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Carbon nanotube adsorbed on a hydrogenated Si-rich β-SiC(100) (3×2) surface: First-principles pseudopotential calculations

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Single wall carbon nanotubes (SWCN's) have attracted scientific interest as a result of their remarkable mechanical and electrical properties. Metallic SWCN's can carry electrical current due to π electrons propagating along their graphitelike surface. This work theoretically considers the effects resulting from the possibility of connecting nanotubes to a partially hydrogenated Si-rich β-SiC(100) (3×2) surface. This is done with the perspective that they can improve the metallic character of the surface. Calculations were performed using a first-principles pseudopotential methodology within the density-functional theory and local-density approximation. Results indicates the formation of a covalent bond between nanotube carbon atoms and surface silicon atoms. The structural and electronic properties of this theoretical system are presented and comparison with previous calculations for related systems is also done.

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I. INTRODUCTION

Since the discovery of carbon nanotubes,[1] nanoscience and nanotechnology have suffered an additional boost towards miniaturization of electronic circuits[2,3] and other potential practical applications.[3] The building of microscopic structures with controlled geometry, density, and dimension for specific applications remains a difficult task for practical realization. Nevertheless, a great amount of work has been reported, not just related to deposition of carbonlike materials but also of other chemical species, either in metals or in semiconductor substrates.[4–6]

Here we report a theoretical study of a nanotube adsorbed on a partially hydrogenated Si-rich β-SiC(100) (3×2) surface. SiC is a wide band-gap semiconductor which, as a result of its characteristics, has important technological applications in a variety of fields such as microelectronics, voltage, temperature, and frequency high resistant electronic devices, matrix composites, and biocompatibility applications.[7–12] It was experimentally observed[13] that the hydrogen saturated Si-rich β-SiC(100) (3×2) surface shows an unusual behavior. It starts to present a metallic character after the hydrogen deposition on the clean surface becomes saturated. This behavior was theoretically reproduced[14–17] by DFT calculations.

Figure 1 shows the structure of the hydrogen saturated β-SiC(100) (3×2) surface, after Si deposition and the necessary treatments for establishing a 3×2 long-range order, as presented by Brito *et al.*[14] The (3×2) unit cell, in respect to bulk square lattice of 3.18 Å, have dimensions of 9.54 and 6.36 Å. In the top layer there are rows of Si dimers resting on similar dimers found on the second layer, these rotated by $\pi/2$ compared to previous ones. The dimers of the first layer, represented by d_1, are perpendicular to the direction where there is a formation of rows.[18] In the second layer there are Si dimers too, represented by d_2, perpendicular to the dimers of the first layer. The third layer is also a Si layer, corresponding to the top layer of the Si-terminated β-SiC(100), with Si-H-Si bonds.[14] The Si-rich β-SiC(100) (3×2) clean surface has the top layer with dangling bonds that can be saturated by the presence of a monovalent atom, like hydrogen, while the second layer presents dimerization, which prevents dangling bonds. The third layer presents formation of Si-H-Si that occurs by insertion of a hydrogen atom into a long Si-Si bond.[13] The work by Brito *et al.*[14] refers to calculations about structural and electronic properties of three phases: the Si-rich β-SiC(100) (3×2) clean surface, the hydrogenated phase (corresponding to the clean surface plus

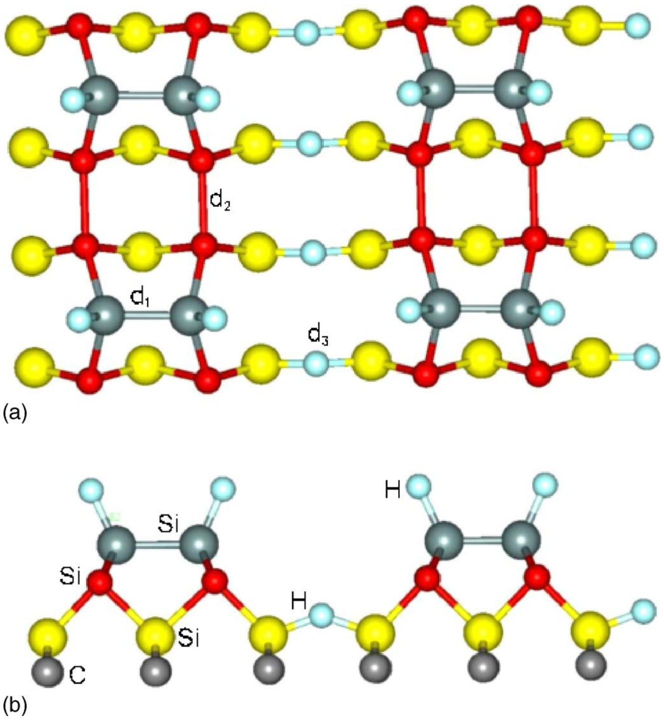

FIG. 1. (Color online) Structure of the hydrogen saturated Si-rich β-SiC(100) (3×2) surface: (a) top view; (b) side view, with C atoms [not shown in (a)] on the fourth layer. For adsorption of the SWCN the hydrogen atoms bounded to the silicon atoms of the first layer were removed.

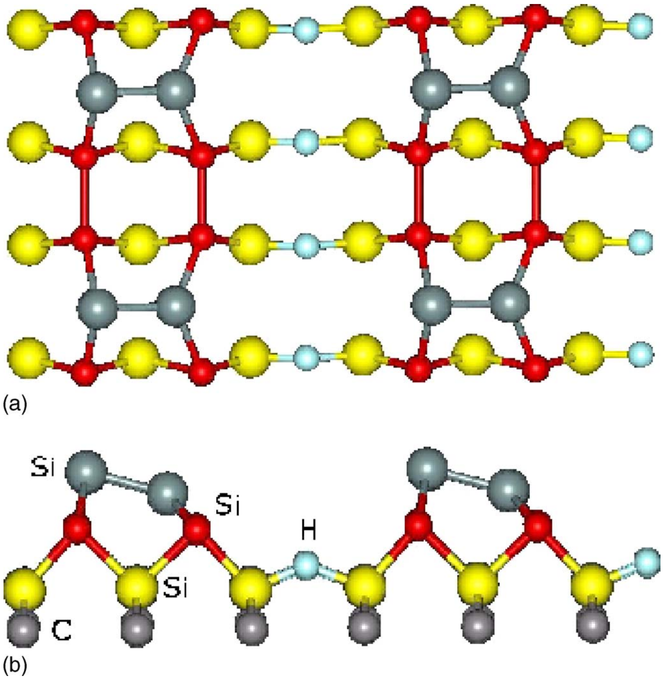

FIG. 2. (Color online) Slab of the hydrogen partially saturated Si-rich β-SiC(100) (3×2) surface: (a) top view showing three Si planes; (b) side view, showing four planes, with C atoms [not shown in (a)] below the third-layer Si atoms.

the hydrogen atoms of the top layer shown in Fig. 2) and a hydrogen saturated one, as shown in Fig. 1. It is worth mentioning that additional deposition of hydrogen, if we compare structures of Figs. 2 and 1, causes the removal of the tilt in Si atoms of the first layer dimers.

Single wall carbon nanotubes (SWCNs) can be either metallic or semiconducting, depending on its diameter and chiral vector.[2,19] The interaction of a semiconductor SWCN and a metal surface has been proposed as the origin of the FET operation, where they are used as channels,[20–22] while the connection of a conducting SWCN to a semiconducting one has been explored for rectification purposes.[2]

In this work we theoretically consider the possible removal of hydrogen atoms from the top layer of the hydrogen saturated Si-rich β-SiC(100) (3×2) surface, shown in Fig. 1 with subsequent insertion, in their place, of a specific single wall (4,1) carbon nanotube (SWCN). We discuss the possible properties resulting from adsorption of such a conducting nanotube on the partially hydrogenated Si-rich β-SiC(100) (3×2) surface, as a way to improve the metallic character of this surface and to model the drain current from a metallic surface.

II. METHODOLOGY

Calculations of the structural and electronic properties were performed using the density-functional theory (DFT) (Refs. 23 and 24) approach. To determine the exchange-correlation energy we adopted the procedure proposed by Perdew,[25] within the approach of the local-density approximation (LDA), with valence electrons treated with Troullier-Martins' pseudopotential.[26] The electronic wave functions were expanded in a numeric atomic orbitals basis set corresponding to a double-zeta basis set with polarized functions (DZP). The ionic positions were relaxed until reaching a minimization of Hellmann-Feynman[27] forces, down to a point where they had become smaller than 0.05 eV/Å. For this work we have used the SIESTA code[28] and adopted the supercell approach, with four special k points in the Brillouin-zone sampling within the Monkhorst-Pack[29] scheme. The density of states (DOS) was obtained by convolution with Gaussian functions centered at the Kohn-Sham[24] one-electron level, with a dispersion of 0.2 eV.

The approach adopted for calculating the SWCN adsorbed on the Si-rich β-SiC(100) (3×2) surface consisted of three steps. First the lattice parameter and atomic positions of just the SWCN were optimized and its electronic properties were calculated. Then, we considered just a slab, representing the support, i.e., the already mentioned partially hydrogenated Si-rich β-SiC(100) (3×2) surface. The slab consists of nine atomic planes plus a plane of hydrogen atoms, bounded to the silicon atoms situated at the bottom of the nine planes in order to saturate their dangling bonds. The lattice parameter and atomic positions of the slab were also optimized with electronic and structural properties then being calculated. Finally, the SWCN-adsorbed slab (SWCN+slab) was built (starting from the final values of the previous steps) with the lattice parameter of the SWCN+slab system being changed slightly until reaching the minimal stress. As in the two steps before, the atomic positions were relaxed in order to minimize the Hellmann-Feynman forces, with structural and electronic properties then being calculated.

III. CALCULATIONS AND RESULTS

The possibility of commensurate nanotube adsorption on a surface and simultaneous formation of a regular two-dimensional (2D) pattern depends on relative sizes of the nanotube dimensions and surface substrate parameters. A SWCN with a chiral vector $(4k,k)$, $k=1,2,3,\ldots$ corresponds to a family of nanotubes that presents the characteristic of having a lattice parameter which is close to the smaller dimension of the Si-rich β-SiC(100) (3×2) primitive cell. The nanotubes of this family differ from each other in diameter, with a well-known relationship between diameter and length (lattice parameter).[31] The SWCN we have considered was a (4,1) conducting carbon nanotube consisting of a total of 28 carbon atoms. After full relaxation of the atomic positions and translational vector, the SWCN had a lattice parameter of 6.40 Å and a diameter of 3.59 Å.

The surface slab considered for further SWCN adsorption was the mentioned 3×2 surface unit cell, as compared with the SiC bulk squared lattice, this one having a parameter of 3.18 Å. The surface unit cell then had dimensions of 6.36 and 9.54 Å. The slab was formed by 56 atoms: 30 silicon atoms, 18 carbon atoms, and 8 hydrogen atoms. Figure 2 shows, in the top view, four unit cells (a) and the first four atomic planes in profile (b). The first, second, and third planes are of silicon while the fourth is carbon. Below these planes the structure is SiC bulklike. The atomic structure was

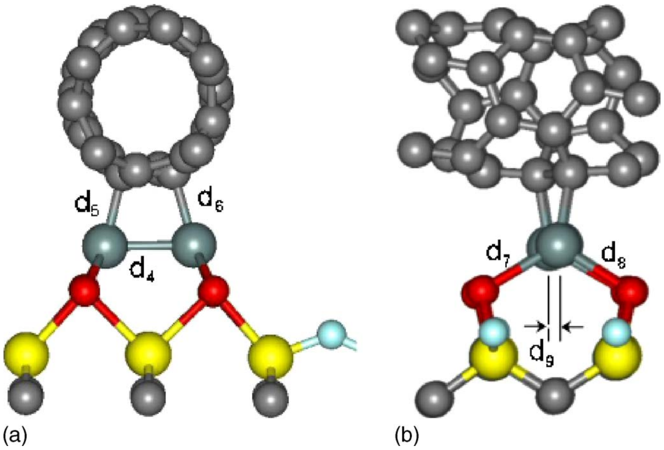

FIG. 3. (Color online) SWCN on hydrogen partially hydrogenated Si-rich β-SiC(100) (3×2) surface: (a) front view; (b) side view.

fully relaxed, until the Hellmann-Feynman forces were smaller than 0.05 eV/Å.

After independent and separate relaxation of each system, SWCN and slab, the nanotubes are supposed to adjust with each other along the dimers rows of the slab top layer. Initially a classical potential[30] was used in the search for best adjustment. Thus rotation of the nanotube around its axis was performed, allowing different adjustments among nanotube and substrate atoms, so that several possibilities were explored in order to get an initial minimum-energy position. From this classical approach, subsequent quantum-mechanical calculation was performed. It is worthwhile to mention that the nanotube length was 6.40 Å, close to the smaller dimension of the slab unit cell (6.36 Å). The dimer bond length was 2.36 Å, being then changed to 2.33 Å [d_4 in Fig. 3(a)] after the interaction with the SWCN. The Si top dimer inclination was of about 15° and disappeared after the SWCN interaction, similar to what would occur in the presence of additional amounts of hydrogen,[14] in the process leading from a partially hydrogenated surface to a saturated phase. The mismatch of the lattice parameters of the SWCN and the slab, separately optimized, was less than 1%. After optimization, the lattice parameter of the SWCN+slab system became 3.19 Å. Figure 3 shows the SWCN+slab system. The interaction between the SWCN and the slab is through the silicon dimer atoms of the slab and the SWCN carbon atoms, with C and Si atoms making a covalent bond. In Fig. 4 we can see an isodensity map of the total charge distribution, which suggests formation of a covalent bond between SWCN carbon atoms and Si dimers. It is worthwhile to mention that the covalent bond lengths between the C and Si atoms are not equal. In each unit cell there is a bonding between two pairs of SWCN carbon atoms and two Si dimers from the slab. The bond lengths are different, as a result of the fact that the silicon dimers are not aligned to the two SWCN carbon atoms. This causes a small torsion on the dimer, with the bond length d_5 being 1.98 Å and d_6 equaling 2.01 Å, as shown in the front view of Fig. 3. Orellana *et al.*[32] reported a first-principles calculation on the absorption of a metallic (6,6) SWCN on the Si(001) surface, for which they found the Si-C bond length as being 2.11 Å, a value 5.0% higher than ours. As a consequence of the torsion, there is also a shift in the Si atom causing distance d_9 to become 0.22 Å instead of zero. As a consequence, the bond lengths d_7 and d_8 for the dimers shown in front of Fig. 3(b), are different from the ones on the back (not shown). The system is not symmetric, with d_7=2.39 Å and d_8=2.33 Å for the front atoms shown in Fig. 3(b) and d_7'=2.31 Å and d_8'=2.37 Å for the pairs on the back.

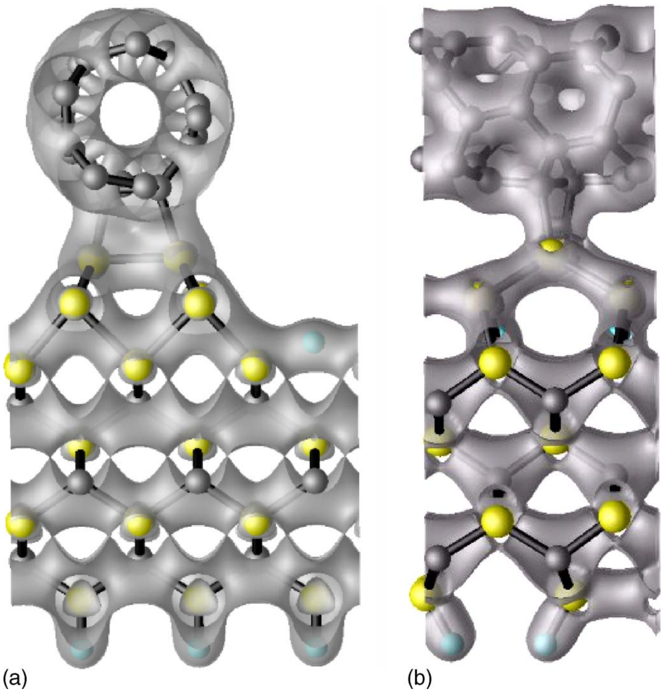

FIG. 4. (Color online) Total electronic charge distribution. (a) front view; (b) side view.

In order to study the energetics of the system we considered two models. To characterize these systems it is necessary to mention the possibility of relaxation towards convergence either of the electrons or of the atomic positions. In the first case, a rigid system (RS), we computed the energies of the SWCN plus slab and the energies separately calculated for the SWCN and for the slab. In this case we have calcu-

TABLE I. A comparison between the binding energies (E_b) of models.

Total energy model	A (eV) SWCN	B (eV) slab	C (eV) SWCN+slab	$C-(A+B)$ E_b (eV)	$C-(A+B)$ E_b (eV/Å)	$C-(A+B)$ E_b (eV/bond)
Rigid systems	−4330.55	−6149.61	−10484.30	−4.14	−0.65	−2.07
Relaxed systems	−4331.57	−6150.00	−10484.30	−2.73	−0.27	−1.36

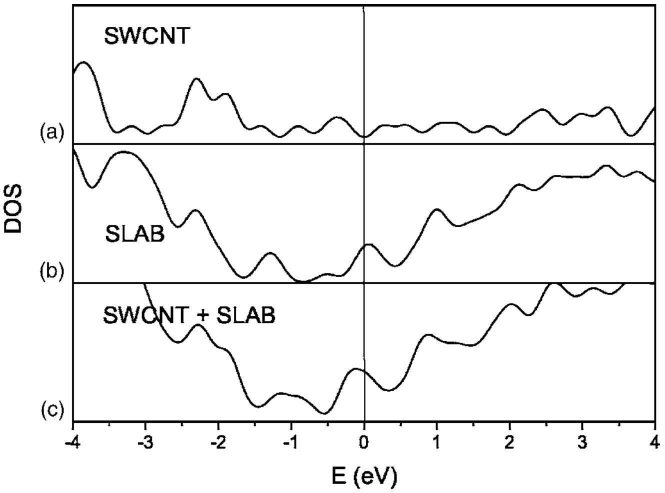

FIG. 5. Electronic density of states. (a) SWCN system; (b) slab system; (c) SWCN+slab system.

lated the binding energy as the energy associated to the SWCN+slab system minus the energies of the SWCN and slab separated and completely unrelaxed, i.e., the separated systems with the same atomic positions and electronic distribution. The second case is a completely relaxed system (XS). In this model we calculated the binding energy as the energy of the SWCN+slab minus the energy of the SWCN and slab, separately considered and relaxed both electronically and also concerning the atomic positions. Table I shows the total and binding energies for each model. The binding energy of the RS model is −0.65 eV/Å, the lowest one. The XS model has a binding energy of −0.27 eV/Å, this larger difference of 0.38 eV/Å being due to the energy involved in the relaxation of the positions of the atoms in the separated systems. The binding energies of our XS model is −0.07 eV/Å less than the value found by Orellana *et al.*[32] for the mentioned system, i.e., −0.21 eV/Å.

The electronic density of states (DOS) have also been separately calculated for the SWCN, slab, and SWCN+slab. The Fermi level (E_F), i.e., the highest occupied state, has been chosen as the origin of energy. The DOS for the SWCN is presented in Fig. 5(a). As can be seen, the tube is metallic as would be expected for a chiral (4,1) nanotube. Figure 5(b) presents the DOS for the slab. The slab is also metallic. This confirms a more detailed discussion about the hydrogenated SiC(100) system of previous works.[14,16,17] In the paper by Brito *et al.*,[14] three systems were considered: (i) the clean SiC(100) surface; (ii) the clean surface partially hydrogenated, with H atoms bonded to the Si atoms of the top layer; (iii) the saturated phase, i.e., besides the H atoms of the previous phase, additional ones bonded to the Si atoms of the third layer. In that paper the partially hydrogenated phase is a nonconducting one. Additional amounts of H atoms, bonded to the Si atoms of the third layer, led to a conducting phase. This has led those authors to associate conduction to the bonding of H atoms to the third Si atoms layer. In the present calculation this conclusion is corroborated by observing that hydrogen atoms bonded to the third layer Si atoms leads to the presence of states in the Fermi level [see Fig. 5(b)]. The DOS for SWCN+slab system can be seen in Fig. 5(c). We observe that the presence of the SWCN increases the numbers of states at the Fermi level, enhancing the metallic character of the surface. The creation of a new channel for conduction, as a result of the SWCN deposition, is apparently reasonable to assume.

IV. CONCLUSIONS

In this work we have been able to theoretically show the possibility of a covalent bonding between a nanotube and a surface, in contrast with previous considerations of just a van der Waals binding.[22] This possibility is apparently eased as a result of the almost exact coincidence between the nanotube length (6.40 Å) and one of the dimensions of the (3×2) cell (6.36 Å). Similarly to what occurs when additional amounts of hydrogen are deposited on a surface like the one shown in Fig. 2,[14] the nanotube deposition removes the tilting of the top dimers and enhances electrical surface conductivity of the supporting slab. Consistently with the induced metallic character of the saturated deposition of hydrogen on the SiC(100) (3×2) surface, the bonding of H atoms to the third layer of Si atoms is responsible for this induced mechanism, instead of H bonding to the Si atoms of the top layer. This can be corroborated by comparison of the present results with the ones by Brito *et al.*[14] There, the presence of hydrogen bonded to the Si atoms of the third layer enhances the metallic character of the surface, different from H atoms bonded to the Si ones of the first layer. In the present case, besides the presence of H atoms bonded to the third layer, the metallic character is also enhanced by the SWCN, as can be seen in Figs. 5(a)–5(c).

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