 \text{ \AA}$ . From the Mulliken population analysis we find that a charge equivalent to  $0.75$  electrons ( $0.75e$ ) per unit cell is transferred from the CNT to the surface, mainly at the dimers where C–Si bonds are formed [see Fig. 2(a)], which increase their charge in  $0.19e$  per unit cell. The total charge-density isosurface plot for the  $T0$  geometry, shown in Fig. 3(a), confirms the formation of C–Si chemical bonds between the CNT and the lower-Si dimer atoms. Similarly to our results on CNTs, organized arrangements of  $C_{60}$  molecules on the Si(001) surface trench has been experimentally observed [12]. Moreover, evidences of C–Si chemical bonds have been recently reported [13,14]. From a calculation of the adsorbed CNT shifted by  $\Delta x$  along the trench, we estimate the shear force ( $F$ ) and shear stress ( $\sigma$ ) for the CNT in the  $T0$  geometry, using  $F = \Delta E / \Delta x$  and  $\sigma = F / A$ . Here,  $\Delta E$  is the difference in energy between the  $T0$  geometry and the shifted geometry, and  $A$  is the area of the CNT–surface contact per unit cell. For  $\Delta E = 0.69 \text{ eV}$ ,  $\Delta x = 0.62 \text{ \AA}$ , and  $A = 45 \text{ \AA}^2$ , we find that  $F \sim 1.8 \text{ nN}$  and  $\sigma \sim 4 \times 10^9 \text{ N/m}^2$ . Following the same procedure, we estimate the force needed to remove the CNT from the  $T0$  geometry in  $\sim 1 \text{ nN}$  per unit cell.

Fig. 2(b) shows a second lower-energy structure for the CNT in the  $T15$  geometry. The CNT

binding energy in this structure is calculated to be  $0.15 \text{ eV/\AA}$ . The shortest C–Si distance is found to be about  $3 \text{ \AA}$ . However, no significant distortions at the CNT–surface junction are observed suggesting a weaker interaction as compared with the  $T0$  geometry. In fact, the total charge density plot of the  $T15$  geometry, shown in Fig. 3(b), do not exhibit the formation of strong chemical bonds as can also be inferred by the small charge transferred from the CNT to the surface dimers [see Fig. 2(b)].

Fig. 4 shows the density of states (DOS) for the clean Si surface [Fig. 4(b)] and for the Si surface

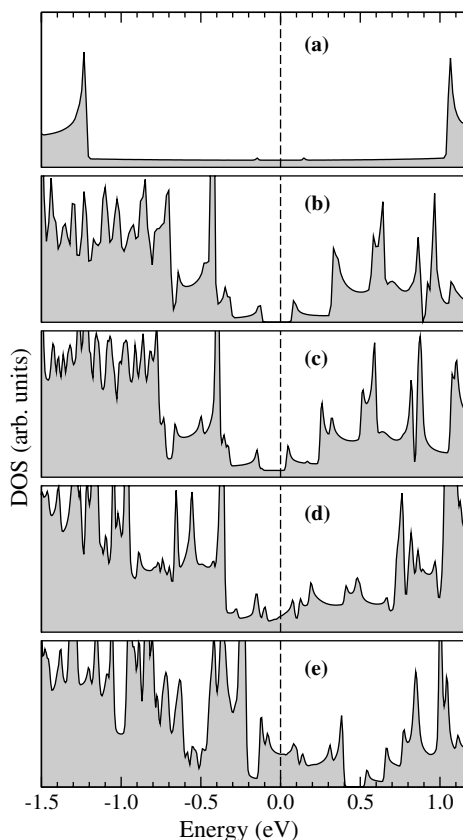


Fig. 4. Density of states for the Si(001) surface and the CNT along the direction of the dimer rows or the tube axis. (a) For the isolated CNT. (b) For the clean surface. (c) For the surface plus the CNT at a height of  $5 \text{ \AA}$  from the surface dimers. (d) For the CNT adsorbed on the trench in the  $T15$  geometry. (e) For the CNT adsorbed on the trench in the  $T0$  geometry. The zero of energy is taken as the Fermi level, indicated by dashed lines.

plus the CNT at a height of 5 Å from the surface [Fig. 4(c)]. We verify that at this distance there is a small interaction between the CNT and the surface, where the metallic character of the system can be associated entirely to the DOS of the isolated CNT [see Fig. 4(a)]. The DOS of the adsorbed nanotube in the *T15* geometry [Fig. 4(d)] shows a relatively small variation of states at the Fermi level comparing with the non-interacting systems [Fig. 4(c)]. However, for the adsorbed CNT in the lowest-energy *T0* geometry [Fig. 4(e)] we find an increase of states at the Fermi level and a strong perturbation in the valence and conduction bands, as compared with the non-interacting systems [Fig. 4(c)]. These results suggest an enhancement of the metallic character of the CNT along the contact with the Si surface induced by the formation of C–Si bonds. It is important to note that the increase in the DOS only occur along the CNT–surface junction, where the bands associated to the C–Si bonds (not shown) are highly dispersive. The wave functions associated to these bands overlap each others characterizing an electronic channel along the CNT–surface junction.

#### 4. Conclusions

We have shown from first-principles calculations that (6,6) metallic CNTs can be chemisorbed on Si(001) surfaces. The electronic states associated to the C–Si chemical bonds increase the density of states at the Fermi level forming an electronic channel at the CNT–surface contact.

These properties may lead to consider CNTs as contact and wiring materials for future silicon-based nanoelectronic devices.

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