Stability and bonding properties of finite single-walled carbon nanotubes adsorbed on Si(001)

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The stability and bonding properties of capped single-walled carbon nanotubes (CNTs) adsorbed on the Si(001) surface are addressed by density-functional theory calculations. We study the armchair (5,5) and the zigzag (9,0) CNTs with a similar length of about 24 Å, which are adsorbed parallel and perpendicular to the dimer direction of the reconstructed Si(001) surface. At the equilibrium geometries, both CNTs form covalent bonds with the substrates with binding energies ranging from 0.40 to 0.62 eV per C–Si bond. These bonds only form when neighboring C and Si atoms are closer than 2.13 Å. We find a preferential direction for the CNT adsorptions along the dimers where the zigzag CNT is found to be the most stable. Changes in the Si(001) band structures after the CNT adsorption are also discussed. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2889471]

Recent advances in the manipulation and characterization of single-walled carbon nanotubes (CNTs) supported on silicon substrates have opened interesting perspectives for the future realization of an hybrid device, taking advantage of both the outstanding CNT properties and the well-established silicon technology.[1–3] Experiments using ultra-high vacuum scanning tunneling microscope are able to stabilize isolated single-walled CNTs supported on hydrogen-passivated Si(001) surface after desorbing H atoms from the interface,[1] supporting theoretical predictions that CNTs attach covalently on the clean Si(001) surface.[4–7] These and other theoretical works have also suggested that the electronic properties of the supported CNT depend on the surface reconstructions at the interface and on the hybridization between silicon and carbon surface states.[8–11]

However, one point not clearly understood in the interaction between CNTs and the Si(001) surface is the mechanism of the C–Si bond formation. *Ab initio* calculations require that lattices of the nanotube and the surface commensurate in order to describe an infinite nanotube-surface system without artificial strain. For armchair CNTs on the Si(001) surface, the commensurability conditions can be applied by stretching the CNT or compressing the surface by 3%. Although calculations have shown that the influence of this strain in the electronic properties of hybrid systems is minor, the description of CNT binding energy and C–Si bond formation may be artificially affected.[4,8] Thus, there is a timely need for a detailed theoretical study to elucidate artificial strain effects in the stability of adsorbed armchair CNTs on Si(001). The case of zigzag CNTs on the same surface is even more difficult to describe because their unit cells commensurate within 6%, hindering supercell calculations. On the other hand, a few chiral CNTs on the Si(001) surfaces have been studied considering large supercells; in this way, the commensurability condition is achieved within 2%.[10]

In this letter, we investigate from *ab initio* calculations the stability and bonding properties of finite armchair and zigzag CNTs adsorbed parallel and perpendicular to the Si dimers of the reconstructed Si(001) surfaces without any artificial strain. Our results reveal that the flexibility of the Si dimers, which can slightly change their lengths, favor the formation of stronger bonds with both armchair and zigzag CNTs when they are adsorbed along to the dimers.

The calculations were carried out in the framework of density functional theory,[12] within the generalized gradient approximation.[13] We use localized atomic orbital basis sets[14] and norm-conserving pseudopotentials as implemented in the *ab initio* simulation package SIESTA.[15] We consider the zigzag (9,0) and armchair (5,5) CNTs with both ends capped. At the equilibrium geometry, they have lengths of 23.8 and 24.3 Å and diameters of 7.2 and 6.8 Å, respectively. The reconstructed Si(001) surface is simulated by using the slab geometry with six Si monolayers and surface periodicity of 4×8 plus a vacuum region of about 18 Å. The bottom Si ML is saturated with hydrogen. The area of the unit cell is $L \times 2L$, where $L = 15.545$ Å, ensuring separation between CNT images of 8.5 Å at the sides and 6.5 Å along the tubes. Due to the large size of the supercells, which contain up to 460 atoms, only the Γ point was used for the Brillouin zone sampling. The geometry optimization is performed for topmost 5 ML Si atoms plus the CNT atoms until the force components become smaller than 0.05 eV/Å. The CNT binding energy is calculated as the energy difference between the CNT adsorbed on the substrate and the CNT suspended 5 Å from the substrate.

We investigate the CNT adsorption on two regions of Si(001): (i) along the trench or between two Si dimer rows [defined as $Si(001)_T$], as shown in Figs. 1(a) and 1(c), and (ii) between two Si dimer lines, with the tube axis parallel to the dimers [defined as $Si(001)_D$], as shown in Figs. 1(b) and 1(d). In a previous calculation, we consider another adsorption region for CNTs on Si(001): on the top of the dimers with the tube axis perpendicular to the dimers.[5] However, this region was found to be unstable and it is not considered in the present work.

The similar size of the CNTs considered allowed us to compare their stability on the adsorption sites, where they can interact with six dimers when adsorbed on $Si(001)_T$ and four dimers on $Si(001)_D$, giving the main features of the CNT-surface interaction. Initially, both CNTs were released at 3 Å from the surface in two configurations obtained by

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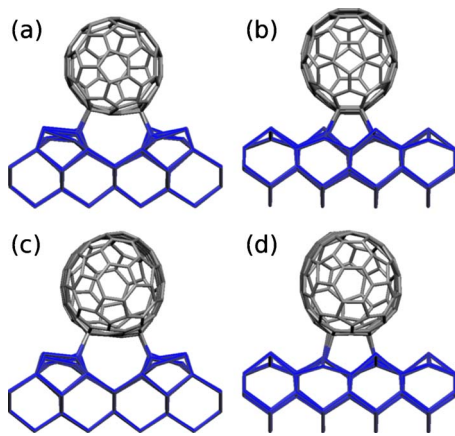[a)]Electronic mail: worellana@unab.cl.

FIG. 1. (Color online) Front view of the equilibrium geometries of capped CNTs adsorbed on the Si(001) surface. (a) The (5,5) CNT along the trench, (b) the (5,5) CNT along the dimers, (c) the (9,0) CNT along the trench, and (d) the (9,0) CNT along the dimers.

rotating the CNT around its axis [20° and 36.5° for (9,0) and (5,5), respectively]. We note that the CNTs adsorbed on unstable positions tend to slide and rotate driven by the force field in order to find the most stable configurations. Figure 1 shows the resulting stable structures as obtained from all the initial geometries considered.

We first study the adsorption of the armchair (5,5) CNT on $Si(001)_T$. Here, two equilibrium structures are found, with the bottommost C–C bonds oriented normal to the trench and with the bottommost C–C bonds forming a zigzag line along the trench. The latter, shown in Fig. 1(a), is found to be the most stable structure by about 1 eV with respect to the second one. We found eight C–Si bonds at the CNT-surface interface with lengths varying from 2.038 to 2.124 Å and a CNT binding energy of 3.73 eV. Figure 2(a) shows the charge density isosurface for the (5,5) CNT on $Si(001)_T$. Here, we note two kinds of bond arrangements along the trench: with asymmetric C–Si bonds at alternate dimers and with symmetric C–Si bonds at consecutive dimers. On the other hand, two previous *ab initio* calculations of infinite armchair CNTs on the trench of Si(001), performed with a
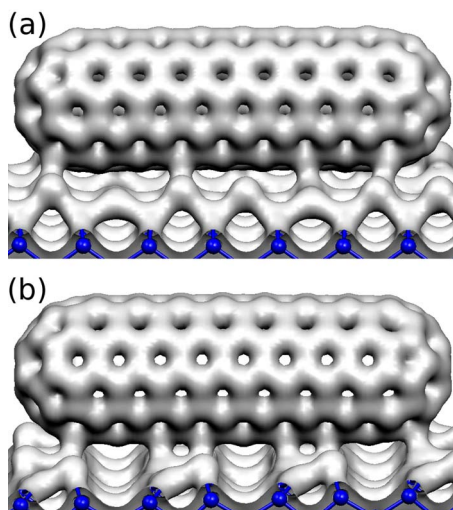

FIG. 2. (Color online) Total charge density isosurfaces for the armchair CNT adsorbed on the Si(001) surface. (a) The (5,5) CNT along the trench and (b) the (5,5) CNT along the dimers. The surface corresponds to a charge density of 0.28 $e/Å^3$.
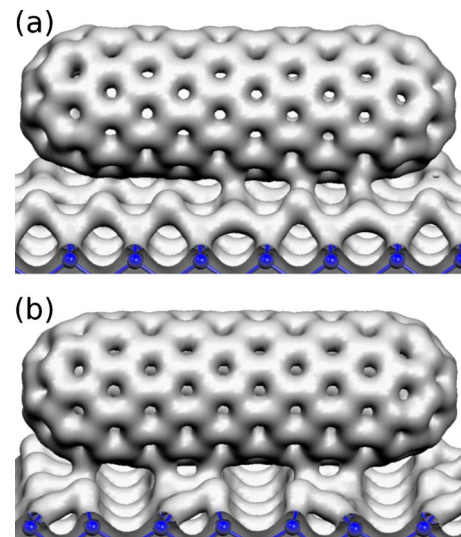

FIG. 3. (Color online) Total charge density isosurfaces for the zigzag CNT adsorbed on the Si(001) surface. (a) The (9,0) CNT along the trench and (b) the (9,0) CNT along the dimer lines. The surface corresponds to a charge density of 0.28 $e/Å^3$.

2×4 surface unit cell, have arrived to different structures. In one case, two C–Si bonds per unit cell at alternate dimers were found,[4] whereas in the other case, four C–Si bonds at consecutive dimers.[8] However, according to our results, both equilibrium geometries would form throughout the CNT-surface interface. Therefore, supercell calculations of infinite armchair CNTs along the trench of Si(001) are not representing properly the equilibrium geometry of the system because of the small supercell considered. It seemed clear that the two bond arrangements were presented due to the mismatch between the CNT and surface lattices.

Figure 1(b) shows the equilibrium geometry of the (5,5) CNT on $Si(001)_D$. Here, the CNT is adsorbed with the bottommost C–C bonds parallel to the dimers; no other stable geometry was found. As can be seen in the charge density plot [Fig. 2(b)], both atoms of the dimers bind with the nanotube symmetrically at each dimer line, forming 12 C–Si bonds with lengths varying from 2.056 to 2.106 Å. The (5,5) CNT on $Si(001)_D$ has a binding energy of 4.77 eV, which is 1.04 eV higher in energy than on the trench. Because of this strong binding, the CNT suffers an oval deformation, as can be seen in Fig. 1(b).

The equilibrium geometry of the zigzag (9,0) CNT on $Si(001)_T$ is shown in Fig. 1(c). We observe a small CNT torsion due to the formation of asymmetric bonds at each side of the CNT. Here, a group of three consecutive C–Si bonds alternate between both dimer rows along the trench without mirror symmetry. The charge density isosurface of Fig. 3(a) shows this bond arrangement at one side of the CNT. Our results show that the (9,0) CNT adsorbed on the trench is the less stable structure with a binding energy of 3.39 eV and C–Si bond lengths varying between 2.025 and 2.096 Å.

Figure 1(d) shows the equilibrium geometry of the (9,0) CNT on $Si(001)_D$. In this structure, both Si-dimer atoms form bonds with the nanotube, in the same way that we found for the (5,5) CNT. However, the (9,0) binding energy of 5.54 eV is 0.77 eV higher than (5,5) at the same adsorption site, turning the zigzag CNT adsorbed along the dimers into the most stable structure on Si(001). Nine C–Si bond are

TABLE I. Energetic and structural properties of (5,5) and (9,0) CNTs on Si(001) oriented along the dimers [Si(001)$_D$] and along the trench [Si(001)$_T$]. E_b is the CNT binding energy (absolute and per CNT length), d is the mean C–Si bond distance. D is the mean distance between the bottommost CNT atoms and the third Si monolayer and N is the number of C–Si bonds at the CNT-surface interface.

System	E_b (eV)	E_b (eV/Å)	d (Å)	D (Å)	N
(9,0) on Si(001)$_D$	5.54	0.23	2.05	4.52	9
(5,5) on Si(001)$_D$	4.77	0.20	2.09	4.62	12
(5,5) on Si(001)$_T$	3.73	0.15	2.08	4.11	8
(9,0) on Si(001)$_T$	3.40	0.14	2.06	4.32	6

formed at the CNT-surface interface with lengths varying from 2.023 to 2.076 Å. The energetic preference for the adsorption of the (9,0) CNT along the dimers with respect to the trench is found to be of 2.14 eV.

Table I summarizes our results for the energetics and equilibrium geometries of the adsorbed nanotubes. We observe that the most stable sites for both CNTs occur along the dimers. This is consistent with the formation of two C–Si bonds per dimer and the absence of Si dangling bond at the CNT-surface interface. For (5,5) on Si(001)$_D$, the dimers that bind the CNT decrease their lengths in average by about 1% with respect to those of the clean surface (2.402 Å). Whereas for (9,0) on Si(001)$_D$, the dimers decrease by 0.3%. This suggests that the C–Si bond formation along Si(001)$_D$ is favored by a dimer relaxation. The smallest relaxation results in the most stable CNT on Si(001) which is independent of the number of C–Si bond formed. From the equilibrium geometry of (5,5) on Si(001)$_T$, which shows the wider C–Si bond variation, we estimate the maximum distance between C and Si atoms that forms a bond in 2.13 Å, which is about 10% longer than the calculated C–Si bond length of zinc blende SiC (1.907 Å).

Finally, we investigated changes in the electronic properties of Si(001) after the CNT adsorption, keeping in mind that our (5,5) and (9,0) CNTs are big molecules with calculated highest-occupied and lowest-empty energy states of 0.27 and 0.40 eV, respectively. The clean Si(001) surface has a calculated band gap of 0.28 eV; after the CNT adsorption, we find that (5,5)-Si(001)$_T$ becomes metallic along the tube axis, whereas (5,5)-Si(001)$_D$ reduces its energy gap of up to 0.07 eV. On the other hand, (9,0)-Si(001)$_T$ and (9,0)-Si(001)$_D$ show semiconducting characters with respective energy gaps of 0.12 and 0.14 eV. If we consider that infinite (5,5) and (9,0) CNTs have metallic and semiconducting characters, respectively, in the light of our results, it is highly likely that infinite achiral CNTs would preserve their electronic properties after being adsorbed on Si(001)$_T$ and Si(001)$_D$.

In conclusion, we have found that the energetically favorable adsorption region for both armchair and zigzag CNTs on Si(001) locates between two dimer lines, where both Si-dimer atoms bind with CNT atoms removing the dangling bonds from the interface. At this site, the zigzag CNTs is about 0.8 eV lower in energy than the armchair one, turning into the most stable CNT on the Si(001) surface. We also suggest that the electronic properties of the nanotube-surface system would be ruled by the nanotube electronic character.

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