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Materials

Growth of graphite film over the tops of vertical carbon nanotubes using Ni/Ti/Si substrate

Chia-chih Chuang[1], *Wei-long Liu*[2], *Wen-jauh Chen*[3], *and Jin-hua Huang*[1]

1) Photovoltaics Technology Center, Industrial Technology Research Institute, Hsinchu, China Taibei
2) Department of Materials Science and Engineering, Formosa University, Yunlin, China Taibei
3) Graduate School of Materials Science, Yunlin University of Science and Technology, Yunlin, China Taibei

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Abstract: A substrate with Ni/Ti/Si structure was used to grow vertical carbon nanotubes (CNTs) with a graphite film over CNT tops by thermal chemical vapor deposition with CH_4 gas as carbon source. The carbon nanotubes and the substrate were characterized by a field emission scanning electron microscope for the morphologies, a transmission electron microscope for the microstructures, a Raman spectrograph for the crystallinity, and an Auger electron spectrometer for the depth distribution of elements. The result shows that when the thickness ratio of Ni layer to Ti layer in substrate is about 1, a graphite film with relatively good quality can be formed on the CNT tops.

Key words: carbon nanotubes (CNTs); graphite film; CH_4 gas; thermal chemical vapor deposition (TCVD)

1. Introduction

Since carbon nanotubes (CNTs) were discovered in 1991 by Iijlma [1], it has attracted considerable attention from the world and has been studied extensively. It has been demonstrated that CNTs have remarkable properties including high aspect ratio, high specific surface area, high chemical stability, high mechanical strength, and so on. Owing to their outstanding characteristics, CNTs can be applied to several fields. To give some examples, CNTs are a good emitter for field emission display [2-4]; CNT can be used as a sensor [5-6], a micro or nano-electrode [7-8], and an element in semiconductor devices [9-12]; CNTs can also replace micro-carbon fiber and carbon black to improve the electricity and heat conductance and the mechanical performance of composite materials. For suiting various applications, CNTs need different properties, which can be obtained using various manufacture processes [13].

The CNT is one of the new materials for solving the problem of miniaturization of semiconductor devices. In semiconductor devices, CNTs can replace copper for electron conductance to avoid the electron-migration effect when the device size is gradually decreased. Horibe [14] achieved success in integrating CNTs as an interconnection into large scale integrated circuit (LSIC) with Cu/low-*k* interconnect processes. Graham *et al*. [15] also proposed that CNTs can be used as electron conducting material in microelectronics in the near future. It is quite clear that the CNT is an important material for the semiconductor device with a size equal to and even smaller than 45 nm.

For the conduction of electricity in microelectronics or nanoelectronics, CNTs need to contact with other conductors at their two ends. Up to date, the contact of CNTs with other conductors is still a problem to be solved. Andriotis *et al*. [16] suggested that the early 3-d elements (Sc, Ti and V) can be expected to be good candidates for making metal-single wall carbon nanotube contacts with low resistance. Lee *et al*. [17] formed low-resistance ohmic contacts between CNTs and metal electrodes by rapid thermal annealing method. It was shown by Wakaya *et al*. [18] that the contact resistance between multiwall CNTs and the metal formed the tunnel resistance in coulomb blockage unlike the case of single wall CNTs. Lieban *et al*. [19] used electroless nickel deposition to improve the contact between CNTs and gold/iron, palladium, or cobalt. Single bundles of CNTs were selectively de-

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Corresponding author: Wen-jauh Chen, **E-mail:** chenwjau@yuntech.edu.tw

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posited from suspensions onto sub-micron electrodes with alternating electric fields by Krupke *et al.* [20]. Ando *et al.* [21] demonstrated the improvement of electrical contact at CNT/Pt by selective electron irradiation. Single-wall CNT field-effect transistors have been shown to behave as Schottky barrier devices by Chen *et al.* [22]. Manohara *et al.* [23] demonstrated CNT Schottky diodes using Ti-Schottky and Pt-ohmic contacts for high frequency applications. Wu *et al.* [24] evaporated a 1-μm-thick Al layer on the top of CNT array, which served as a heat current collector. Nosho *et al.* [25] found that the barrier height of the metal/CNT contact was dependent on the work function of the contact metal. Zhang *et al.* [26] used AC dielectrophoresis to deposit one bundle of single-wall CNTs between a pair of predefined Pd electrodes for fabrication of CNT field effect transistors.

In this study, a substrate with Ni/Ti/Si structure was used to grow vertical carbon nanotubes with a carbon film over these vertical CNT top by thermal chemical vapor deposition with CH_4 gas as carbon source. Since the carbon film on the vertical CNT top was continuous and quite even, several materials, such as metal, semiconductor, dielectrics *etc.* can be deposited or coated on it for various applications.

2. Experimental

In this study, a substrate with Ni/Ti/Si structure was used to grow vertical carbon nanotubes (CNTs) with a graphite film over these CNT tops. The thickness of Ti layer in the substrate was kept as 40 nm and the Ni layer was varied from 8 to 80 nm. The Ti and Ni layers were successively formed on Si at a pressure of 2×10^{-6} torr in an electron beam deposition system. The Ni layer was used as catalyst for CNT growth and the Ti layer as interlayer for the adjustment of CNT growth.

The CNTs were grown on substrate by chemical vapor deposition (CVD) in which CH_4 gas was used as carbon source. Before the growth process, the Ni/Ti/Si substrate was adhered to a holder of SiC by silver glue. A microwave was guided to heat the SiC holder and substrate whose temperature was measured by a thermal couple and controlled by the microwave power. Before the entrance of CH_4 gas, the pressure of the growth chamber was 10^{-1} torr and kept at 1 atm in CH_4 atmosphere in the CNT growth process.

The morphologies of CNTs were observed by a field emission scanning electron microscope (FESEM, JEOL JSM-6500F) and the microstructures of CNTs and substrates were viewed using a transmission electron microscope (TEM, JOEL JEM-2010). A micro-Raman spectrograph (Reni Shaw 2000) was used to analyze the crystallinity of CNTs. An Auger electron spectrometer (CILVAC PHI, AES 650) was used to obtain the depth distributions of C, Ni, Si, Ti, and O in various substrates.

3. Results and discussion

Fig. 1 shows the FESEM views of CNTs grown on Ni(8-80 nm)/Ti(40 nm)/Si substrates at 680°C in l atm

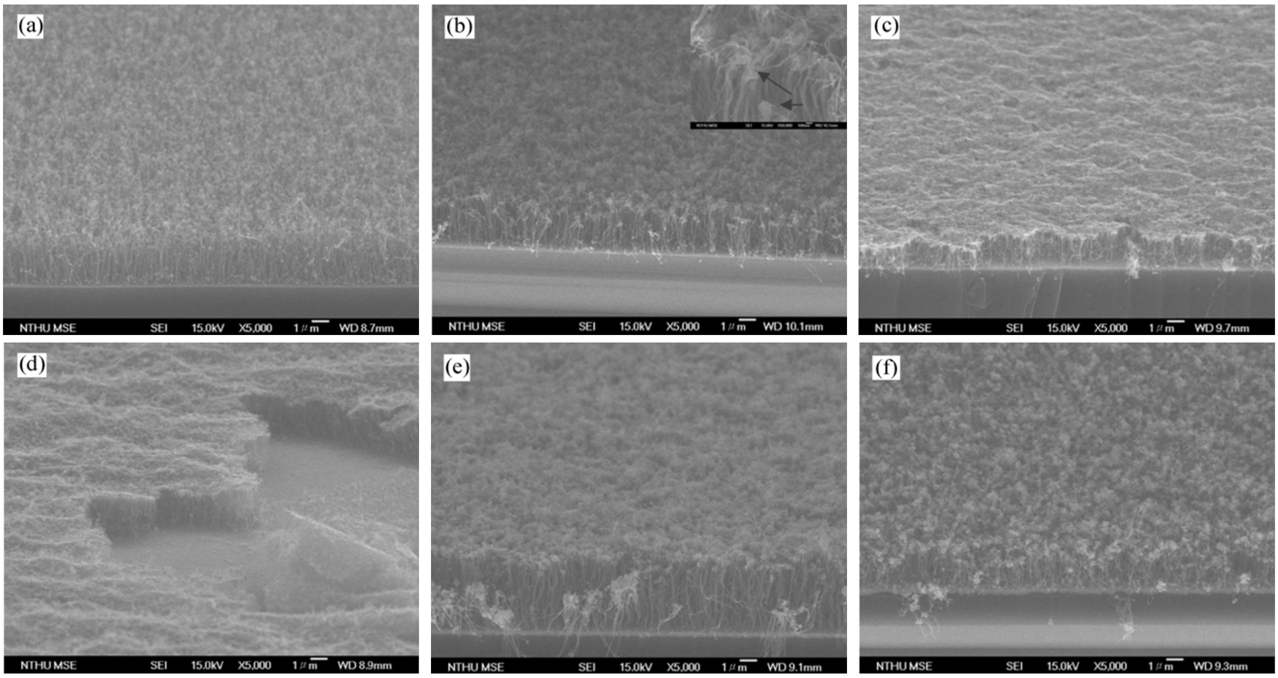

Fig. 1. FESEM views of CNTs grown for 18 min on Ni(8-80 nm)/Ti(40 nm)/Si substrates at 680°C in CH_4 gas with a flow rate of 200 cm^3/min for different thicknesses of Ni layer in substrate: (a) 8 nm; (b) 16 nm; (c) 32 nm; (d) 40 nm; (e) 60 nm; (f) 80 nm.

CH_4 gas with a flow rate of 200 cm^3/min for 18 min. The CNTs in Fig. 1(a) grown on a substrate with a Ni layer of 8 nm in thickness are about 3 nm in length, and 20-60 nm in diameter, and stand quite vertically on the substrate. The CNTs shown in Fig. 1(b), grown on a substrate with a Ni layer of 16 nm thickness, have a length about 3 nm and a diameter ranging from 20 to 90 nm. It can be seen from the inset of Fig. 1(b) that there are discontinuous, irregular, and very thin carbon films formed on some CNT tails. As seen in Figs. 1(c) and 1(d), when the thickness of Ni layer in substrate is increased to 32 or 40 nm, a carbon film, which has graphite structure confirmed by high resolution view of TEM, is formed on the tops of CNTs and is quite even and continuous. If the Ni layer in the substrate is 60 or 80 nm in thickness, the carbon films on CNT top in Figs. 1(c) and 1(d) are replaced by carbon particles as shown in Figs. 1(e) and 1(f).

Figs. 2(a) and 2(b) show the TEM views of CNTs grown on Ni(8 nm)/Ti(40 nm)/Si substrate. These CNTs have a bamboo structure indicated by arrows in

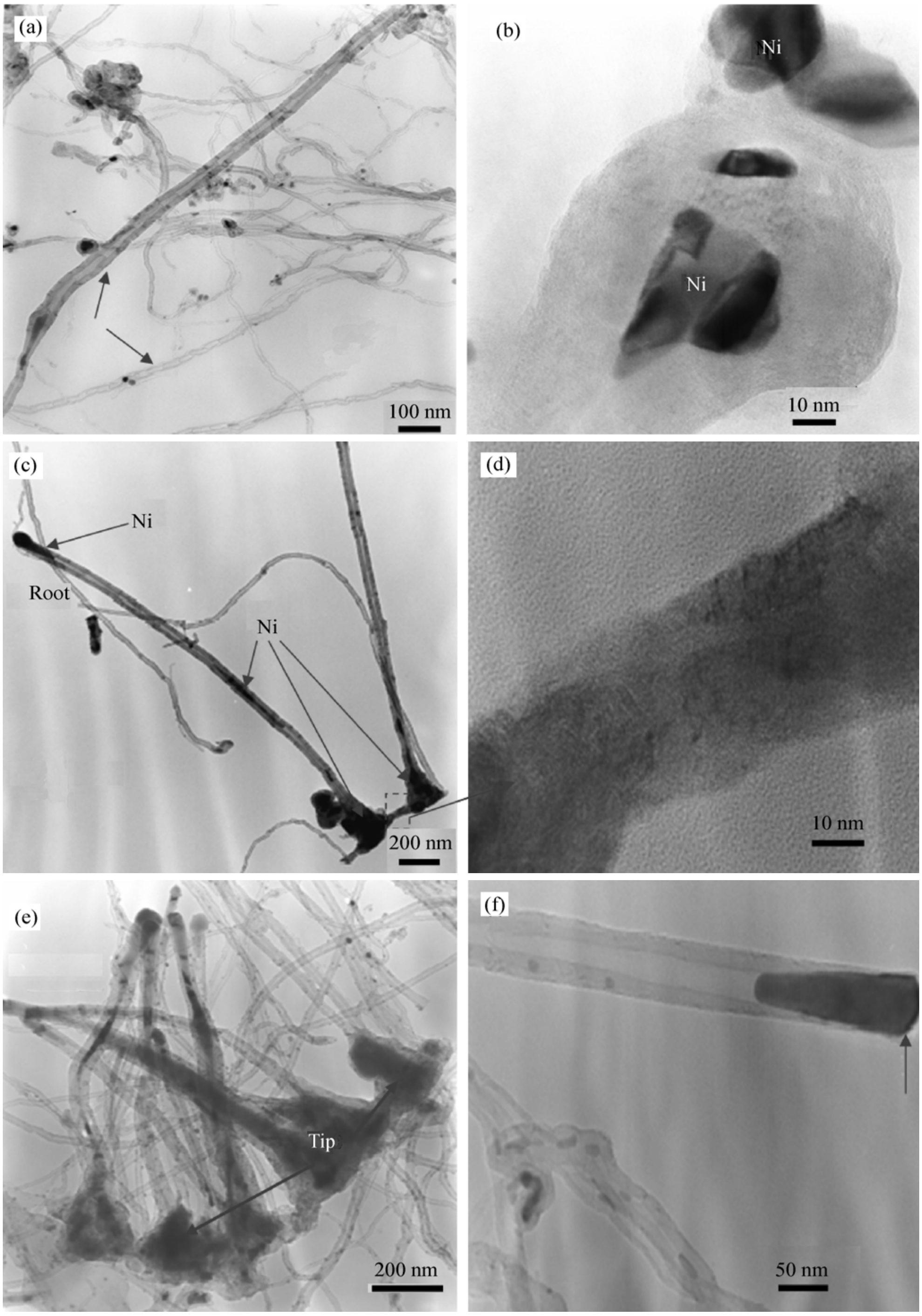

Fig. 2. General and high resolution TEM views of CNTs grown under the same growth condition as for the samples of Fig. 1 for (a) and (b) 8, (c) and (d) 16, and (e) and (f) 40 nm thickness of Ni layer in substrate.

Fig. 2(a) and Ni particles at the CNT top shown in Fig. 2(b) may be enclosed in CNT or naked on CNT top surface. CNTs shown in Fig. 2(c) is grown on Ni(16 nm)/Ti (40 nm)/Si substrate. There are Ni particles at the root, middle part, and top of CNT, and the Ni particle at the top is larger than that at the root or middle part. The two CNTs shown in Fig. 2 (c) are connected together at their tops by a carbon film, which has graphite structure and is about 50 nm in thickness and 150 nm in length as shown in Fig. 2(d). As seen in Figs. 2(e) and 2(d), the CNTs grown on Ni(40 nm)/Ti(40 nm)/Si substrate have more Ni particles, and the Ni particles at tops are considerably larger than that at root or middle part. These CNTs shown in Fig. 2(e) are also connected together at their tops by carbon films.

The Raman spectra for CNTs grown on Ni(8-80 nm)/Ti(40 nm)/Si substrates are shown in Fig. 3. The intensity peaks at wave numbers of 1350 and 1590 cm^{-1} are respondent to the disorder and order part in CNTs, respectively, which are the so-called D mode and G mode. The intensity ratio of D mode to G mode, ID/IG, is roughly equal to 0.9 for all CNTs grown on Ni(8-80 nm)/Ti(40 nm)/Si substrates, in other words, all CNTs have nearly the same crystallinity.

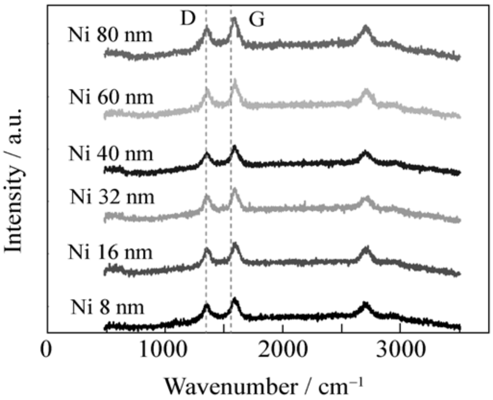

Fig. 3. Raman spectra for CNTs grown under the same growth condition as for the sample of Fig. 1.

Fig. 4 shows the AES depth profiles of C, Ni, Si, Ti, and O in substrates of Ni(8-80 nm)/Ti(40 nm)/Si after CNT growth at 680°C in 1 atm CH_4 gas with a flow rate of 200 cm^3/min for 18 min. Fig. 4(a) is the AES depth profiles of C, Ni, Si, Ti, and O for the Ni(8 nm)/Ti(40 nm)/Si substrate. It can be seen that the quantity of Ni diffused into the substrate is quite small. The C exists only in the region near the substrate surface. The Ti and O have similar depth profiles, and only small quantity of Si diffuses outward. From these depth profiles, it can be reasonably deduced that in the CNT growth process, almost the entire Ni layer of 8 nm in thickness had become Ni particles and was kept in CNTs. The Ti layer of 40 nm had become an alloy layer with O. From the depth profiles shown in Figs. 4(b)-4(f) for the substrates with an Ni layer of 16, 32, 40, 60, and 80 nm in thickness, it can be seen that a part of Ni diffuses inward and forms a Ni_xSi_y layer with Si. The Ti layer becomes an alloy layer containing Ti, O, and C. The Ni_xSi_y layer seems to be able to block the diffusion of Ti, O, and C; the depth and width of Ni distribution are increased with the increase of Ni layer thickness, and the depth of Ti alloy layer is also increased with the increase of Ni layer thickness.

Fig. 5 shows the FESEM views of CNTs grown on Ni(40 nm)/Ti(40 nm)/Si substrate at 680°C in 1 atm CH_4 gas with a flow rate of 200 cm^3/min for 0, 6.5, and 20 min, respectively. The Raman spectra for these CNTs are shown in Fig. 6. It can be seen that a carbon film with graphite structure has formed on the substrate surface when the substrate temperature is increased to just 680°C, as shown in Fig. 5(a). This carbon film will be lifted up by the growing CNTs during the growth process, as shown in Figs. 5(b) and 5(c). Comparing the intensity ratios of D mode and G mode, ID/IG, for CNTs grown for 0, 6.5, and 20 min, as shown in Fig. 6, it can be seen that the crystallinity of CNTs varies with growth time. The ID/IG for the CNTs grown for 6.5 min is larger than that for 0 and 20 min; in other words, the CNTs grown for 6.5 min are relatively disorderly.

From the results and discussion stated above, the growth behavior of CNTs grown on Ni(8-80 nm)/Ti(40 nm)/Si substrate at 680°C in 1 atm CH_4 gas with a flow rate of 200 cm^3/min could be reasonably deduced as follows. In this study, CH_4 gas was introduced into the growth chamber at once when the substrate just began to be heated by microwave. The CH_4 gas could be decomposed into C and H under the catalysis of Ni. If the thickness of Ni layer in Ni/Ti/Si substrate was 8 nm, nearly the entire Ni layer would become Ni particles dispersed on substrate surface and only very small quantity of Ni could diffuse into the substrate. These separated Ni particles could catalyze the decomposition of CH_4 and make CNTs grow up by root growth mechanism. Finally, a film of CNTs could be vertically grown on Ni(8 nm)/Ti(40 nm)/Si substrate as shown in Fig. 1(a). If the Ni layer in Ni/Ti(40 nm)/Si substrate had relatively large thickness, a part of Ni would diffuse into substrate and formed an Ni_xSi_y layer with Si, and the other Ni would become Ni particles for CNT growth. The quantities of Ni_xSi_y and Ni particles were increased with increasing the thickness of Ni layer. A part of these Ni particles acted as role for CNT growth and the other Ni particles were carried to the middle and upper parts of CNTs as shown in Figs. 2(c) and 2(e). When the Ni layer was too thick to form separated Ni particles, the C decomposed from CH_4 gas would form a

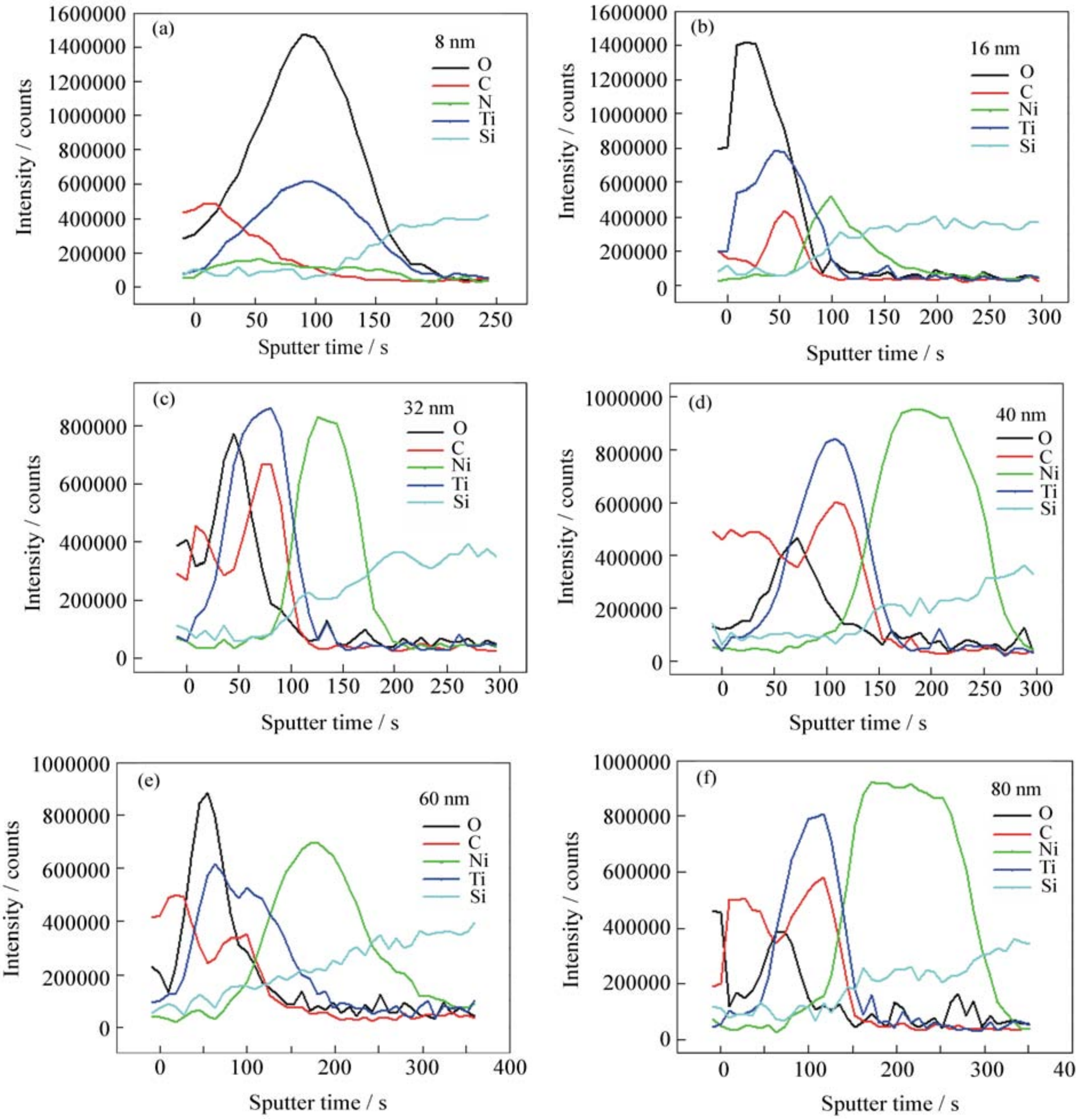

Fig. 4. AES depth profiles of C, Ni, Si, Ti, and O in substrates of Ni(8-80 nm)/Ti(40 nm)/Si after CNT growth under the same growth condition as for the samples of Fig. 1.

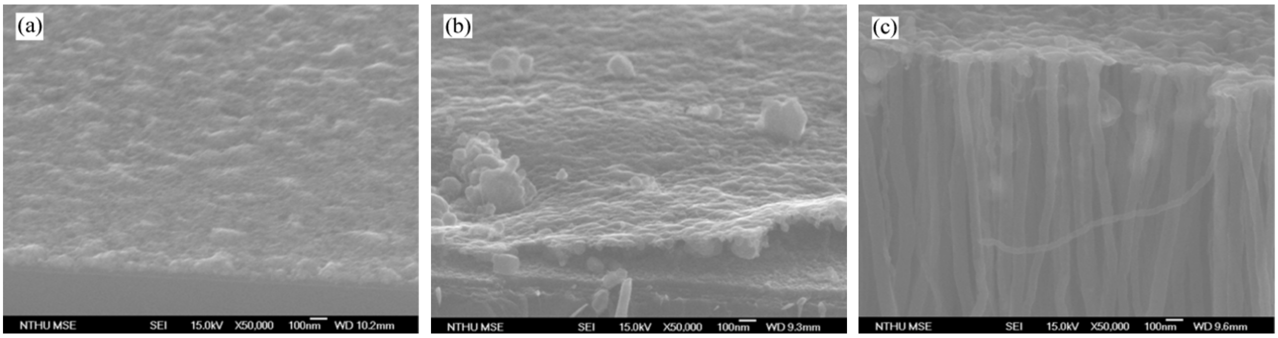

Fig. 5. FESEM views of CNTs grown on Ni(40 nm)/Ti(40 nm)/Si substrate at 680°C in 1 atm CH_4 gas with a flow rate of 200 cm^3/min for different growth time: (a) 0 min; (b) 6.5 min; (c) 20 min.

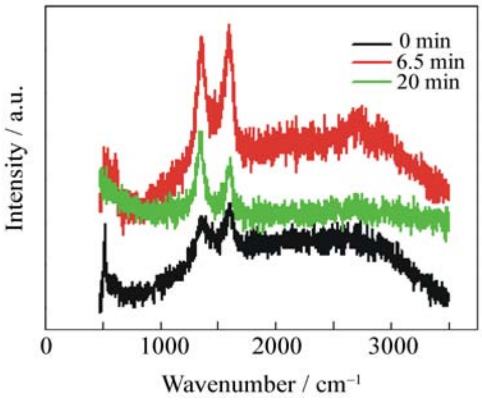

Fig. 6. Raman spectra for the CNTs in Fig. 5.

continuous film covered on the surface of the Ni layer. Since a part of C in the carbon film could diffuse into the Ni layer, hence, CNTs were able to be grown under this carbon film and the carbon film rose by CNTs as shown in Fig. 5 and Figs. 1(c) and 1(d). In the process of CNT growth, the CH_4 gas could continue to be supplied to Ni catalysts by means of the voids in the carbon film and the space between CNTs; therefore, CNTs could grow up continuously. When the thickness of Ni layer was increased to 60 or 80 nm, the carbon film over the CNT top would break down, as shown in Figs. 1(e) and 1(f), owing to too many Ni particles at CNT tops. As for the details about the carbon film formed on CNT tops, a further study is needed.

4. Conclusions

CNTs can be vertically grown on Ni(8-80 nm)/Ti(40 nm)/Si substrate at 680°C 1 atm CH_4 gas with a flow rate of 200 cm^3/min by thermal chemical vapor deposition. If the thickness of Ni layer in Ni/Ti(40 nm)/Si substrate is 32 nm or 40 nm, an additional graphite film can be formed on the top of vertical carbon nanotubes; however, this graphite film over the CNT top will break down when the thickness of Ni layer in Ni/Ti(40 nm)/Si substrate is increased to 60 or 80 nm. Whether a graphite film can be formed on CNT top or not, the key factor is the thickness ratio of Ni layer to Ti layer in Ni/Ti(40 nm)/Si substrate. When the thickness ratio of Ni/Ti is about 1, the graphite film has a relatively good quality; in other words, a continuous and even graphite film can be formed on the CNT top.

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