EFFECT OF THE TEMPERATURE AND CATALYST LAYER OF MO/FE/AL ON GROWTH OF CARBON NANOTUBES

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ABSTRACT: *Carbon nanotubes (CNTs) were synthesized by thermal chemical vapor deposition method using a three layer Mo-Fe-Al metal catalyst. All metal layers were deposited by DC sputtering method. By analysis with SEM and Raman spectra, we investigated the effect of temperature and the role of Mo layer on the quality of synthesis CNTs.*

Keywords: *Carbon nanotube; Chemical vapor deposition.*

1. INTRODUCTION

In 1991 [1], Iijima reported about the new material with several particular properties and ability of large applications. Their structure is many graphitic carbon sheets which are rolled to nanotube, with from 4 to 30 nm in diameter and up to 1 μm in length [1]. They were called carbon nanotubes (CNTs) with two kinds: single-wall nanotube (SWNT) and multi-wall nanotube (MWNT).

Since their discovery, carbon nanotubes have been attracted the attention of scientist and researcher due to their particular microstructures, unique physical and chemical properties [2]. Today, CNTs are interesting materials in wide range of applications in chemical sensor, catalytic support, structural composite, SPM tips, fuel cell, hydrogen storage and field emission [3-5].

CNTs can be synthesized by various methods such as arc discharge, laser ablation, catalytic chemical vapor deposition (CCVD) and flame synthesis [7]. In arc discharge and laser ablation, carbon source is made by vaporization of solid carbon targets. For the growth of CNTs by CVD, different gasses can be used as carbon feedstock (methane, ethylene, acetylene, CO,...) [7]. Besides the commonly employed Fe, Co and Ni catalysts, many bimetallic catalysts like Fe-Mo, Co-Mo, Co-Ni and Fe-Co have also been effectively utilized [5].

In this work, CNTs were grown by thermal CVD technique using a three layer Mo-Fe-Al metal catalyst. These metal layers were deposited by DC sputtering method. Acetylene (C_2H_2) gas was used as the carbon feedstock. The hydrogen gas was used to pretreat the catalytic layers into their nano particles, and remove amorphous carbon produced in the growth of CNTs [6]. CNTs were characterized by using scanning electro microscopy (SEM) and Raman spectroscopy. The effect of temperature on the growth of CNTs and the relation between the thickness of metal layer and the morphology of CNTs were investigated.

2. EXPERIMENT

2.1. Preparation of metal catalyst

The metal catalyst films were prepared by DC sputtering method. First, a n-type silicon wafer was cleaned by sonication with methanol, ethanol and DI water. It was then transferred to a DC sputtering chamber (CoreVac, Korea). The chamber was pumped down to the base pressure of 10^{-6} Torr and then Ar was added with the flow of 30 sccm. The Al layer with a thickness of 15 nm was first deposited on Si substrate. Followed a 3 nm thick of Fe catalytic layer, the thickness of Mo 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 halogen lamp at the pressure of a few Torr with a gas mixture (argon and hydrogen). These gases were run by the mass flow controller. The flow rate of Ar and H_2 were 800 and 100 sccm, alternately. The growth of CNTs was performed for 10 min by adding C_2H_2 with the rate of 50 sccm. The CNTs were synthesized on the metal catalytic with C_2H_2 as carbon precursor. Finally, the reactor was cooled down in Ar and H_2 environment. The growth of temperature is from 600°C to 900°C.

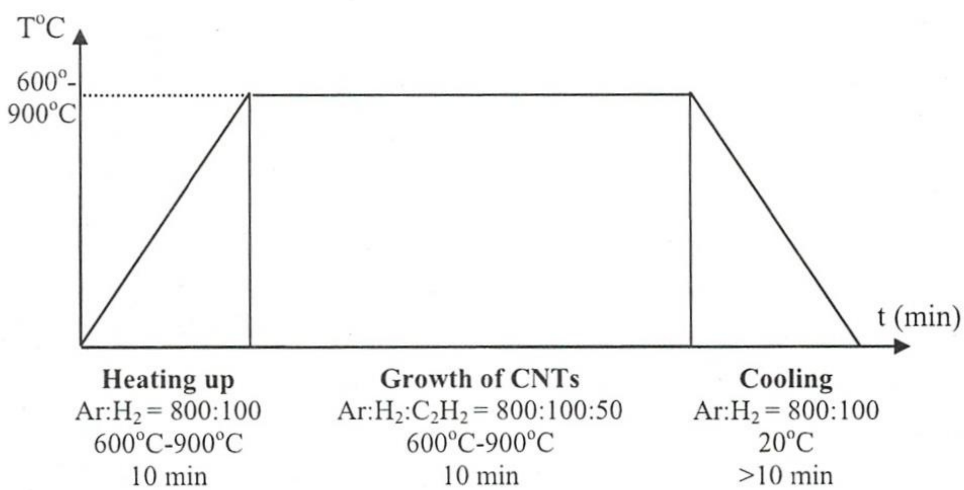


Fig.1. The growth of carbon nanotubes process

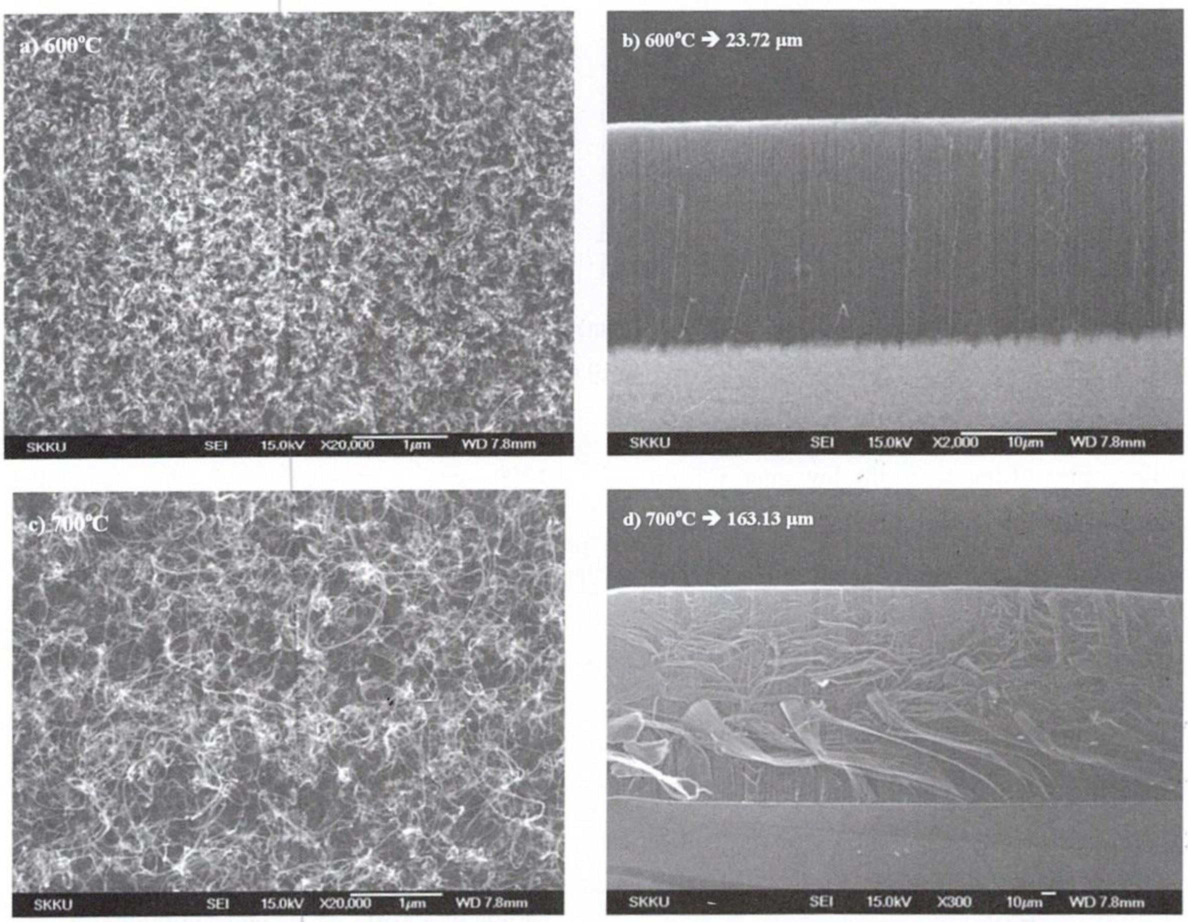
2.3. Sample characterization

The morphology of CNTs was investigated with a JEOL JSM 6700F scanning electron microscope (SEM). The Raman spectra of as-grown CNTs was recorded by micro Raman system (Renishaw Invia Basic) with an excitation of 514 nm (Ar ion laser).

3. RESULTS AND DISCUSSION

3.1. Effect of temperature on the growth of carbon nanotubes

In this experiment, we investigated the effect of temperature on the growth of carbon nanotubes in 600°C-900°C. CNTs were synthesized on Fe(3nm)/Al(15nm) substrate. Fig.2 shows the SEM images of CNTs grown at 600°C, 700°C, 750°C and 800°C with 10 min growth. The density and diameter of CNTs were decreased when it increased the temperature. The CNTs tend to be a uniformly aligned at 600, 700, and 750°C. At 800°C, CNTs were formed a random orientation on the substrate.



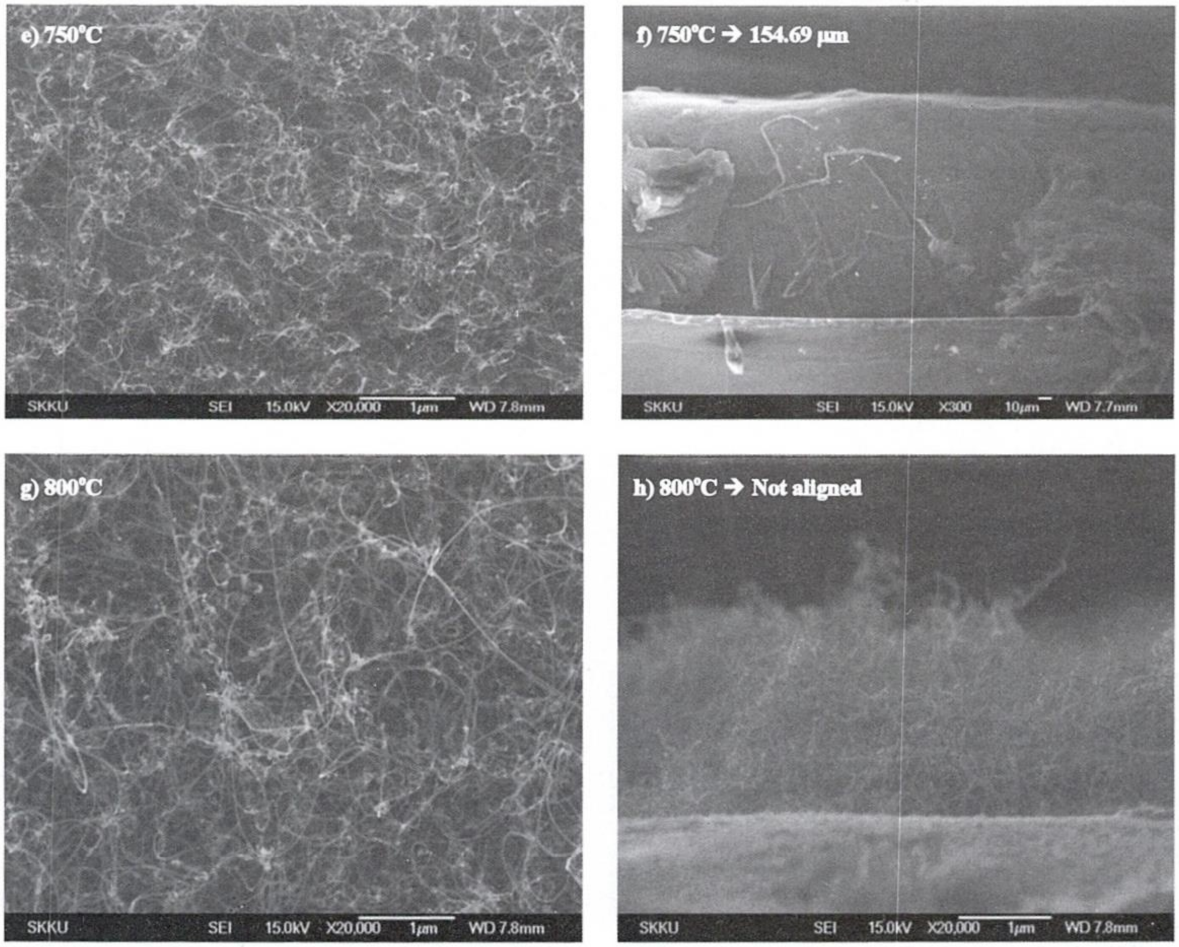


Fig.2. SEM images of CNTs grown on Fe(3nm)/Al(15nm) at [a,b] 600°C; [c,d] 700°C; [e,f] 750°C and [g,h] 800°C in 10 min

In the Raman spectra of CNTs, it was two main groups of bands: in the low-energy from 100 to 300 cm^{-1}, and the high-energy with wavelength from 1.000 to 3.000 cm^{-1} [8]. The oscillations (ω_{RBM}) in the low-energy were called the radial breathing modes (RBM), in which can be used to study the nanotube diameter (d_t) of SWNTs through the relation [3,8]:

$$\omega_{RBM} \approx \frac{248}{d_t} \qquad (1)$$

G-mode is a board band in the range 1500-1700 cm^{-1}, associated to the tangential stretching modes (G-band) [3]. And D-mode is another band in the range 1200-1400 cm^{-1}, which is assigned to a symmetry-lowering effect, such as defect of nanotube cap, bending of nanotubes, or the presence of nanoparticles and amorphous carbon [9]. The relatively high intensity of the G-mode relative to the D-mode (I_G/I_D) indicates a small amount of amorphous carbon or a lower defect concentration in CNTs [3].

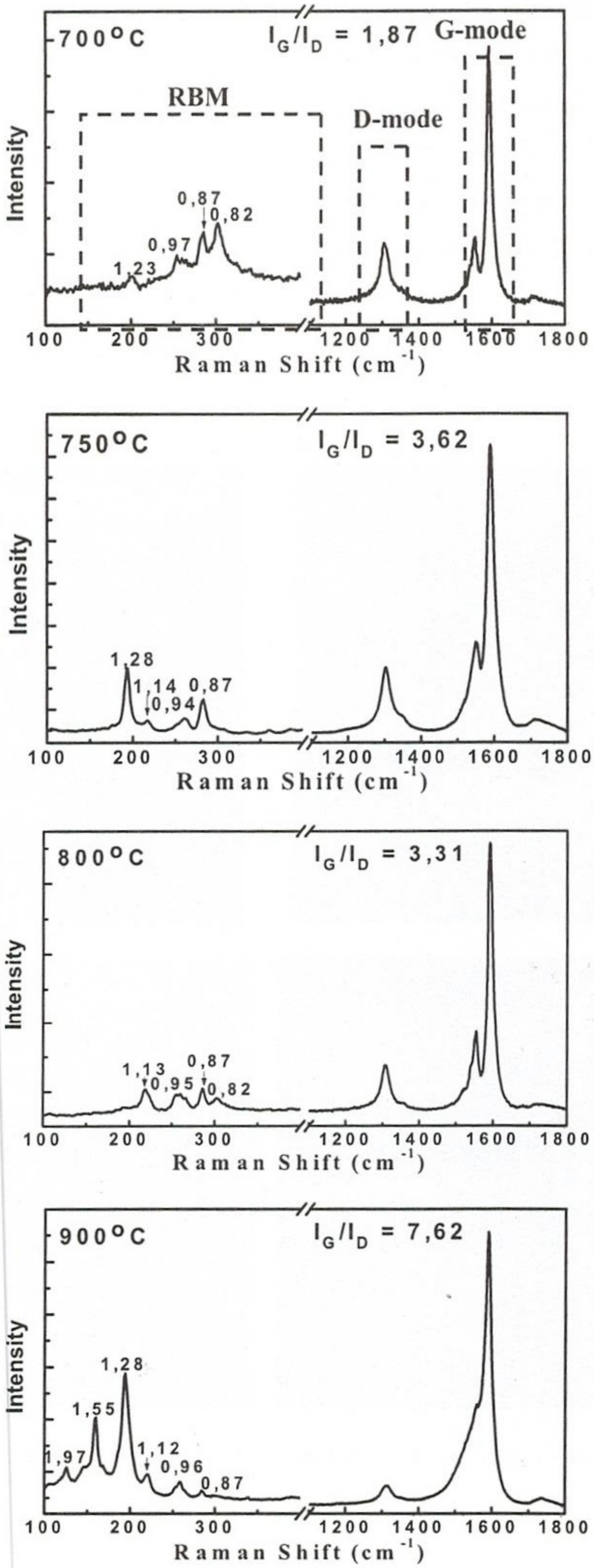


Fig.3. Raman spectra of CNTs at 700°C; 750°C; 800°C and 900°C with RBM mode, D-mode and G-mode

In the Raman spectra of CNTs, fig.3, the intensity ratio I_G/I_D of CNTs was increased as the temperature was increased. It means the defect concentration of CNTs decreased. Therefore, the structure and quality of carbon nanotubes could be controlled by changing the growth temperature.

3.3 Effect of the Mo top-layer

Finally, the role of Mo top-layer was studied on the synthesis of CNTs by using a three layer of Mo/Fe/Al. These metal layers were deposited by DC sputtering with a 3 nm thickness catalytic Fe layer on 15 nm of Al layer. The thickness of Mo layer from 0.5 to 5 nm was used as the barrier layer to control the diameter and density of CNTs.

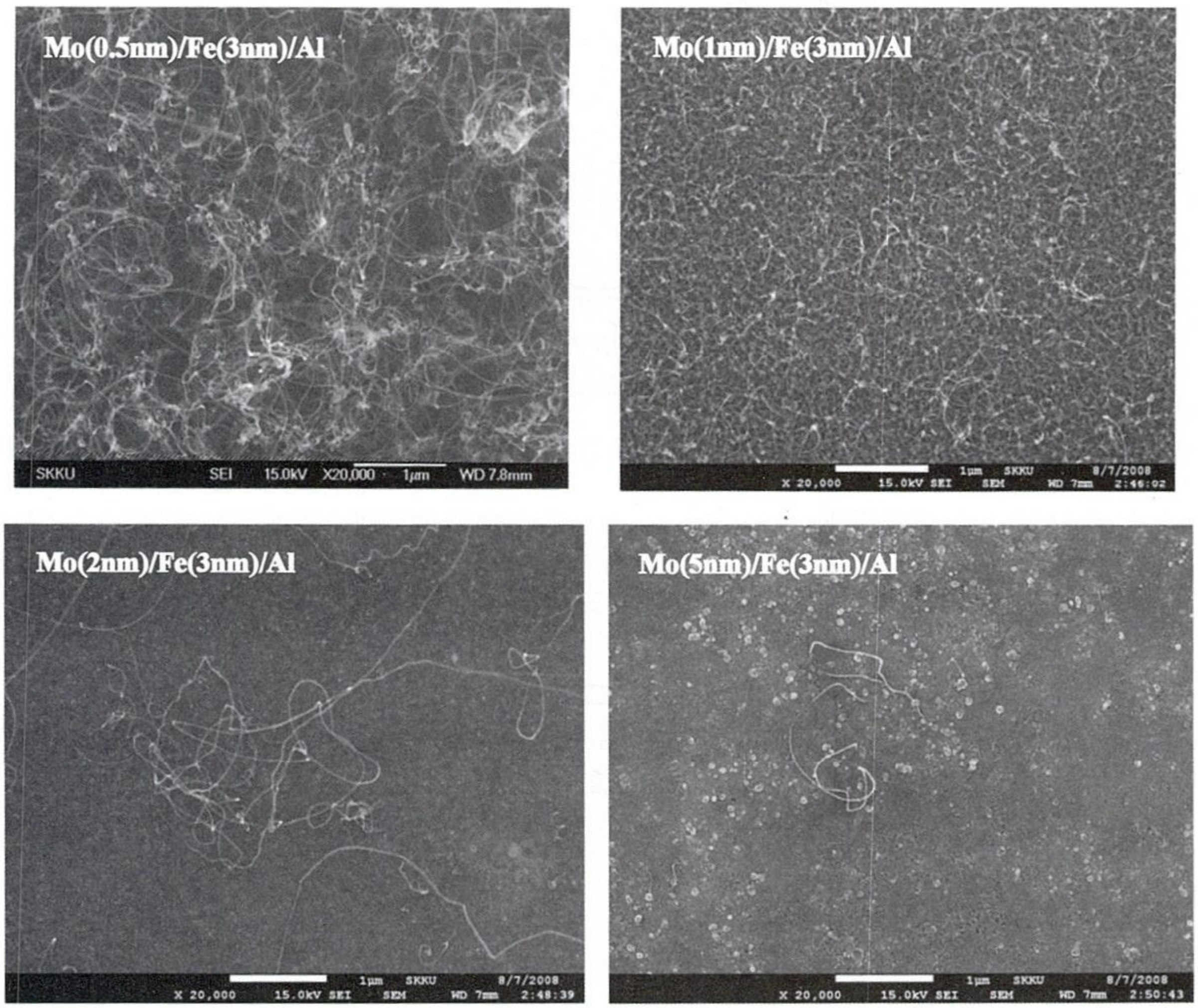


Fig.4. SEM images of CNTs grown at 800°C using the multi-layer Mo/Fe/Al with the thickness of Mo layer from 0.5 – 5 nm

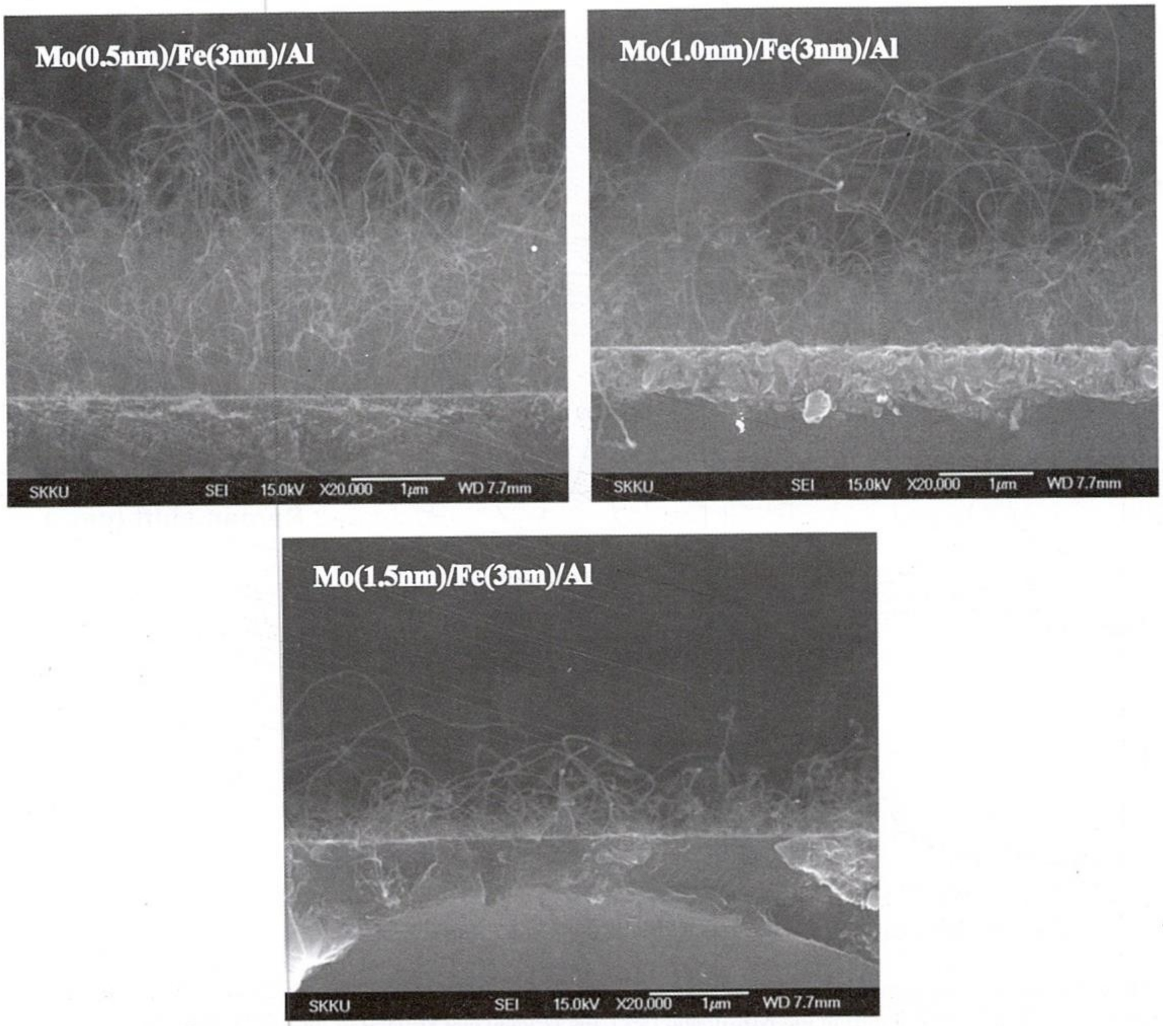


Fig.5. The cross-sectional view of CNTs grown at 800°C using the multi-layer Mo/Fe/Al with the different the thickness of Mo layer: 0.5, 1.0 and 1.5 nm

As SEM images, fig.4 and fig.5, the density of CNTs grown by Mo/Fe/Al catalytic layer was decreased with an increasing thickness of Mo top-layer.

And the Raman scattering spectral, the intensity ratio G/D was increased with increasing thickness of Mo. This is showed that if the thickness of Mo top layer is increase, it improves the synthesis of SWNTs by RCVD. In case of Mo 5 nm, strong RBM peak was occurred at 250 cm^{-1}, it was the present of SWNTs with diameter of tube was 0.95 nm.

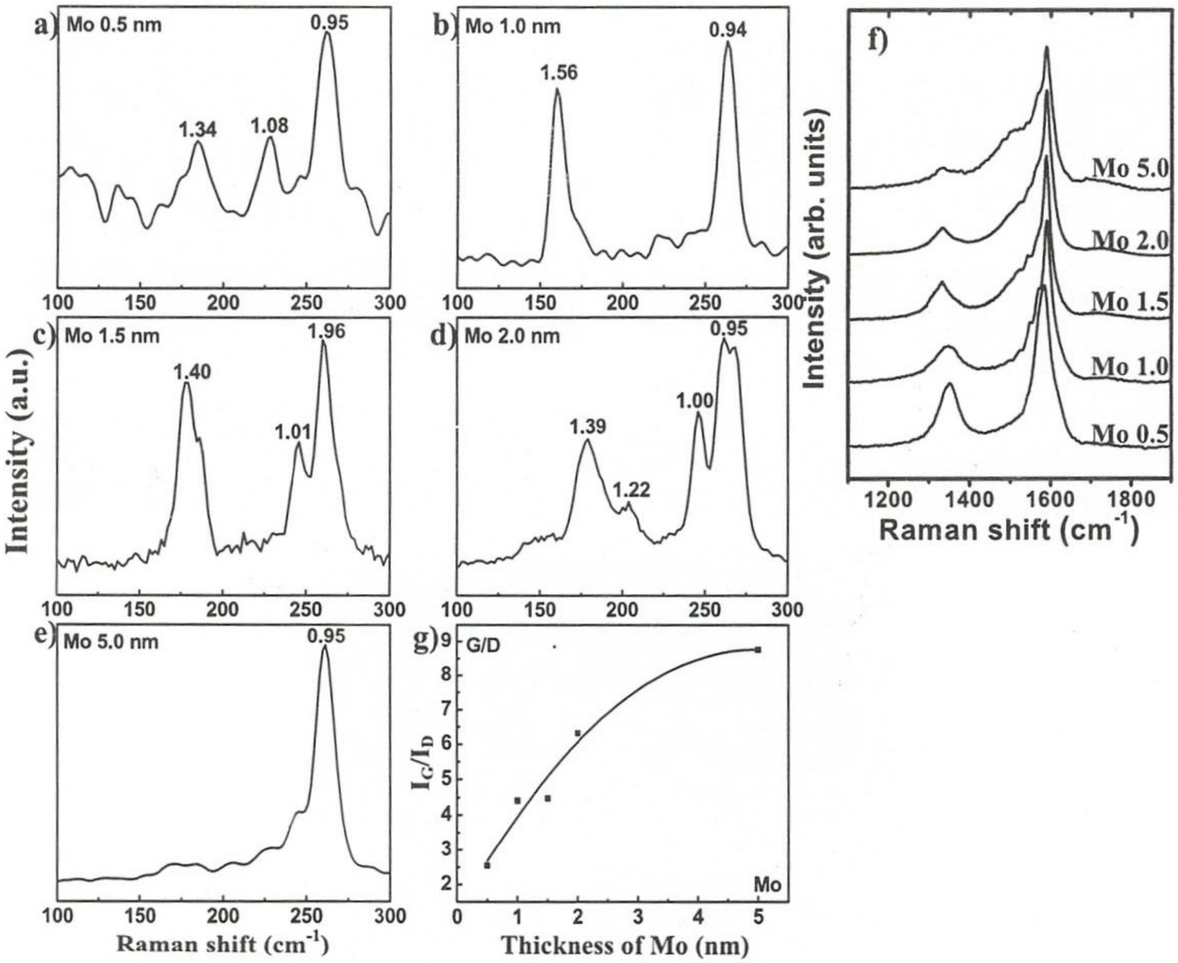


Fig.6. Raman scattering spectral for the nanotubes samples synthesized with different thickness of Mo top-layer (0.5; 1.0; 1.5; 2.0 and 5.0 nm) in the RBM band [a-e]; the D-band and G-band of the CNTs samples [f]; and [g] show the relative of I_G/I_D with thickness of Mo

4.CONCLUSION

In our experiments, we investigated the effect of temperature and thickness of catalytic layers on the growth of carbon nanotubes. It was showed that the temperature was an important parameter on the synthesis of CNTs. The structure and quality of CNTs could be controlled by changing the growth temperatures. With a three layer Mo/Fe/Al metal catalyst, the role of Mo top-layer was as the barrier layer to control the diameter and density of CNTs. The G&D ratio of CNTs grown by using Mo/Fe/Al catalytic layer were increased with increasing thickness of Mo top-layer. These results indicate that thickness of Mo top-layer were increased which leads to decrease the density of CNTs. In case of Mo 5 nm, strong RBM peak was occurred at 250 cm^{-1}, as the single-wall nanotubes with 0.95 nm of diameter.

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ẢNH HƯỞNG CỦA NHIỆT ĐỘ VÀ LỚP XÚC TÁC MO/FE/AL TRONG SỰ TỔNG HỢP ỐNG NANO CARBON

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TÓM TẮT: *Ống nano carbon (CNTs) được tổng bằng phương pháp lắng đọng nhiệt hơi hóa học, sử dụng lớp xúc tác kim loại 3 lớp là Mo-Fe-Al. Tất cả các lớp kim loại được phủ bằng phún xạ DC. Bằng phân tích SEM và phổ Raman, chúng tôi khảo sát sự ảnh hưởng của nhiệt độ và vai trò của lớp Mo đối với sự tổng hợp CNTs.*

Từ khóa: *ống nano carbon; lắng đọng hơi hóa học.*

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