Multi-barrier layer-mediated growth of carbon nanotubes


School of Advanced Materials Science and Engineering and Center for Nanotubes and Nanostructured Composites, Sungkyunkwan University, Suwon, 440-746, South Korea

Abstract

Variation in the height of carbon nanotubes (CNTs) grown has been co-related to the type of multi-barrier-layer used. Initially, various types of barrier-layers such as Al, Al₂O₃, Al/SiO₂, Al₂O₃/SiO₂ were prepared onto a n-type Si (100) substrate. The thickness of SiO₂ was ~550 nm, whereas, Al₂O₃ and Al were ~15 nm thick. These samples were covered with ~1 nm thick Fe catalyst layer. The coated samples were subjected to the thermal chemical vapor deposition (T-CVD) process. SEM analysis showed that, for Al₂O₃/SiO₂ barrier layers, the average height of the CNTs was ~10 μm, whereas, for other types of samples it was less than ~1 μm. To investigate this, multi-barrier layers were characterized by dynamic secondary ion mass spectrometry (D-SIMS). The observed variation in height of CNTs is attributed to the variation in diffusivity of Fe atoms into multi-barriers-layers. The results showed that, diffusion of Fe catalyst atoms could severely affect height of CNTs.

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1. Introduction

The layer sandwiched between catalyst and substrate is termed as barrier-layers (buffer layers). Role of barrier-layers in CCVD synthesis of CNTs is an important class of issue. Various materials such as, SiO₂, TiO₂, TiN, Al₂O₃, Cr, MgO could be used as the barrier layers [1–4]. These layers could prevent the diffusion of catalyst atoms into the substrates, improve the adhesion of CNTs to substrate and influence the characteristics of the CNTs. A considerable amount of work, related to barrier-layer-mediated growth of CNTs has been carried out. Cao et al. [1] has studied substrate-selective growth of CNTs, Arecos et al. [2] has observed the influence of buffer layers type on the CNT characteristics by carrying out in-situ XPS measurements. In so far, the systematic investigations on diffusion of Fe atoms in multi-barrier-layer have rarely been reported [5–7].

That is the topic of this communication. Here we report on our first attempts to investigate diffusion of Fe into multi-barrier-layers. CNTs were grown on various types of barrier-layers (Al, Al₂O₃, Al/SiO₂, Al₂O₃/SiO₂ and no barrier layer) coated with Fe catalyst, on Si (110) substrate. The CNT characteristics were determined by SEM, TEM techniques. The diffusion dynamics of the Fe atoms into the multi-layer-barriers was investigated by Dynamic-Secondary Ion Mass Spectroscopy (D-SIMS) technique and surface chemical analysis of as prepared and CNT-grown multi-barrier layer samples was carried out by X-ray photoelectron spectroscopy (XPS). The details of the analysis are presented.

2. Experimental

2.1. Deposition of multi-barrier-layer samples

Initially, a n-type Si (100) wafer (resistivity ~132 kΩ and thickness ~450 μm) has been cleaned up with the chemicals. The wafer was cut into several pieces and subjected to the different treatment to obtain multi-barrier layers. SiO₂ layers were grown onto the Si samples by wet-thermal oxidation process. For this purpose, a few samples were loaded into the high temperature furnace. The temperature of the chamber was raised upto ~1300 °C and maintained for a period of ~12 h. During thermal oxidation process H₂O vapors were passed onto the samples. Following this process these samples were removed from the thermal reactor and kept under dry atmosphere for next treatment. The thickness of the SiO₂ was found to be ~550 nm.
To grow Al layers on to the samples a few Si and SiO<sub>2</sub>/Si samples were subjected to the e-beam evaporation technique. An aluminum pellet of purity $\sim 99.999\%$ was loaded into the evaporation chamber and high voltage $\sim 15$ kV was applied. The chamber temperature was raised upto $\sim 90^\circ$C, however, the substrate temperature was maintained at $\sim 40^\circ$C. During the e-beam evaporation, the deposition rate was kept $\sim 0.1$–$0.2$ Å per second. The evaporation process was carried out for a period of 5 h to obtain $\sim 15$ nm thick Al layer.

To obtain Al<sub>2</sub>O<sub>3</sub> coating, a few Al/Si and Al/SiO<sub>2</sub>/Si samples were subjected to thermal evaporation process. These samples were loaded into the annealing chamber and temperature was increased upto $\sim 300^\circ$C. Thermal oxidation process was carried out for a period of 1 h to obtain $\sim 15$ nm think Al<sub>2</sub>O<sub>3</sub> layer. A few Si and multi-barrier-layers samples were subjected to e-beam evaporation process. In similar fashion the Fe catalyst layer of thickness $\sim 1$ nm was coated on each sample. The prepared samples were kept in dry environment under the high vacuum conditions $\sim 10^{-5}$ Torr to avoid the catalyst oxidation and contamination. The batch of the Fe/Si substrates are designated as sample S<sub>1</sub>, Fe/Al/Si as sample S<sub>2</sub>, Fe/Al/SiO<sub>2</sub>/Si as S<sub>3</sub>, Fe/Al<sub>2</sub>O<sub>3</sub>/Si and Fe/Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>/Si as S<sub>4</sub> and S<sub>5</sub>, respectively.

2.2. Synthesis of the carbon nanotubes (CNTs) on the multi-barrier-layer samples

A few S<sub>1</sub> and all S<sub>2</sub>–S<sub>5</sub> samples were subjected to the Thermal–Chemical Vapor Deposition (T-CVD) treatment. Initially, samples were loaded in the thermal reactor and evacuated to a base pressure of $\sim 20$ mTorr. The reactor temperature was raised with ramp rate of $\sim 10$ °C/min and the growth of CNTs was carried out at a temperature $\sim 650^\circ$C, for a period of 30 min. Moreover, C<sub>2</sub>H<sub>2</sub>/NH<sub>3</sub> feed stocks were used to grow the CNTs with flow rate 40 sccm /120 sccm. T-CVD process was repeated for 4–5 times to cover all category of samples.

The morphological investigation of the CNTs grown on the samples was carried out by Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). In order to simulate the diffusion conditions for the Fe atoms a few S<sub>1</sub>–S<sub>5</sub> samples were subjected to the annealing process at a temperature $\sim 650^\circ$C, for a period of 30 min. These samples were characterized by Dynamic Secondary Ion Mass Spectroscopy (D-SIMS).

In another experiment, a few CNT-grown S<sub>1</sub>–S<sub>5</sub> samples were subjected to the sonication process to remove the over-layer

Fig. 1. Typical SEM micrographs (cross-section view) recorded for (a) Fe/Si, (b) Fe/Al/Si, (c) Fe/Al/SiO<sub>2</sub>/Si, (d) Fe/Al<sub>2</sub>O<sub>3</sub>/Si and (e) Fe/Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>/Si multi-barrier-layer samples (scale bar: 2 μm).

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CNTs grown onto the surface and these samples were characterized by X-ray Photoelectron Spectroscopy (XPS) technique.

3. Results and discussion

Fig. 1 is the five typical SEM micrographs (cross-section view) recorded for (a)–(e) the CNT-grown S1–5 samples. The scale bar in each micrograph is \( \sim 2 \) \( \mu \)m. It can be seen that, a marginal amount of the CNTs has been observed on the S1–4 samples; whereas, a considerable amount of yield is observed on the surface of the S5 sample. Moreover, the average height of the CNTs is measured for all categories of the samples. The analysis revealed that, height of the CNTs ranges from 0.5 to 1 \( \mu \)m for the S1–4 samples. In contrast, height of the CNTs was found to be \( \sim 9.5 \) \( \mu \)m for the S5 sample. The result lead to a speculation that, either there could be considerable amount of the Fe catalyst sites available or the oxidation rate of catalyst samples differs substantially, for the S5 sample as compared to that of the S1–4 samples.

To investigate the diffusion of the Fe atoms into the barrier layers, a few S1–5 samples, after annealing treatment, were subjected to the Dynamic-Secondary Ion Mass Spectroscopy (D-SIMS). One sample at a time was loaded in the mass spectroscopy chamber and the chamber was evacuated to the base pressure of \( 1.4 \times 10^{-9} \) mbar. The sample was exposed to the \( O_2^- \)-ions with energy 800 eV and the beam current was varied from \( 9.71 \times 10^3 \) pA to \( 1.07 \times 10^4 \) pA. Spectra of the sputtering yield as a function of the sputtering time was collected for a period of \( \sim 10 \) min, for each sample. Fig. 2 shows the variation in the sputtering yield of Fe atoms, for S1–5 samples, as a function of the sputtering time. It can be seen that for the Fe/Si, S1, sample the sputtering yield is almost constant, \( \sim 10^5 \) ions/cm\(^2\) s, over the time measured for \( \sim 7 \) min. Similarly, the sputtering yield was found to almost constant for the Fe/Al/Si and Fe/Al\(_2\)O\(_3\)/Si samples. However, for the Fe/Al/SiO\(_2\)/Si, S3, sample the sputtering yield \( \sim 10^3 \) ions/cm\(^2\) s decreases after a period of \( \sim 2.5 \) min. Furthermore, for the Fe/Al\(_2\)O\(_3\)/SiO\(_2\)/Si, S5, sample the sputtering yield of \( \sim 10^5 \) ions/cm\(^2\) s decreases markedly after \( \sim 0.5 \) min. This shows that, the diffusion of the Fe atoms is hindered by the Al\(_2\)O\(_3\)/SiO\(_2\) barrier layer and almost all catalyst layers reside on the surface of the S5 sample. However, it seems that diffusion of Fe atoms is not prevented by the barrier layers in the S1–4 samples. The time of sputtering was calibrated with respect to the depth of diffusion for each sample. The analysis revealed that for the pristine Si sample the sputtering rate is \( \sim 100 \) Å/min.

To investigate the surface chemical states, a few, S1–5, samples were studied by the X-ray photoelectron spectroscopy (XPS). For this purpose, these samples were subjected to the sonication process to remove the over-layer CNTs. Each sample was immersed in the ethanol solution and sonicated for a period of \( \sim 10 \) min. Surface morphology of the sonicated samples was investigated by SEM technique to confirm the removal of the CNTs from the sample surface. Following this process the samples were subjected to the XPS characterization by using Mg K\(_\alpha\) (1253.6 eV) or Al K\(_\alpha\) (1286.6 eV) X-ray source of power 200 W was used. All samples were loaded in the XPS chamber and the system chamber was evacuated to a base pressure of \( \sim 10^{-9} \) Torr. One sample at a time was exposed to the X-ray beam and for each sample wide scan as well as narrow scan was taken for a period of \( \sim 2 \) min and \( \sim 10 \) min (per element), respectively. Pass energy for the wide scan and
the narrow scan was 100 eV and 20 eV, respectively. Fig. 3 is the recorded narrow scan of the O-1s peak for (a) before and (b) after annealing of the S1–5 samples. From Fig. 3(a) one can see that, the over all intensity of the ejected photo-electrons for the O-1s is less than 6000 for the S1–5 samples before CNT growth. After the CNT deposition the intensity of the O-1s peak is found to be increased up to ~8000. The increase in the intensity of O-1s peak suggests that, the number of photo-electrons participating in the scattering process is increased, which in-turn suggests the increase in concentration of O-species in the surface region of the sample. However, the increase in the intensity seems to be marginal. This leads to a conclusion that, the oxygen sites that are available for the samples, S1–5, before and after annealing are remained almost same. In addition, Fig. 3(a) shows that, O-1s peak consists of a doublet for the samples S1–5, which seems to be submerged into a single peak after the deposition of the CNTs. The O-1s peak at ~530.56 eV is attributed to the FeO species which is almost un-shifted after the growth of CNTs, for the Fe/Si, S1, sample. In addition, the peak at ~530.27 eV gradually shifts to 531.87 eV for the Fe/Al2O3/SiO2/Si, S5, sample after the growth of CNTs.

Fig. 4(a) is the variation in the intensity of Fe-2p peak as a function of binding energy for the S1–5 samples. It can be seen that, two peak exists for Fe-2p one at ~712 eV and other at higher binding energy ~725 eV. The peak at lower binding energy is attributed to the Fe2O3 where as, the peak at higher binding energy is attributed to the FeO [8,9]. It is interesting to note that, the overall intensity of Fe-2p peak is less than 4000 for the S5 sample, where as, the intensity of peak for the S1–4 samples is ~6500. This shows that number of photoelectron

![Fig. 3. Variations in the intensity of O-1s peak as a function of binding energy for the samples, S1–5, (a) before and (b) after annealing.](image)

![Fig. 4. (a) Variations in the intensity of Fe-2p peak as a function of binding energy for the samples, S1–5, and (b) typical TEM micrograph of the CNTs grown on the sample, S1.](image)

### Table 1

<table>
<thead>
<tr>
<th>Type of samples</th>
<th>Substrate</th>
<th>Barrier layers</th>
<th>Catalyst</th>
<th>Height (μm)</th>
<th>Diameter (nm)</th>
</tr>
</thead>
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<tr>
<td>S1</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>Fe</td>
<td>12–15</td>
</tr>
<tr>
<td>S2</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>Fe</td>
<td>12–15</td>
</tr>
<tr>
<td>S3</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>Fe</td>
<td>11–14</td>
</tr>
<tr>
<td>S4</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>Fe</td>
<td>12–15</td>
</tr>
<tr>
<td>S5</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>Fe</td>
<td>8.5</td>
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</table>

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sites for Fe-2p sites are reduced for the S5 sample. This is consistent since the growth of CNTs occurred by tip growth mode and most of the Fe is removed due to the removal of the CNTs from the surface of the substrate. Fig. 4(b) is a typical TEM image recorded for the CNTs grown on the surface of the S5 sample. It can be seen that the nanotube consists of 4–5 concentric graphene layers and the head of the CNT is decorated by the Fe cluster.

It is noteworthy that the diameter of the CNTs was found to be relatively small for the S5 samples as compared to the other category of samples. Table 1 enlists the height and diameter of the CNTs grown on various substrates. Thus we have observed relatively greater height and small diameter for the Fe/Al2O3/SiO2/Si samples. The observed variation in the height of CNTs could be co-related with the quantity of Fe atoms available on the surface region of the barrier-layer. The observed decrease in the height shows that, a large number of Fe atoms are diffused into the Al layer for Si/Al samples. In contrast the diffusivity seems to be reduced for the Si/SiO2/Al2O3 samples.

4. Conclusion

We have studied the barrier-layer-mediated variation in the height of the CNTs. It seems that, thermal diffusivity of the Fe atoms into barrier layer plays an important role in observed variation in the height of CNTs, as suggested by D-SIMS analysis. The diffusivity of the Fe atoms seems to be hindered by the Al2O3/SiO2 type of barrier layer and hence a large number of active catalyst sites are available for the growth of CNTs. Lowering of the diffusivity enhanced the number of Fe atoms contributing CNT growth process, which in turn enhanced the height of CNTs. Furthermore, XPS analysis revealed that, peak intensity of O-1s is almost same for as prepared and CNT-deposited multi-barrier-layer samples. This suggests that, the role of thermal diffusivity of Fe atoms into barrier layers seems to be superior as compared to that of catalyst layer oxidation.

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References