Effect of temperature and role of Mo top layer on the growth of carbon nanotubes

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Abstract
Carbon nanotubes (CNTs) were synthesized by a thermal chemical vapor deposition method using a three-layer Al/Fe/Mo metal catalyst. All metal layers were deposited by dc sputtering. With a scanning electron microscope (SEM) and Raman spectra, we investigated the effect of temperature and the role of the Mo top layer on the structure and quality of grown CNTs. The results showed that the growth temperature was an important parameter for the synthesis of CNTs. With an Al/Fe/Mo triple layer catalyst, the role of the Mo top layer was as the barrier layer to control the diameter, density and the peak intensity ratio of the G-peak to D-peak (I_G/I_D) of the CNTs. These results indicate that the thickness of the Mo top layer increased, which leads to decrease of the density of the CNTs. In the case of Mo 5 nm, the radial breathing mode (RBM) of the CNTs was observed in Raman spectra at 250 cm⁻¹ and corresponds to the single-wall carbon nanotube with 0.95 nm diameter.

Keywords: carbon nanotube, chemical vapor deposition, Mo top layer

Classification numbers: 5.00, 5.14

1. Introduction

In 1991 [1], Iijima reported on a new material with several particular properties and its potential for large applications. They were called carbon nanotubes (CNTs) and consisted of two kinds: single-wall nanotubes (SWNTs) and multi-wall nanotubes (MWNTs).

Since that discovery, carbon nanotubes have attracted the attention of scientists due to their particular microstructures and unique physical, chemical and electronic properties. Today, CNTs are attractive materials with a wide range of applications in chemical sensors, catalytic support, structural composites, scanning probe microscopy (SPM) tips, fuel cells and field emission [2–4].

In this work, CNTs were grown by a thermal chemical vapor deposition (CVD) technique using an Al/Fe/Mo tri-metallic catalyst. These metal layers were deposited using a dc sputtering method. Acetylene (C₂H₂) gas was used as the carbon feedstock. CNTs were characterized using scanning electron microscopy (SEM) and Raman spectroscopy. The effect of temperature on the growth of CNTs and the relation between the thickness of the Mo top layer and the morphology of the CNTs were investigated.
Figure 2. SEM images of CNTs grown on Al(15 nm)/Fe(3 nm) at (a, b) 600 °C, (c, d) 700 °C, (e, f) 800 °C and (g, h) 900 °C in 10 min.
Figure 3. Raman spectra of the CNTs grown by thermal CVD at 600 °C, 700 °C, 800 °C and 900 °C.

Figure 4. SEM images of CNTs grown at 800 °C using Mo/Fe/Al with thickness of the Mo layer from 0.5 to 5 nm.

2. Experiment

2.1. Preparation of the metal catalyst

The metal catalyst films were prepared by dc sputtering. First, an n-type silicon wafer was cleaned by sonication with methanol, ethanol and deionized (DI) water. It was then transferred to a dc sputtering chamber (CoreVac, Korea). The chamber was pumped down to a base pressure of 10⁻⁶ Torr and then Ar was added with 30 sccm flow. An Al layer with thickness of 15 nm was first deposited on the silicon substrate.
Figure 5. Raman spectrum for the CNTs samples synthesized with different thickness of the Mo top layer (0.5; 1.0; 1.5; 2.0 and 5.0 nm) in the RBM band (a–e); (f) shows the ratio $I_G/I_D$ versus the thickness of Mo.

Then, a Fe catalytic layer was deposited with thickness of 3 nm. Mo with thickness from 0.5 to 5 nm was finally deposited as a barrier layer.

2.2. Growth of carbon nanotubes
Carbon nanotubes were synthesized by rapid thermal chemical vapor deposition, RTCVD. The as-deposited sample was placed into a tube chamber. The substrate was heated up by a halogen lamp at a pressure of a few Torr with argon and hydrogen gases. The flow rates of Ar and $H_2$ were 800 and 100 sccm, respectively. The growth of CNTs was performed for 10 min by adding $C_2H_2$ at a rate of 50 sccm. The hydrogen gas was used to pretreat the catalytic layers into their nano particles, and remove amorphous carbon produced in the growth of CNTs [5].

Finally, the reactor was cooled down under Ar and $H_2$ gases. The growth temperature is changed from 700 °C to 900 °C.

2.3. Sample characterization
The morphology of CNTs was investigated with SEM (JSM 6700F, Japan). The Raman spectrum of as-grown CNTs was recorded by Fourier transform (FT) Raman spectroscopy (Renishaw inVia, England) with excitation at 514 nm.

3. Results and discussion

3.1. The effect of temperature on the growth of carbon nanotubes
In this experiment, we investigated the effect of temperature on the growth of carbon nanotubes at 700 °C–900 °C. CNTs were synthesized on the Al/Fe sample. Figure 2 shows SEM images of CNTs grown at 600 °C, 700 °C, 800 °C and 900 °C with 10 min growth. As shown in figure 2, when the growth temperature increased from 700 °C to 900 °C, the diameter and the length of the CNTs increased.
In cross-view (b, d and f), the CNTs tend to be uniformly aligned at 600°C, 700°C and 800°C with increasing their height from 24 to 175µm. At 900°C, the CNTs formed a random orientation and were entangled on the substrate. It can be seen that the length of the CNTs increased with the increase of the growth temperature.

Figure 3 shows FT-Raman spectra from 1200 to 1700 cm\(^{-1}\). The quality of carbon nanotubes can be identified by using the peak intensity ratio of the G-peak (1580 cm\(^{-1}\)) to D-peak (1320 cm\(^{-1}\)). With the increase of the growth temperature, the \(I_G/I_D\) ratio increased. This means the defect concentration of the CNTs decreased [6]. Therefore, the structure and quality of carbon nanotubes could be controlled by changing the growth temperature.

3.2. The effect of the Mo top layer

Finally, the role of the Mo top layer on the synthesis of CNTs was studied using a tri-layer Al/Fe/Mo. An Mo layer with thickness ranging from 0.5 to 5 nm was deposited on a layer of Al/Fe. Except for the thickness of the Mo top layer, carbon nanotubes were grown under the same conditions, with Ar/H\(_2\)/C\(_2\)H\(_2\) flow rates of 800/100/50 sccm and a growth time of 10 min at 800°C.

As seen in the SEM images of figure 4, the density of the CNTs grown by the Mo/Fe/Al catalytic layer decreased with increasing thickness of the Mo top layer from 0.5 to 2 nm.

In the Raman spectrum of the carbon nanotubes, the radial breathing modes (RBM), which exist at 100–300 cm\(^{-1}\), could be used to investigate the single-wall nanotubes. The nanotube diameter \(d_t\) of a single-wall nanotube is calculated from the RBM equation, \(\omega_{\text{RBM}} \approx 248/d_t\), where \(\omega_{\text{RBM}}\) is RBM frequency (in cm\(^{-1}\)) [7]. In figure 5, \(d_t\) is calculated in the range 0.94–1.34 nm, dependent on the thickness of the Mo top layer. In the particular case of Mo 5 nm, a strong RBM peak is observed at 250 cm\(^{-1}\). It indicates the presence of SWNT with 0.95 nm diameter of tube.

In figure 5(f), the ratio \(I_G/I_D\) versus the thickness of the Mo top layer is plotted. It showed that if the thickness of the Mo top layer increased, the \(I_G/I_D\) ratio increased.

4. Conclusions

In our experiments, we investigated the effect of growth temperature and thickness of the Mo top layer in a tri-layer Al/Fe/Mo on the growth of carbon nanotubes. It was shown that temperature was an important parameter in the synthesis of CNTs. The structure and quality of the CNTs could be controlled by changing the growth temperature. Also, a Mo top layer was used as a barrier layer to control the density and \(I_G/I_D\) ratio of the CNTs. These results indicate that increasing the thickness of the Mo top layer, the \(I_G/I_D\) ratio could increase and the density of the grown CNTs decrease. In the case of Mo 5 nm, strong RBM of the CNTs was observed in the Raman spectrum at 250 cm\(^{-1}\), corresponding to the single-wall carbon nanotube with 0.95 nm diameter.

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References

[1] Iijima S 1991 Lett. Nature 354 56
[2] Se J K, Yong H L, Chan W K, June H L and Geun-Y Y 2006 Carbon 44 1530
[3] Chen Y S, Huang J H, Hu J L, Yang C C and Kang W P 2007 Carbon 42 3007
[4] Singh B K, Sung W C, Bartwal K S, Nguyen D H and Ryu H 2007 Solid State Commun. 144 498
[5] Alexandru R B, Li Z, Dervishi E, Lupu D, Xu Y, Saini V, Watanabe F and Alexandru S B 2008 Phys. Lett. A 372 3051
[6] Dresselhaus M S, Dresselhaus G, Saito R and Jorio A 2005 Phys. Rep. 409 47
[7] Ouyang Y, Conga L M, Chena L, Liub Q X and Fang Y 2008 Physica E 40 2386