Ni-Grain Size Dependent Growth of Vertically Aligned Carbon Nanotubes by Microwave Plasma-Enhanced Chemical Vapor Deposition and Field Emission Properties

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Abstract

Vertically aligned carbon nanotubes were synthesized on Ni-coated Si substrates using microwave plasma-enhanced chemical vapor deposition. The grain size of Ni thin films was varied with the RF power density during the RF magnetron sputtering process. It was found that the diameter, growth rate, and density of carbon nanotubes could be controlled systematically by the grain size of Ni thin films. With decreasing the grain size of Ni thin films, the diameter of the nanotubes decreased, whereas the growth rate and density increased. High-resolution transmission electron microscope images clearly demonstrated synthesized nanotubes to be multiwalled. The number of graphitized wall decreased with decreasing the diameter. Field emission properties will be further presented.

Introduction

Synthesis of carbon nanotubes (CNTs) for mass production has been achieved by several methods such as laser vaporization [1], arc discharge [2], and pyrolysis [3]. Different diameter, length, and chirality of nanotubes give rise to diverse physical and mechanical properties. However, controlling diameter, length, and chirality has never been easily accessible with such approaches. In particular, growth of vertically aligned nanotubes is of practical importance for applications to the field emitters.

Chemical vapor deposition (CVD) method has several advantages to control the structures with various growth parameters. Recently, vertically aligned CNTs have been grown by hot-filament plasma-enhanced CVD on Ni-coated glass substrates pre-treated with NH_3 gas [4]. Aligned CNTs can be also grown on mesoporous [5] and Fe-patterned porous silicon [6] using the thermal CVD method. Control of the CNT-diameters has been attempted using different transition metals deposited on Si substrates followed by the HF treatment [7]. Despite such breakthroughs in the growth, a way to systematically control the diameter and chirality of CNTs has not been clearly demonstrated.

In this report, we have grown vertically aligned CNTs on Ni-coated Si substrates using microwave plasma-enhanced CVD (MPECVD). It was found that the diameter, growth rate, and density of CNTs could be controlled by the grain size and morphology of the Ni thin films that are altered by changing RF power density during the RF magnetron sputtering process. The diameters of multiwalled CNTs range from 10 nm to 35 nm. The growth rate and the density of CNTs increase with decreasing RF power density. The number of graphitized carbon walls decreased with decreasing the diameter. Effective field emission properties were observed from the nanotubes .

Experimental Procedure

Ni thin films with a thickness of 70 nm were deposited using RF magnetron sputtering on Si substrates. An array of Ni dots was prepared using a shadow mask with a size of 2 cm × 2 cm. The diameter of a Ni dot and the distance between dots are 250 μm and 750 μm, respectively. Before the deposition of Ni thin films, the chamber was evacuated to a base pressure of 1.0×10^{-6} Torr. The pressure was adjusted to 3.7 mtorr by feeding Ar gas and the substrate temperature was elevated to 350 °C. Ni films were then deposited at various RF power densities. CNTs were grown on Ni-coated Si substrates using MPECVD at 700 °C with gas mixtures of CH_4 (20 %) and H_2 (80 %). The applied microwave power and the pressure during the growth of CNTs were 400 W and 10 torr, respectively. The growth time of CNTs was maintained for 5 min. The surface morphologies of Ni thin films were investigated by atomic force microscopy (AFM). The growth rates and densities of CNTs were observed by scanning electron microscopes (SEM). FT-Raman spectroscopy was used to confirm the graphitized structure. Transmission electron microscope (TEM) was used to measure the diameters of CNTs and the number of graphitized carbon wall.

Results and Discussion

Figure 1(a-c) are the AFM images in contact mode showing the surface morphologies of Ni film dots prepared at RF power denisities of 0.25, 0.5, and 1.0 W/cm^2, respectively. The grain size decreased drastically with decreasing RF power density, whereas the grain density increased. Some amount of larger size of Ni grains are also shown non-uniformly at higher RF power density, as shown in Fig. 1(c). Figure 1(d) shows the average grain sizes of Ni thin films with error bars as a function of RF power density during the sputtering process. The grain size increases with increasing RF power density at the power densities ranging from 0.25 to 1.0 W/cm^2, and tends to saturate at higher power densities. However, grain sizes are widely distributed at RF power densities above 1.0 W/cm^2, although the average grain size is not varied significantly with the RF power density. At lower power density, smaller Ni particles will be sputtered from the target. Particles arriving at the substrate will start aggregating depending on the substrate temperature. We thus expect smaller grain size on the substrate at lower power density. At higher power density, however, we expect larger Ni particles as well as smaller particles to be ejected from the target, giving rise to wide distribution of the grain sizes. This analysis suggests that the size and the density of Ni thin films can be easily controlled by the RF power denisity during the magnetron sputtering process.

Figure 2(a-c) show the oblique (45°) SEM images of vertically

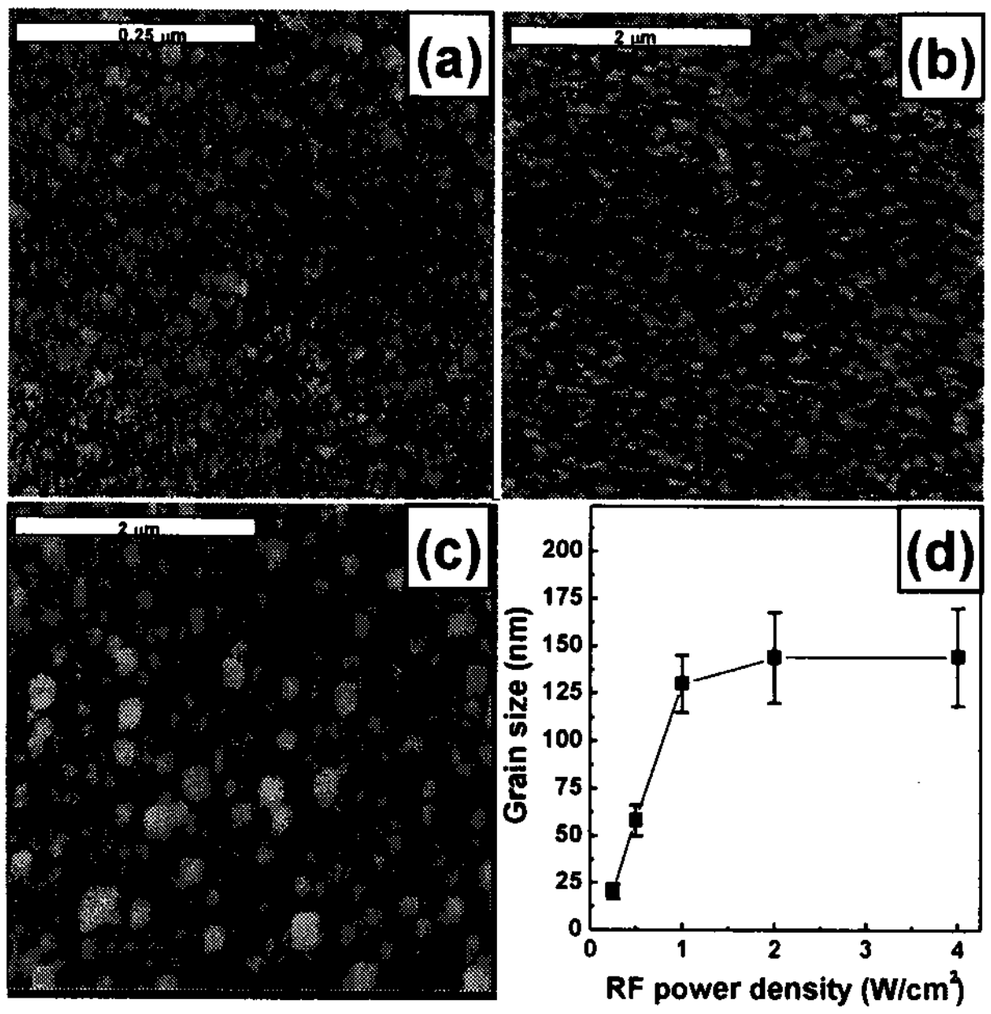

Fig. 1. AFM images of Ni thin films deposited at RF power densities of (a) 0.25, (b) 0.5, and (c) 1.0 W/cm^2, and (d) average grain size as a function of the RF power density.

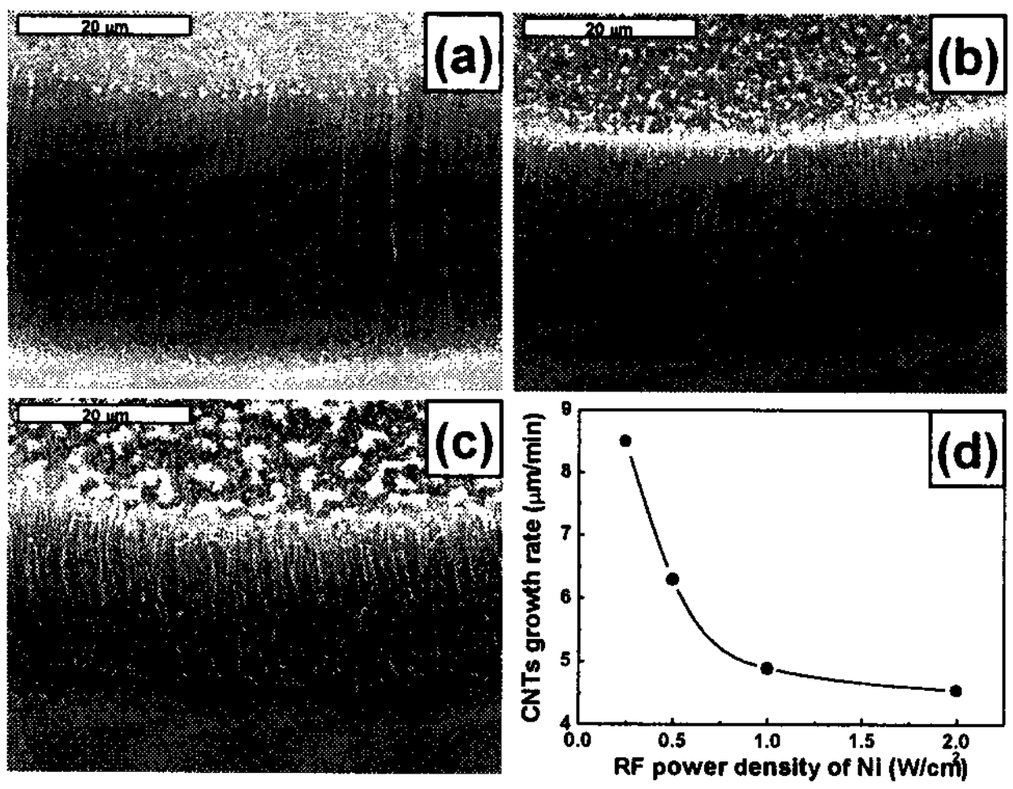

Fig. 2. SEM images (45 °-tilted) of vertically aligned carbon nanotubes synthesized on Ni films deposited at the RF power densities of (a) 0.25, (b) 0.5, and (c) 1.0 W/cm^2, and (d) the growth rate of carbon nanotubes as a function of the RF power density during the Ni-sputtering process.

aligned carbon nanotubes grown on Ni dots which was deposited at the previously described conditions. Vertically aligned CNTs were obtained by the MPECVD, as shown in the figures. We here note that any pretreatments for the surface of catalyst-metal thin films, i.e., an exposure to NH_3 gas [4] and the dipping in HF solution [7] were not necessary for growing CNTs in our case. In spite of the identical growth conditions of the CNTs, the growth rate increases markedly with decreasing the RF power density. The growth rate of CNTs grown on Ni film deposited at the RF power density of 0.25 W/cm^2 is 8.5 μm/min, much faster than the previously reported results by other groups [4-6]. The density of CNTs is also affected by the RF power density of Ni films. The density of Ni grains increased with decreasing RF power density, as shown in Fig. 1. Hence, the density of the CNTs increases with increasing the density of Ni grains, as shown in Fig. 2. Some carbonaceous particles are placed on top of the nanotubes particularly at higher RF power density, as can be seen in Fig. 2(c). We also synthesized the nanotubes on Ni film prepared at the RF power density of 2.0 W/cm^2. CNTs were aligned vertically, but had rather larger amount of carbonaceous particles on top of nanotubes. At higher RF power density, larger size of Ni particles appears on uniformly distributed smaller particles, as shown in Fig. 1(c). The number of these larger particles increased with increasing RF power density. It seems that larger Ni particles do not act as nucleation seeds for CNTs but form carbonaceous particles, since more carbonaceous particles were observed on top of CNTs when grown on Ni films having more particles with larger size.

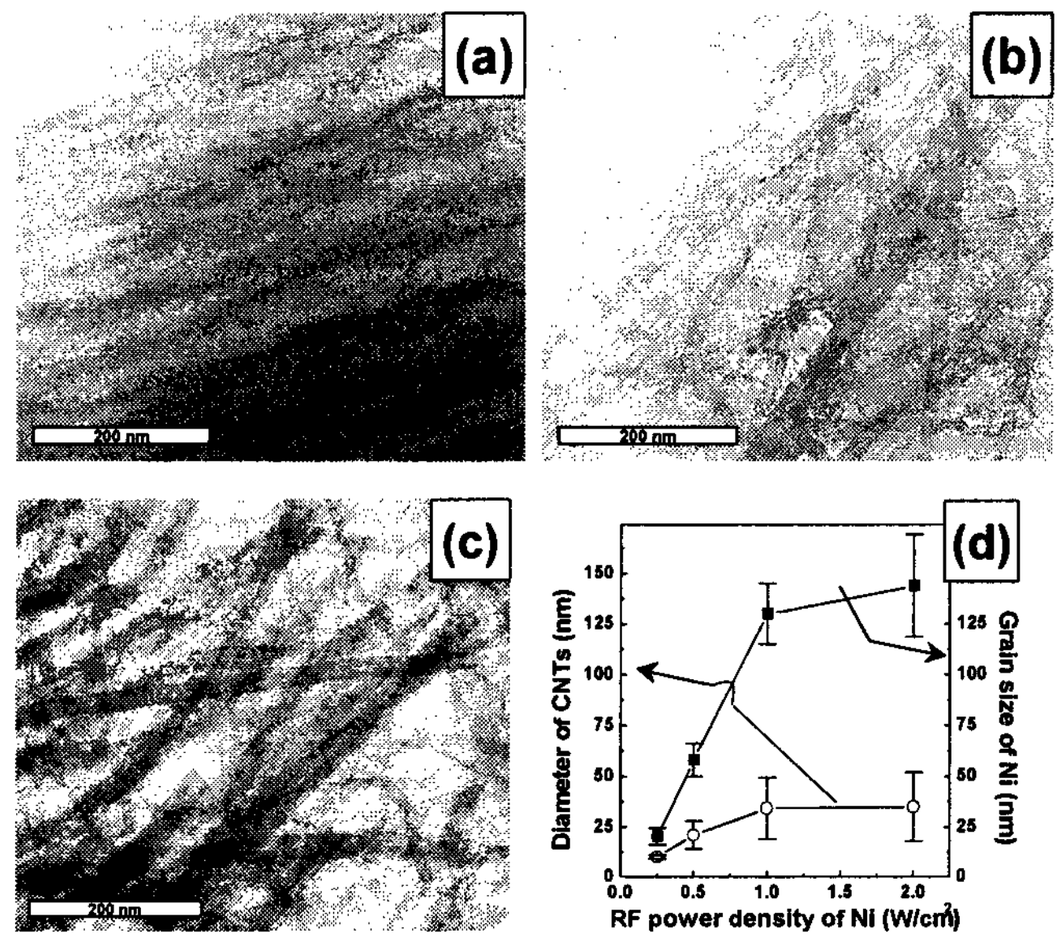

Fig. 3. TEM images of carbon nanotubes grown on Ni films prepared at the RF power densities of of (a) 0.25, (b) 0.5, and (c) 1.0 W/cm^2, and (d) the diameter of carbon nanotubes and grain size of Ni as a function of the RF power density during Ni-sputtering.

Figure 3(a-c) show the corresponding TEM images of CNTs synthesized on Ni thin films prepared at RF power densities of 0.25, 0.5, and 1.0 W/cm^2, respectively. Peeled nanotubes were dispersed on a copper carbon-microgrid for the TEM measurement. It is clearly seen that diameters of the CNTs are strongly correlated with the RF power density during Ni-sputtering process, indicating that the diameter is proportional to the grain size of Ni catalyst-metals. Lower RF power density results in the smaller diameter of the CNTs. Figure 3(d) represents diameters of grown nanotubes and the grain sizes of Ni thin films as a function of the RF power density. Average diameters of the CNTs are smaller than the grain sizes of Ni thin films, although the general trends are similar to each other. This is in good contrast with the previous report that the diameter of the CNTs was almost the same as the grain size of transition metals when the thermal CVD was used [7]. Ni surface is etched away by the microwave plasma at the early stage of the growth in our MPECVD, resulting in smaller Ni grain sizes than as-prepared ones and correspondingly smaller sizes of nucleation seeds.

Therefore, diameters of the CNTs grown on such nucleation seeds are presumably to be smaller than the grain sizes of Ni thin films. Since the Ni thin film deposited at higher RF power density has wider distribution of grain sizes, the CNTs synthesized on such film shows the CNTs with more widely distributed diameters, as shown in Fig. 3(d). We emphasize that CNTs grown on Ni film prepared at the RF power density of 0.25 W/cm^2 reveal very uniform diameters of 10±1 nm. This high selectivity is attributed to the uniform sizes of Ni grains, as shown in Fig. 1(a).

The role of transition metals and the related growth mechanism have long been argued. It is noted that the transition metal particles were observed at top of CNTs from the HRTEM measurement [9]. Therefore, we believe that the metal cap may play an important role in CNT-growth during the CVD. We also observed that aligned CNTs were grown at temperatures as low as 600 °C, although larger amount of carbonaceous particles were produced [10]. This clearly indicates that the transition metal particle plays as a catalyst to decompose the methane gases more efficiently. The CNT-diameter is strongly correlated to the Ni grain size, and the smaller grain size gives higher growth rate. These suggest that Ni grains play as nucleation seeds and the carbon diffusion is limited within the Ni grains. Hydrocarbon gases are first decomposed by the catalyst-metals, and diffused efficiently in carbon-metal eutectic alloy. The diffusion of carbon atoms is limited by the grain wall, where carbon atoms start aggregating and form nucleation seeds for nanotubes. Thus, the diameter of a carbon nanotube is determined by the grain size of catalyst-metals. A part of catalyst-metal grain is being pushed upward by growing nanotubes, resulting in continuous cap growth. Therefore, decreasing grain size causes the diffusion length of carbon atoms to be shortened, resulting in accelerating the formation rate of nanotubes.

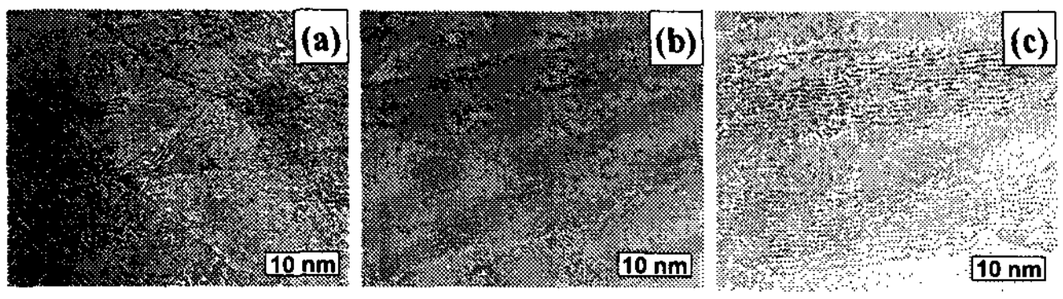

Fig. 4. HRTEM images of carbon nanotubes grown on Ni films prepared at the RF power densities of of (a) 0.25, (b) 0.5, and (c) 1.0 W/cm^2.

Figure 4 (a-c) show the high-resolution TEM images of CNTs synthesized on Ni films which had been deposited at various RF power densities. It is clearly demonstrated that the diameter is decreased by decreasing the grain size of Ni film that is influenced by RF power density. The number of graphitized carbon walls was found to be decreased with decreasing the diameter.

Figure 5 shows FT-Raman spectra of vertically aligned CNTs grown on Ni thin films deposited at three different RF power densities. CNTs on the Ni film deposited at lower RF power density shows stronger intensity of G-peak (1599 cm^{-1}). This is in good agreement with the variation of CNT-density, as demonstrated in Fig. 2. As shown in the spectra that is very interesting are the peaks located at 1750 cm^{-1}, which is a characteristic of single-walled CNTs [11]. However, CNTs grown in this study were found to be multiwalled by HRTEM measurements. We believe that the peaks at 1750 cm^{-1} may be attributed to small number of graphitized walls, for instance 3 walls of CNTs on Ni film prepared at 0.25 W/cm^2, as shown in HRTEM images. The intensity of peak at 1750 cm^{-1} increases with decreasing RF power density during Ni-sputtering. As shown in Fig. 4, the number of graphitized walls decreased with decreasing the RF power density. It can be therefore said that CNTs on the Ni film deposited at lower RF power are closer to single-walled CNTs than those on Ni film prepared at higher RF power, which results in the increasing the intensity (1750 cm^{-1}) with decreasing the RF power density during Ni-sputtering.

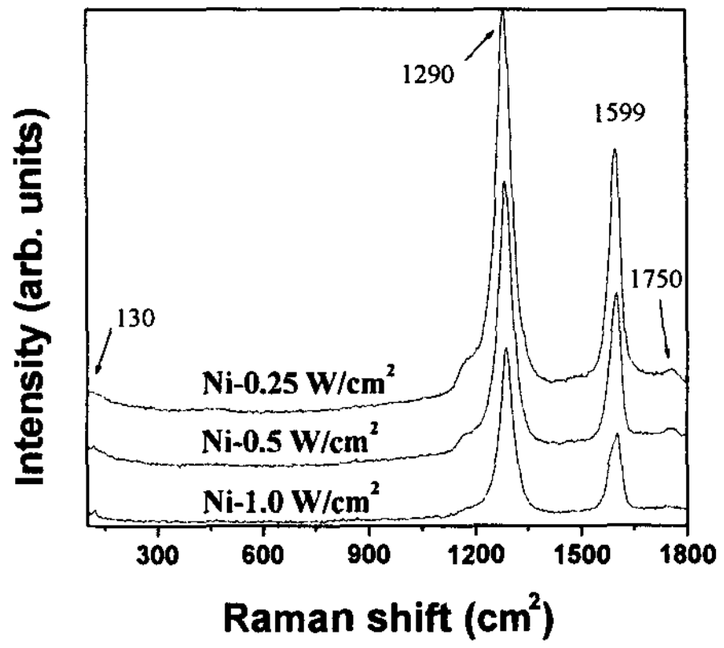

Fig. 5. FT-Raman spectra of CNTs on Ni films prepared at three different RF power densities.

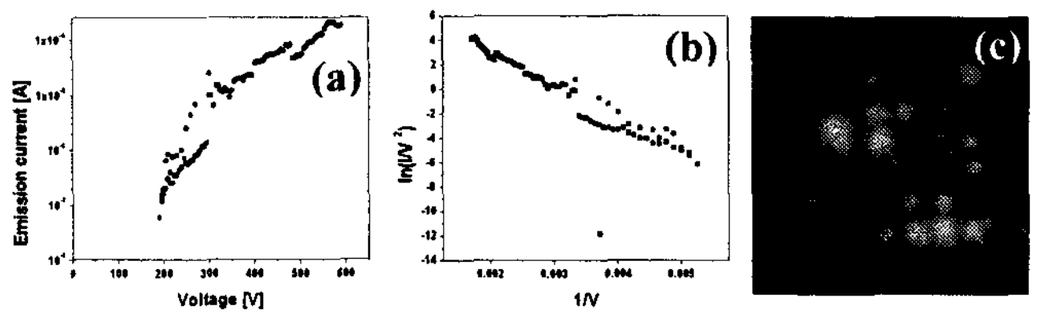

Fig. 6. Field emission properties of CNTs on Ni film dots deposited at 0.25 W/cm^2. (a) I-V curve, (b) F-N plot, (c) FE pattern

Figure 6 represents field emission (FE) properties of CNTs on Ni film dots (250 μm in dia.) that had been deposited at 0.25 W/cm^2. Figures 6 (a) and (b) show the current-voltage curve and corresponding Fowler-Nordheim (F-N) plot, respectively. The spacers with 200 μm thick were used. As shown in Fig. 6 (a), turn-on filed was as low as about 1 V/μm. The obtained data were well fitted to F-N equation, indicating that the emission was due to F-N tunneling. Figure 6 (c) is a FE pattern obtained at 2 V/μm. Effective FE property was observed at very low applied field. Some non-uniformly bright images may be due to unintentionally protruded nanotubes.

Conclusion

In summary, vertically aligned carbon nanotubes were synthesized by microwave plasma-enhanced chemical vapor deposition on Ni thin films deposited using RF magnetron sputtering. The surface morphology of Ni thin films such as the grain size and the grain density could be controlled by changing the RF power density during sputter-deposition process. The diameter, growth rate, and density of vertically aligned carbon nanotubes were found to be closely related to the microstructure of Ni thin

films. FT-Raman spectra as well as HRTEM images reveal well graphitized structure. Field emission was observed at very low applied filed.

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