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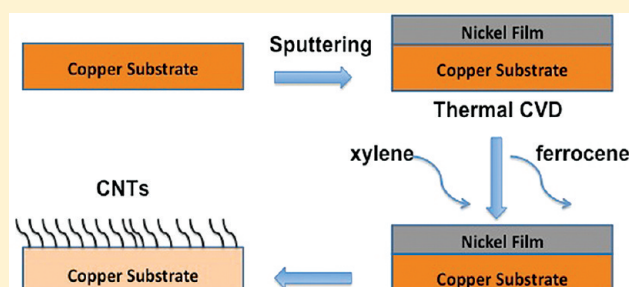
Nickel Catalyst-Assisted Vertical Growth of Dense Carbon Nanotube Forests on Bulk Copper

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ABSTRACT: Vertical growth of carbon nanotubes using thermal chemical vapor deposition (CVD) is demonstrated on bulk copper substrates by first sputtering a thin Ni film on the surface of copper. Vertical growth of carbon nanotubes occurred when the nickel film thickness was 20 nm and the carbon nanotubes were grown using a xylene source and additional ferrocene catalyst during CVD. These results show the effectiveness of this method in directly integrating carbon nanotubes with highly conductive substrates for applications where a conductive carbon nanotube network is desirable.



INTRODUCTION

There has been ongoing interest in understanding and controlling the synthesis of carbon nanotubes (CNTs) ever since their initial discovery.¹ This is required in order to successfully integrate them into new devices and applications that exploit their excellent physical properties, including high mechanical strength, high aspect ratio, and conductivity.^{2,3} There have been extensive publications in recent years to demonstrate the growth of nanotubes under different conditions.^{4–7} These studies show that the resulting structure and the morphology of the nanotubes determine what types of applications they may be useful for. For example, randomly oriented, entangled CNTs have been suggested to be of use in capacitors because of the large surface area of the nanotubes, which is ideal for charge storage.⁸ For use in applications such as electrodes, where the nanotubes might serve as an electrically conducting array or conducting support structure, vertically aligned carbon nanotube growth directly on a common conducting substrate such as copper would be ideal. Copper is one of the most common conductive metals used in many applications because of its excellent thermal and electrical conductivity with respect to cost. The direct growth of nanotubes on Cu would provide good electrical contact to the nanotubes. These conductive, vertically aligned structures could be used as a conductive support for fabricating new structures for a variety of applications including energy storage, sensing, and nanoelectronic devices.⁹

Typically, nanotubes are grown using a method such as chemical vapor deposition on metal catalyst particles or islands that are deposited on top of a semiconducting or insulating substrate such as SiO₂. These nonconducting substrates facilitate the formation of small islands or nanoparticles of the catalyst metal on their surfaces, which are necessary for forming the CNTs. By

comparison, fewer studies have been done on bulk metallic substrates. Although it has been demonstrated that Cu nanoparticles may act as a catalyst for carbon nanotube growth,^{10,11} it is difficult to grow CNTs directly on bulk Cu without the aid of an additional catalyst. Copper is a poor catalyst for CNT growth as carbon shows very little solubility in copper.^{12,13} Deck and Vecchio¹² have reported that for transition metals to act as successful catalysts for CNT growth about 1 atom % carbon solubility in the solid solution is required. Among the transition metals, Fe, Co, Ni, and their alloys serve as the best catalysts for achieving directed growth of carbon nanotubes.^{13–16} Growth of CNTs on copper has been reported using a multilayer structure consisting of titanium nitride as a barrier layer and a second layer of iron as the catalyst.¹⁷ Recently, Li et al.¹⁷ reported the growth of CNTs on copper using a thermal CVD technique and multilayer structures consisting of a Ti buffer layer, an alumina layer, and finally a metal catalyst layer. In all of these cases, it is expected that the barrier layers may increase the electrical resistance between the copper and the nanotubes. However, if only a single thin film metallic catalyst layer is deposited on the copper, in this case, the increase in resistance may be limited to just the remaining native oxide on the copper surface and conductive catalyst particles at the base of the nanotubes.

Beyond simply finding a way to grow CNTs on copper, forcing them to grow in a primarily vertical direction is an additional challenge. Vertically aligned growth using thermal CVD is typically more difficult because of the absence of any electric fields or plasma. The plasma in a plasma-enhanced CVD (PECVD) system is

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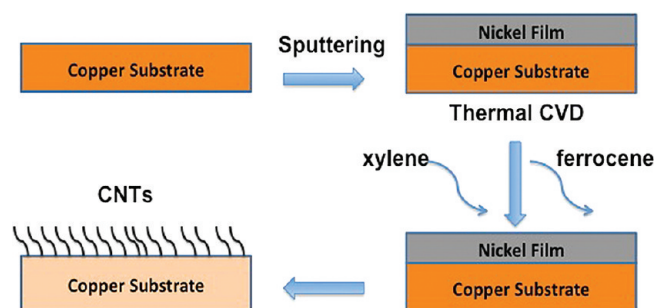


Figure 1. Sequence of steps involved in the growth of CNTs using sputtering and thermal chemical vapor deposition.

widely regarded to aid in the alignment of vertical nanotubes.¹⁸ In the experiments described here, the goal was to find thermal CVD growth conditions under which a single thin film catalyst layer could be used to promote the vertical growth of dense nanotubes on copper substrates. Nickel specifically was chosen for the experiments described here because of its demonstrated superior capabilities for attaining directed carbon nanotube growth.^{19–22} In these experiments, we have explored the use of a thin nickel layer, 45 nm or less, deposited on commercial copper foil substrates, which is combined with an additional catalyst (ferrocene) that is supplied during the actual CVD growth. This additional supply of catalyst in combination with the Ni film promotes the dense vertical growth of carbon nanotubes that is desired.

EXPERIMENTAL METHODS

The general processing sequence followed is shown in Figure 1. Oxygen-free copper foils ($\sim 18 \mu\text{m}$ thick) purchased from Insulectro were used as the substrates for all CNT growth studies. The copper substrates were cleaned ultrasonically first in acetone followed by isopropyl alcohol for 10 min before loading them into the sputtering system for thin film deposition. No attempt was made to remove any native oxide from the surface of the copper foil. The nickel thin film deposition was done using an AJA Orion RF magnetron sputtering system with a base pressure of 1.3×10^{-9} Torr and a process pressure of 3.0×10^{-3} Torr. The sputter rate for nickel was 0.21 \AA/s at 150 W RF power. The substrate–target distance was maintained at 6 in. for all the samples. The nickel target used was 2 in. in diameter, 0.125 in. thick, and 99.999% pure and was purchased from Kurt J. Lesker Company. The sputtering was done at room temperature.

For CVD growth of the nanotubes, a mixture of *m*-xylene/ferrocene feedstock was used with a concentration of 0.01 g/mL and was introduced into a subchamber at 200°C with a 0.11 mL/min feed rate (for the sake of simplicity, *m*-xylene will be simply referred to as xylene). Flow rates of Ar (85%) and H_2 (15%) were set at 85 and 15 sccm, respectively. Xylene vapors (boiling point of about 140°C) enter the growth chamber from the preheated subchamber. Ferrocene then decomposes into iron particles on the substrate that act as a catalyst for nanotube growth. The deposition time was maintained at 30 min for a temperature range between 700°C and 850°C .²³

Scanning electron microscopy (SEM) was used to study the surface morphology of the CNTs using a Philips XL30 SEM operating at 5–10 kV. All SEM images were obtained by tilting the stage to 60° to examine the degree of CNT alignment. Transmission electron microscopy (TEM) analysis and TEM-EDS (energy-dispersive X-ray spectroscopy) of the nanotubes were

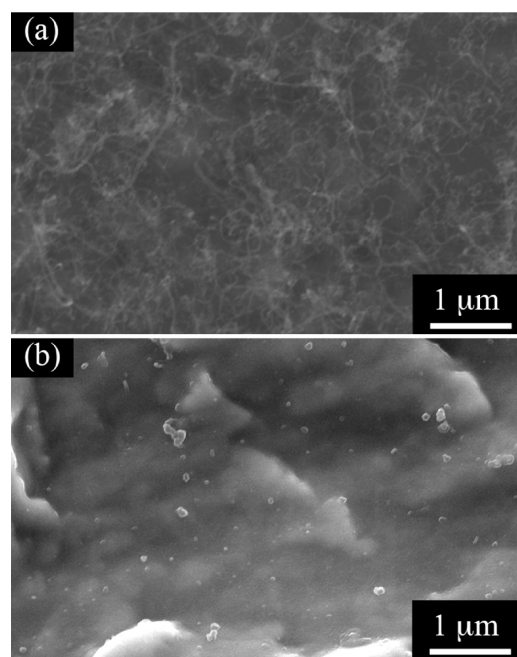


Figure 2. Representative SEM images of the samples grown at (a) 700°C where poor CNT growth and coverage was observed and (b) 850°C where no CNT growth was seen.

done using a JEOL JEM-2100F (Schottky field-emission electron gun operating at 200 kV). Raman measurements on the nanotubes were done using a Renishaw inVia Raman microscope (633 nm wavelength) to evaluate the quality of the CNTs grown on the basis of the I_d/I_g ratios obtained. X-ray photoelectron spectroscopy (XPS) measurements were done using Thermo Scientific K-Alpha XPS, and the X-ray spot size in all the cases was $400 \mu\text{m}$.

RESULTS AND DISCUSSION

For all experiments, the thickness of the nickel film was varied between 20 and 45 nm to study the effect of film thickness on the quality and alignment of CNTs. Three CVD growth temperatures, 700, 770, and 850°C , were investigated, keeping all other parameters constant. CNT growth, in terms of alignment, coverage, and density, was poor for 700°C , and no CNTs were seen at 850°C for the three film thicknesses that were tried. Representative images for CNTs grown at 700 and 850°C are shown in Figure 2. The best results in terms of alignment and density were obtained for 770°C (Figure 3). This temperature for optimum CNT growth is in agreement with Pal et al.²³ who investigated the effect of temperature in terms of growth rate and saturation length of the CNTs. Thinner films appear to work better as the greatest density and alignment of the CNTs was obtained on the 20 nm thick Ni film as seen in Figure 3c. TEM images reveal that CNTs grown on the 20 nm Ni films are multiwalled, and the diameter on average is approximately 40 nm (Figure 4). From the Raman spectrum in Figure 5, we report a lower I_d/I_g ratio of 0.72 than the ratios reported by Li et al.¹⁷ There is a sharp G' peak indicating a very good long-range order for the CNTs. The intensity ratio (I_d/I_g) is indicative of the purity of the CNTs that are grown on substrates. Purity in this context refers to the degree or index of crystallinity in the carbon nanotubes; a smaller intensity ratio corresponds to a greater degree of graphitic crystallinity and less defects and amount of disordered amorphous carbon.²⁴ This

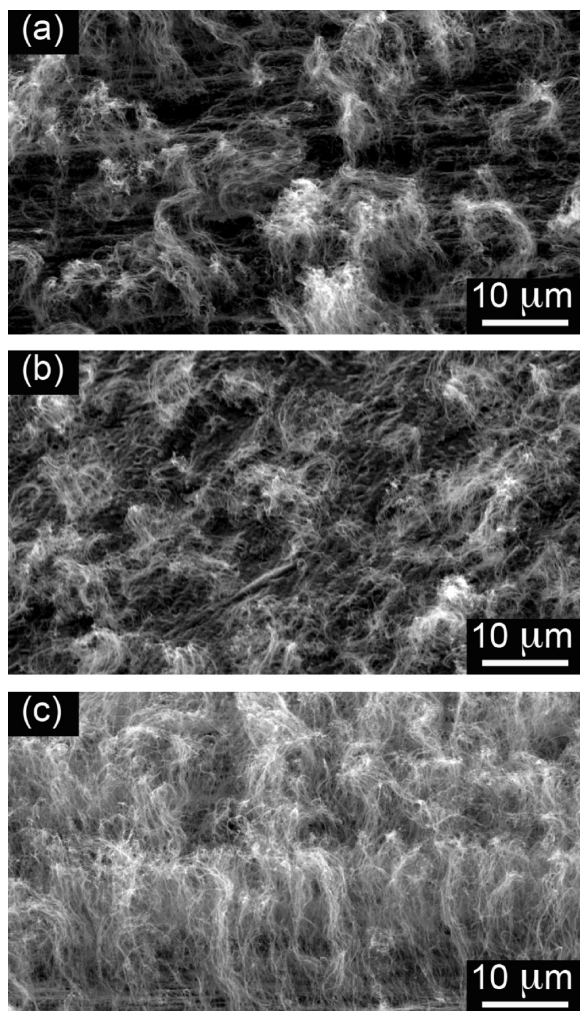


Figure 3. SEM images of CNTs grown using different nickel film thicknesses with xylene as the carbon source: (a) 45 nm, (b) 30 nm, (c) 20 nm.

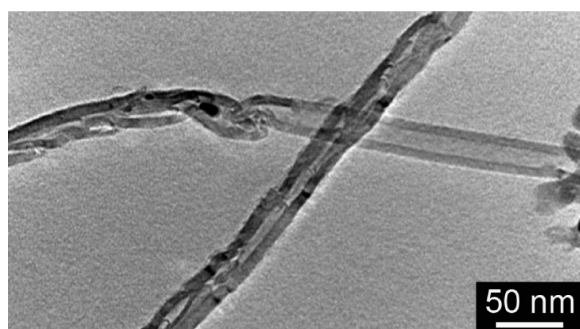


Figure 4. TEM image of multiwalled CNTs grown using 20 nm Ni film with xylene as the carbon source.

intensity ratio may be thought of as an entropic value with the degree of crystallinity pertaining to the degree of order.

CNT growth on the 30 and 45 nm Ni films shows less vertical alignment. Therefore, there appears to be a critical thickness of around 20 nm for the best possible vertical alignment of dense CNTs on nickel. One explanation is that the thinner films result in the formation of very small Ni enriched surface sites after heating in the CVD chamber. The thicker nickel may instead

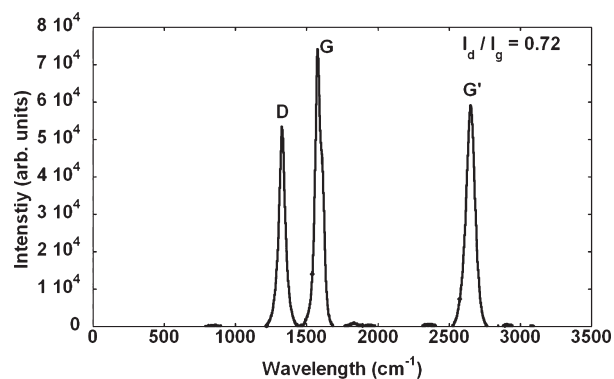


Figure 5. Raman spectrum from the CNTs grown using 20 nm Ni film.

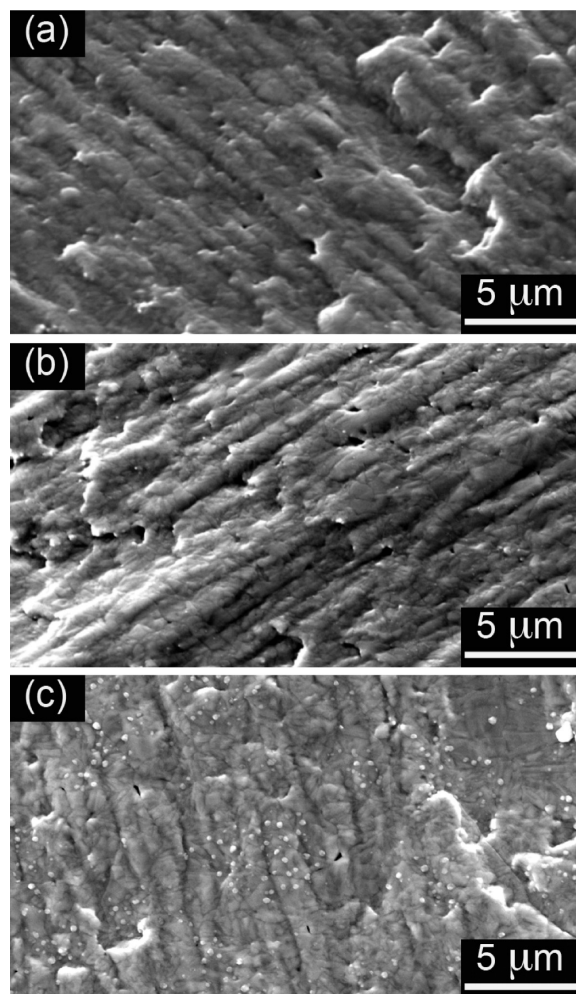


Figure 6. SEM images of the surface of the copper substrate with 20 nm Ni film (a) before annealing and (b) after annealing and (c) with 45 nm Ni film on copper substrate after annealing.

result in Ni surface islands that are too large after heating and therefore are not as conducive to nanotube growth. This theory is supported by SEM images taken of the surface of the as-deposited Ni film on copper before and after annealing for a time and temperature that replicates the CVD conditions. For a 20 nm Ni film deposited on a copper foil, there is basically no observable change in the surface topography after annealing at 770 °C for the magnification shown (Figure 6a, b). However, for the 45 nm

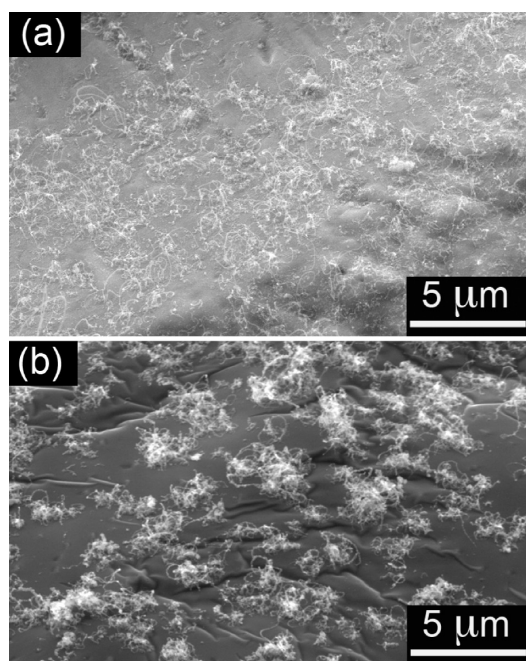


Figure 7. SEM images of the surface of the copper substrate with CNTs grown using xylene source with (a) 20 nm Ni film but no ferrocene and (b) with ferrocene but no Ni film.

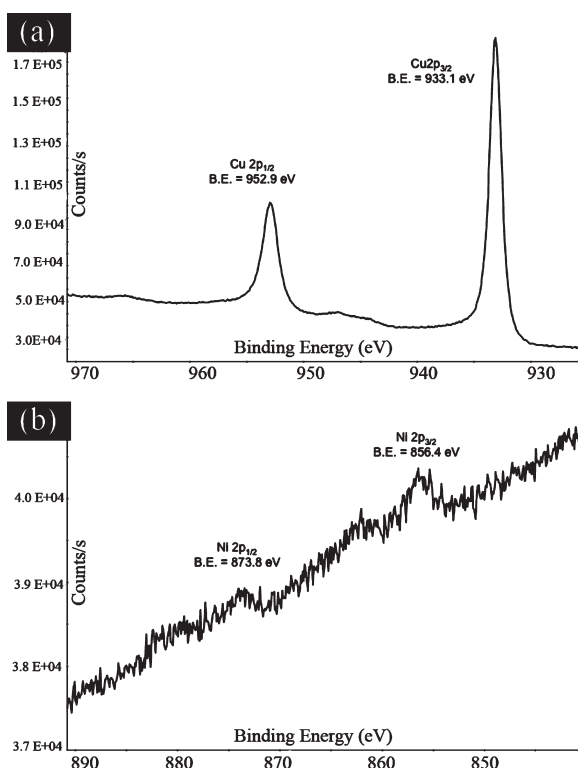


Figure 8. Near-surface high-resolution XPS spectra of 20 nm Ni sample after annealing for 30 min at 770 °C indicating the presence of (a) copper oxide and (b) nickel oxide.

film, islands are visible on the surface (Figure 6c). The islands have a broad diameter distribution ranging from about 250 nm to 3 μm . It therefore appears that the excessive nickel has the propensity to form into islands on the surface. Because the Ni films

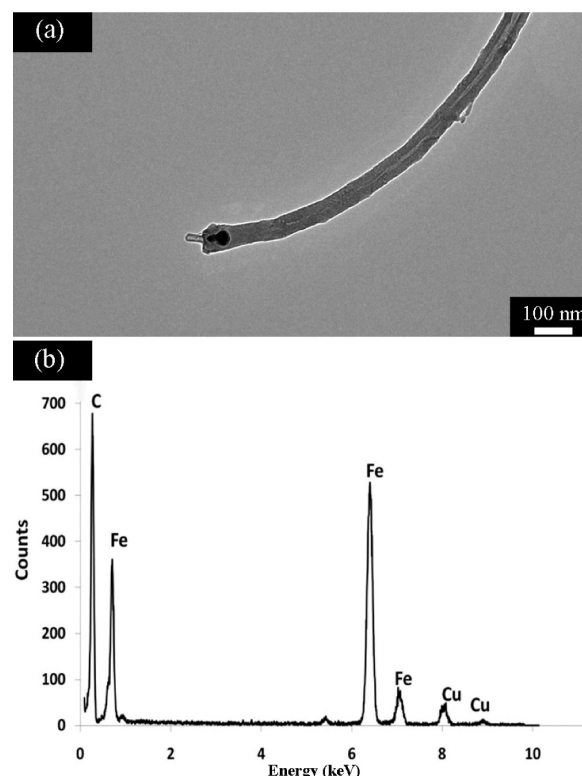


Figure 9. (a) Representative TEM image showing CNT with catalyst particle. (b) EDS data taken from multiple CNTs indicating that the catalyst particle is iron.

are actually deposited on the native copper oxide that is present on the surface of all the copper foils, it is possible that this oxide plays a role in the formation of Ni islands upon heating in the CVD chamber. Copper is known to oxidize rapidly^{25,26} on exposure to ambient conditions. It has been proposed that metal oxide layers such as chromium oxide aid in alignment by improving the breakup of catalyst islands. These results also correlate with the diffusion model for CNT growth, which predicts that if the island sizes are larger than the diffusion length of carbon, CNT growth is more difficult.^{27,28} The presence of large Ni islands for the thicker film appears to obstruct the efficiency of iron acting as a catalyst since there is poor growth and alignment when thicker Ni films are used (Figure 3a, b). Thus, thicker nickel films ($t > 20$ nm in this case) result in the growth of fewer CNTs, which in turn can grow in random directions because of a lack of crowding from other nanotubes. A high density of CNT nucleation and growth is required for preferential, vertical CNT growth.

To determine if the Ni film is still necessary when using the xylene/ferrocene mixture, growth of CNTs on bare copper (no Ni film) was also attempted, and random carbonaceous structures with extremely poor coverage and large amorphous carbon chunks were observed as seen in Figure 7a. We, therefore, also hypothesize that the nickel film acts as a surface modifier that supports the Fe catalyst from the ferrocene source. The ferrocene, therefore, is important for obtaining the high density of CNTs that forces the vertical growth to occur, but the presence of the nickel layer is also necessary. This finding can be compared to a study by Miao et al.²⁷ which found that copper nickel alloy substrates with iron thin films are much better than only nickel alone for growing aligned CNTs. On the other hand, CNT growth using just xylene (no ferrocene) on Ni films was also

performed and resulted in random CNT growth with poor coverage as seen in Figure 7b. Therefore, the addition of the Fe, from ferrocene, provides a greater amount of catalyst for CNT growth. Ferrocene may also play another role by providing intermediate decomposition products that could aid in dehydrogenation of the hydrocarbon feedstock.²⁹ Thus, it is clear that a 20 nm Ni film with the addition of the iron catalyst (from ferrocene) during CVD growth is the best combination for aligned, dense CNT growth.

To understand the effect of the Ni film better, X-ray photoelectron spectroscopy (XPS) was used for qualitative and quantitative surface analysis and chemical state information. A 20 nm nickel film (the thickness that yielded the best nanotube growth, Figure 3c) was annealed in the CVD chamber under flowing argon and hydrogen at 770 °C and then was removed to analyze the surface composition before nanotube growth using XPS. XPS data in Figure 8a reveals the presence of copper oxide present on the surface of the substrate in addition to nickel oxide. Quantitative XPS results show that the copper-to-nickel ratio in terms of atomic percentage is about 64% on the surface of the copper foil. In addition to acting as a catalyst for nanotube growth, it is possible that the remaining surface Ni will change the surface energy of the substrate. Studies by De Los Arcos et al.³⁰ and Wright et al.³¹ state that the contact angle of the catalyst particle on the substrate plays an important role in the wetting of the catalyst particle promoting faster growth and better aligned CNTs. Kanzow and Ding³² had also proposed that an increased contact angle for the catalyst particle would provide an increased surface area for carbon to precipitate in accordance with the diffusion model for CNT growth. Therefore, a similar effect may be occurring in these experiments. The Ni enrichment of the Cu surface may impact the wetting behavior of the Fe particles on the Cu substrate in a manner that promotes the enhanced formation of CNTs. To ascertain whether iron alone or some nickel–iron compound acts as a catalyst in the CVD growth process, TEM-EDS data from multiple CNTs was analyzed. The analysis revealed that the catalyst particles attached to the nanotubes were composed of only iron from the ferrocene decomposition in the CVD chamber (Figure 9). No Ni was found.

CONCLUSIONS

The results conclusively show that a Ni enriched surface is beneficial in obtaining dense vertically aligned CNT growth on bulk copper foil substrates when using a thermal CVD method with additional Fe catalyst supplied during growth. The results are comparable to what has previously been reported for PECVD growth of CNTs. The method proposed here, using a single thin Ni layer, is relatively simple in comparison to others that use multiple barrier films of different thicknesses that would also add to the contact resistance. To obtain these results, the xylene/ferrocene mixture is critical as CNTs grown using only a nickel film or only iron, from ferrocene, as the catalyst show poor coverage and alignment. For the case of the xylene/ferrocene growth, the Ni enriched surface acts as a support for the Fe catalyst that results in densely aligned CNT growth. It is believed that thinner nickel films result in better alignment because of compositional modification of the surface of the Cu on a smaller scale as opposed to thicker films where the nickel can form large surface islands, which may hinder CNT growth because of their size.

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