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Atomic and Electronic Structures of Carbon Nanotubes on Si(001) Stepped Surfaces

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We report first-principles total-energy calculations that provide energetics and electronic structures of adsorbed carbon nanotubes (CNTs) on stepped Si(001) surfaces. We find that adsorption energies strongly depend on the directions of CNTs, and that there are several metastable adsorption sites both on terraces and near step edges. We also find that the electronic structure of adsorbed metallic CNTs becomes semiconducting or remains metallic, depending on the adsorption site. Charge redistribution upon adsorption is prominent mainly at the CNT-surface interface.

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Carbon nanotubes (CNTs) [1], consisting of graphite layers rolled up to seamless, nanometer-wide cylinders, emerged as one of the most promising materials for future electronics applications. Some practical applications have already been demonstrated [2], albeit not at a mass production scale. On the other hand, the current electronics industry benefits from huge expertise on Si technology, which will certainly be inherited in the future. The inclusion of CNTs in nanoelectronics devices therefore requires integration with Si substrates, gates, and contacts. The electronic properties of such hybrid structures are expected to be sensitive to local chemical environments [3–6]. The atomistic understanding of the adsorption of a CNT on Si surfaces and then the resulting modification of properties is, however, largely lacking.

In this Letter, we present *ab initio* total-energy electronic-structure calculations of CNTs adsorbed on Si(001) stepped surfaces. When Si(001) is slightly misoriented along the $\langle 110 \rangle$ direction with a few degrees, double-atomic-layer steps named D_B are present and almost equally separated from each other [7–9]. This offers a possibility to produce well aligned CNT arrays on a technologically important substrate. We have searched all possible adsorption sites of a CNT on stepped Si(001) for the first time. We find that adsorption energy exhibits strong site and direction dependence. For a metallic (5, 5) CNT, adsorption on a terrace in perpendicular direction to the Si dimer row is found to be energetically most favorable. The D_B step edge also provides a metastable adsorption site. The bonds formed between a CNT and the surface show covalent character, resulting in highly rehybridized electron states. Calculated energy bands show that metallic CNTs become nonmetallic due to the insertion of sp^3 bonded atoms in a sp^2 bond network.

Density functional theory (DFT) structure optimization and electronic-structure calculations are performed in supercell technique, where the surface is simulated by periodic slabs. Exchange correlation is treated at the local density approximation level [10]. Interaction between valence electrons and the atomic core is handled by the norm-conserving Troullier-Martins pseudopotentials [11] that have been used to study similar systems successfully [12,13]. Wave functions are expanded into the plane-wave basis set with a 40 Ry energy cutoff. We find the use of the plane-wave basis set necessary since they provide unbiased basis functions, which could be crucial in adsorption studies. Prior to full structure relaxation, the energy landscape is explored by rigidly moving the nanotube on the surface and then rotating around its axis until all possibilities are exhausted.

We use 2 × 4 lateral periodicity to study the adsorption of a (5, 5) CNT on terraces of Si(001). For the CNT adsorption near D_B step edges, we use a (1, 1, 11) vicinal surface where adjacent step edges are separated from each other by ≈21 Å. The two-dimensional Brillouin zone is sampled by up to 8 special k points. The surface geometry in our study consists of 5 Si monolayers, and the bottom layer of the slab is terminated by a monolayer of H atoms. The bottommost Si layer and terminating H atoms are fixed during structure optimizations. The positions of other atoms are relaxed until all force components are less than 5 m Ry/bohr. Our unit cell contains 60 C atoms in a (5, 5) nanotube, corresponding to 3 times the primitive unit cell. The energy values given throughout the text are for 1 unit cell. The total number of atoms in the unit cell is 116–140. The commensurability condition is applied by stretching the carbon nanotube by 3% [14].

The possible adsorption sites of CNTs on Si(001) stepped surfaces, considered in this study, are depicted in Fig. 1. Adsorption sites A–D are terrace adsorption sites and could be grouped into two, based on the adsorption direction, namely, perpendicular (A and C) or parallel (B and D) to the dimer rows. The nanotube axis at site A lies in between dimers, while at site C it lies on top of the dimers. In the case of the adsorption parallel to the dimer rows, the CNT could adsorb on the trench of the surface, site B, or on top of the dimer rows, site D. The adsorption at step edges possess also 2 metastable adsorption sites with unequal stability that could be distinguished by the existence or lack of covalent bonding with the lower terrace atoms. All adsorption sites depicted in Fig. 1 are at least metastable configurations, but we will focus our electronic-structure

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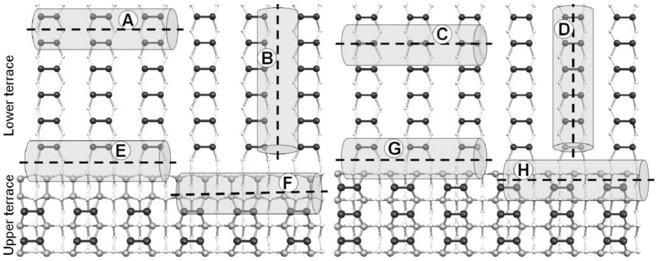

FIG. 1. Adsorption sites of carbon nanotubes on Si(001) stepped surfaces. The Si dimers formed as the reconstruction of the surface are highlighted by dark shading. The left panel contains a rebonded D_B edge, and the right panel an unrebonded D_B edge. The positions of the nanotube are depicted by transparent cylinders, and the tube axes are indicated by dashed lines. Adsorption sites are labeled by the capital letters referred throughout the text.

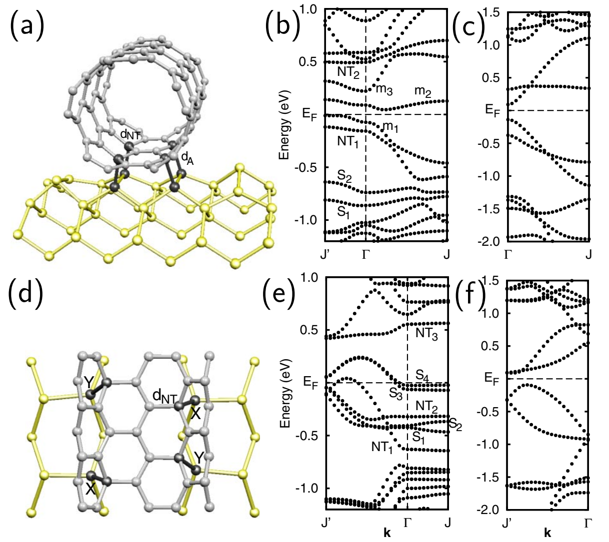

FIG. 2 (color online). The atomic and electronic structure of the (5, 5) CNT adsorbed on the terraces of Si(001). (a) The relaxed structure and (b) the band structure of the CNT adsorbed on Si(001) at site A, which compares with (c) the band structure of 4 H atoms bonding to the side wall of the nanotube. (d) The atomic geometry (top view) and (e) the band structure of the CNT adsorbed at site B, which is energetically less stable than site A. (f) The band structure of the (5, 5) CNT bonded with 4 H atoms. The Fermi levels E_F are shown by the horizontal dashed lines.

investigation on 4 configurations, A, B, E, and G, selected by choosing the most stable one among similar adsorption sites.

The optimum atomic structure of the (5, 5) CNT adsorbed at site A is depicted in Fig. 2(a). The Si dimer atoms capped by the nanotube displays a symmetric configuration; i.e., the heights of the dimer atoms are the same within the numerical accuracy. The CNT adsorption prevents energy gain due to the charge transfer upon the buckling of dimers. On the contrary, other Si dimers on the surface keep their asymmetric geometry. Close inspection of the total charge density reveals that 4 C-Si bonds with covalent characters are formed, which are highlighted by the dark sticks in Fig. 2(a). The bond lengths of these C-Si bonds $d_A \approx 1.97$ Å are larger than the Si-C bond length of 1.89 Å in silicon carbide. The carbon atoms that make bonds with the surface atoms, highlighted by dark balls in Fig. 2(a), are displaced outwards. The C-C bonds d_{NT} around those outward moving C atoms are extended to ≈1.5 Å.

In the band structure of the CNT adsorbed at site A, shown in Fig. 2(b), the tube axis is in the Γ to J direction. The most striking feature is the disappearance of the metallic character along the tube axis. The Fermi level (E_F) does not cross any energy bands along Γ to J, indicating a semiconducting behavior in the tube direction. The second main feature is the substantial rehybridization of the CNT and surface states. The bands labeled by m_1, m_2, and m_3 are considerably mixed CNT-surface states, while s_1 and s_2 could be assigned to the Si surface. Because of substantial rehybridization, state NT$_1$, which has a large amplitude on the CNT, fails to show a flat band line perpendicular to the tube axis, J' to Γ. The adsorption induces structural deformations on the CNT, which may cause drastic changes in the electronic structure. In order to understand the origin of the gap opening, we calculate the electronic structure of this deformed CNT, isolated by removing Si and H atoms from the optimized combined structure. Even the deformed tube shows a metallic character. Next, the effect of sp^3-type bonding is investigated by attaching 4 H atoms to the deformed nanotube at 4 carbon atomic sites that are highlighted by dark shading in Fig. 2(a). Only this explicit introduction of sp^3 bonding reproduces the gap opening, as shown in Fig. 2(c). The bands around the E_F of the isolated (5, 5) CNT are π bands, and the introduction of sp^3 bonded atoms into the π electron network results in the gap opening and the flattening of the π bands.

We define the adsorption energy of a CNT on Si surface as the energy difference between the total energy of the combined system and the summation of the total energies of an isolated CNT and a clean surface in the same simulation box, calculated with the same parameters. Note that the surface resumes asymmetric dimer geometry in our reference relaxed structure. Positive adsorption energies indicate that adsorption is favorable starting from the reference structures. Adsorption at site A has the highest calculated adsorption energy of 2.77 eV. The least favorable adsorption site, C, has almost zero adsorption energy, and the adsorption energies for the other less favorable adsorption sites, D, F, and H, are 0.89, 0.6, and 1.0 eV, respectively.

The second most favorable adsorption site on the terrace is on the surface trench, which has 1.76 eV adsorption energy. The relaxed atomic structure of the CNT adsorbed on the trench is depicted in Fig. 2(d). The C-Si bond lengths are ≈ 2.0–2.05 Å, and the C-C bond lengths d_{NT}

around 4-coordinated C atoms are expanded to 1.51 Å. The interface positions X and Y shown in Fig. 2(d) are distinguishable: The Si dimer bond at Y is tilted with respect to the $\langle 110 \rangle$ direction and thus the C-Si bonds are stretched. We have found that the Si dimers under the CNT are almost symmetric due to the formation of 4 C-Si bonds, which contradicts the previous DFT calculations employing a localized-orbital basis set [4]. We provisionally ascribe this discrepancy to the difference in the completeness of the basis set. Because of the strained bonds at the interface, the adsorption energy is ≈ 1 eV less than at site A.

The band structure of the CNT adsorbed on the surface trench, site B, is shown in Fig. 2(e). Since the CNT is rotated by 90° with respect to the surface, the tube axis is in the direction J' to Γ. It is possible to assign energy bands near the E_F to either the CNT or the surface based on wave function analysis, in spite of the sizable mixing of nanotube and surface states. States S_1, S_2, S_3, and S_4 are localized on Si dimers and have the character of remaining dangling bonds on the Si surface. The bands labeled NT_1, NT_2, and NT_3 are mainly localized on the CNT, and they show no dispersion in the direction Γ to J, which is perpendicular to the tube axis and also to the dimer rows. As is analyzed in the case of site A, the energy bands of the distorted CNT bonded with 4 H atoms [Fig. 2(f)] are useful to interpret the energy bands for site B. The Fermi level E_F crosses CNT bands, indicating metallic behavior along the tube axis, in sharp contrast with the adsorption at site A. The insertion of sp^3 bonding in the π network induces a gap opening, as deduced from the band plot in Fig. 2(f). Yet, surface states S_3 and S_4, which are not occupied originally, draw electrons from the CNT band, and the CNT band becomes partially occupied. The availability of surface states accessible in the proximity of the CNT makes the adsorption on the trench different from the adsorption at site A. The surface bands near the E_F could be eliminated by the H passivation of the surface after the adsorption of the nanotube, which should result in a semiconducting behavior.

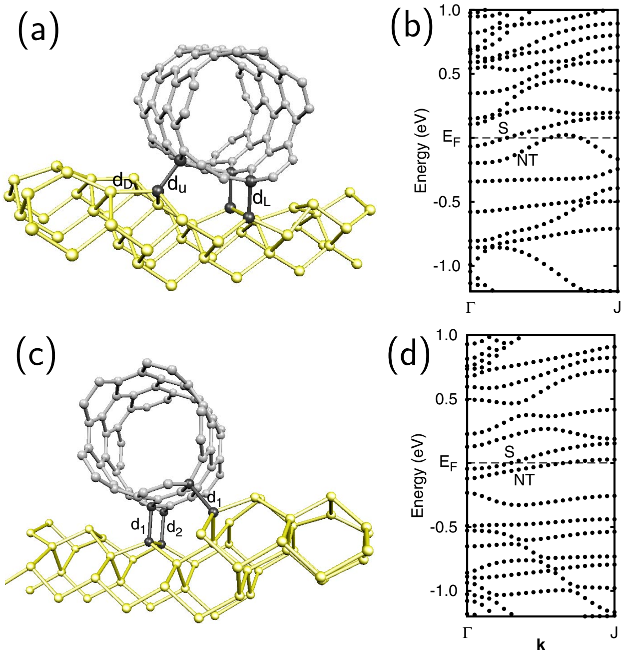

FIG. 3 (color online). The atomic structure of the (5, 5) CNT adsorbed (a) at rebonded D_B step edge, site E, and (c) at unrebonded D_B step edge, site G. The energy bands of the CNT adsorbed at the (b) rebonded and (d) unrebonded step edges are plotted around the Fermi levels E_F, shown by dashed lines.

We now discuss the adsorption of the (5, 5) CNT near D_B step edges. The CNT at the step edge forms only 3 covalent bonds with the Si surface atoms, as depicted in Figs. 3(a) and 3(c), because of geometric restrictions. The optimum adsorption geometry of the CNT at the rebonded step edge has 2 covalent bonds with the lower Si terrace atoms, and 1 with the edge atoms, although it is possible to identify weak bonds between the nanotube atoms and the other step edge atoms. As a result of these weak bonds, not shown in Fig. 3(a), all dangling bonds at the step edge are more or less terminated, and the dimers at the rebonded step edge are in a symmetric configuration in contrast to the clean rebonded D_B step. The C-Si bond $d_u \approx 1.99$ Å is slightly longer than the bonds with terrace atoms $d_L \approx 1.96$ Å, and the bond length of rebonding dimer at the edge d_D is ≈ 2.5 Å. The C-Si bond lengths of the CNT adsorbed at the unrebonded edge, depicted in Fig. 3(c), $d_1 \approx 1.99$ Å and $d_2 \approx 1.96$ Å are also in the same range. The calculated adsorption energy for the rebonded edge ≈ 1.88 eV is slightly higher than the corresponding value for the unrebonded edge ≈ 1.76 eV. In spite of the fact that the number of covalent bonds formed with the surface is smaller, the additional weak extended bonds with the

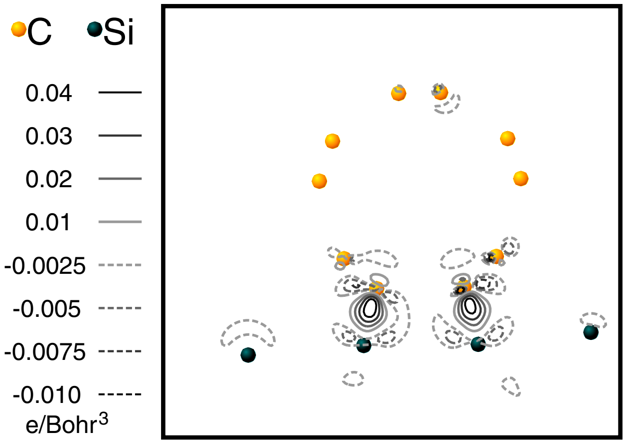

FIG. 4 (color online). Charge redistribution upon the (5, 5) CNT adsorption on site A is depicted as a contour plot of the density $\rho_{\mathrm{NT+Si}} - \rho_{\mathrm{NT}} - \rho_{\mathrm{Si}}$ on the plane perpendicular to the tube axis. C-Si bonds are almost contained in the plane. Atoms within 0.5 Å to the plane are indicated by small balls. Positive and negative densities are shown by solid and dashed lines, respectively. The scale used in the contour plot is displayed on the left.

edge atoms make the adsorption energy as large as, or even larger than, that for the terrace trench, site B. The band structures of the CNTs adsorbed at step edges calculated along the tube direction, Γ to J, are shown in Figs. 3(b) and 3(d). The E_F crosses both a nanotube and a surface band, labeled NT and S, respectively. The electrical conduction along the nanotube should preserve the metallic character of an isolated nanotube.

The charge redistribution upon CNT adsorption at site A is illustrated as a contour plot of the electron density difference of the combined system from the superposition of electron densities of the isolated CNT and the surface $\rho_{\mathrm{NT+Si}} - \rho_{\mathrm{NT}} - \rho_{\mathrm{Si}}$ in Fig. 4. The biggest change upon the adsorption of the CNT on the Si surface happens around C-Si bonds. Electrons are accumulated in the interface region, assisting in forming the C-Si bonds. Contour plots for other adsorption sites, not shown here, exhibit the same general features with negligible charge transfer. Only at site B does sizable charge transfer from the CNT to the surface take place, as is deduced from the energy bands [Fig. 2(e)]. Our finding of charge accumulation mostly in the bond region leads to a doubt about the accuracy of previously reported charge transfer values [4] calculated by the Mullikan population analysis.

Experiments suggest that CNTs may stick more to clean surfaces [15] than to H-terminated surfaces [16]. Based on our exploration of the energy landscape, the translation of a nanotube along its axis requires only small energy barriers (0.05–0.25 eV) except for site A. During the translation, the energy loss due to the weakening of some C-Si bonds is compensated by the strengthening of other C-Si bonds. But, all C-Si bonds at site A are equally affected from such a translation, resulting in the energy barrier of $\approx$0.6 eV. Comparing the relative total energy of different adsorption sites with parallel tube direction, we conclude that moving the (5, 5) CNT perpendicular to the tube axis requires energy barriers higher than 1 eV per $\approx$7.68 Å tube length, corresponding to ≈ 0.13 eV/Å. It is not likely to move a nanotube in a single step since the energy barrier is proportional to tube length. However, a CNT could be moved to the next stable adsorption position in multiple steps. Such a mechanical manipulation may be the combination of the translation and rotation of tube segments and could induce additional stretching and twisting strain energy on the CNT.

The CNT used in this study has a relatively small diameter for computational reasons. The adsorption energies of moderate diameter CNTs should be proportional to the number of C-Si bonds allowed by geometrical constraints. Smaller curvature in larger diameter CNTs should reduce the energy gain per C-Si bond while bigger number of bonds are made. The adsorption at the step edge could become more favorable than the adsorption on terrace in moderate diameter ranges once the bonding with the upper terrace becomes effective. In the case, ordered alignments of CNTs at D_B step edges may be self-organized. The silicon atoms that offer new bonds have desirable separation in the direction perpendicular rather than parallel to the dimer rows, making the directional adsorption preference valid also for large diameter armchair tubes.

In summary, our DFT calculations have unequivocally determined stable atomic geometries and corresponding electronic structures for the adsorption of (5, 5) armchair carbon nanotubes on Si(001) stepped surfaces. The CNT adsorption perpendicular to the dimer rows is energetically favorable compared with the adsorption parallel to the dimer rows. Silicon D_B step edges also provide metastable adsorption sites, opening the possibility of self-organized alignments of CNTs. An adsorbed metallic CNT becomes semiconducting or remains metallic, depending on the adsorption site.

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