Mechanism of Horizontally Aligned Growth of Single-Wall Carbon Nanotubes on R-Plane Sapphire

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As a promising one-dimensional material for building nanodevices, single-wall carbon nanotubes (SWNTs) should be organized into a rational architecture on the substrate surface. In this study, horizontally aligned SWNTs with two alignment modes were synthesized on the same R-plane sapphire wafer by chemical vapor deposition with cationized ferritins as catalysts. In the middle part of the wafer, SWNTs were aligned on the R-plane sapphire in the direction $[1\bar{1}0\bar{1}]$. At the edge of the wafer, SWNTs were aligned in the tangential direction to the wafer edge. The comparison of these two groups of SWNTs suggests the competition between the two alignment modes and indicates that atomic steps in high density have superior influence on the SWNTs' alignment to the crystal structure on the surface of the sapphire substrate. A "raised-head" growth mechanism model is proposed to explain why catalysts can stay active during the horizontally aligned growth of relatively long SWNTs with the strong interaction between SWNTs and the sapphire substrate.

Introduction

The unique electronic properties and native small size of single-wall carbon nanotubes (SWNTs) make them important candidates for nanoelectronic materials.[1] The controls on the length, direction, and chirality of these one-dimensional (1D) materials are major challenges to realize their applications in nanoelectronics. The horizontal alignment of SWNTs is essential for the fabrication of most electronic devices and has already been explored through a postgrowth approach by self-assembly[2] and in situ growth approaches by external forces, including the gas flow[3] and the electrical field.[4] However, these methods have limitations, such as low density, poor reliability, small area coverage, and peculiar equipment requirements.

Recently, the horizontal alignment of SWNTs through an in situ growth approach was discovered[5−9] on sapphire and quartz substrates without external forces. Two growth modes have been discovered with different mechanisms. In one mode, the growth directions of SWNTs have a definite relation with the crystallographic indices of R- and A-plane sapphire substrates. The mechanism of this alignment has been attributed to the minimum Lennard-Jones potential when SWNTs grow in a certain direction[6] or to the strong interaction between C atoms of SWNTs and Al atoms of the sapphire substrate.[7] In the other mode, SWNTs could align themselves along atomic steps[5,9] or faceted nanosteps.[8] It is of great importance to investigate the competition of these two growth modes. With these two alignment mechanisms, another critical question is yet to be answered for better understanding the alignment phenomenon: why can catalysts stay active for the growth of relatively long (over 100 μm) SWNTs with the strong interaction between SWNTs and substrates? Previous studies[3,4] indicated that, in the horizontally aligned growth of SWNTs by chemical vapor deposition (CVD), SWNTs should be suspended or floated to avoid large friction due to SWNTs' van der Waals binding on the substrate surface. If an entire SWNT has a strong interaction with the substrate, the catalyst may not be active either because the high friction of lateral movement of the SWNT prevents the base-mode growth[10] or because the composition, morphology, and size of the catalyst may be modified to lose the activity due to the skidding of the catalyst on the substrate[11] in the tip-mode growth. All of these may limit the length and growth rate of horizontally aligned SWNTs. In this article, the horizontally aligned growth of SWNTs on R-plane sapphire substrates is reported and a model is proposed to explain why SWNTs can grow relatively long without the inactivity of catalysts.

Experimental Methods

SWNTs were synthesized by chemical vapor deposition (CVD) of methane on the R-plane sapphire substrate from Montco Silicon Technologies with the miscut angle $<2°$. Cationized ferritins (10 mg/mL) from Aldrich were deposited on the sapphire substrate as catalysts. The purpose of using cationized ferritins, but not common ferritins, is that cationized ones can be adsorbed effectively on the sapphire substrate due to the electrostatic interaction. Through this method, the aggregation of the ferritins, which may lead to the growth of multiwall carbon nanotubes, was avoided. Cationized ferritins were diluted 200 times with deionized water before being applied. The sapphire substrate was soaked in the catalyst solution for 30 s, followed by rinsing with deionized water and blowing dry with nitrogen. After the substrate was calcined in air at 800 °C for 5 min, SWNTs were grown at 800 °C for 20

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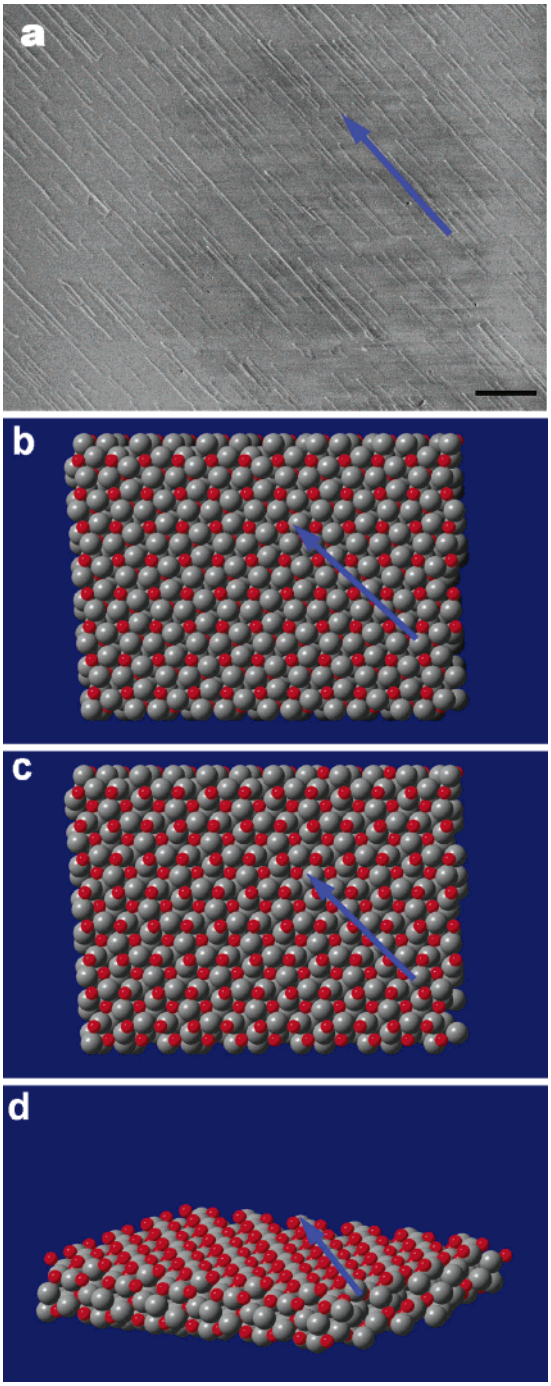

Figure 1. (a) SEM image of SWNTs grown in direction [1$\bar{1}$0$\bar{1}$] on R-plane sapphire substrate. Scale bar is 20 μm. (b) Simulation of the surface structure of the stoichiometric R-plane sapphire substrate. (c and d) Simulation of the surface structure of the oxygen-depleted R-plane sapphire viewed at different angles. The red and gray atoms indicate Al and O, respectively. The blue arrows indicate the direction [1$\bar{1}$0$\bar{1}$].

min in a flow of methane (150 sccm) and argon (650 sccm) at atmosphere pressure. SWNTs were characterized by scanning electron microscopy (SEM, LEO 1525 field emission), atomic force microscopy (AFM, Veeco Nanoscope IIIa), and Raman microscopy (Renishaw Micro-Raman System 1000).

Results and Discussion

A typical SEM image of SWNTs grown with the alignment on the middle part of the R-plane sapphire substrate is shown in Figure 1a. The density could be as high as 5 SWNTs/μm. SWNTs are up to 100 μm long and about 1 nm thick, as determined by AFM. Sharp RBMs in the Raman spectrum (Supporting Information) were observed, and diameters from the RBM data vary from 0.87 to 1.11 nm. Gas flows, atomic and faceted steps, and the atomic arrangement on the substrate may align SWNTs. In our experiments, no correlation between the gas flow and the growth direction of SWNTs was observed. The possible reason the gas flow cannot affect the growth direction of SWNTs is that SWNTs nestle closely to the substrate as they grew, and the gas flow rate at the surface of substrate is very low due to the friction effect. Comparing the interaction between the substrate and SWNTs, the force from the gas flow at the surface of the substrate is too small to align SWNTs. No directional correlation between SWNTs and atomic steps was observed either based on the AFM. All SWNTs that were not close to wafer edge grew along the direction [1$\bar{1}$0$\bar{1}$], which was determined by crystallographic parameters of the wafer flat provided by Montco Silicon Technologies. This growth direction agrees with recent experiments by Han[6] and Ago.[7]

The layout of Al (red) and O (grey) atoms in R-plane is shown in Figure 1b. This horizontally aligned growth was attributed to the strong interaction between C atoms in SWNTs and Al atoms in a certain crystallographic direction on the substrate,[7] where the total interaction between SWNTs and the substrate can be maximized to minimize the total system energy. With the experiments and the calculation using empirical force potentials, Su[10] indicated that the maximization of the interaction is the reason for the aligned growth of SWNTs in the certain crystallographic directions on the Si surface. However, from the atomic layout in the R-plane, [1$\bar{1}$0$\bar{1}$] is not the direction that allows the most bonding between Al and C atoms. The actual atomic layouts of Al and O atoms may be different from what is depicted in Figure 2b. Previous research shows that the surface of the C-plane sapphire substrates could be depleted of O atoms and become terminated by Al atoms by heating in ultrahigh vacuum at 900 °C or by hydrogen plasma.[12] It is also demonstrated that O atoms on the R-plane were partially depleted at the high temperature.[13] Although hydrogen was not applied in our CVD, a significant amount of hydrogen can be produced on the sapphire surface by the decomposition of methane[14] through the catalysis by Fe nanoparticles at high temperature. In our SWNT growth experiments, with the effects of the high temperature and the presence of hydrogen, the most outside layer of O atoms of the sapphire substrate may also be depleted and then the surface is terminated by Al atoms, as shown in Figure 1c and d at different angles of view. With the depletion of oxygen in the most outside layer, [1$\bar{1}$0$\bar{1}$] becomes the direction of the compact arrangement of Al atoms on the surface. From the angle of view in Figure 1d, a series of grooves aligned in the direction [1$\bar{1}$0$\bar{1}$] were observed, and the arrangement of Al atoms builds the pseudo-one-dimensional arrays. It appears that the oxygen depletion on the surface of R-plane sapphire plays an important role for the alignment of SWNTs.

On the area with 150 μm from the edge of the sapphire wafer, the aligned SWNTs always grow in the directions tangential to the edge of the rounded wafer; by contrast, in the middle part of the wafer and at the cleaved edges, the SWNTs always grow in the direction [1$\bar{1}$0$\bar{1}$]. Two typical images at the different locations of the edge of the sapphire substrate are shown in Figure 2a and b, where blue arrows indicate the direction [1$\bar{1}$0$\bar{1}$] and red arrows are located at the edge and indicate the tangential directions to the edge. As previous research,[5,8,9] atomic steps or faceted nanosteps play an important role in SWNTs'

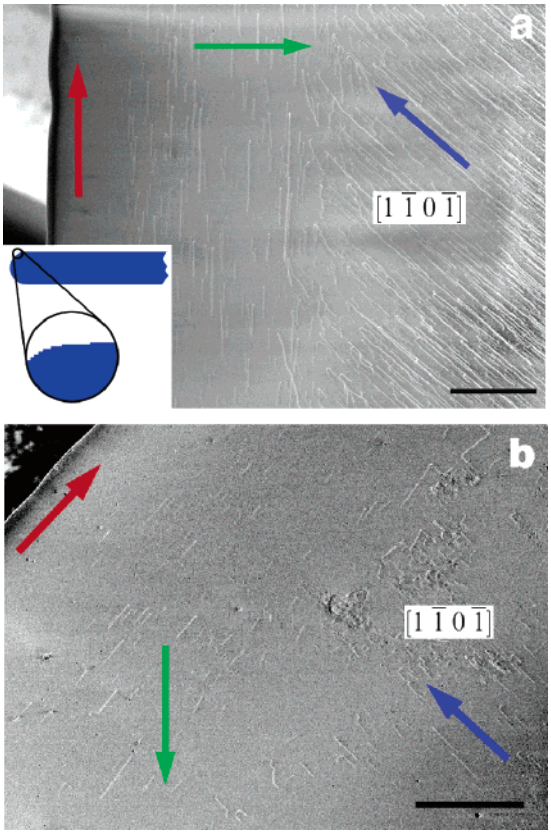

Figure 2. SEM images of the SWNTs at two typical locations around the edge of the wafer. Red arrows indicate that SWNTs grow along the tangential direction to the edge. Blue arrows indicate the direction [1$\bar{1}$0$\bar{1}$] in which the SWNTs grown at the inner area of the wafers. Green arrows indicate gas flow directions. Scale bars are 50 μm. The angles between the SWNTs grown at the edge and at the inner location of the wafer are about 45° (shown in a) and 90° (shown in b). The inset in (a) shows the cross-sectional schematic of the edge of the wafer where the density of steps increases significantly.

alignment at the edges of the wafers. A schematic illustration of the cross section of wafer edge is shown in the inset of Figure 2a. The cross-section image of the sapphire wafer, which was cleaved along radial direction, is shown in Figure 3a. Within the 150 μm from the edge, the profile of surface is an arc. However, at the place more than 150 μm away from the edge, the profile of the surface is a straight line. In Figure 3b and c, AFM images show atomic steps along the direction tangential to the edge within the 150 μm from the edge, but no clear steps at the middle part of the wafer. Because of the round angle of the edge, the density of the atomic steps or nanosteps increases significantly and the directions of these steps are along the tangential directions to the edge. The electrostatic interaction between the atomic step and a SWNT can be about 50 eV/nm without considering the surface relaxation and reconstruction,[5] which may be strong enough for the aligned growth. At the edge of the wafer, the compact arrangement of Al atoms in direction [1$\bar{1}$0$\bar{1}$] have inferior influence to atomic steps on the dominant effects on the SWNTs' alignment with the possible reason that it is difficult for SWNTs to conform themselves in the step profiles in the direction [1$\bar{1}$0$\bar{1}$].

Previous experiments suggested that high-density Fe nanoparticles could not yield the aligned growth of SWNTs when Fe nanoparticles were prepared by heating Fe thin films.[6,15] It was postulated that the high-density catalyst and SWNTs disturbed the interaction between sapphire substrates and SWNTs and thus impeded the growth of aligned SWNTs. Figure 4 depicts an interesting AFM image of aligned SWNTs on the

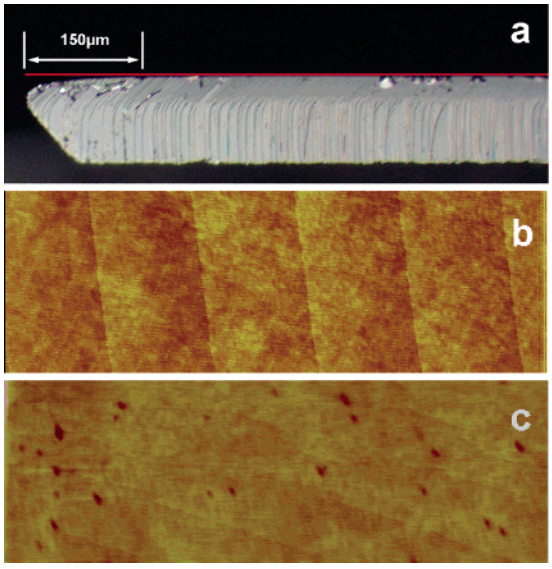

Figure 3. (a) Cross-section image of the sapphire wafer, which was cleaved along radial direction. (b and c) AFM images of the edge and middle of the sapphire wafer in (a). The size of images is 3 μm × 1 μm.

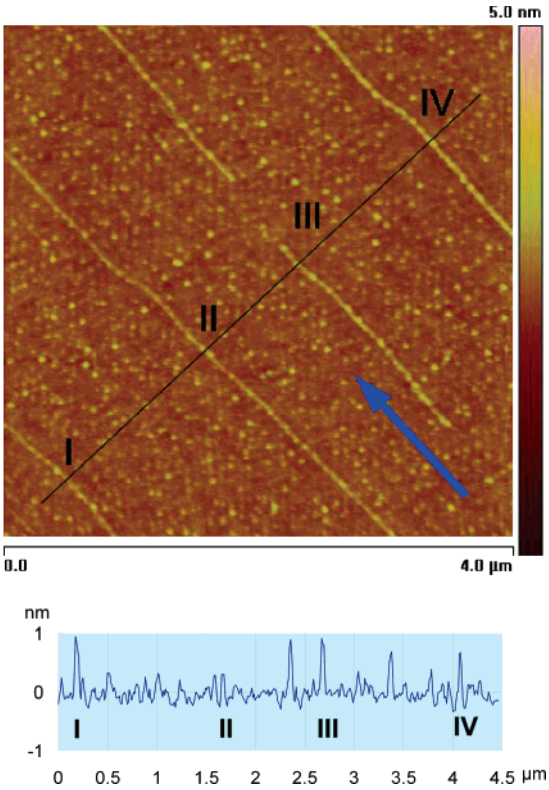

Figure 4. Typical AFM image (upper panel) and the corresponding cross-sectional height profile (lower pane) of the SWNTs at the inner place of the sapphire wafer. The blue arrow indicates the direction [1$\bar{1}$0$\bar{1}$] in which the SWNTs were grown. The height peaks of the four SWNTs are labeled in the cross-sectional height profile and the other peaks come from nanoparticles.

sapphire substrate, where many Fe nanoparticles were also observed. In our experiments, the disturbance of aligned growth of SWNTs by nanoparticles was not observed, although with higher density of nanoparticles, the disturbance may happen.

In Su's research on aligned SWNTs on Si substrates,[10] the growth mode is the base mode, where both ends of SWNTs are in contact with substrates, according to the AFM images before and after the regrowth of SWNTs**.** In his experiments,

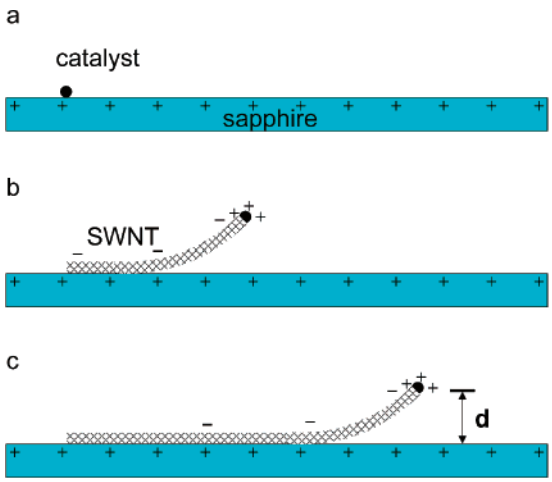

Figure 5. Scheme of horizontally aligned growth of SWNTs on the sapphire substrates as the "raised-head" model. (a) Surface of the sapphire substrate has positive charges in the growth environment because of the oxygen depletion on the surface. (b) When a section of SWNT grows out of the catalyst, the catalyst is also positively charged due to the contact potential at the interface of the catalyst and the SWNT. (c) Repulsion between the catalyst and substrate can keep the catalyst from touching the ground during the growth.

the typical length of SWNTs is 1−2 μm. However, it is difficult to apply the base mode to explain the SWNT growth on sapphire substrates considering the SWNTs can grow 100 μm long. The barrier energy for such long SWNTs may be large enough to restrain the growth of SWNTs in the base mode. In general, the relatively long SWNTs with horizontal alignment should grow in the tip mode, where the growing end of a SWNT with a catalyst moves forward and leaves the growing SWNT as a wake. In the tip mode, the segment of the SWNT near the tip should float above the substrate.[3,4,11] Otherwise, the catalyst may touch the surface of the substrate to make wavy SWNT, and the catalyst becomes inactive due to the frictional force between the catalyst and the substrate or the change of the composition, morphology, and size from the interaction. However, during the aligned growth of a SWNT on a sapphire substrate, the entire SWNT seems to have a strong interaction with and nestles tightly to the substrate for alignment. A question should be answered why catalysts still seem active and SWNTs grow straight with the high possibility that the catalysts fall down on the substrate. A model named the "raised-head" model is built into this report to explain this phenomenon. The principle of this model is that the sapphire substrate tends to be positively charged by Al−O dipoles at the surface in the growth environment and the Fe catalyst is also positively charged owing to a contact potential at the interface between the SWNT and the catalyst. The electrostatic force between the catalyst and substrate keep the catalyst from touching the substrate during the growth, although the greater part of the SWNT still nestles closely on the substrate.

As mentioned above, the surface of the R-plane sapphire may be oxygen depleted and terminated with Al atoms. Therefore, the surface tends to be positively charged because of the Al−O dipole, as shown in Figure 5. To the best of our knowledge, no one has measured or calculated the work function of iron with saturated carbon before. In this article, the work function of iron, $\phi_{Fe} = 4.67$ eV, from ref 16, is used to represent that of iron with saturated carbon. The work function of SWNTs has a wide range from 4.5 to 5.7 eV based on different experiments and theoretical calculations.[17−19] Most of these works focused on the tips of the capped carbon nanotubes for the field emission properties. For the purpose of calculating charge transfer between the iron catalyst and SWNTs, the work function $\phi_{SWNT} = 5.44$ eV is used from the theoretical calculation of the SWNT's body.[20] Once a segment of the SWNT grows out of the catalyst, electrons in the catalyst are transferred to the SWNT driven by the difference in work functions, i.e., the catalysts are positively charged and carbon nanotubes are negatively charged because of $\phi_{Fe} < \phi_{SWNT}$, as shown in Figure 5b. Because of the poor screening of the long-range Coulomb interaction in 1D carbon nanotubes,[21,22] (1) for metallic SWNTs, the transferred electrons in carbon nanotube locate in a large range from the junction with a low density, and (2) for the semiconductive ones, the transferred electrons locate in an even larger range than the metallic ones due to the dielectric property of the semiconductor. So at the tips of SWNTs, the net charge is positive, which is the same type charge as on the sapphire substrate. The repulsive force between the catalyst and the substrate balances with the bending force of the SWNT and the gravitational force of the tip section of the SWNT. This balance of forces keeps the catalysts from falling down to the substrate. Although there is not enough information to decide the charge density on the surface of the substrate and the net charge amount at the tip of SWNT, we would like to simplify this model to see whether the balance of force is possible. It is supposed that the integrated Coulomb interaction between the charges, including the positive and negative charges at the section around the tip of the SWNT and the positive charges on the surface of the substrate, is equivalent to the interaction of two one-unit positive charges where one is at the catalyst and the other one is on the substrate surface just under the catalyst. For a 1 nm thick SWNT with a 100 nm bent section, the catalyst will rise up to 12 nm due to the repulsion of the substrate.[1] The bending force is calculated by $f = 3dYI/l^3$, where Young's modulus $Y = 1060$ GPa, areal moment of inertia $I = 4.85 \times 10^{-38}$ m,[4] and the length of bending section $l = 100$ nm. The areal moment of inertia is calculated by $I = \pi(r_o^4 - r_i^4)/4$, where r_o and r_i are the outer and inner radii of an elastic cylinder, respectively. The gravitational force is neglected here because of its trivial amount. The amplitude of thermal vibration σ at such high temperature is a significant amount[23] and it can be calculated by $\sigma = \{0.8486l^3kT/[Y2r_oG(4r_o^2 + G^2)]\}^{1/2} = 5.6$ nm, where k is the Boltzmann constant, T is temperature, and $G = 0.34$ nm is the van der Waals distance in graphite. Thus, the thermal fluctuation will not cause the catalyst to touch ground. From the above simplified consideration, the "raised-head" model is a possible explanation of how catalysts can stay active with the strong interaction of SWNTs and substrates.

Previous research[5,8] proposed a "wake-growth" model to explain horizontally aligned growth of SWNTs along atomic steps and nanosteps. "Wake-growth" model is also plausible; however, one of the assumptions in it maybe questioned. In the "wake-growth" model, it is assumed that there is "better wetting of the atomic steps by the Fe metal catalyst nanoparticles, because of capillarity and higher coordination." However, with good wetting of atomic steps by the Fe catalyst in two directions, the Fe nanoparticle is not a ball anymore. Depending on the extent of wetting, the Fe catalyst may be far from the symmetric shape in radius direction of SWNT. Whether a SWNT that has a symmetric shape can grow out from an asymmetric nanoparticle is unknown and with doubts. Furthermore, in the "wake-growth" model, the whole SWNT is supposed to lie on the substrate. So when a SWNT meets a nanoparticle, it may stop growth because of the obstruction or the size change of the catalyst by merging the nanoparticle.

However, previous research[6,15] showed that the high density of the catalyst cannot stop the growth of SWNTs on sapphire substrates, but made them in random directions. The raised-head SWNTs with the thermal vibration are a more reasonable explanation for the growth in random directions. When a SWNT meets a nanoparticle, the thermal vibration of this raised-head SWNT makes it bend to other direction for further growth.

From the "raised-head" model, the horizontally aligned growth of SWNTs is not limited to the sapphire substrate anymore. Other substrates may also be used in the horizontally aligned growth of SWNTs if the surface atoms have a strong interaction with the SWNTs in a certain crystallographic direction and they are also positively charged in the growth environment.

Conclusions

In conclusion, we have grown horizontally aligned SWNTs on R-plane sapphires. Two different alignment mechanisms influence the growth direction on the sapphire substrate: (1) in the middle parts of the wafers, the interaction between Al atoms in the $[1\bar{1}0\bar{1}]$ direction on the oxygen-depleted sapphire and SWNTs is attributed to the alignment, and (2) at the edges of the wafers, atomic steps or nanosteps align SWNTs. The "raised-head" model is built to explain the horizontally aligned growth in which catalysts stay active with the strong interaction between SWNTs and the substrates. The electrostatic repulsion between the catalysts and the substrate prevent the falling of the catalyst to the ground.

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Supporting Information Available: Raman data taken with 780 nm excitation laser. This material is available free of charge via the Internet at http://pubs.acs.org.

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