Alignment of Carbon Nanotubes on Sapphire Surfaces with Strong Interactions

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1. Introduction

Nanodevices using single-walled carbon nanotubes (CNTs) are regarded as one of the next-generation devices in post-Moore era that can get over the physical limitations rendered by miniaturization. To exploit the fascinating electronic structures of CNTs [1,2], they should be aligned on solid surfaces in controllable ways for fabrication of such CNT devices [3]. Growth of the CNTs with high quality requires the delicate control of the external forces such as electric field [4] and gas flow [5], or utilizes the interaction of CNTs with the stepped [6] and flat substrates [7-12]. Chemical vapor deposition (CVD) on the template-free sapphire surfaces produces well-aligned and ultralong CNTs along particular directions [8-12].

It is clear that the selective growth of CNTs on the sapphire surfaces is strongly related with the anisotropic arrangements of the substrate atoms. Regarding the interaction between the CNTs and the substrates, the van der Waals (vdW) interaction [10,11] or the strong chemical interaction [9,12] is proposed to be responsible for the selective growth of CNTs. However, the physical and chemical origins for such selective alignment of CNTs are not clarified yet. In this paper, we present our first-principles calculations [13] for single-walled CNTs on the sapphire surfaces to elucidate the nature of interactions between CNT and substrate, which gives rise to the selective alignment of CNTs.

2. Results and Discussion

Calculation Method

Calculations are performed using the Vienna ab-initio simulation package [13] which incorporates projector-augmented wave and local-density approximation for the exchange-correlation energy. The surface is simulated by a repeated slab model. We choose an armchair (9,9) and a zigzag (10,0) CNTs for R(1120) and A(1102) plane, respectively, to be consistent with experimental observations for CNT chirality [10].

Results and Discussion

We put a (9,9) CNT along both the [$\underline{1}$ 101] direction (growth direction) on the stoichiometric R plane and along its perpendicular direction to see whether the CNT along the growth direction is energetically preferred. For the [$\underline{1}$ 101] direction, the CNT is located above the trough be-

tween Al-O chains (not shown). The shape of the CNT rarely changes from its isolated state, suggesting 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. These values are much larger than the Al-C distances in Al carbides, $1.90 \sim 2.21$ Å. The equilibrium structure for the [1120] direction shows the similar features to those for the [1101] direction. The calculated interaction energies E_I , the energy gain involved in adsorption of a CNT on a surface, are almost the same, i.e., 0.19 eV/unit [14] for both the $[\underline{1}101]$ and $[\underline{11}20]$ directions. This negligible difference of E_I is inconsistent with the experiments reporting the selective growth along the [1101] direction, which should have a lower E_I than any other CNT direction. Inclusion of the vdW interaction [15] produces E_1 of 0.48 and 0.51 eV, for the [1101] and [1120] directions, which cannot still explain the anisotropic interaction.



Fig. 1 Lowest-energy structures of a (9,9) CNT on (a-b) Al-rich R-plane along [<u>1</u>101], (c-d) Al-rich R-plane along [<u>1120</u>]. Dashed lines in the top views of (b) and (d) indicate the boundaries of the super cells. Gray, red, and light-yellow balls represent Al, O, and C atoms, respectively. In the enlarged views of (b) and (d), dark-yellow balls indicate the C atoms that make bonds with Al atoms.

Surface treatments taken at high temperatures could 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. Thus, we investigate the adsorption of CNTs on the Al-rich surfaces that also have one-dimensional structures.

Figures 1 illustrates the lowest-energy structures of CNTs on the Al-rich R-plane in the [1101] and [1120] directions, respectively. Unlike the stoichiometric surfaces, the equilibrium structure suggests formation of covalent bonds between C and Al atoms. The bond lengths between C and Al atoms are $2.02 \sim 2.14$ Å and $2.05 \sim 2.20$ Å for the CNT aligned along the [1101] and [1120] directions, respectively. All these values fall within the Al-C atomic distances, $1.90 \sim 2.21$ Å in aluminum carbide. In addition, the charge transfer takes from the Al layers to the CNT, implying that the Al-C bonds is partially ionic. The amount of the transferred charge is ~0.4e per Al-C bond calculated by the Bader method. The bond networks around the C atoms that make bonds with Al atoms transform to pyramidal shapes, implying sp^3 rehybridizations and thus breaking of the π bonds around the C atoms. Indeed, the C-C bonds 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 [1101] direction participate in the bonding with CNT [Refer to the side view of Fig. 1(a)]. In the central chain, all the Al atoms are bonded to the CNT and half of the Al atoms in the two neighboring chains make bonds with the CNT. The calculated E_I of the (9,9) CNT on the Al-rich R-plane is 1.46 eV/unit, much larger than that on the stoichiometric surface.

The equilibrium structure for the [1120] direction shown in Figs. 1(c) and (d) is very similar to that for the the [1101] direction: Bond formation between Al and C atoms, flattening of the CNT near the interface, the average amount of the charge transfer per Al-C bond. However, the adsorption energy, 0.71 eV/unit, is nearly half of that of the $[\underline{1}101]$ direction, meaning that the CNT in the $[\underline{1}101]$ direction is the most stable. This is the origin why the CNTs on the R-plane prefer to grow in the [1101] direction. The main reason for the anisotropic E_I is due to the different number of the Al-C bonds per CNT unit, i.e., 2 vs. 1.5 for the $[\underline{1101}]$ and $[\underline{1120}]$ directions, respectively (Fig. 1). Furthermore, since the different amount of transferred charges is almost proportional to the number of the Al-C bonds, the electrostatic interaction by the different charges will contribute to the different adsorption energies.

The arguments for the strong interaction between the CNT and the substrate persist to the A-plane since the adsorption structures and energetics of a CNT on the A-plane are quite similar to those on the R-plane as shown in Fig 2. E_I anisotropy is significant on the Al-rich plane (0.67 vs. 0.31 eV/unit) while negligible on the stoichiometric surface (0.24 vs. 0.20 eV/unit). The lowest-energy structure shows that the covalent bonds with ionic characters are formed



Fig. 2 Lowest-energy structure of a (10,0) CNT on Al-rich A-plane along $[1\underline{1}00]$, the growth direction. Dashed lines in the top views of (b) indicate the boundaries of the super cells.

between the Al and the C atoms.

3. Conclusions

Using a first-principles method, we have investigated the interactions between the CNTs and the sapphire surfaces in order to unravel the origins of the selective alignment of CNTs on the surfaces. We have found that the vdW interaction shows no directional preference and that the strong interactions including the covalent and electrostatic interactions between the C atoms and the Al atoms are responsible for the selective alignment of CNTs.

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