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Carbon nanotube adsorbed on hydrogenated Si(0 0 1) surfaces

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Abstract

The structural and electronic properties of a metallic single-walled carbon nanotube (CNT), adsorbed on hydrogenated Si(0 0 1) surfaces, have been investigated by first-principles calculations. We find that the electronic properties of the adsorbed CNT can be ruled by the H concentration along the CNT–H/Si(0 0 1) contact region. (i) On the fully hydrogenated Si(0 0 1), the CNT is physisorbed, preserving almost unchanged its metallic character. (ii) Removing half the H atoms along the adsorption site, we find an enhancement on the metallicity of the adsorbed CNT. (iii) When all the H atoms along the adsorption site are removed, the adsorbed CNT becomes semiconducting, exhibiting an energy gap. These results suggest that metallic CNTs adsorbed on H/Si(0 0 1) could be transformed into metal–semiconductor junctions by grading the H concentration along the CNT–surface interface.
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The electronic properties of CNTs can be manipulated by incorporation of impurities [1], deformations [2,3], and topological defects [4]. For instance, by the introduction of a pentagon and a heptagon into the hexagonal CNT structure, a single CNT can exhibits different atomic and electronic properties, resulting in new types of metal–metal, metal–semiconductor, and semiconductor–semiconductor junctions made of a single molecular element, a carbon nanotube. This property opens the possibility to realize CNT devices based on molecular metal–semiconductor junctions. The direct integration of CNTs into the well-established silicon technology is an efficient alternative to achieve nanoscale devices and circuits in the near future. Recently, Albrecht and Lyding have demonstrated the feasibility to characterize single-walled CNTs adsorbed on H-passivated silicon surfaces using ultra-high vacuum scanning–tunneling microscopy (UHV-STM) techniques [5]. Following this way, the study of atomistic processes occurring at the CNT–surface interface and the effect of the substrate in the electronic properties of the adsorbed CNT, are important questions for the future realization of silicon-based nanoelectronics.

In this paper, the electronic and structural properties of a metallic single-walled CNT adsorbed on fully

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and partially 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 changing the H concentration at the nanotube–surface interface. This interesting property suggests the possibility to construct metal–semiconductor junctions with a single metallic CNT adsorbed on H/Si(0 0 1), by the selective removal of H atoms along the surface adsorption site, instead of changing the CNT structures.

The calculations were performed in the framework of the density functional theory, using a basis set of numerical atomic orbitals as implemented in the SIESTA code [6]. For the exchange-correlation potential we adopt the generalized gradient approximation [7], and standard norm-conserving pseudopotentials to describe the electron–ion interaction [8]. We consider a split-valence double-zeta basis set plus the polarization functions. Our surface model consists of eight Si-atom monolayers (ML) plus one H-atom coverage ML in a 2×4 surface unit cell, describing a hydrogen-terminated (2×1)-reconstructed Si(0 0 1) surface. The dangling bonds of the bottom Si ML are passivated by H atoms. We consider a (6,6) metallic 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 distance between image CNTs is 6.5 Å. For the Brillouin zone sampling we use three k points along the CNT axis [9]. The positions of the topmost surface atoms (the first H-atom ML plus six Si-atom MLs), 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 [$H_{1.0}$/Si(0 0 1)] and on partially hydrogenated Si surfaces, considering two different H coverages: (i) 0.75 ML [$H_{0.75}$/Si(0 0 1)] and (ii) 0.50 ML [$H_{0.50}$/Si(0 0 1)]. For $H_{0.75}$/Si(0 0 1), half the H atoms are removed from the adsorption site, whereas for $H_{0.50}$/Si(0 0 1), all the H atoms are removed from the adsorption site. Following previous calculations [10], the site for the CNT adsorption is chosen to be the surface trench, which is the space between two consecutive Si-dimer rows.

Fig. 1 shows the equilibrium geometries, total charge densities and the charge transfers of the CNT adsorbed on the H/Si(0 0 1) surface. For the CNT adsorbed on $H_{1.0}$/Si(0 0 1), we find a CNT stable position at 5.98 Å from the second-sublayer Si atoms [Fig. 1(a)]. The total charge density, depicted in Fig. 1(b), shows that there are no chemical bonds between the CNT and $H_{1.0}$/Si(0 0 1), with a slight charge transfer from the CNT towards the $H_{1.0}$/Si(0 0 1) surface [Fig. 1(c)]. The CNT binding energy is calculated to be 0.08 eV/Å, thus, indicating that the CNT is weakly adsorbed (physisorbed) on the fully hydrogenated Si surface. Fig. 1(d) shows the equilibrium geometry for the CNT adsorption on $H_{0.75}$/Si(0 0 1). We observe that the depassivated Si-dimer atoms and the nanotube C atoms approach each other, forming C–Si chemical bonds [Fig. 1(e)]. The charge transfer diagram [Fig. 1(f)] indicates very localized charge transfer, increasing the charge density along the C–Si bonds. Our total-energy results indicate that the adsorption process of the CNT on $H_{0.75}$/Si(0 0 1) 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 π orbitals of the CNT. The buckling of the passivated Si dimers is a clear indication of that. For the CNT adsorption on $H_{0.50}$/Si(0 0 1), we find that all the depassivated Si atoms form chemical bonds with the closer C atoms of the CNT, as shown in Fig. 1(g) and (h). The adsorption reaction is exothermic, with an energy gain of 0.20 eV/Å. The formation of the C–Si bonds is clearly verified by the total charge-density contour plot shown in Fig. 1(h). The charge transfer diagram [Fig. 1(i)] indicates a localized charge transfer along the CNT surface contact region. The stability of the CNT on the partially hydrogenated surface trench indicates that the depassivated sites are energetically favorable for the CNT adsorption. Since H atoms can be removed from passivated Si surfaces with atomic precision by using STM nanolithography [11], it is possible to create an atomic resolved depassivated nanostripe along the trench of H/Si(0 0 1) where the CNT can be deposited.

Fig. 2 shows the electronic band structure, density of states (DOS) and charge density of the adsorbed CNT on H/Si(0 0 1). The charge densities correspond to the states lying in an energy range of 0.15 eV above the Fermi energy. In the figure, Γ–J'(Γ–J) is the direction of the wave vector parallel (perpendicular) to

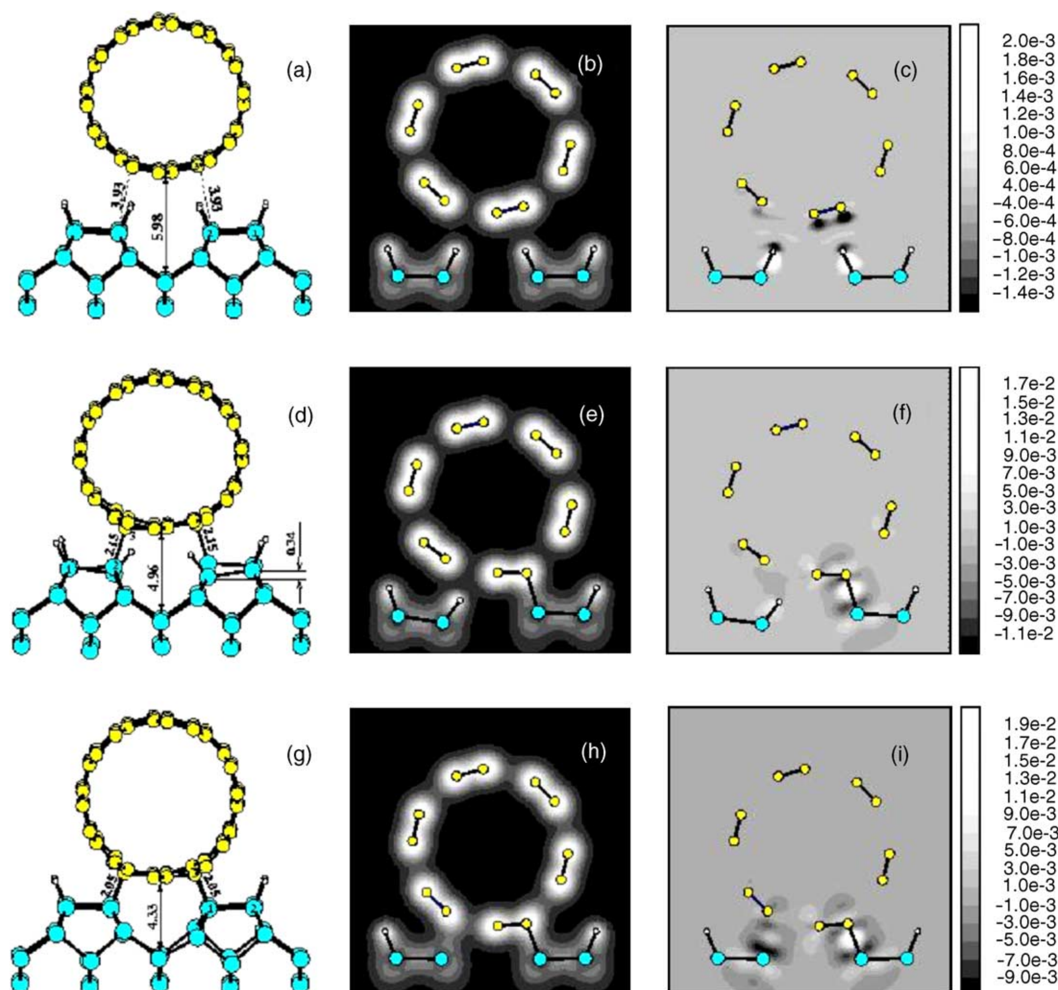

Fig. 1. Equilibrium geometries (left), the total charge densities contour plots (central), and the charge transfers for the carbon nanotube adsorbed on the hydrogenated Si surfaces: (a)–(c) $H_{1.0}$/Si(0 0 1), (d)–(f) $H_{0.50}$/Si(0 0 1), and (g)–(i) $H_{0.75}$/Si(0 0 1). The numbers represent distances in Å.

the CNT axis. The DOS is plotted along the Γ–J' direction. The electronic band structure of the CNT adsorbed on $H_{1.0}$/Si(0 0 1) [Fig. 2(a)] is essentially a superposition of the bands of the isolated systems, the CNT plus the $H_{1.0}$/Si(0 0 1) surface. This confirms the weak electronic interaction between the CNT and the fully passivated Si surface. The dispersionless sub-bands along Γ–J are identified as the bidegenerated CNT π states. Note that the empty π state has a slight energy split. From Fig. 2(b) we clearly see that the CNT π states give the metallicity of the system along Γ–J', showing the inert character of the H-terminated Si surface. Fig. 2(c) shows the band structure and DOS of the adsorbed CNT on $H_{0.75}$/Si(0 0 1). 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 0.14Γ–J'. These two partially occupied states are mainly localized at the bottommost C atoms (which form a zigzag C–C bonds along the CNT axis), with some electronic contribution from the C–Si bonds, as shown in Fig. 2(d). Along Γ–J, the delocalized CNT π states split into c_1 and c_2 (v_1 and v_2) states with energy split of 0.32 eV (0.25 eV). These results are similar to those previously found for the CNT adsorption on the clean Si(0 0 1) [10]. In

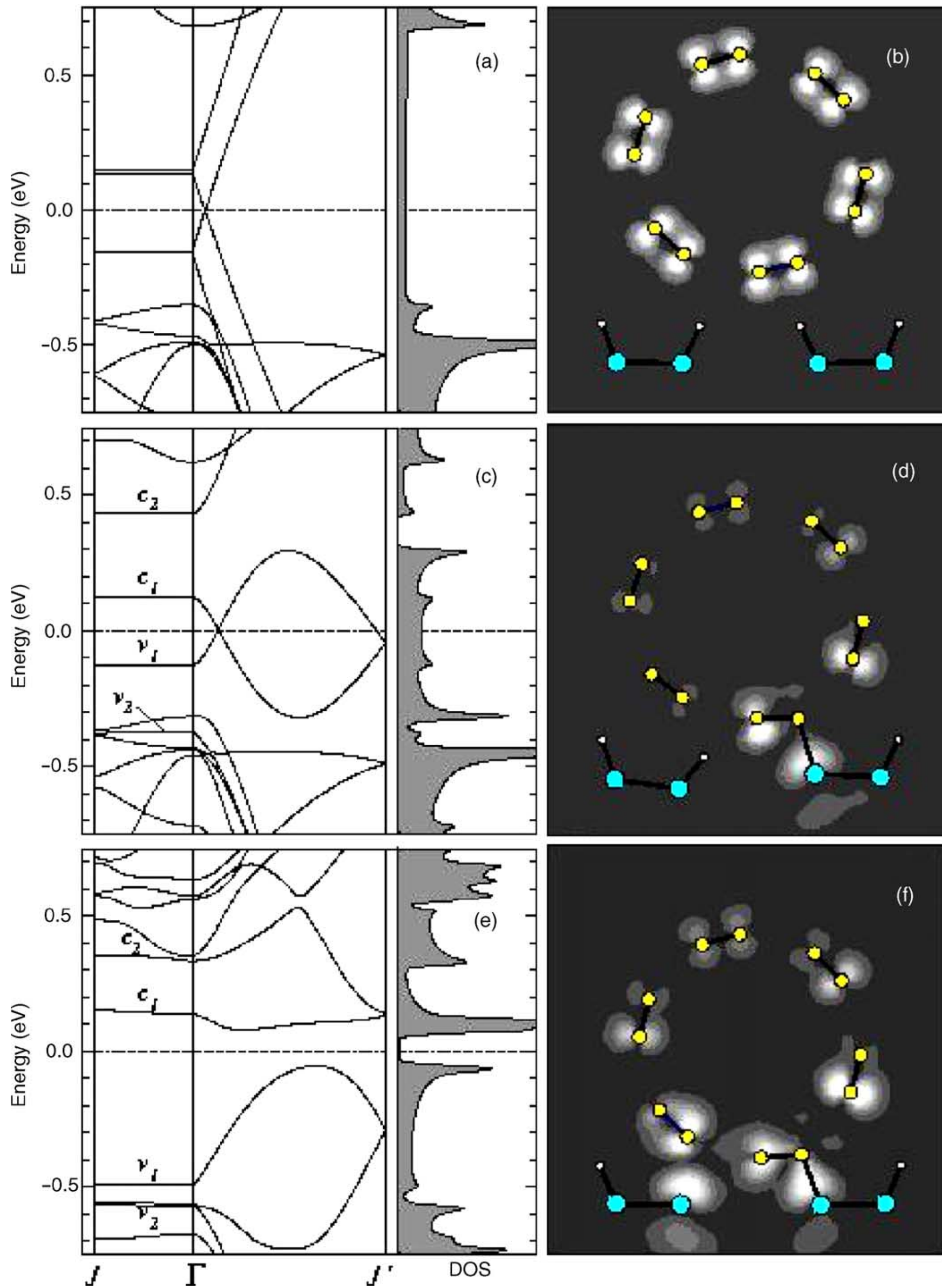

Fig. 2. Electronic band structures plus density of states (left), and charge density contour plots for states just above Fermi level (right), for the CNT adsorbed on hydrogenated Si surfaces. (a, b) The adsorbed CNT on $H_{1.0}$/Si(0 0 1). (c, d) The adsorbed CNT on $H_{0.75}$/Si(0 0 1). (e, f) The adsorbed CNT on $H_{0.50}$/Si(0 0 1). The Γ–J' (Γ–J) is the direction of the wave vector parallel (perpendicular) to the CNT axis. The density of states (DOS) is plotted along Γ–J' direction. The zero of energy is taken as the Fermi level, indicated by dashed lines.

striking contrast with the above described system, our results for the CNT on $H_{0.50}$/Si(0 0 1) 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. We also note a strong hybridization between CNT and surface states along Γ–J', notably different than the CNT on $H_{0.75}$/Si(0 0 1). In the CNT–$H_{0.50}$/Si(0 0 1) interface, all the depassivated Si atoms bind with the closer C atoms of the nanotube. The charge density plot of c_1 (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 (HOMO) state.

Metal–semiconductor junctions based on a single CNT have been proposed and realized by the introduction of topological defects [4,12]. In this work we propose an alternative way to realize this junction which would provide an electronic device similar to a Schottky barrier. In our CNT–H/Si(0 0 1) structure containing a metal–semiconductor junction, the Fermi energy of the metallic segment would be aligned with the middle of the energy gap of the semiconductor segment. So that, we estimate a valence-band offset for the adsorbed CNT heterojunction of $\approx$0.08 eV.

In summary, using first-principles total-energy calculations, we have investigated the structural and electronic properties of a metallic single-walled CNT adsorbed on the fully and partially hydrogenated Si(0 0 1) surfaces. On the fully hydrogenated Si(0 0 1) the CNT is physisorbed, preserving almost unchanged its metallic character. Removing half the H atoms from the H/Si(0 0 1) surface trench (the adsorption site), we observe an enhancement in the metallicity of the adsorbed CNT which can be attributed to the formation of one C–Si bond per dimer plane, inducing a delocalized charge density along the CNT. Removing all the H atoms from the H/Si(0 0 1) surface trench, the adsorbed CNT becomes semiconducting, having a band gap of 0.15 eV. Here, all the Si atoms at the CNT–surface interface bind with CNT atoms. Thus, the semiconducting behavior can be attributed to the charge density localization at the C–Si bonds. Our results suggest the possibility to construct metal–semiconductor junctions with a single metallic CNT by grading the H concentration at the CNT–surface interface without changing the CNT structure.

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