

Low Temperature Growth of Carbon Nano-materials on Different Catalysts by the Surface-wave Plasma Technique

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In this work, the microwave surface wave plasma (MWSWP) equipment is used to grow the carbon nano-materials at low temperature on different catalysts prepared by the so-called plasma assisted sol-gel synthesis method. Without any additional heating method, the plasma itself can heat up the substrate to about 280°C. By applying the -600V bias voltage, the substrate temperature can reach more than 330°C. The Ar/H₂ plasma was utilized for pretreatment, and Ar/CH₄ plasma for the growth of carbon nano-materials. The optical emission spectroscopy (OES) was used to diagnose the components of plasma. At this low temperature, we would like to present different results. Without any bias voltage, Molybdenum (Mo) exhibited good catalytic property, and solid carbon nano-wires were obtained. Co and Ni proved to be better catalysts in the case of biasing the substrate, and carbon nanotubes (CNT) and carbon nanocones (CNC) growth on the Co and Ni, respectively.

Keywords: Low temperature growth, surface wave plasma, OES, carbon nano-material

1. Introduction

The one dimensional carbon nano-materials research, can be traced back to 1952,^[1] and was greatly boosted by the report made by Iijima on Nature in 1991.^[2] During the recent decade, applications of carbon nanotubes (CNT) have been widely researched.^[3] Among those prospective applications, the field emission displays (FED) based on the CNT emitters^[4] have considerable improved. However, the CVD^[5] and PECVD^[6] were yet the main methods for CNTs growth, requiring typically growth temperatures around 500 ~ 700°C. The high growth temperature limits the use of cheap substrate such as glass and polymer.^[3] This fact made unclear the commercialization of FED based on CNT emitters, in the competition with liquid crystal displays (LCD) and organic light-emitting diode displays (OLED). Although Z. F. Ren and his colleagues reported that it is possible to grow the CNTs on the display glass with the strain point at 666°C,^[7] it is still quite expensive. Despite this, some other solutions, such as screen printing,^[8] were used to overcome this problem and deposit the CNTs on the glass substrate. Several disadvantages of this method, such as the restriction of feature size, were reported.^[9] Therefore, new requirements to grow CNT on glass substrate with the purpose of fabricating the low cost FED were necessary^[10], and some progress had also been done.^[10-13]

In this work, we tried to prepare the carbon nano-materials at low temperature by using the MWSWP equipment. The catalyst was also synthesized by the so-called "surface wave plasma assisted sol-gel method". During MWSWP treatment, no additional heating source

was employed, the substrate was only heated by the plasma itself. The maximum temperature of the substrate during the growth was about 280 °C ~ 350 °C, (depending on whether the bias voltage is applied or not). The temperature was measured using thermo label (Nichiyu Giken Kogyo Co., Ltd). This temperature range made feasible the normal ITO glass as substrate.

Optical emission spectroscopy (OES) was used to diagnose the plasma during the growth. The morphology of the carbon nano-materials production was analyzed by the FE-SEM and TEM. We found a strong relation between the materials morphology and the type of catalyst, and the value of the negative bias voltage applied to the substrate stage.

2. Experiment

The catalyst precursor was prepared using a modified version of the reported traditional sol-gel method.^[14] The (NH₄)₂MoO₄, Co(Ac)₂ · 4H₂O and Ni(Ac)₂ · 4H₂O were dissolved in ethanol. The obtained solution was diluted to a concentration of about 10⁻⁵ mol/L serving as the catalyst precursor solution. Then, the precursor was dropped onto the cleaned (100) n-type silicon wafer substrate with a pipette. The substrate was then put in the vacuum chamber of the surface wave plasma equipment and dried by pumping. Surface-wave plasma CVD (SWPCVD) was applied, without extra heating, for the catalyst pre-treatment and the carbon nano-material growth. Fig. 1 shows a schematic drawing of the experimental setup. The SWP was produced in a 400 mm-diameter, cylinder vacuum chamber by introducing 2.45 GHz

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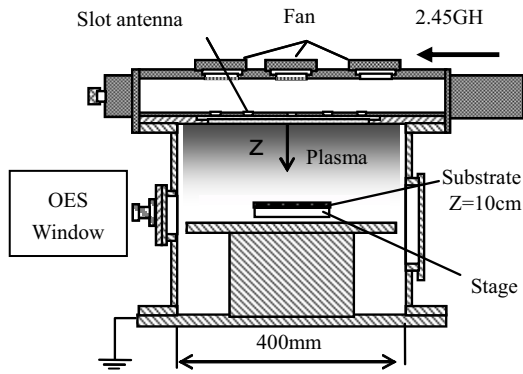


Fig.1 Schematic drawing of the experiment setup

microwaves through a quartz window via slot antennas. The samples were placed on a stage situated at 10 cm from the top of the chamber. A gas flow of Ar/H₂ with 50/50 sccm was introduced for the pre-treatment to reduce the metal oxidation and make the catalyst active. Then the Ar/CH₄ mixture gas of 100 sccm total gas flow rate was used to grow the carbon nano-materials. The working pressure of both the plasma pre-treatment and the growth process was 13.3 Pa. The Ar/H₂ plasma reducing time was 15 min to get relatively stable growth temperature and the growth process lasted also for 15 min. The applied microwave power was 900W. The temperature of the substrate was measured by thermo label. The samples morphology after treatment was determined by FE-SEM and TEM.

3. Results and discussion

3.1 OES measurement

The OES measurements were carried out to diagnose the plasma. Figure 2(a) shows a plasma spectrum of typical experimental conditions. We can distinguish a very strong C₂ emission peak (about at 516.5nm).^[15, 16] The C₂ swan system corresponding to $\Delta v=+2, +1, 0, -1, -2$ vibration sequences of the (D³Π_g-A³Π_u) electronic transition was also found. Besides, due to CH₄ decomposition, we observed peaks at 431.5 nm and 387.5 nm corresponding to CH A-X(²Δ-²Π), and CH B-X(²Σ-²Π) electron transition, respectively. These revealed the existence of CH and the appearance of H_α (656.5 nm) proving also the

existence of atomic hydrogen. The Ar⁺ ions (lines at 433.5 nm and 696.5 nm) are considered to facilitate the CH₄ decomposition, and C₂ production from resulted C atoms. Applying the negative bias voltage on the substrate, the energy of Ar⁺ ions that bombard the substrate increases, and a part of it is transferred to the substrate. The main lines of optical emission are listed in Table. 1.

Table.1 Main optical emission lines in the Ar/CH₄ plasma

Species	Transition	Wavelength (nm)
H _α	Balmer (n=3→2)	656.5
C ₂	Swan(D ³ Π _g →A ³ Π _u) Δv=0	516.5
C ₂	Swan Δv=+1	470.0
C ₂	Swan Δv=-1	563.5
C ₂	Swan Δv=+2	436.5
C ₂	Swan Δv=-2	618.0
CH	A-X(² Δ- ² Π)	431.5
CH	B-X(² Σ- ² Π)	387.5
Ar ⁺	4s ^o [1/2]-5p ^π [1/2]	433.5
Ar ⁺	4s ^o [1/2]-4p ^π [1/2]	696.5

C₂ species are thought to be a very important precursor in the carbon materials growth, such as CNT^[17] and diamond like carbon (DLC)^[18,19], by both CVD^[17] and PECVD^[18,19] methods. In order to optimize the plasma for the low temperature growth of carbon nano-materials, some adjustments to the gas ratio and the introduced microwave power were done. The results for the latest are presented in Fig. 2 (b) and (c) reflected on OES measurements. It is clearly shown that, for the same introduced power (900 W), the intensity of the C₂ emission peaks increases, while the CH₄ ratio of the mix gas decrease, from 40% to 2.5%. In the case of raising the microwave power from 700 W to 1000 W, CH₄ ratio (5%), the intensity of the C₂ emission peaks increased.

The OES results suggest that high introduced power and low CH₄ ratio are beneficial for the production and of C₂. According to this result, we reduced the CH₄ ratio in the mixed gas and increased the introduced power to optimize the plasma status of the low temperature growth of carbon nano-materials using the MWSWP method. Therefore, in our experiment, the work values are 5% CH₄ ratio, and 900 W microwave power.

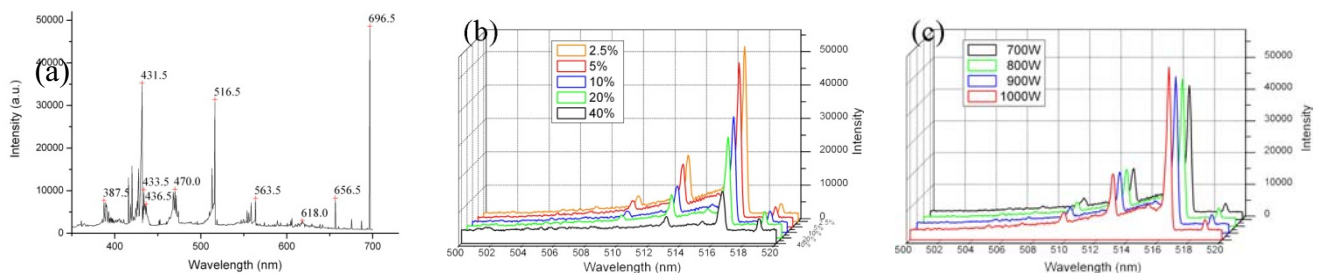


Fig.2 Optical emission spectra of CH₄/Ar plasma: (a) Full spectrum with 5% ratio of CH₄ and 900W introduced power; (b) C₂ swan-band peak ($\Delta v=0$) strength variation to the CH₄ ratio of the mixture gas at 900W; (c) C₂ swan-band peak ($\Delta v=0$) strength variation to the introduced power with CH₄ ratio of 5%; the pressure is 13.3 Pa and the mixture gas flow rate is 100 sccm.

3.2 Bias effect

Fig. 3 shows the variation of the current density versus the applied bias voltage. The relationship is linear and implies that the conductivity of the plasma remains constant during the increasing of bias voltage. The current density is given by:

$$J = \sigma E = \sigma \frac{U}{d}$$

where the conductivity is given by,

$$\sigma = (e^2 n_e) / (m_e v_{ce})$$

Therefore, it is concluded that by applying no more than -600 V bias voltage, only minor changes of the plasma density and electron temperature were produced in our

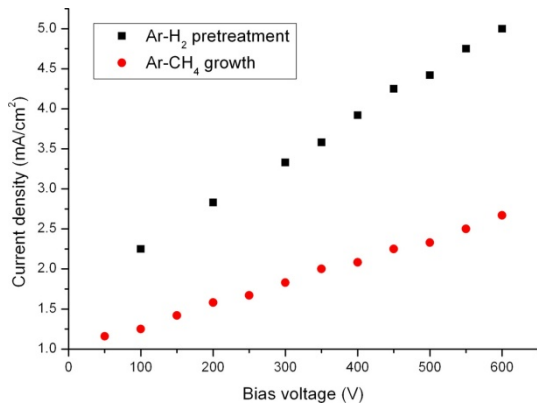


Fig.3 Current density variation to the bias voltage

experiment. This is a very important evidence, proving that no additional discharge occurred when the substrate is biased. Hence, we can affirm that the carbon nano-materials obtained in our experiment were synthesized by MWSWP method. However, the additional power introduced by the bias voltage supply heated up the substrate stage to about 330~350°C, according to the

thermo label. The substrate temperature was about 280°C when the bias voltage was not applied.

3.3 FE-SEM measurement

Figure 4 shows the FE-SEM images of the grown carbon nano-materials morphology at low temperature. According to Fig.4 (a), randomly grown carbon nano-fibers were obtained, with diameters of several tens nanometers on the Mo catalyst without bias voltage. However, no long fiber or wire structure was found in the materials grown on the Ni and Co catalysts, as shown in Figs.4 (b) and (c). The network-like film materials developed on the Ni catalyst, while on the Co, an amorphous structure was observed. In this case the substrate temperature was 280 °C.

Higher carbon deposition rates were found for all the catalysts when a -600 V voltage was applied on the substrate. This may be due to the increasing of substrate temperature caused by stronger ion bombardment in the high electrical field. In this case the substrate temperature turned a little higher to about 330~350°C. On catalyst samples no carbon nano-fibers grown, only cone-shape structures being found. They had several micro-meters in diameter, as Fig.4 (d) shows. Co and Ni exhibited better catalytic properties, as Fig.4 (e) and (f) show. In the FE-SEM image the carbon nano-materials grown on the Ni catalyst seem to be carbon nano-cones (CNC). Although the materials grown on Mo have a similar structure, the size of the cone structure grown on Ni was much smaller than in the case of Mo. The materials grown on Co are carbon nano-tube arrays, as also proved in the TEM measurements presented later in this work.

3.4 TEM measurements

Figure 5 shows two important images of the carbon nano-materials of our experiment. From the TEM image in

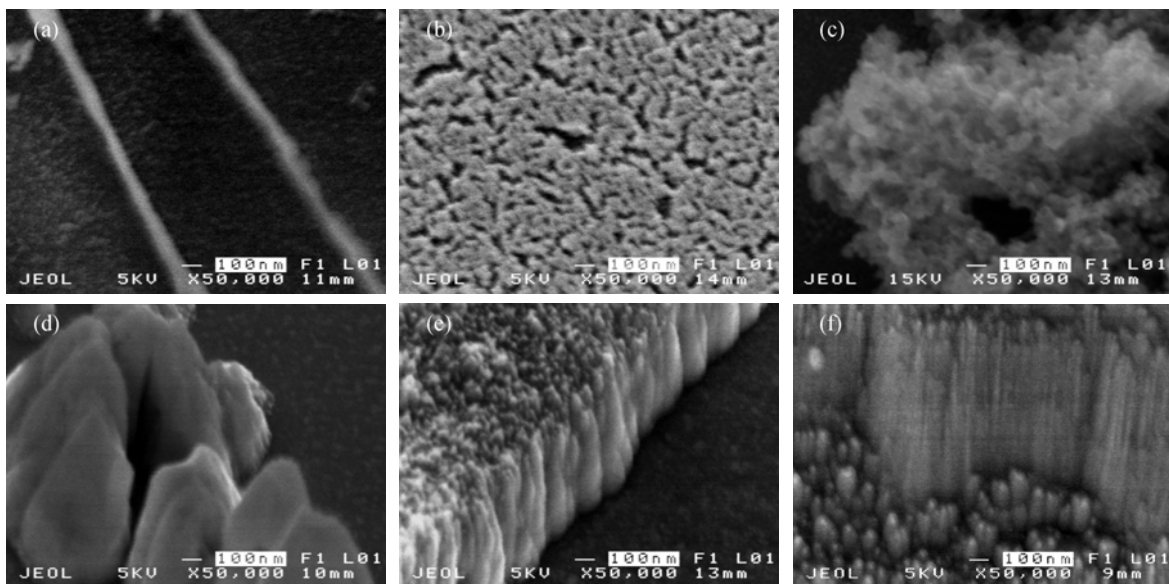
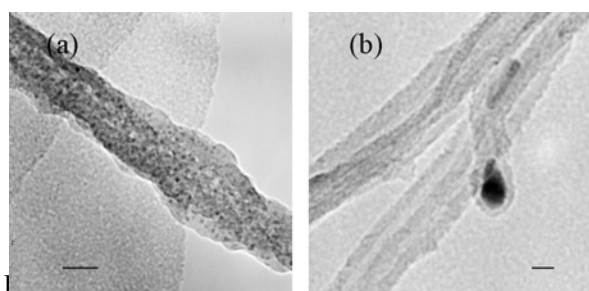


Fig.4 FE-SEM images of the carbon nano-material obtained: (a) Mo catalyst without bias; (b) Ni catalyst without bias; (c) Co catalyst without bias; (d) Mo catalyst with -600V bias; (e) Ni catalyst with -600V bias; (f) Co catalyst with -600V bias.

Fig. 5(a), we can confirm that on the Mo catalyst without applying a bias voltage, solid carbon wire grew. Fig. 5(b) presents the case of a -600 V biased substrate, when CNTs were produced on Co as catalyst.

In Fig. 5(b) we can clearly distinguish the catalyst particles in the tips of CNT. Fig. 5(a) shows many small black particles dispersed in the body of the wire. We speculate these particles were Mo particles. This result indicates a totally different growth mode of the carbon nano-wire other than vacuum-liquid-solid (VLS) growth model.^[20, 21]



(a) Mo catalyst without bias voltage; (b) Co catalyst with -600V bias voltage. Scale bar: (a) 20nm; (b) 10 nm.

4. Conclusion

In this work, MWSWP method was employed to produce low temperature growth of carbon nano-materials. The Ar/CH₄ plasma conditions were studied using OES for different gas ratio and microwave power in order to optimize the conditions for the carbon nano-materials growth. The analysis suggested that high introduced microwave power and low CH₄ ratio facilitate the C₂ species forming.

The morphology of the grown carbon nano-materials is also influenced by the type of catalyst material and applied bias on the substrate. Mo showed better catalytic properties without bias, and solid carbon nano-wires were obtained in this case. In contrary, Co and Ni exhibited a better catalytic role when the substrate was biased. CNT, and CNC vertical aligned arrays growth on the Ni and Co catalysts, respectively in these conditions.

Prof. Ostrikov demonstrated by model simulation that in the plasma the ion bombardment to the substrate helped the CNC growth.^[22] However, in our situation, it was revealed that the carbon species, such C₂, only deposited on the surface on the nucleus. But to grow CNT, the carbon species should be diffused through the catalyst particles, according to the VLS mode.^[21] As the condition of CNT array and CNC array were obtained under exactly same condition, (the samples with different catalysts in same dispersing densities were treated in the same time and the same chamber) the Co catalyst seems to have lower activation energy for the CNT growth. Therefore we concluded that, by applying the -600 V bias voltage in the plasma, the Co would obtain enough

energy for the CNTs to grow, while Ni received inadequate energy and only CNCs could develop.

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