Functionalization of carbon nanotubes through the chemical binding of atoms and molecules

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We present a proposal for altering the electronic properties of single wall carbon nanotubes (SWNT's) through the chemical binding of atoms and molecules. This binding would be performed at Si substitutional defect sites, which would guarantee a high stability to the system. We argue that, by appropriately choosing the atom or radical bound to the Si atom, one can have a greater doping flexibility than has been achieved so far, and can, in principle, engineer transport, optical, or other properties of SWNT's. These conclusions are based on detailed first-principles calculations for a Si-X doped semiconducting (10,0) SWNT, for $X=\{$F, Cl, H, CH$_3$, and SiH$_3\}$.

I. INTRODUCTION

Carbon nanotubes[1] have attracted a lot of attention as a promising form of nanoscale material with possible applications in nanoscale devices.[2–5] In particular, the possibility of modifying their properties through doping has become a field of growing interest, both from an experimental[6–15] as well as a theoretical[16–21] point of view. One of the reasons for this interest in doping is the possibility of altering the transport or optical properties of the nanotubes, which is usually a necessity in device engineering. If one considers semiconducting nanotubes, the natural way to introduce either acceptor or donor levels would be through substitutional boron or nitrogen doping, respectively. However, it could be useful to have other options. Here we suggest that complexes formed from a Si substitutional atom plus another atom or molecule chemically bonded to it can be used to alter, with greater flexibility, the transport properties of semiconducting nanotubes. We show that all these systems introduce a half filled level close to the top of the nanotube's valence band. Moreover, the specific position of this level in the gap depends on which species is bonded to the Si atom. Therefore one can now modify the transport properties of nanotubes not only by changing the concentration of dopants, as could be done in the case of N and B doping, but also by choosing which species is attached to the Si atom.

The main criticism that can be raised about our proposal is the difficulty, in principle, of doping a nanotube with Si, given that it would prefer an sp^3 rather than an sp^2 hybridization. In fact, we have studied such doping in a previous paper,[19] and we have shown that its formation energy is somewhat high,[22] of the order of 3.1 eV. However, there is by now vast experimental evidence[23–27] about the possibility of substitutional doping of fullerenes by Si atoms, which indicates that it should also be possible to similarly dope nanotubes with Si. Moreover, different routes can be used to incorporate the Si atom, or the Si-X complex (e.g., radially deforming the nanotubes[20]). Once inserted, this defect should be quite stable, and could then be used as the trapping site for the chemisorption of other atoms or molecules. Finally, it

might be easier to insert the Si-X complex at once, using appropriate chemical routes.

We have previously[19] presented predictions about the electronic and structural properties of silicon-doped carbon nanotubes. In particular, for a semiconducting (10,0) SWNT's it was demonstrated that Si substitutional doping introduces an empty level in the gap at approximately 0.2 eV below the bottom of the conduction band. The presence of this empty level is intimately related to the structural relaxation that happens around the Si atom.[28] As the Si substitutional atom has now a more sp^3-like character, we suggested[19] that the silicon impurity could be used as an effective center to capture other atoms or molecules, since in this way the Si atom would be fourfold coordinated.

Therefore we present a study of the interaction of this site with atoms and molecules that have different binding energies to the Si atom in order to establish general trends. In particular, we will present results for F, Cl, H, CH$_3$, and SiH$_3$.

II. METHOD

The calculations are similar to what was done before for Si on SWNT's.[19] They are based on first-principles density-functional theory calculations[29] using numerical orbitals as basis sets. We have used the SIESTA code,[30] which performs a fully self-consistent calculation solving the standard Kohn-Sham equations. For the exchange and correlation term we use the local-density approximation with the parametrization of Perdew and Zunger.[31] In all calculations we have used a split-valence double-zeta basis set with polarization function.[32] Standard norm-conserving Troullier-Martins pseudopotentials[33] are used. A cutoff of 120 Ry for the grid integration was utilized to represent the charge density. Our calculations were all performed using a (10,0) semiconductor SWNT (diameter of 8.14 Å). We use periodic-boundary conditions and a supercell approximation with lateral separation of 18 Å between tube centers to make sure that they do not interact with each other. The supercell had 120 atoms for both the doped and undoped nanotubes, which results in the

value of 12.78 Å for the distance between a Si atom and its image in the next supercell. We have used three Monkhorst-Pack **k** points for the Brillouin-zone integration along the tube axis, and the structural optimizations were performed using the conjugate gradient algorithm until the residual Hellmann-Feynman forces were smaller than 0.05 eV/Å.

III. RESULTS AND DISCUSSION

For all the systems considered the final relaxed structures are rather similar. They all present an outward local structural distortion along the radial direction ("bump"), a feature that was already observed in the Si-only doped tube.[19] This bump is clearly related to two factors: (i) a tendency of Si to have an sp^3 hybridization; and (ii) the larger Si-C bond when compared to the C-C bond. The bump in the Si-only doping was equal to 0.78 Å. For all the systems considered this number increased to values between 0.84 and 1.03 Å, except for SiH_3, where it decreased to 0.65 Å. The angle between X-Si-C, where X is any one of the atoms or molecules considered, is always between 114° and 117°, whereas the angle between C-Si-C is always between 100° and 103°. The Si-C distances are all between 1.7 and 1.8 Å, a feature already observed for the Si-only doping.[19] Finally, the Si-X distances are all very similar to what is obtained in organosilicon compounds,[34] with deviations between 1% and 3%.

In Fig. 1 we present the band structures around the nanotube energy gap for the pure Si doping system [Fig. 1(a)] and all the Si-X systems considered [Figs. 1(b)–(f)]. As mentioned above, once a Si atom has been inserted into the tube network, it is expected that it will be highly reactive because: (i) it prefers a tetra-coordinated configuration (sp^3 hybridization); (ii) studies of organic silicon compounds indicate[35] that Si usually forms stronger bonds than C with other elements. We indeed obtain that all the species considered are strongly bonded to the Si site (our estimated *ab initio* binding energies give values larger than 3.5 eV for all bonds). As can be seen comparing Fig. 1(a) with Figs. 1(b)–(f), a consequence of the formation of these strong bonds is the disappearance of the empty level above midgap, for all cases considered.

In order to better understand this universal behavior, let us consider a simple three level model, where we have: (i) a pure nanotube orbital, called $|T\rangle$, which corresponds to a situation where we (theoretically) removed one p_z orbital (for an sp^2 carbon atom, we call the p orbital perpendicular to the three sp^2 hybrid orbitals a p_z orbital) from the system. Both a simple tight-binding calculation and an *ab initio* calculation where we removed a C atom from the (10,0) nanotube (with the three σ bonds that were created saturated with H atoms) show that this $|T\rangle$ orbital is positioned close to the middle of the gap; (ii) the Si atom sp^3-like orbital, which we call $|Si\rangle$; (iii) the ligand X orbital, called $|X\rangle$. When we have simply the Si-doped nanotube, the somewhat weak π-like interaction, between the $|T\rangle$ and the $|Si\rangle$ orbitals result in the above midgap level shown in Fig. 1(a). However, with the X
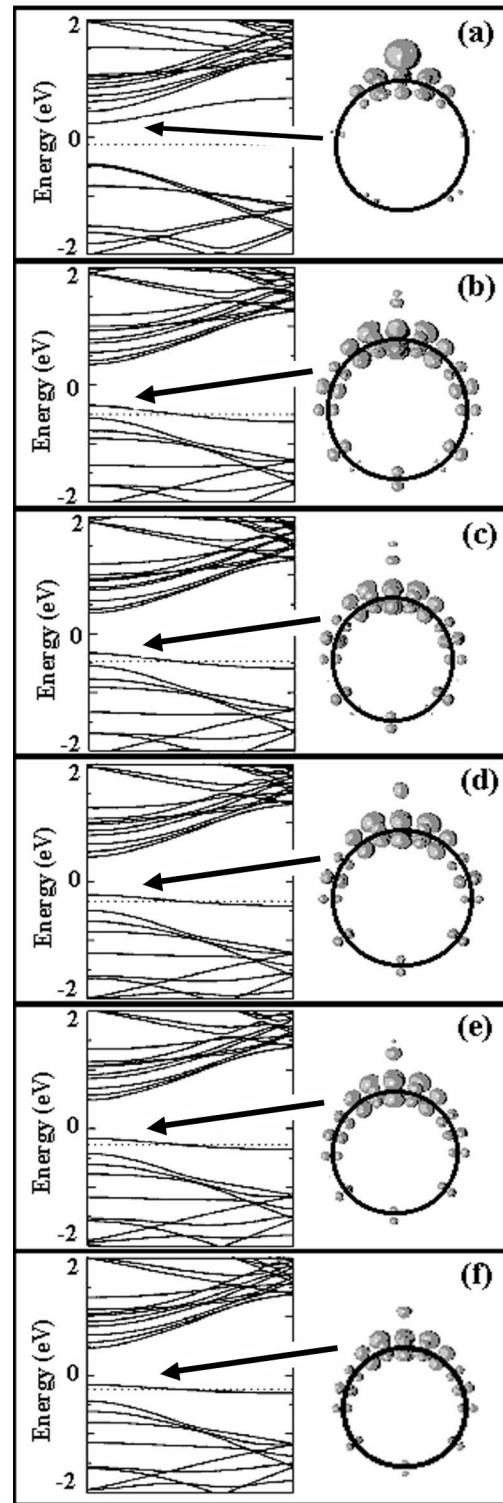

FIG. 1. Band structures (from the Γ to the π/a point) around the band gap, and electronic-charge densities for the half filled levels close to the top of the valence band for all the systems (nanotube $+Si+X$), except in the case of a (nanotube$+Si$), where the charge density is for the orbital at $\simeq 0.6$ eV above the top of the valence band. (a) nanotube$+Si$; (b) $X=F$; (c) $X=Cl$; (d) $X=H$; (e) $X=CH_3$; (f) $X=SiH_3$. The circles are guides to the eye.
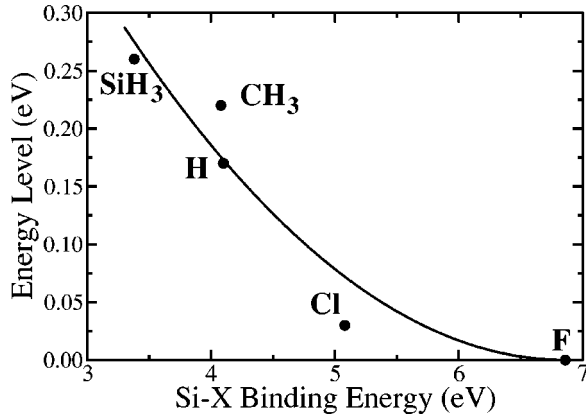
FIG. 2. Position of the half filled level in the band gap, relative to the top of the valence band. The dots are the calculated values as a function of the experimental Si-X binding energies for Me$_3$Si-X molecules, where Me is a methyl group and $X = \{$F, Cl, H, CH$_3$, and SiH$_3\}$. The curve is a fitting to the data points, and corresponds to the equation $y = 0.0227(x - 6.86)^2$, where x is the Si-X binding energy and y the level position, both in eV.

atom or molecule present, the Si atom forms a much stronger bond with the ligand X (a σ-like bond), resulting in a bonding ($|B\rangle$) level and an antibonding ($|A\rangle$) level, which will be resonant in the valence and conduction bands, respectively. The resulting bonding $|B\rangle$ level will couple very weakly to the tube $|T\rangle$ orbital. Therefore the final situation can be viewed as a coupling between the tube level $|T\rangle$ and the antibonding level $|A\rangle$, resulting in the appearance of a half filled level ($|L\rangle$) in the gap, somewhere between midgap and the top of the valence band.

As expected from the above argument, the character of this level is basically the same, independently of what atom or molecule is bound to the Si site. Plots of charge density for all the systems considered (see Fig. 1) show that they have a strong tube character, being somewhat delocalized but with the stronger weight on the C atoms nearby the Si atom. If we write for the $|A\rangle$ level $|A\rangle = a|\text{Si}\rangle - b|X\rangle$ (a, $b > 0$), one can show that the position of the level $|L\rangle$ depends on a^2 approximately as $\varepsilon_L = \varepsilon_T - (\beta_{TSi}^2 a^2)/(\varepsilon_A - \varepsilon_T)$, where ε_S is the level position for the state $|S\rangle$, for $S = A$, T, or L, and β_{TSi} is the effective coupling between $|T\rangle$ and $|\text{Si}\rangle$. For a stronger bond between the ligand X and the Si atom, the weight of the $|\text{Si}\rangle$ orbital in the antibonding $|A\rangle$ state is larger, i.e., the a coefficient defined above is larger. As a consequence, the ε_L level will be closer to the top of the valence band. On the other hand, for a weaker bond between X and Si we expect the half filled gap level to move away from the top of the valence band, closer to midgap.

Hence, based on the above argument, we expect the interesting feature for the Si-X doping that, even though the overall characteristics are the same for all the systems considered, the specific position of the level $|L\rangle$ depends on which atom or molecule is bound to the Si atom. In Fig. 2 we show the position of this level relative to the top of the valence band,

as obtained in our *ab initio* calculations,[36] as a function of the experimental binding energies[38] between X and the Si atom for the molecules of the type Me$_3$Si-X, where Me is a methyl group. As can be seen, the higher the binding energy, the closer the level is to the top of the valence band, which is in accord with our previous argument. In this way, one can design the system of interest by picking the appropriate group to bind to the Si sites.

Therefore the picture that we propose for the electronic structure of atoms and molecules bound to a Si substitutional site in SWNT's is the following: (i) if we have the Si-only doping, due to the relaxation of the Si atom, there is the appearance of an empty state "close" to the bottom of the conduction band; (ii) upon chemisorption of an atom or radical to the Si site, there is the formation of a strong bond between the Si and the chemisorbed species, with the formation of bonding and antibonding states, which will be resonating in the valence and conduction bands, respectively; (iii) this leaves in the gap the tube level $|T\rangle$, which will couple mostly to the antibonding level $|A\rangle$. As a consequence there is the presence of a half filled level in the gap, with a strong nanotube character. Even though the general features of this level are independent of the ligand X, its specific position depends on the binding energy between Si and X.

IV. CONCLUSIONS

In conclusion, we present a theoretical suggestion for controlled doping of SWNT's through a system formed by Si substitutional atoms bound to other atoms or molecules. The greatest experimental difficulty is probably the insertion of Si atoms in the SWNT. However, both the previous experimental results about Si doping in fullerenes,[23–27] plus the vast knowledge on organic silicon compounds,[34,35,38] give us great confidence that this problem is perfectly surmountable. Once the Si atom is inserted in the SWNT, the binding of other elements to it will be very strong. This is a very nice property, since most atoms and molecules that have recently been shown to alter the electronic properties of SWNT's (e.g., O$_2$) adsorb weakly on tubes. It is important to stress the fact that, even though we are here presenting a scenario for a larger flexibility of doping when compared to B atoms, the actual possibilities are far reaching. For example, one can think about control of optical properties, quantum dots engineering by alternating the Si-X complex along the nanotube,[21] or tube-tube interactions through Si-X-Si bridges.

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