Carbon nanotube growth enhanced by nitrogen incorporation

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Abstract

It is well known that the growth of carbon nanotubes (CNTs) by chemical vapor deposition using a transition metal catalyst is greatly enhanced in a nitrogen environment. We show here that the enhanced growth is closely related to nitrogen incorporation into the CNT wall and cap during growth. This behavior is consistent with theoretical calculations of CN_x thin films, showing that nitrogen incorporation to the graphitic basal plane reduces the elastic strain energy for curving the graphitic layer. Enhanced CNT growth by nitrogen incorporation is thus due to a decrease in the activation energies required for nucleation and growth of the tubular graphitic layer.

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1. Introduction

Synthesis and characterization of carbon nanotubes (CNTs) have been extensively studied in the last decade owing to their unique properties and potential application to nanoscale devices [1–5]. In chemical vapor deposition (CVD) processes using transition metal particles as the reaction catalyst, it is believed that the CNT forms from the saturated metal catalyst surface that resides at either the base [6–8] or the tip of a growing nanotube [9,10]. The CVD process has many advantages over other deposition methods, including low deposition temperature and control of the diameter of the CNT by varying the size of the metal

catalyst. Furthermore, it is relatively easy to obtain vertically aligned CNTs by increasing nucleation density and the growth rate [11,12]. The microstructure of the vertically aligned CNT thus reflects the enhanced CNT growth in the CVD process.

Most previous results using the CVD process showed that the vertically aligned CNTs were obtained in N_2 or NH_3 gas environments, which reveals the key role of nitrogen in CNT growth. However, the environment gas has only been considered as an etching agent of the catalyst particle [13], a diluting gas to suppress excess decomposition of hydrocarbon precursor [14] or a reducing gas for the oxide layer of the catalyst surface [15]. On the other hand, Jung et al. [16] focused on the activated nitrogen that can enhance CNT growth. They compared the deposition behavior in an NH_3 environment with that in a

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mixed environment of H_2 and N_2 with the atomic ratio $H/N = 3$, as in NH_3 . They observed vertically aligned CNTs only in the NH_3 environment, where the activated nitrogen could be generated by thermal decomposition of NH_3 . In the mixed environment, N_2 acted like an inert gas and only amorphous carbon was deposited, with no CNT growth. Although this result shows that CNT growth is greatly enhanced by activated nitrogen, its role in CNT growth needs to be clarified based on systematic experimental evidence. In the present work, we show that the enhanced CNT growth results from nitrogen incorporation to the CNT wall or cap, which can reduce the elastic strain energy to form a tubular graphitic layer of CNT.

2. Experimental

The nanotubes were grown by using thermal decomposition of acetylene (C_2H_2) at atmospheric pressure. Thin film (3 nm) Ni was deposited on an oxidized Si(100) wafer by DC magnetron sputtering. The specimen was annealed at 800 °C for 15 min in a hydrogen environment to obtain uniformly distributed catalyst particles whose diameter ranged from 17 to 58 nm. The specimen was transferred to the horizontal quartz tube reactor. Details of the reactor are given elsewhere [16]. Before loading the specimen to the reaction zone, the temperature of the reactor was increased to 950 °C in an Ar environment. The specimen was then pushed to the reaction zone by a loading system. If required, pretreatment was performed before the CNT deposition in H_2 , NH_3 or their mixture. Carbon was deposited by adding C_2H_2 to the environment gas with the concentration of C_2H_2 ranging from 1.5 to 100 vol%.

3. Results and discussion

Fig. 1a shows the cross-sectional SEM image of vertically aligned CNT grown for 20 min using 16.7 vol% of C_2H_2 in an NH_3 environment. Before the deposition, the sample was pretreated in a pure NH_3 environment for 1 h. The diameter of the CNTs measured by high magnification SEM and

Fig. 1. SEM (a) and TEM (b) images of the CNTs deposited at 950 °C for 20 min in a 16.7 vol% $C_2H_2 + NH_3$ environment after pretreatment at 950 °C for 1 h in an NH_3 environment. (c) SEM image of amorphous carbon deposited for 20 min in a 16.7 vol% $C_2H_2 + H_2$ environment after pretreatment for 4 h in an NH_3 environment. (d) SEM image of CNTs deposited for 20 min in a 16.7 vol% $C_2H_2 + NH_3$ environment without pretreatment.

TEM ranges from 23 to 79 nm, which is comparable to that of the catalyst particle. The TEM microstructure of the CNT (Fig. 1b) shows that the CNT grows with ‘bamboo-like’ structure. Both the diameter and the TEM microstructure are consistent with the base growth model: the number of graphitic layers deposited on the catalyst surface was separated from the catalyst surface, resulting in the growth of CNT with a closed end [6–8]. The base growth model would suggest two possibilities for the role of activated nitrogen. In the present experimental condition, pretreatment in an activated nitrogen environment results in nitrogen incorporation into the catalyst surface [16]. The modified catalyst surface may change the nucleation behavior of the graphitic layer or the separation of the deposited layer from the catalyst surface to evolve the CNT structure. If this were the major role of the activated nitrogen, pretreatment in the NH_3 environment would be essential for CNT growth. The other possibility is based on

the atomic scale electron energy-loss spectroscopy (EELS) analysis of CNT showing that the nitrogen is incorporated into the CNT wall or cap in the NH_3 environment [17]. If nitrogen incorporation enhances CNT growth, the nitrogen environment during growth would be a prerequisite for the vertically aligned CNT growth.

In the present work, we performed two experiments in order to verify the possibilities. In the first experiment, the sample was pretreated in an NH_3 environment for 4 h. Auger spectroscopy shows that the nitrogen was incorporated in the catalyst surface during the pretreatment. (Because of the limited spatial resolution of Auger spectroscopy, the spectrum includes compositional information on the SiO_2 surface layer as well as the catalyst surface. However, the Auger spectrum analysis of the substrate without catalyst particles showed that the amount of nitrogen incorporated into the SiO_2 surface layer was negligible.) After the pretreatment, NH_3 gas in the reactor was replaced by the mixture of 16.7 vol% C_2H_2 and H_2 gas for carbon deposition. In this experimental condition, only amorphous carbon was deposited on the catalyst surface, as shown in Fig. 1c. In the second experiment, the carbon was deposited without pretreatment by using 16.7 vol% of C_2H_2 in an NH_3 environment. Fig. 1d shows the SEM microstructure of the vertically aligned CNTs grown in the second experimental condition. The same behavior was observed when the sample was pretreated in an H_2 environment. From these results, we can conclude that pretreatment in an NH_3 environment is neither a sufficient nor a necessary condition for the vertically aligned CNT growth. On the other hand, an NH_3 environment during growth significantly enhances CNT growth, regardless of the pretreatment condition (see Fig. 1a,d).

Fig. 2 shows the change in morphologies of the deposited carbon when the concentration of C_2H_2 in NH_3 during growth was varied from 1.5 to 23.1 vol%. In all samples, the carbon was deposited for 20 min after pretreatment for 1 h in an H_2 environment. When the C_2H_2 concentration was 1.5 vol%, only tangled CNTs with a low growth rate were observed (Fig. 2a). This tangled CNT would result from an insufficient supply of carbon for the

Fig. 2. SEM microstructures of the carbon deposited at 950 °C for 20 min after pretreatment for 1 h in an H_2 environment when using (a) a 1.5 vol% C_2H_2 + NH_3 environment, (b) a 5.0 vol% C_2H_2 + NH_3 environment, (c) a 16.7 vol% C_2H_2 + NH_3 environment, and (d) a 23.1 vol% C_2H_2 + NH_3 environment during deposition.

higher growth rate. As the concentration of C_2H_2 increased, both the growth rate and the degree of alignment drastically increased, as can be seen in Fig. 2b,c. The growth rate judged from the thickness of the CNTs increased from 1.1 nm/s at 1.5 vol% of C_2H_2 to 9.6 nm/s at 16.7 vol% of C_2H_2 . However, when the C_2H_2 concentration was larger than about 20 vol%, excess carbon supply seemed to passivate the catalyst surface resulting in amorphous carbon deposition, as shown in Fig. 2d. Chhowalla et al. [18] reported the similar CNT deposition behavior in DC plasma CVD process. As C_2H_2 fraction in NH_3 increased from 5% to 30%, the growth rate rises by 30%. However, the nanotubes become obelisk-like beyond 30% of C_2H_2 fraction.

The composition of the deposited carbon in Fig. 2 was analyzed by X-ray photoelectron spectroscopy (XPS) and Auger spectroscopy. Before the analysis, the sample was cleaned by an Ar ion beam in the analysis chamber to remove surface contaminants. Fig. 3 summarizes the nitrogen content in the deposited carbon measured by Auger spectroscopy. Nitrogen concentration in the

Fig. 3. Nitrogen concentration in the CNTs measured by Auger spectroscopy for various C_2H_2 concentrations in an NH_3 environment.

CNT increased from 1.0 to 2.5 at.% as the C_2H_2 concentration increased from 8 to 16.7 vol%. In the amorphous carbons deposited when the C_2H_2 concentration was larger than about 20 vol%, nitrogen concentration was slightly reduced. This compositional variation would be surprising if one considers that the NH_3 fraction in the reaction gas decreases with increasing C_2H_2 fraction. However, the nitrogen concentration in CNT increased with increasing CNT growth rate and the degree of alignment, which exhibits an intimate relationship between CNT growth and nitrogen incorporation. Fig. 4 shows typical XPS spectra of carbon and nitrogen in the CNTs. The C_{1s} peak at 285 eV corresponds to that of graphite. The N_{1s} spectrum shows two peaks at 400.9 and 398.5 eV. The high binding energy peak (400.9 eV) is due to the nitrogen bonded to sp^2 coordinated C atoms, i.e. substitutional N in the graphite sheet. The other peak at 398.5 eV is believed to correspond to three-coordinated N atoms in an sp^3 rich environment or at peripheries of the graphite sheet [19,20]. The XPS analysis shows that the nitrogen in the CNT is chemically bonded with the carbon atoms of the graphitic basal plane.

Fig. 4. X-ray photoelectron spectra of C and N of the CNTs deposited at 950 °C for 20 min in a 16.7 vol% $C_2H_2 + NH_3$ environment after pretreatment in an H_2 environment.

Morphological change of the graphitic basal plane due to nitrogen incorporation has been widely investigated since the theoretical prediction of a super hard C_3N_4 phase [21]. An ab initio total energy calculation showed that the strain energies of rolling the CN sheets into tubular form are smaller than that for a graphite sheet [22]. A semi-empirical total energy calculation also showed that nitrogen incorporation promotes the pentagons, leading to curving of the basal plane [23]. Several experimental results support the theoretical calculations. Atomic scale EELS analysis of nano onions in CN_x thin film [24] and a CN_x nanotube [17] showed that nitrogen concentration increases as the curvature of the graphitic layer increases. Hence, these results strongly suggested that nitrogen incorporation to the CNT would reduce the strain energy required to form a tubular graphitic layer. The reduced strain energy would in turn enhance the nucleation rate of the graphitic layer on the curved catalyst surface [25]. Further CNT growth also requires continuous deposition of the tubular graphitic layer, where nitrogen incorporation can reduce the strain energy.

4. Conclusion

The most significant result of the present work is to show that the enhanced CNT growth in an N_2

or NH_3 environment is due to nitrogen incorporation into the CNT wall or cap. Because nitrogen incorporation can reduce the strain energy required for the tubular graphitic layer of CNTs, nitrogen incorporation will decrease the activation energy for both the nucleation of the graphitic layer on the curved catalyst surface and the structural evolution of the CNT during growth. Pretreatment of the catalyst in a nitrogen environment is not a prerequisite for the enhancement of CNT growth.

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