

Selective Alignment of Carbon Nanotubes on Sapphire Surfaces: Bond Formation between Nanotubes and Substrates

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We present our first-principles total-energy calculations performed for carbon nanotubes (CNTs) on sapphire substrates. We find that the formation of covalent and partly ionic bonds between Al and C atoms on the Al-rich surfaces causes the selective alignment of CNTs, this being the principal reason for the CNT growth along particular crystallographic directions. We also find that the van der Waals interaction which is important on the stoichiometric surfaces produces no directional preference. The characteristic features in the electron states of the CNT on the substrate are clarified.

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Nanometer-scale devices using single-walled carbon nanotubes (CNTs) are expected to be boosters in postscaling semiconductor technology that is challenged by the physical limitations of its cutting edge miniaturization [1]. In order to utilize the fascinating properties of CNTs [2,3] for devices, however, it is imperative to align them on substrate surfaces in controlled ways, which has not been achieved yet in spite of a lot of effort [4–6].

Chemical vapor deposition (CVD) on sapphire surfaces provides a promising stage: It is found that ultralong CNTs are produced along particular directions on the *A* ($11\bar{2}0$) and *R* ($1\bar{1}02$) crystallographic planes [7–13]. Furthermore, it is reported that the chirality of the grown CNTs is almost controlled by choosing the surface orientation; i.e., zigzag-like CNTs are mainly observed on the *A* plane while armchairlike CNTs on the *R* plane [10].

The interaction between the CNT and the substrate plays an essential role in such selective growth of CNT on sapphire. However, the nature of the interaction is still unclear. Strong chemical interaction [8,12] or van der Waals (vdW) interaction [9–11] is proposed to be responsible for the selective growth of CNTs based on speculative analyses or an empirical simulation [11]: In the latter, the Lenard-Jones potential is used to calculate the interaction energy but no clear directional preference is observed. Furthermore, the CNT-substrate interaction is expected to modify the electronic structures of the CNTs [14], thus being decisive in characteristics of the nanodevices. At this stage, reliable first-principle calculations that reveal the nature of the CNT-interface interaction, the mechanism of the selective growth, and then the interplay between the atomic structures and the electron states are highly demanded.

In this Letter, we explore stable and metastable atomic structures of CNTs on the *A* and *R* planes and calculate the total energy difference, using the density functional theory. On the stoichiometric surfaces, we find that the vdW interaction is dominant between the CNTs and the substrates and causes no directional preference. On the Al-rich surfaces which are also stable from our recent calculations

[15], on the other hand, we find that strong chemical bonds are formed between C and Al atoms and the calculated interaction energy shows strong directional dependence, unequivocally clarifying the origin of the observed selective CNT growth in terms of energetics. The calculated energy bands in the most stable arrangements of the CNTs on sapphire show substantial modification of the corresponding energy bands of isolated CNTs, elucidating the importance of the CNT-substrate interaction.

Calculations are performed using the VASP code [16] which incorporates projector-augmented wave [17] and local-density approximation (LDA) [18] for the exchange-correlation energy. The surface is simulated by a repeated slab model [19]. We use the 30 Ry cutoff energy for the plane-wave basis and *k*-point meshes with a size of $\sim 1/(20 \times 20 \text{ \AA}^2)$ in surface Brillouin zones, which produce well-converged results [15]. We choose armchair (9,9) and zigzag (10,0) CNTs for the *R* and *A* plane, respectively, in accord with experimentally observed chirality [10]. The structural global minimum is searched through two stages. First, we introduce a grid on the surface unit cell with the grid spacing of $\sim 0.5 \text{ \AA}$ and then place a CNT at each grid point and perform the structural relaxation by fixing the shape of the CNT. Next, from the obtained energy surface as a function of the CNT position, probable structures are fully relaxed, including the deformation of the CNT, until the remaining force on each atom is less than $0.02 \text{ eV/\AA}$.

We begin with a description of the sapphire surfaces. For the *R* plane, there are five distinctive ways of surface termination and the most stable surface is the stoichiometric surface [15]. The next most stable is the Al-rich surface labeled Al-II in Ref. [15] with its surface energy higher than that of the stoichiometric surface by $37 \text{ meV/\AA}^2$ in Al-rich condition. As shown in Fig. 1, both the stoichiometric and the Al-rich surfaces have zigzag chains along $[\bar{1}101]$, along which the CNT grows preferentially: The zigzag chain consists of the top-layer O (Al) and the

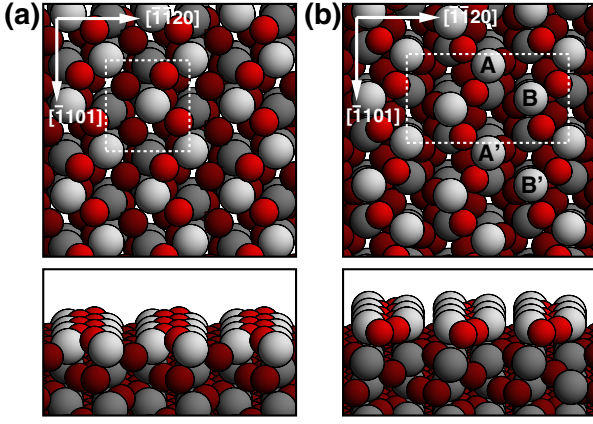


FIG. 1 (color online). Atomic structures of the *R*-plane sapphire surfaces: (a) the stoichiometric and (b) the Al-rich (Al-II) surface. In (b), each Al and O layer is added to (a) instead of removing the outermost layer from (a). The dashed rectangles indicate the surface unit cell. Large and small balls represent Al and O atoms, respectively. The outermost atoms toward the surface are colored brighter.

second-layer Al (O) atoms in the stoichiometric (Al-rich) surfaces. Pairing of Al atoms, indicated by A and B or A' and B' in Fig. 1(b), takes place on the Al-rich surface. As for the A plane, there are also five distinctive ways of surface termination and the most stable surface is the stoichiometric surface [15]. The next most stable is the Al-rich surface labeled O-II at this time with its surface energy higher than that of the stoichiometric surface by $16 \text{ meV}/\text{\AA}^2$ in the Al-rich condition. Being similar to the *R* plane, one-dimensional (1D) troughs and hills run parallel along the $[\bar{1}\bar{1}00]$ direction, i.e., the growth direction on the A plane.

We have explored the most stable configuration for a (9,9) CNT along both the $[\bar{1}\bar{1}01]$ direction and its perpendicular direction, in order to see whether the CNT along the growth direction is energetically preferred. Figures 2(a) and 2(b) display the thus obtained most stable structures of the CNT along the two directions on the stoichiometric surface. For the $[\bar{1}\bar{1}01]$ direction, the CNT is located above the trough between Al-O chains. The shape of the CNT rarely changes, inferring a weak interaction between the CNT and the substrate. The minimum distances from C atoms to Al and O atoms are 3.20 and 3.11 Å, respectively, which are much larger than the Al-C distances in Al carbides, 1.90–2.21 Å [20]. The contour plot of the electron localization function (ELF) [21] in Fig. 3(a) shows no electron accumulation between C and Al, indicating no sign of a chemical bond between the CNT and the substrate. The stable structure for the $[\bar{1}\bar{1}20]$, i.e., the perpendicular direction, shows the similar features to those for the $[\bar{1}\bar{1}01]$. The calculated interaction energy E_I , the energy gained by the adsorption of a CNT on a surface, is 0.19 eV per CNT unit for both the directions (Table I). This negligible difference in E_I between the two directions is unable

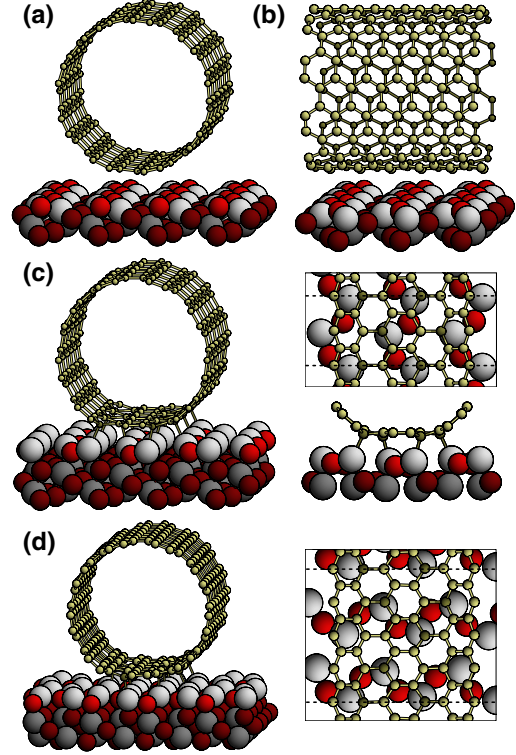


FIG. 2 (color online). Stable structures of a (9,9) CNT along (a) $[\bar{1}\bar{1}01]$ and (b) $[\bar{1}\bar{1}20]$ directions on the stoichiometric surface, and along (c) $[\bar{1}\bar{1}01]$ and (d) $[\bar{1}\bar{1}20]$ directions on the Al-II surface of the *R* plane. Dashed lines in the top views of (c) and (d) indicate the boundaries of the supercells, which contain two and four CNT units, respectively. Large, medium-sized, and small balls represent Al, O, and C atoms, respectively. In the enlarged views of (c) and (d), darker balls indicate the C atoms that make bonds with Al atoms.

to explain the observed selective growth along the $[\bar{1}\bar{1}01]$ direction.

The small directional difference of E_I drives us to consider the contribution of the vdW interaction to the energetics. However, since the present LDA does not describe

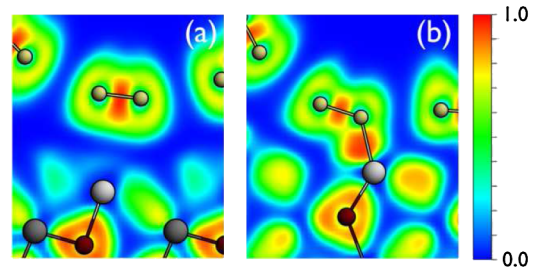


FIG. 3 (color online). Contour plots (on the plane perpendicular to the CNT axes) of the ELF of the stable CNT along the $[\bar{1}\bar{1}01]$ direction on (a) the stoichiometric surface and (b) the Al-II surface of the *R* plane. Large, medium-sized, and small balls represent Al, O, and C atoms, respectively. The CNT is in the upper and the substrate in the lower.

TABLE I. Interaction energy E_I for the (9,9) CNT on the R plane and the (10,0) CNT on the A plane of the sapphire surface. For each plane, two different surfaces, i.e., the stoichiometric and the Al-rich surfaces, are considered. E_I is in eV per CNT unit of the corresponding chirality.

Substrate orientation	CNT direction	E_I	
		Stoichiometric	Al rich
R plane	$[\bar{1}101]$	0.19	1.46
	$[\bar{1}\bar{1}20]$	0.19	0.71
A plane	$[\bar{1}\bar{1}00]$	0.24	0.67
	$[0001]$	0.20	0.31

the vdW interaction properly, we resort to a semiempirical method to estimate the magnitude of the vdW interaction [22]. The resulting interaction energies obtained by the generalized gradient approximation plus the semiempirical vdW energies are 0.48 and 0.51 eV per CNT unit for the $[\bar{1}101]$ and $[\bar{1}\bar{1}20]$ directions, respectively. Still the CNT laid along the $[\bar{1}101]$ direction is less stable than that along the perpendicular direction. Thus, the vdW interaction on the stoichiometric surface cannot be the origin of the observed selective growth.

It is noted that surface treatments at high temperatures are likely to induce O desorption from sapphire surfaces to form Al-rich surfaces. Besides, the dissociated H during CVD could also remove O atoms by combining them to form water molecules. Indeed the appearances of Al-rich surfaces were reported in experiments [23]. Thus, we investigate the energetics of CNTs on the Al-rich surfaces, which also have 1D features as shown in Fig. 1(b).

Figures 2(c) and 2(d) illustrate the most stable structures of CNTs along the $[\bar{1}101]$ and $[\bar{1}\bar{1}20]$ directions, respectively, on the Al-II surface of the R plane. Unlike the stoichiometric surface, the ELF shown in Fig. 3 clearly indicates the formation of covalent bonds between C and Al atoms (note the strong electron accumulation between C and Al atoms similar to Al clusters on a CNT [24]). The bond lengths between C and Al atoms are 2.02–2.14 Å and 2.05–2.20 Å for the CNT aligned along the $[\bar{1}101]$ and $[\bar{1}\bar{1}20]$ directions, respectively. All these values are in the range of the Al-C atomic distances, 1.90–2.21 Å in aluminum carbide [20]. In addition, the electron transfer takes place from the Al layers to the CNT, implying that the Al-C bonds are partially ionic. The amount of the transferred charge is $\sim 0.4e$ per Al-C bond calculated by the Bader method [25]. The bond networks around the C atoms that make bonds with Al atoms transform to pyramidal shapes, inferring sp^3 rehybridizations and thus breaking of the π bonds around the C atoms. Indeed, the C-C lengths around such C atoms increase by ~ 0.1 Å compared to those of the isolated CNT. As a result, the CNT is deformed so as to maximize the interface area between the CNT and the substrate. The three Al-O chains along the $[\bar{1}101]$ direction participate in the bonding with the CNT [refer to the side

view of Fig. 2(c)]. All the Al atoms in the central chain and half of the Al atoms in the two neighboring chains make bonds with the CNT.

The most stable structure for the $[\bar{1}\bar{1}20]$ direction shown in Fig. 2(d) is similar to that for the $[\bar{1}101]$ direction: Bond formation between Al and C atoms, flattening of the CNT near the interface, and the electron transfer from Al to C. However, the interaction energy, 0.71 eV, is nearly half of that for the $[\bar{1}101]$ direction, meaning that the CNT in the $[\bar{1}101]$ direction is energetically the most favorable. This is the origin why the CNTs on the R plane prefer to grow in the $[\bar{1}101]$ direction. The main reason for the anisotropic E_I is due to the different number of the Al-C bonds; i.e., 4 vs 3 per double CNT units for the $[\bar{1}101]$ and $[\bar{1}\bar{1}20]$ directions, respectively (refer to the top views in Fig. 2). Furthermore, since the charge transfer takes place around the Al-C bonds the electrostatic interaction also contributes to the difference in the interaction energy.

The (9,9) CNT is still metallic even after being placed on the Al-II surface of the R plane of sapphire. Figure 4 shows its calculated energy bands along with those of the CNT being attached with 4 H instead of the Al atoms of the surface, to trace the origins of the energy-band modification. The states in Fig. 4(a) contain the surface states that originated from the bonding states (filled squares) of Al atoms, A and B (or A' and B'), and the corresponding antibonding states (empty squares), in addition to the CNT-related states (filled circles and filled and empty diamonds). The CNT-related states indicated by the upper filled circles take part in the bonding with the Al atoms of the substrate. Similar to the isolated (9,9) CNT, the CNT states with π characters, indicated by filled circles and empty diamonds are responsible for the metallic property. The CNT placed along the perpendicular direction is also

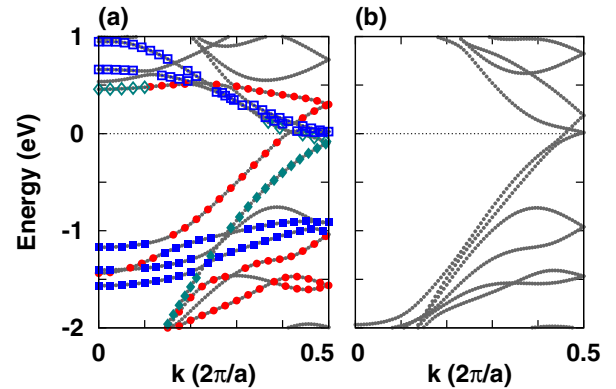


FIG. 4 (color online). Calculated energy bands for (a) the (9,9) CNT placed along $[\bar{1}101]$ on the Al-II surface of the R plane [Fig. 2(c)] and for (b) the same CNT being saturated with 4 H atoms instead of the Al atoms of the substrate. a is the lattice constant along the tube axis, i.e., twice the CNT unit. The energy references are the Fermi energies for both cases. The symbols in the energy bands in (a) indicate the characters of the corresponding bands (see text).

metallic although the detailed features are changed by the bond formation between the Al and C atoms.

We have also performed LDA calculations for the (10,0) CNT on the A plane and found that the strong interaction between the CNT and the Al-rich surface is the central reason for the selective growth of CNTs. It is found that the directional preference of the alignment of the CNT on the A plane is lacking on the stoichiometric surface (Table I). On the Al-rich (O-II) surface, however, the interaction energy is much larger with the CNT along $[1\bar{1}00]$ than that along $[0001]$ (0.67 vs 0.31 eV per CNT unit), clearly indicating that the selective growth of CNT along $[1\bar{1}00]$ is energetically favorable. The geometry-optimized structures (not shown) and the electron-density analyses reveal that formation of covalent and partly ionic bonds between the Al and C atoms is the central reason for the obtained energetics. We also find that the (10,0) SWNTs placed on the A plane are insulating as may be natural for the (10,0) CNT although the detailed band structures are modified substantially.

A couple of growth modes have been proposed for CNT growth through CVD. In the base-growth mode, growing CNTs move along the growth direction with catalytic particles fixed on the substrate [9], while in the tip-growth mode, vice versa [6]. An alternative mechanism called the raised-head-growth mode, in which catalytic particles stay above the surface during growth, is also proposed [12]. The present finding of the bond-formation between Al and C atoms favors the raised-head-growth mode since the bond-breaking and reformation processes are involved in the other two growth modes. Nonetheless, the possibility of the base- or the tip-growth modes is not excluded since the energy barrier for the bond reformation is typically much lower than the interaction energy between the substrate and CNT or the catalyst: The bond breaking could be healed by adjacent atoms simultaneously, leading to the bond reformation.

Effects of step edges on the CNT alignment are of interest. It is likely that low steps rarely affect the alignment since the energetics is determined by the Al-C bond formation on the terrace. It is indeed observed that the selective alignment is achieved or uncorrelated with the existence of monolayer steps [12,13].

In conclusion, we have performed first-principles calculations for CNTs on the R and A planes of sapphire and found that the formation of covalent and partly ionic bonds between Al and C atoms, not the vdW interaction, is the principal reason for the selective growth.

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