Synthesis of carbon nanotubes grown by hot filament plasma-enhanced chemical vapor deposition method

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Abstract

We prepared two kinds of catalytic layers onto n-typed silicon substrate—nickel by r.f.-magnetron sputtering and iron (III) nitrate metal oxide by spin coating. For iron (III) nitrate metal oxide 0.5 mol of ferric nitrate nonahydrate $\text{Fe}_3(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ ethanol solution was coated onto silicon by spin coater at different rotation speeds (rev./min). Carbon nanotubes were synthesized on both Ni and iron (III) nitrate metal oxide layers by the HFPECVD (hot filament plasma-enhanced chemical vapor deposition) method. We used ammonia ($\text{NH}_3$) and acetylene ($\text{CH}_2\text{H}_2$) for the dilution gas and a carbon precursor for the growth of the carbon nanotubes, respectively. We could observe the relationship between the catalytic cluster density and the nanotube density with scanning electron microscopy (SEM) images. The density of carbon nanotubes on iron (III) nitrate metal oxide was controlled by the rev./min of the spin coater. Transmission electron microscopy (TEM) image shows multi-walled carbon nanotube where the catalyst was found in the tip of the carbon nanotube. Electron dispersive X-ray spectrometry (EDS) peaks for CNT’s tip show that it was constituted with nickel and iron, respectively. Raman spectroscopy of nanotubes shows D-band and G-band peaks approximately 1370 and 1590 cm$^{-1}$. © 2003 Elsevier B.V. All rights reserved.

Keywords: Carbon nanotubes; Hot filament plasma; Chemical vapor deposition

1. Introduction

Carbon nanotubes (CNTs) have much potential for being used as materials for future electron devices such as field emission display [1], high capacity battery [2], and nano-electronic devices [3]. Besides this attractive aspect, there is growing recognition that the synthesis of CNTs is complex compared with another material. In order to make it possible to grow CNTs, one must first deposit a catalytic metal layer. The conventional methods for depositing catalytic metal layer are sputtering and evaporation. Unconventional methods were also used to synthesize CNTs—the floating catalyst method [4], the simplified hot filament chemical vapor deposition method [5], the aerosol pyrolysis method [6] and CVD method, using spin coated metal oxide. Single wall carbon nanotubes (SWNTs) represent very good characteristics but SWNTs grow at high temperature (higher than 900 °C) and the alignment of SWNTs is not as good as that of multiwall carbon nanotubes (MWNTs) grown by the plasma-enhanced chemical vapor deposition (PECVD) process [7]. Recently, PECVD attracted attention for carbon nanotube growth to its mass productivity, its high uniformity, and its good alignment of CNTs.

In this work, we prepared two kinds of catalytic layers—nickel and iron (III) nitrate metal oxide, onto n-typed silicon substrate by r.f.-magnetron sputtering and spin coating, respectively, to compare the growth characteristics of CNT depending on the catalytic metal. In order to make it possible to grow CNTs, one must first deposit a catalytic metal layer. The conventional methods for depositing catalytic metal layer are sputtering and evaporation. Unconventional methods were also used to synthesize CNTs—the floating catalyst method [4], the simplified hot filament chemical vapor deposition method [5], the aerosol pyrolysis method [6] and CVD method, using spin coated metal oxide. Single wall carbon nanotubes (SWNTs) represent very good characteristics but SWNTs grow at high temperature (higher than 900 °C) and the alignment of SWNTs is not as good as that of multiwall carbon nanotubes (MWNTs) grown by the plasma-enhanced chemical vapor deposition (PECVD) process [7]. Recently, PECVD attracted attention for carbon nanotube growth to its mass productivity, its high uniformity, and its good alignment of CNTs.

In this work, we prepared two kinds of catalytic layers—nickel and iron (III) nitrate metal oxide, onto n-typed silicon substrate by r.f.-magnetron sputtering and spin coating, respectively, to compare the growth characteristics of CNT depending on the catalytic metal.

2. Experiments

We used two kinds of catalytic layers—nickel and iron (III) nitrate metal oxide, onto n-typed silicon substrate by r.f.-magnetron sputtering and spin coating,
respectively. Before the catalyst layer was deposited, the substrate was cleaned in TCE, acetone, methanol and deionized water for 5 min in each step to remove organic contaminants. Then the silicon substrate was loaded in the r.f.-magnetron sputter and the spin coater for the catalyst layer growth, respectively.

In the r.f.-magnetron sputter, the chamber was pumped down to the base pressure of 0.5 mTorr with a turbomolecular pump and then argon gas was introduced into the chamber in order to maintain a working pressure of 20 mTorr. Once the pressure was stabilized, an r.f.-power of 200 W was applied. Chromium of 130 nm was deposited first to improve the adhesion of the nickel catalyst layer, and then a nickel layer of 30 nm was deposited before growing CNTs.

To obtain the iron (III) nitrate metal oxide catalytic layer, 0.5 mol of ferric nitrate nonahydrate [Fe(NO₃)₃·9H₂O] ethanol solution was coated onto silicon by a spin coater at various rotation speeds (rev./min) and each substrate was coated at two different rotation speeds. Each rotation speed was maintained for 30 s. After spin coating, the substrate was dried for 24 h in a clean room.

The substrate with the Cr/Ni catalytic layer was cleaned again by using the cleaning step mentioned previously before CNT synthesis. However, the substrate with the iron (III) nitrate metal oxide catalytic layer was not cleaned because the metal oxide was soluble.

The pretreatment and CNT synthesis were accomplished with HFPECVD system, which was described in detail in Han et al. [8] Acetylene (C₂H₂) gas was used as the carbon precursor and ammonia (NH₃) was used as dilution gas. The chamber was pumped down to the base pressure of 20 mTorr by mechanical rotary pump and then ammonia gas of 126 sccm was introduced into the chamber in order to maintain a working pressure of 1 Torr. Once the working pressure was stabilized, DC powers for plasma and the tungsten filament were turned on. The plasma bias voltage was maintained at 700 V and the current was 18 mA. The current of the filament was varied automatically to maintain the substrate temperature of 600 °C. The substrate temperature was measured on the surface of the cathode with the K-type thermocouple. The pretreatment of catalyst layer was carried out in the ammonia plasma for 5 min to create seed from which CNTs started to grow and then acetylene of 47 sccm was introduced into the chamber for the growth of carbon nanotubes. After the introduction of acetylene, the current of DC power for plasma was automatically increased to 39 mA. The substrate size was 2×2 cm.

Table 1 shows the preparation condition of iron (III) nitrate metal oxide catalytic layer. From S₁ to S₄, each substrate was rotated at two different speeds for 30 s in each stage. For example, the S₁ substrate was rotated in spin coater with 2000 rev./min for 30 s and 3000 rev./min for 30 s. For each preparation condition of the catalyst layer, the growth characteristics of carbon nanotubes were observed.

The pretreated catalyst layer and CNTs were investigated with scanning electron microscopy (SEM) for the morphology of the catalyst layer with different kinds of catalytic metal—nickel and iron (III) nitrate metal oxide. Transmission electron microscopy (TEM) was used to investigate the structure of nanotube, and electron dispersive X-ray spectrometry (EDS) was also used to investigate the elements of carbon nanotube and its tip. Triple Raman spectrometer (Jobin–Yvon T6400) with the excitation wavelength of 640 nm argon laser was used to investigate the chemical information of carbon nanotubes.

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>1st speed (rev./min)</th>
<th>2nd speed (rev./min)</th>
<th>CNT diameter (μm)</th>
<th>CNT length (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S₁</td>
<td>2000</td>
<td>3000</td>
<td>88</td>
<td>6</td>
</tr>
<tr>
<td>S₂</td>
<td>4000</td>
<td>5000</td>
<td>47</td>
<td></td>
</tr>
<tr>
<td>S₃</td>
<td>6000</td>
<td>7000</td>
<td>21</td>
<td>7.04</td>
</tr>
<tr>
<td>S₄</td>
<td>8000</td>
<td>9000</td>
<td>35</td>
<td>6</td>
</tr>
<tr>
<td>Ni</td>
<td></td>
<td></td>
<td>24</td>
<td>1.36</td>
</tr>
</tbody>
</table>

3. Results and discussion

To find out the characteristics of catalytic metal after pretreatment, we prepared Ni and iron (III) nitrate metal oxide [Fe₂(NO₃)₃] catalytic layer coated silicon substrate. The plasma bias was 700 V and the substrate temperature was 600 °C during pretreatment. Fig. 1 shows the surface of catalyst layer pretreated for 5 min.

The entire layer was transformed into the catalytic seeds for the growth of CNTs. In the case of Ni coated substrate, the seeds were distributed uniformly. Also the pretreatment of iron (III) nitrate metal oxide was dependent on the spin coating speed. The shape and the size of seeds were very random at low speed. However, with increased rotation speed, the uniformity of catalytic seeds was improved. Especially, we got very similar image of catalytic seeds in S₁ to the case of Ni catalytic layer.

Fig. 2 shows typical SEM images of CNTs grown on Si substrate for 20 min with the pretreated Ni and iron (III) nitrate metal oxide [Fe₂(NO₃)₃] catalytic layer. All other deposition conditions were kept the same as the pretreatment. In Ni coated substrate, as we could see in Fig. 2a, CNTs were well oriented, but the density of CNTs were not so high compared with other cases. In iron (III) nitrate metal oxide coated substrate, with the increased revolutions per minute, the density of CNTs was improved and their diameter decreased. The diameter for each sample and the length of CNT are shown.
in Table 1. However, in the case of iron (III) nitrate metal oxide coated substrate, the orientation of CNTs was not as good as those with Ni coated substrate, and especially S2 got intertwined with one another.

It was observed by TEM image that CNTs synthesized in this work had multiwall structure.

However, further analysis is needed to observe how many walls are included in each sample. Catalyst particles were sitting on the top of the tube and CNTs had hollow. In the case of CNTs grown on Ni, the diameter was larger than that of CNTs grown on iron (III) nitrate metal oxide for the same growth time. CNTs grown on iron (III) nitrate metal oxide had a bamboo structure and some of them did not have catalyst tip. This could be explained in two ways. While making the TEM sample, we used a CNT ethanol solution and during this procedure the iron (III) nitrate metal oxide was dissolved in ethanol. Another possibility is that CNT's tip was off during the ultrasonic cleaning for the preparation of the TEM sample. This explanation is better supported by Fig. 3b. However, further observation is needed for these possibilities.

Fig. 1. SEM images of catalyst layer pretreated with plasma bias of 700 V at 600 °C. (a) Ni layer, (b) Iron (III) nitrate metal oxide layer (2000 rev./min for 30 s and then 3000 rev./min for 30 s), (c) Iron (III) nitrate metal oxide layer (4000 rev./min for 30 s and then 5000 rev./min for 30 s), (d) Iron (III) nitrate metal oxide layer (6000 rev./min for 30 s and then 7000 rev./min for 30 s), and (e) Iron (III) nitrate metal oxide layer (8000 rev./min for 30 s and then 9000 rev./min for 30 s).
Fig. 2. SEM images of CNTs grown in plasma bias 700 V, 600 °C (a) on Ni layer, (b) on Iron (III) nitrate metal oxide layer (2000 rev./min for 30 s and then 3000 rev./min for 30 s), (c) on Iron (III) nitrate metal oxide layer (4000 rev./min for 30 s and then 5000 rev./min for 30 s), (d) on Iron (III) nitrate metal oxide layer (6000 rev./min for 30 s and then 7000 rev./min for 30 s), and (e) on Iron (III) nitrate metal oxide layer (8000 rev./min for 30 s and then 9000 rev./min for 30 s).

Fig. 4 shows EDS spectra of CNT tip grown on Ni and iron (III) nitrate metal oxide [Fe$_2$(NO$_3$)$_3$] catalytic layer, respectively. Each figure shows that the tip of CNT is constituted with the same catalyst metal as one coated on the substrate. In lower graph, Cu peak was observed because we used copper TEM grid. However, in the upper graph, we could not observe Cu peak, which was considered to be overlapped to Ni peak.

The samples were measured with Raman spectrometer with an excitation wavelength of 640 nm of an Ar laser to investigate CNTs' chemical information. Fig. 5 represents triple Raman spectra of CNTs synthesized with different catalyst. The G line (1598 cm$^{-1}$) is assigned to $E_{2g}$ mode of highly oriented pyrolytic graphite and demonstrates the presence of crystalline graphite carbon. The D line (1360 cm$^{-1}$) can be related with either defective graphitic layer or carbonaceous particles [9].

The position of the G and D lines was the same for every sample. In the case of iron (III) nitrate metal oxide catalyst substrate, the intensity ratio of D- to G-line peak ($I_D/I_G$) increased as the revolutions per minute increased, which indicates that the amounts of amorphous carbonaceous and defective structure in MWNT increased, and a decreasing degree of crystallinity in the sample. In the case of Ni, we could observe sharp peaks compared with iron (III) nitrate oxide catalyst case,
Fig. 3. TEM images of CNT grown in plasma bias 700 V, 600 °C. (a) on Ni layer, (b) on Iron (III) nitrate metal oxide layer (2000 rev./min for 30 s and then 3000 rev./min for 30 s), (c) on Iron (III) nitrate metal oxide layer (4000 rev./min for 30 s and then 5000 rev./min for 30 s), (d) on Iron (III) nitrate metal oxide layer (6000 rev./min for 30 s and then 7000 rev./min for 30 s), and (e) on Iron (III) nitrate metal oxide layer (8000 rev./min for 30 s and then 9000 rev./min for 30 s).

Fig. 4. EDS spectra of CNT tip grown in plasma bias 700 V, 600 °C. (a) on Ni layer, and (b) on Iron (III) nitrate metal oxide layer (8000 rev./min for 30 s and then 9000 rev./min for 30 s).

which implies that CNT films on Ni were well graphitized in these samples [10]. Also the peak at 500 cm$^{-1}$ for each material is considered to be from Si substrate.

4. Conclusion

CNTs grown on two kinds of catalyst—nickel and iron (III) nitrate metal oxide [Fe$_2$(NO$_3$)$_3$], at 600 °C were obtained by using hot filament plasma-enhanced chemical vapor deposition. In the case of the iron (III) nitrate metal oxide [Fe$_2$(NO$_3$)$_3$] catalytic layer, the uniformity of pretreated catalyst particle was improved, and the diameter of CNT decreased as the catalytic layer was deposited with higher speed. In the case of Ni coated substrate, CNTs were oriented perpendicularly and the growth rate was not so high as for the iron (III) nitrate metal oxide.

TEM measurement showed typical image of MWCNTs with hollow bodies and we could observe very thin CNTs whose diameter was few nanometers. EDS spectra showed that the tip of the CNT was composed of its original catalytic material.

The position of the D and G bands from Raman spectra did not vary with the catalyst and its coating condition. Also the intensity ratio of $I_D/I_G$ increased with the increased spin coating velocity.

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References