

Research Article

Growth of Carbon Nanotubes on Carbon/Cobalt Films with Different sp^2/sp^3 Ratios

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The need of barrier layer such as SiO_2 for carbon nanotubes (CNTs) growth limits their performance in electronic applications. In this study, conductive carbon/metal (carbon/cobalt—C:Co) composite films with the same metal content, but different sp^2/sp^3 ratios, were deposited using dual-source filtered cathodic vacuum arc (FCVA) technique. Three different C:Co composite films were deposited at different temperatures; visible Raman spectroscopy indicates that the sp^2 -rich C:Co composite film forms at high temperature (500°C), and high-resolution transmission electron microscopy (HRTEM) shows the formation of conducting graphitic-like sp^2 clusters and with Co nanoclusters embedded within them. Electrical measurement shows a significant decrease in film resistivity as sp^2/sp^3 ratio increases. CNTs were successfully grown on the composite films by plasma-enhanced vapor deposition (PECVD) approach. Scanning electron microscopy (SEM) shows minor effect on the density of CNTs by varying the sp^2/sp^3 ratio. The dependence of defect level of the as-grown CNTs is found to reduce as sp^2/sp^3 ratio increases.

1. Introduction

Carbon nanotubes (CNTs) have attracted a lot of attention in the fields of nanoscience and nanotechnology because of their superior physical, electrical, and thermal properties [1, 2]. A substantial amount of work has been done to promote them in the industry, and one of the requirements is growth of CNTs on conductive metal or substrates [3, 4]. The conventional way of growing CNTs is a multistep process, the first of which is to deposit a barrier layer, which can be an insulating material such as silicon oxide (SiO_2) or conductive material such as titanium nitride [5]. Secondly it requires the deposition of a catalyst layer such as nickel (Ni), cobalt (Co), or iron (Fe). However, the effective electrical conductivity of the CNTs is higher when CNTs are grown directly on a conductive substrate [6]. An alternative approach to eliminate the use of barrier layer during growth

is to deposit amorphous carbon a-C metal (C:Me) composite film, such as C:Ni, C:Fe, and C:Co, as the catalyst layer.

Previous studies had shown that composite film serving as catalyst layer results in better density control of CNTs [7, 8] and also better performance in CNTs field emitter array (FEA) applications [9, 10]. Other than serving as the catalyst layer of CNTs growth, another advantage of incorporation of metal within C film is to increase the conductivity of the film. Takeno et al. found that the electrical conductivity is proportional to the amount of metal incorporated into the C:Me composite film [11–13]. However the focus was only on tuning the metal content of the film. The relationship between the CNTs growth and the intrinsic properties of C:Me composite film, such as the sp^2/sp^3 ratio, is not well understood yet. Recent work has shown that by in-situ thermal annealing and ex situ laser annealing, sp^2 -rich high electrical conducting nanostructured C film can be synthesized [14–17], which can

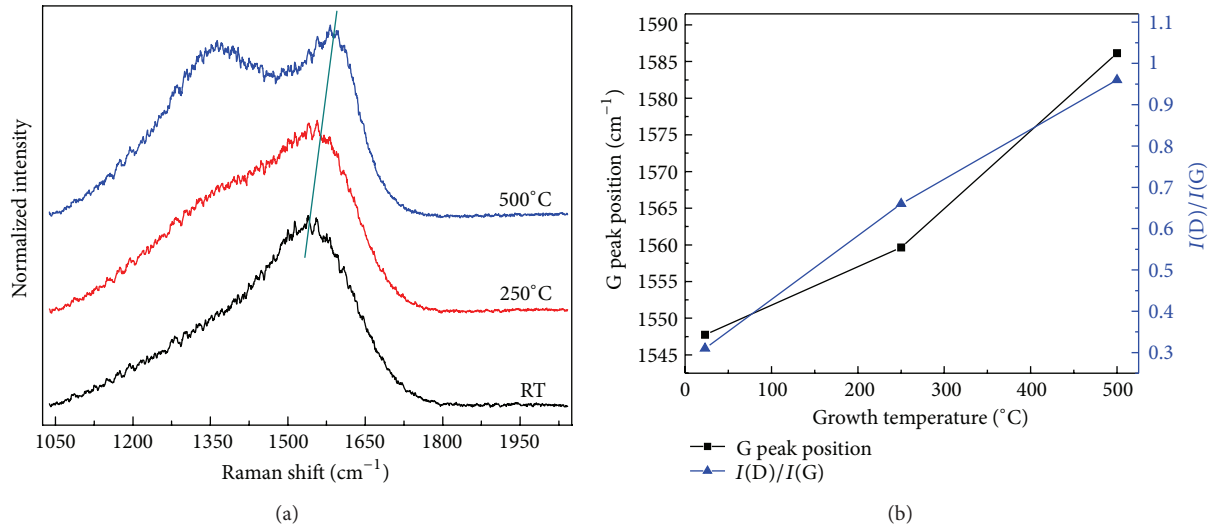


FIGURE 1: (a) Raman spectra of C:Co composite film grown using different growth temperatures and (b) Raman features as a function of growth temperature.

then be adopted in future electronic applications. Hence the electrical properties of C:Me composite film can be varied by only changing the sp^2/sp^3 ratio of the amorphous carbon.

In this work, C:Co composite film has been adopted as the catalyst layer of CNTs growth. We reported the feasibility of CNTs growth on conducting C:Co composite film, by only varying the sp^2/sp^3 ratio of the film. It adequately shows that CNTs can be grown on a conducting catalyst layer without the use of a barrier layer.

2. Materials and Methods

C:Co composite films were deposited on n-doped (100) silicon wafer, which was firstly cleaned using acetone, followed by ultrasonic isopropanol (IPA) to remove the surface particles. The films were deposited using dual-source FCVA which consists of two off-plane double bend (OPDB) filtering bends, each of them is connected to individual cathode source as described in our past work [18]. In this work, 99.999% pure graphite rod and 99.9% pure nickel rod were used to form the C and Co ions. The composition was controlled by the arc current of the cathode source which was fixed at 70 A for C and 120 A for Co. Film depositions were carried out in the vacuum ($\sim 10^{-5}$ Torr), and no bias was applied to the substrate. The substrate heating temperature was varied from room temperature to 500°C to obtain the various sp^2/sp^3 ratios. The thickness of different C:Co composite films was measured to be 50 nm using the Tencor P-10 surface profilometer. The resistance of different C:Co composite films was measured using a cascade of 200 nm probe station with a Hewlett Packard 4156A precision semiconductor parameter analyzer, with a voltage step of 0.01 V.

The three C:Co composite films were then cut into a dimension of 1 cm by 1 cm and placed into a plasma-enhanced chemical vapor deposition (PECVD) chamber where the CNT growth would be carried out. The CNT growth was

performed at 600°C with a plasma power of 85 W for 30 min. The ramp rate was set at maximum. The heater stage reached 600°C in less than 10 sec, and the carbon feedstock gas (C_2H_2) was immediately introduced to reduce the influence of annealing on the samples. The pressure in the chamber during CNT growth was maintained at 4.5 Torr with a C_2H_2/NH_3 gas ratio of 1:5.

The atomic fraction of Co within the films was estimated using energy dispersive X-ray spectroscopy (EDX). In this work, Co is detected to be $\sim 5\%$ in atomic ratio for all three films. Before CNT growth, the microstructure of different C:Co composite films was characterized using WITec visible Raman spectroscopy with a 532 nm diode-pumped solid state laser. The obtained Raman spectra were fitted using a Breit-Wigner-Fano (BWF) line shape for the G band and a Lorentzian line shape for D band if the spectra cannot be fitted by only the BWF line shape [19, 20]. To confirm the formation of graphitic-like sp^2 clusters, JEOL JEM 2100 high-resolution transmission electron microscopy (HRTEM) was used. The images of the grown CNTs were acquired using scanning electron microscopy (SEM), and the CNT quality was also characterized using visible Raman spectroscopy.

3. Results and Discussions

Figure 1(a) shows the Raman spectra of C:Co composite films deposited using different substrate temperatures. The main changes of the Raman spectra are the shift of G peak position and the increase in D peak density. The G band relates to both breathing and stretching modes of sp^2 bonds, and the D band only reflects the existence of the breathing mode of sp^2 bonds, which are normally in the form of nanometer-size graphitic-like clusters [19, 20]. The spectra of the C:Co composite film at room temperature show that only one peak and a neighbor peak at around 1350 cm^{-1} started to emerge with increasing substrate temperature.

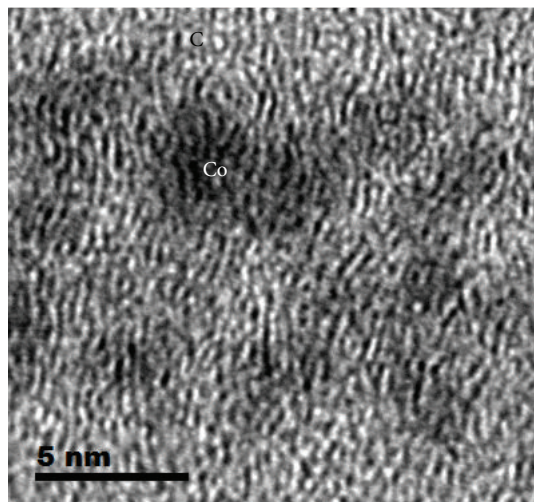


FIGURE 2: Cross section view of HRTEM image of C:Co composite film deposited at 500°C.

The microstructure subjected to different growth temperatures is shown in Figure 1(b)—the rightward shift of G peak position is due to the conversion of sp^3 bonding to sp^2 bonding [14, 20, 21]. Based on the three-stage model [20], the film grown under RT is estimated to be 30% in sp^2 content, and as the growth temperature increases, the sp^2 content in the film rises to more than 80%. Besides the rise in sp^2 content, the six-ring graphitic-like sp^2 bonds also become dominant, which is shown by the increase in $I(D)/I(G)$ ratio [20], in Figure 1(b).

To confirm the formation of the graphitic-like sp^2 clusters, HRTEM analysis has been performed on the C:Co composite film deposited at 500°C. Figure 2 shows the HRTEM image of the film; due to higher density of Co atoms (8.9 g/cm^3) compared to the C atoms (3.515 g/cm^3 for diamond, 2.267 g/cm^3 for graphite, and $1.8\text{--}2.1 \text{ g/cm}^3$ for amorphous carbon), fewer electrons are able to transmit from Co region; hence the dark contrast on Co nanoclusters is presented in the HRTEM image. It clearly shows that the Co nanoclusters are embedded within the graphitic-like clusters. The graphitic-like clusters form the electron-conducting paths, and the free electrons contributed by the Co also enhance the electrical conductivity of the film [22].

The changes in the microstructure of C:Co composite film influence the electrical properties of the film as represented by the I - V curve of these three films in Figure 3. The film grown under RT has high resistance of $\sim 10^9$ ohm, and the resistance reduces with the growth temperature. The film grown under 500°C has a much lower resistance of about 10^1 ohm. The reduction of resistance is attributed to the increase in sp^2 content, the formation of more graphitic-like sp^2 clusters, which has been reported in a previous study [14–16], and also the incorporation of Co nanoclusters.

Figures 4(a), 4(b), and 4(c) show the CNTs grown on different C:Co composite films. CNTs of the same length ($\sim 1 \mu\text{m}$) can be synthesized on all these three types of C:Co

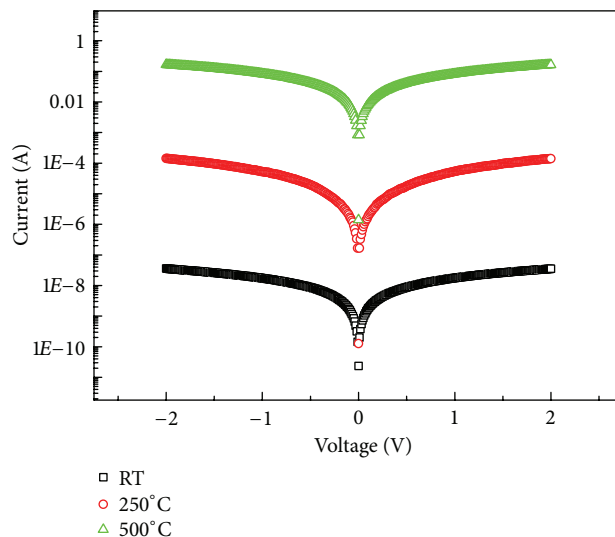


FIGURE 3: I - V characteristic of C:Co composite films grown using different growth temperatures.

composite film. However, the density of CNTs does not have a significant change among these three kinds of C:Co composite film. Zhang et al. have reported that the density of CNTs grown on C:Me film has a strong relation with the content of metal [7]. In this work, it was demonstrated that the initial sp^2/sp^3 ratio does not affect the density of CNTs grown on the C:Co composite film. The quality of the CNTs is characterized and shown in Figure 5. The two peaks detected in the spectra are D peak and G peak which fall in the range of $1370\text{--}1400 \text{ cm}^{-1}$ and $1580\text{--}1600 \text{ cm}^{-1}$. Unlike C film, D peak for CNTs represents defects and G peak is an indication of crystalline graphite [23]. The inserted table lists the $I(D)/I(G)$ ratios of these CNTs. CNTs 3 has the lowest ratio which indicates the lowest defect level. Although the defect level is desired to be zero, it is difficult to be eliminated in the PECVD process [24].

4. Conclusions

C:Co composite films with the same Co content but different initial sp^2/sp^3 ratios were deposited using dual-source FCVA technique, with varying growth temperatures. The change in microstructure of the film leads to the formation of the sp^2 -rich C:Co composite film, with the presence of conducting graphitic-like sp^2 cluster. The electrical resistance is reduced to approximately 10^1 ohm. CNTs can be successfully synthesized on C:Co composite film regardless of the change of initial sp^2/sp^3 ratio of the film. There is no clear evidence to show the influence of initial sp^2/sp^3 ratio on the density of CNTs grown on C:Co composite film; however the quality, such as defect level, is shown to be dependent on the initial sp^2/sp^3 ratio of the C:Co composite film, which can be reduced by using film with higher initial sp^2/sp^3 ratio.

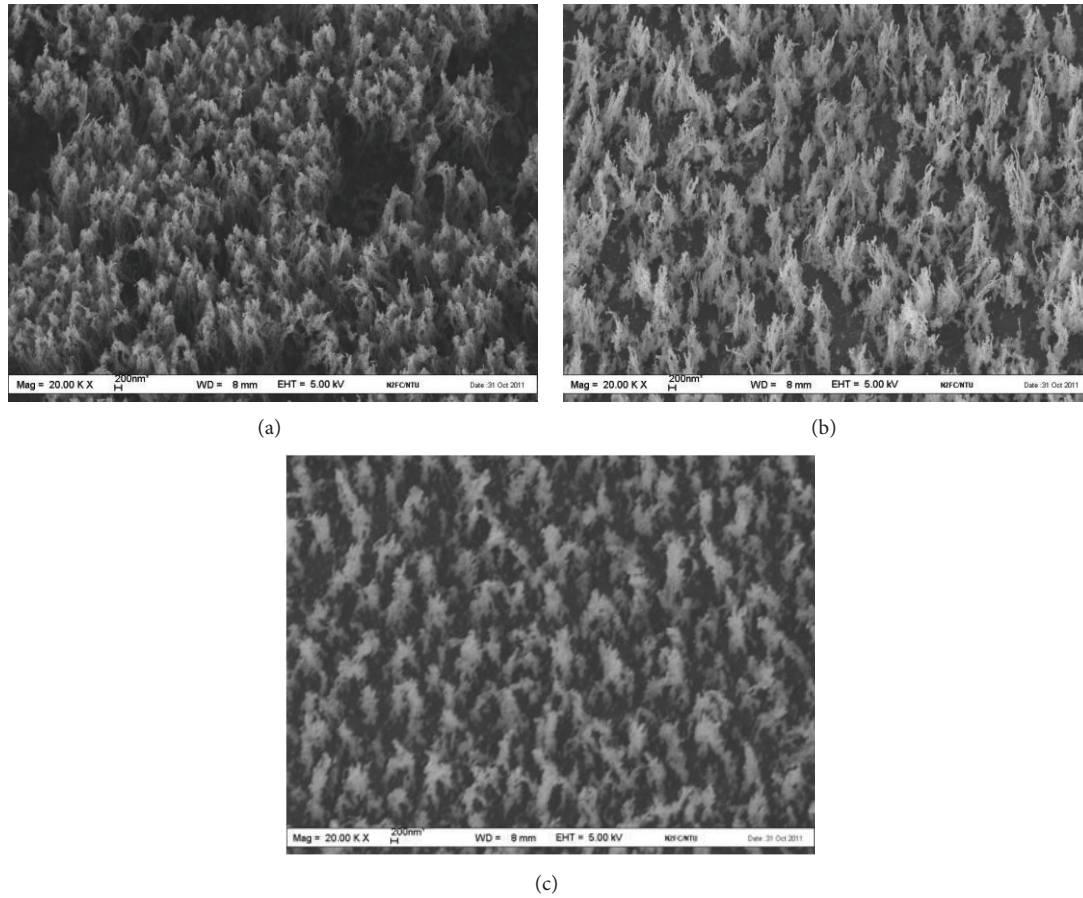


FIGURE 4: SEM images of CNTs grown on different C:Co composite films: (a) RT, (b) 250°C, and (c) 500°C.

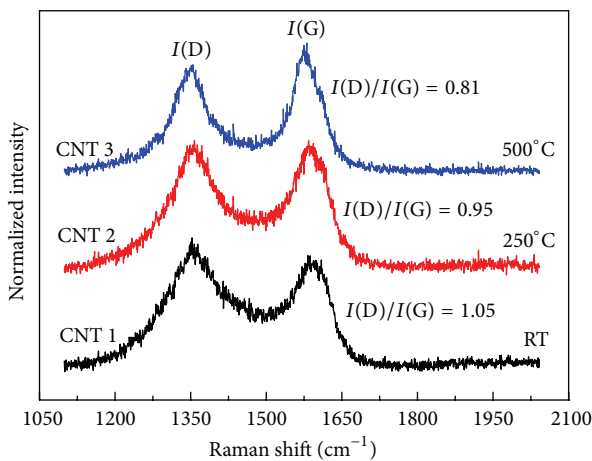


FIGURE 5: Raman spectra of CNTs grown on different C:Co composite films (inserted table shows the $I(D)/I(G)$ ratios).

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