

## Substrate-dependent electronic properties of an armchair carbon nanotube adsorbed on H/Si(001)

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The adsorption of an armchair single-walled carbon nanotube (CNT) on fully and partially hydrogenated Si(001) surfaces are studied from first-principles calculations. Our results indicate that the electronic properties of the adsorbed CNT can be ruled by the H concentration along the CNT–H/Si(001) contact region. On the fully hydrogenated Si(001), the CNT is physisorbed, preserving almost unchanged its metallic character. Removing a few of H atoms along the adsorption site, we find an enhancement on the CNT metallic character. In contrast, removing all the H atoms along the adsorption site, the adsorbed CNT becomes a semiconductor, exhibiting an energy gap. These results suggest that armchair CNTs adsorbed on H/Si(001) could be transformed into metal–semiconductor junctions by grading the H concentration along the CNT–surface interface. © 2005 American Institute of Physics. [DOI: 10.1063/1.1931027]

The control of the electronic properties of carbon nanotubes (CNTs) have been proposed by incorporating impurities,<sup>1</sup> deformations<sup>2</sup> and topological defects in their structure.<sup>3</sup> For instance, by the introduction of a pentagon and a heptagon into the hexagonal CNT structure, a single CNT can exhibit different electronic character at each side of the defects, resulting in new types of metal–semiconductor junctions. Experimental results have shown that similar junctions exhibit rectifying behavior.<sup>4</sup> This property opens the possibility to realize CNT devices based on atomic-scaled metal–semiconductor junctions.

The direct integration of CNTs into the well-established silicon technology may be an efficient alternative to achieve molecular devices and circuits in the near future. Recently, Albrecht and Lyding have demonstrated the feasibility to characterize single-walled CNTs adsorbed on H–passivated Si(001)– $2 \times 1$  surfaces, using ultrahigh vacuum scanning-tunneling microscopy (STM) techniques.<sup>5</sup> In addition, STM nanolithography has been successfully used to construct atomic-scale lanes of clean silicon by desorbing hydrogen from H/Si(001)– $2 \times 1$ .<sup>6</sup> This mechanism enables the creation of single Si-atom dangling bond patterns with the potential for the adsorption of individual molecules at specific locations on silicon.<sup>7</sup> In this letter, the electronic and structural properties of an armchair (6,6) single-walled CNT adsorbed on hydrogenated silicon surfaces are explored through first-principles calculations. We find that the metallic character of the adsorbed CNT can be switched to a semiconducting one by reducing the H concentration at the nanotube–surface interface, allowing the formation of

carbon–silicon chemical bonds. These findings may provide a way to perform metal–semiconductor junctions with armchair CNTs without significantly altering their structure.

The calculations were performed in the framework of the density functional theory (DFT), using a basis set of numerical atomic orbitals as implemented in the SIESTA code.<sup>8</sup> For the exchange–correlation potential we adopt the generalized gradient approximation (GGA),<sup>9</sup> and standard norm-conserving pseudopotentials to describe the electron-ion interaction.<sup>10</sup> We consider a split-valence double- $\zeta$  basis set plus the polarization functions. Our surface model consists of eight Si-atom monolayers (ML) plus a H-atom cover layer in a  $2 \times 4$  surface unit cell, describing a hydrogen-terminated ( $2 \times 1$ )-reconstructed Si(001) surface. The dangling bonds of the bottom Si ML are passivated by H atoms. We consider a metallic (6,6) single-walled CNT with a diameter of 8.2 Å containing 72 atoms. Our supercell has vacuum region of 20 Å separating the image surfaces, whereas the lateral distance between image CNTs is 6.5 Å. For the Brillouin zone sampling we use three  $k$  points along the CNT axis.<sup>11</sup> The positions of the topmost surface atoms (the first H-atom layer plus six Si-atom layers), as well as the CNT atoms, were fully relaxed until all the force components were smaller than 0.05 eV/Å.

We investigate the CNT adsorption on the fully hydrogenated Si surface [H<sub>1.0</sub>/Si(001)] and on several H-deficient surfaces, where the H atoms are removed only from the lane where the CNT is adsorbed. The site for the CNT adsorption on H/Si(001) is chosen to be the trench, which is the space between two consecutive Si-dimer rows. This adsorption site has been found to be energetically favorable for the CNT adsorption on clean Si(001).<sup>12,13</sup> We consider hydrogen coverage on the trench of 75% [H<sub>0.75</sub>/Si(001)],

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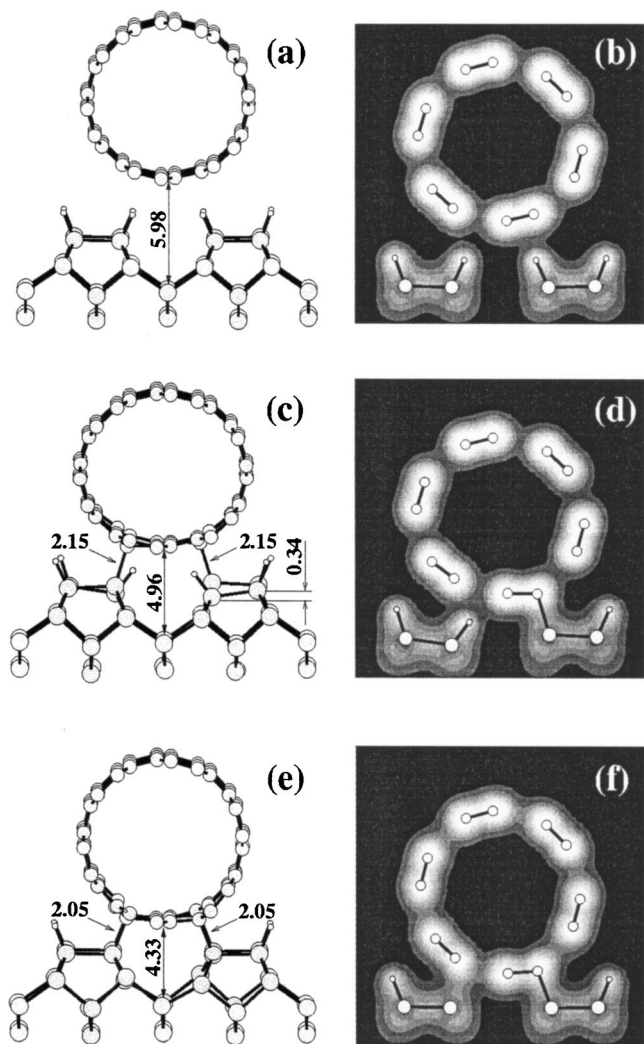


FIG. 1. (Left) equilibrium geometries and (right) total charge density plots of the adsorbed CNT on the trench of H/Si(001) for different H concentrations: (a), (b)  $H_{1.0}/Si(001)$ ; (c), (d)  $H_{0.5}/Si(001)$ ; (e), (f)  $H_{0.0}/Si(001)$ . The charge densities are depicted on a plane passes through the Si dimers. The numbers represent distances in angstroms.

50% [ $H_{0.50}/Si(001)$ ], 25% [ $H_{0.25}/Si(001)$ ], and 0% [ $H_{0.0}/Si(001)$ ].

We first study the fully hydrogenated Si(001) surface without the CNT, our results for the equilibrium geometry show perfectly aligned hydrogenated Si dimers with Si-Si and H-Si bond lengths of 2.41 and 1.52 Å, respectively. The band structures of  $H_{1.0}/Si(001)$  show a band gap of 1.05 eV. Figures 1(a) and 1(b) show the equilibrium geometry of the CNT adsorbed on  $H_{1.0}/Si(001)$  and the respective charge-density plot through a dimer plane. We find that the CNT has a stable position at 5.98 Å from the second sublayer Si atoms, approximately 4 Å from the Si-dimer rows [see Fig. 1(a)]. The CNT binding energy is calculated to be 0.08 eV/Å. As Fig. 1(b) shows, there are no chemical bonds between the CNT and  $H_{1.0}/Si(001)$ , indicating that carbon nanotubes are physisorbed on fully hydrogenated Si(001).

We now examine the structural properties of the CNT adsorption on the H-deficient sites. We begin with the  $H_{0.75}/Si(001)$  substrate, corresponding to three H atoms at the adsorption site per unit cell. We find that the CNT is physisorbed on this substrate exhibiting a similar equilibrium geometry and binding energy than those found on

$H_{1.0}/Si(001)$  [see Fig. 1(a)]. Our results for the CNT adsorption on  $H_{0.50}/Si(001)$  (two H atom at the adsorption site per unit cell) are shown in Figs. 1(c) and 1(d). We observe that the depassivated Si atoms and their neighboring C atoms approach each other, forming C-Si chemical bonds in alternate dimer planes [see Fig. 1(d)]. The C-Si bond lengths are found to be 2.15 Å. On the other hand, the passivated Si atoms move downward, with their attached H atoms, buckling the dimer by 0.34 Å. Our total-energy calculations indicate that the adsorption process of the CNT on  $H_{0.50}/Si(001)$  is slightly endothermic, with an energy cost of 0.05 eV/Å. This result can be attributed to a competing process between the attractive interaction involved in the formation of the C-Si chemical bonds, and the repulsive interaction between the occupied orbitals of the H-Si pair and the partially occupied  $\pi$  orbitals of the CNT. We also analyze other configurations for the  $H_{0.50}/Si(001)$  adsorption site, removing H atoms in an irregular manner in order to investigate commensurability or ordering effects. Our results always show the formation of C-Si chemical bonds and similar electronic properties among all possible configurations. For the adsorbed CNT on  $H_{0.25}/Si(001)$ , with one H atom at the adsorption site per unit cell, we find the same trend for the CNT chemisorption process. This adsorption reaction is exothermic with a energy gain of 0.09 eV/Å. Finally, Figs. 1(e) and 1(f) show our results for the CNT adsorption on  $H_{0.0}/Si(001)$ , here all the H atoms at the adsorption site are removed. This reaction is exothermic with a energy gain of 0.20 eV/Å, resulting in the energetically most favorable structure for the CNT adsorption because all the depassivated Si atoms form chemical bonds with the tube.

Figure 2 shows the electronic band structure plus the density of states (DOS) and charge density plots for the adsorbed CNT on the different substrates. The charge densities correspond to the states lying in an energy range of 0.15 eV above the Fermi energy. In the figure,  $\Gamma-J'$  ( $\Gamma-J$ ) is the direction of the wave vector parallel (perpendicular) to the CNT axis. The DOS is plotted along the  $\Gamma-J'$  direction. The electronic band structure of the CNT on  $H_{1.0}/Si(001)$  [Fig. 2(a)] is essentially a superposition of the bands of the isolated systems, the CNT and the  $H_{1.0}/Si(001)$  surface. This confirms the weak electronic interaction between the CNT and the fully passivated Si surface. The dispersionless subbands along  $\Gamma-J$  are identified as the bidgenerated CNT  $\pi$  states. From Fig. 2(b) we clearly see that the CNT  $\pi$  states give the metallicity of the system along  $\Gamma-J'$ , showing the inert character of the H-terminated Si surface.

Figure 2(c) shows the band structure and DOS of the CNT on  $H_{0.50}/Si(001)$ . Here, we observe an increase of the DOS at the Fermi level, enhancing the metallic character of the adsorbed CNT. The two partially occupied states, labeled as  $c_1$  and  $v_1$ , cross the Fermi level at  $0.14\Gamma J'$ . These two states are mainly localized at the bottommost C atoms (which form zigzag C-C bonds along the CNT axis), with some electronic contribution from the C-Si bonds, as shown in Fig. 2(d). Along  $\Gamma-J$ , the delocalized CNT  $\pi$  states split into  $c_1$  and  $c_2$  ( $v_1$  and  $v_2$ ) states with energy split of 0.32 eV (0.25 eV). For the CNT on  $H_{0.25}/Si(001)$  we also find a metallic system along the CNT axis, which is entirely due to the  $v_1$  state. This state crosses the Fermi level at  $0.35\Gamma J'$ , exhibiting lower dispersion and consequently a more localized character than that observed in Fig. 2(c).

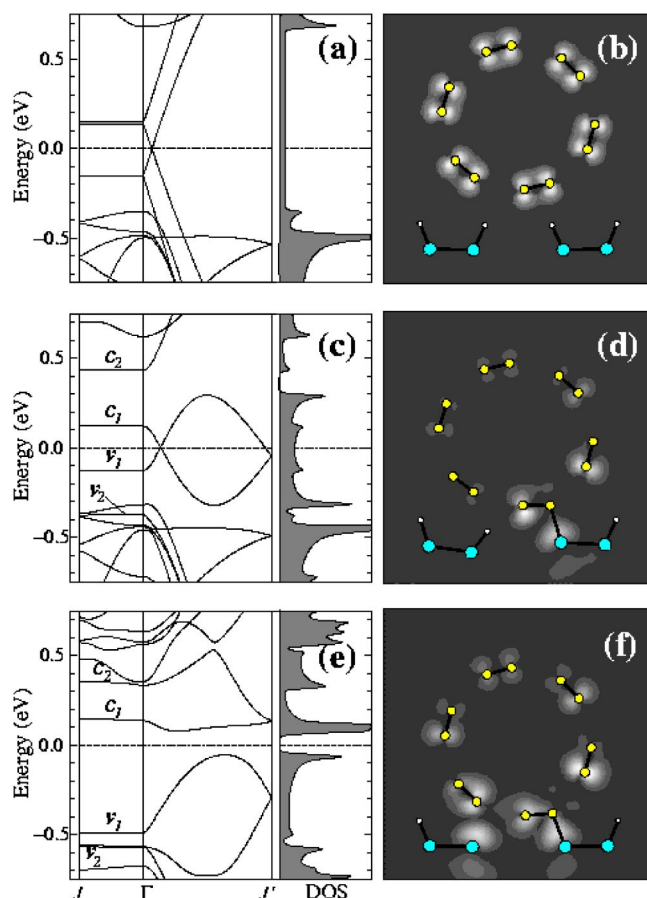


FIG. 2. (Left) electronic band structures plus density of states (DOS) and (right) charge density plots for the states just above the Fermi level for the adsorbed CNT on the trench of H/Si(001) for different H concentrations: (a), (b)  $H_{1.0}/Si(001)$ ; (c), (d)  $H_{0.5}/Si(001)$ ; (e), (f)  $H_{0.0}/Si(001)$ . The  $\Gamma-J'$  ( $\Gamma-J$ ) is the direction of the wave vector parallel (perpendicular) to the CNT axis. The DOS is plotted along  $\Gamma-J'$  direction. The zero of energy is taken as the Fermi level, indicated by dashed lines.

In striking contrast with the above described systems, our results for the CNT on  $H_{0.0}/Si(001)$  exhibits a semiconducting character. The band structure of Fig. 2(e) shows that the  $c_1$  ( $v_1$ ) state moves upward (downward), becoming empty (fully occupied), giving rise to an energy gap of 0.15 eV. It is important to note that this gap value was obtained within the DFT-GGA approach, which means that its real value should be expected to be larger in an experimental measurement. In the CNT- $H_{0.0}/Si(001)$  interface, all the de-passivated Si atoms bind with the closer C atoms of the nanotube. The charge density plot of  $c_1$  [lowest unoccupied molecular orbital (LUMO)] state [Fig. 2(f)] shows a strong concentration of charge at the interface, mainly at the Si atoms that form the C-Si bonds. Similar results are found for the  $v_1$  [highest occupied molecular orbital (HOMO)] state. Based on the charge density diagrams of Figs. 2(d) and 2(f) we can infer that the metallic to semiconducting transition occurs due to the  $\pi$  states localization at the newly formed C-Si bonds on the 0 ML H coverage. The metallic character

of the CNT- $H_{0.50}/Si(001)$  system is due to the delocalized  $\pi$  states lying along the bottommost zigzag C-C bonds parallel to the CNT axis, Fig. 2(d) shows a transversal section of these states. On the other hand, Fig. 2(f) shows that the  $c_1$  and  $v_1$  states of CNT- $H_{0.0}/Si(001)$  are mainly localized at the C-Si bonds. Thus, the delocalization of the  $\pi$  states along the CNT is suppressed when all the H atoms are removed from the contact region and the de-passivated Si atoms form chemical bonds with nearest-neighbor C atoms of the tube, giving rise to a semiconducting system.

Metal-semiconductor junctions based on a single CNT have been proposed by the introduction of topological defects in its structure.<sup>3</sup> Based on our results we suggest that similar heterojunction could be constructed with a single armchair CNT adsorbed on a previously prepared H-deficient lane on H/Si(001). The metallic and semiconducting character of the CNT would be induced by its chemical interaction with the H-deficient substrate, for H concentrations of 50% and 0%, respectively. This junction would provide an electronic device similar to a Schottky barrier.

In summary, we have investigated the structural and electronic properties of an armchair (6,6) CNT adsorbed on H/Si(001). We find that on the fully hydrogenated Si(001) the CNT is physisorbed, preserving almost unchanged its metallic character. Removing about half the H atoms from the adsorption site, we observe an enhancement in the metallicity of system along the CNT. However, when all the H atoms of the adsorption site are removed, the system becomes semiconductor, having a band gap of 0.15 eV. This interesting property suggests the possibility to construct metal-semiconductor junctions with armchair CNTs by grading the H concentration at the contact with the substrate where it is supported.

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