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RESEARCH PAPER

Changing the chirality of single-wall carbon nanotubes during epitaxial growth : A density functional theory study

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Abstract: The energetic of the change in the chirality of single-wall carbon nanotubes (SWCNTs)during epitaxial growth from (n, m) to (n±Δ, m∓Δ)(Δ=1, 2) was investigated by density functional theory calculations. The calculated energies for changing the chirality of different SWCNTs show a nearly linear decrease with decreasing tube diameter. In the case ofΔ=1, more energy input is needed for near armchair (nAC) SWCNTs to change their chiralities than those for near zigzag (nZZ) SWCNTs with comparable diameters, due to the larger formation energies of pentagon-heptagon defects (5,7-defects) introduced in the nAC-SWCNTs. These larger formation energies for the nAC-SWCNTs come from the larger angles between the orientation of a 5,7-defect and the tube axis than those for nZZ-SWCNTs. The topological connection oftwo adjacent 5,7-defects, which is indispensable for changing the chirality during growth in the case of Δ=2, is found to be energetically most stable. The energies needed to change chirality in the case of Δ=2 are calculated to be less than twice those in the case of Δ=1 for SWCNTs with comparable diameters. These results may help us understand the change in chirality during the epitaxial growth of SWCNTs and guide the future synthesis of SWCNTs with a single-chirality .

Key Words: Single-walled carbon nanotube; chirality-changed; pentagon-heptagon defect; epitaxial growth; density functional theory

1 Introduction

A single-walled carbon nanotube (SWCNT) can be conceptually considered as a cylinder rolled up from a graphene sheet. The geometry structure of a SWCNT is exclusively determined by a pair of chirality indices (n, m) according to the rolling direction of the graphene sheet[1]. The electronic properties of SWCNTs are closely related to their geometry structures. For example, SWCNTs can be either metallic (m-SWCNTs) or semiconducting (s-SWCNTs) depending on their chiralities. To be specific, when (2n+m)/3 is an integer, the SWCNTs are metallic, and otherwise semiconducting[2]. The unique electronic properties of SWCNTs show appealling potential applications in many fields. For instance, s-SWCNTs can be used for high mobility nano transistors[3] and computers[4], while m-SWCNTs are suitable for fabricating transparent electrically conductive films[5], field-emission electron sources[6], nanocables[7], and so on. Unfortunately, as-grown SWCNT samples are always a mixture of m-SWCNTs and s-SWCNTs[8] due to the negligible formation energy difference among different SWCNTs with comparable diameters[9], highly limiting their widespread applications. Basically, the above issue can be possibly solved by a direct synthesis of uniformly metallic (or semiconducting) or even single-chirality nanotubes through controlling the composition, morphology and/or size of catalysts for SWCNT growth by chemical vapor deposition [10]. For example, dominantly semiconducting SWCNTs with a narrow distribution of diameter and chirality were synthesized by using bimetallic CoMn[11], FeRu[12] catalysts, or monometallic Co nanoparticles with a well-defined crystal structure[13]. Moreover, SWCNTs with only a few specific chiralities were realized by a fine regulation and design of catalysts[14-20]. Also, the chirality distribution of as-grown SWCNTs can be altered by varying the composition of Ni_xFe_{1-x} nanocatalysts based on an epitaxial growth model[21]. Very recently, Yang et al. reported a direct growth of the (12,6) tube with an abundance higher than 92% using WCo bimetallic nanocatalysts[22], and Fasel et al. have achieved single-chirality SWCNTs with only one chirality of (6, 6) by using surface-catalyzed cyclodehydrogenation of $C_{96}H_{54}$ precusors on Pt(111) surface[23]. However, despite enormous efforts and remarkable progress, real achievements of uniformly conducting and even chirally pure SWCNTs in a large amount by a direct growth is still highly impractical due to the insufficient understanding of the growth mechanism and the multiple factors (catalyst structure and morphology[24], temperature[25], and so on) relating to the growth of SWCNTs.

On the other hand, we also noted that the chirality of SWCNTs could be uniformly controlled by an epitaxial growth with open-end short SWCNT seeds, namely “cloning growth”. For example, Yao et al. grew SWCNTs with a controlled chirality by using open-end SWCNTs as seeds[26], Liu et al. synthesized SWCNTs with predefined chiralities using purified single-chirality nanotubes as seeds[27]. It is also found that the diameter or even the chirality of SWCNTs can

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be finely controlled via a tube junction formation by changing the temperature during SWCNT growth[28], which is a typical case for a chirality-changed. In principle, such a chirality-unchanged (cloning growth) or chirality-changed epitaxial growth would achieve a chirally pure SWCNT growth in a large amount with finely controlled growth conditions. However, the underlying mechanism of this cloning or chirality-changed epitaxial growth of SWCNTs is still unclear, thus highly hindering the experimental progress in this aspect.

In this work, we systematically studied the thermodynamics for the cloning and chirality-changed growth of SWCNTs by DFT calculations, aiming to obtain guideful hints to achieve single-chirality SWCNTs by an epitaxial growth. Taking the SWCNTs with diameters ranging from 0.4 to 1.3 nm as examples, we have calculated the energy changes (ΔE) for SWCNTs with chirality change from (n, m) to ($n\pm\Delta$, $m\mp\Delta$), Δ=1 and 2. The energy changes for the chirality-changed epitaxial growth of SWCNTs increase linearly with increasing the tube diameters, ranging from 1.1 (2.0) to 3.7 (4.4) eV in the case of Δ=1 (2). It is also found that the energy changes in the case of Δ=1 are about 0.2- 0.4 eV larger for near armchair (nAC) tubes than those for near zigzag (nZZ) tubes, resulting from the larger angle difference between pentagon-heptagon defects (5,7-defects) and the tube axis for nAC tubes. In the case of Δ=2, the topological connection with two adjacent 5,7-defects, which are indispensable for the chirality-changed growth of SWCNTs in this case, is found to be the most energetically stable. Similar to the case of Δ=1, the energy needed to change chirality of a SWCNT for Δ=2 case increases with increasing the tube diameter. Our DFT results provide a deep understanding on the thermodynamics of the chirality-changed epitaxial growth and may guide for the chirality-controlled synthesis of SWCNTs.

2 Computational methods

In this work, all calculations were carried out within the framework of DFT implemented in the Vienna Ab Initio Simulation Package (VASP)[29], using the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof[30]. The electron-ion interactions were described by using the frozen-core projector augmented wave approach[31, 32]. Testing calculations show that the total energy of a (5, 1)/(4, 2) tube junction obtained by using a cut-off energy of 450 eV is only 30 meV lower than that by using the cut-off energy of 280 eV, which is negligible in comparison with the energy input for changing a (5, 1) tube to a (4, 2) tube (1.1 eV). Thus, the energy cut-off for plane waves was set to be 280 eV for all calculations in this work. Considering that different tube junctions were constructed based on the cluster model to simulate the chirality-changed epitaxial growth for different SWCNTs, only Gamma point was used to sample the first Brillouin zone for all calculations in this work. Optimized geometry structures for all tube junctions considered in the present work were determined until the residual forces acted on each atom were less than 0.01 eV/Å.

Different tube junctions consisting of two short segments of different SWCNTs with chirality of (n, m) and ($n\pm\Delta$, $m\mp\Delta$) (Δ=1, 2) were constructed to study the atomic structure change and corresponding energy change induced by the chirality-changed epitaxial growth of different SWCNTs. Eight nZZ (n, 1) (n=5-11 and 15) and eight other tubes including (5,2), (5,3), (6,3), (6,4), (7,4), (7,5), (8,5) and (10,7) were considered for the case of chirality change with Δ=1, and twelve (n, m) tubes with m= 2, 3, 4 and n ranging from m+4 to m+7 for case of chirality change with Δ=2, in order to achieve a convincing comparison of the energy change among different tubes in this work. It should be noted that, one of the initial purposes of this work is to understand the difference of energy changes between highly symmetrical tubes, like ZZ and AC tubes, during their chirality-changed epitaxial growths. Unfortunately, both ZZ and AC tubes will change their helicities from the left-handed to the right-handed (or from right-handed to left-handed) when their chiralities are changed from (n, m) to ($n\pm\Delta$, $m\mp\Delta$) (Δ=1, 2). Alternatively, we choose these nZZ and nAC tubes in this work without considering the possible influence of the tube helicity on the energy changes during the chirality-changed epitaxial growth. We use the cluster models for all the calculations in this work since the periodic models for a tube junction are too large for standard DFT calculations, and a large supercell containing a short tube (or a tube junction) was constructed to model the chirality-changed epitaxial growth of SWCNTs. The inter-tube distance was set to be 10 Å to minimize the periodic image interactions for all calculations. For comparison, a monolayer graphene sheet with a 5,7-defect (or two 5,7-defects) was constructed to model the hypothetically chirality-changed growth of a SWCNT with an infinite diameter.

3 Results and discussion

It is intuitively easy to understand that the cloning growth of a SWCNT just grows the tube length along the direction of the tube axis by continuously adding carbon atoms at the open-end without inducing any defects, while the chirality-changed epitaxial growth for the SWCNTs inevitably induces topological defects at the tube junction position to change the tube chirality of (n, m) to (n', m'). As for the chirality-changed epitaxial growth considered in this work, we only focus on the cases in which the tube diameters do not change too much, for example from (n, m) to ($n\pm\Delta$, $m\mp\Delta$) with Δ=1 and 2, since it is very difficult to enlarge or reduce the tube diameters in a typically epitaxial growth without catalyst at the open-end. As well demonstrated, at least one and two pentagon-heptagon topological defects have to be introduced for the (n, m)/($n\pm1$, $m\mp1$) and (n, m)/($n\pm2$, $m\mp2$) tube junctions, respectively[33]. In energetics, the topological 5,7-defects in sp^2 carbon materials like graphene and carbon nanotubes contribute the minimum energy gain to the total energy due to the zero net curvature change, which