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Role of thin Fe catalyst in the synthesis of double- and single-wall carbon nanotubes *via* microwave chemical vapor deposition

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Synthesis of vertically aligned small diameter (single- and double-wall) carbon nanotube films on thermally oxidized n^+-Si(001) wafers, with acetylene diluted with ammonia gas mixture using a microwave plasma-assisted chemical vapor deposition technique, is reported. Experiments show that by continuous reduction in the thickness of the iron catalyst film to ~0.3–0.5 nm, or alternately, smaller catalyst particles produces hollow concentric tubes with a fewer number of walls. Double- and single-wall carbon nanotubes with diameters ranging from 1 to 5 nm were identified using transmission electron microscopy and Raman spectroscopy. A relatively higher deposition temperature (~850 °C) in conjunction with a controlled catalyst and rapid growth (<40 s) allowed for the growth of well-graphitized, high areal density ($\sim 10^{12}$-$10^{13}/cm^2$) nanotubes with reduced amorphous carbon and iron. Our results also indicate that the base growth is the most appropriate model to describe the growth mechanism for the nanotube films. © *2004 American institute of Physics*. [DOI: 10.1063/1.1796529]

Carbon nanotubes (CNTs) with either single-, double-, or multilayered graphene cylinders have been produced using different methods, such as dc electric arc discharge (EA), pulsed laser vaporization (PLV), and now chemical vapor deposition (CVD) (both thermal and plasma excitations).[1] Vertically aligned and/or patterned CNT films are highly desirable, so that their *structure-property* relationship can be assessed and they can be effectively incorporated into complex device architectures. Consequently, CVD may prove to be the preferred synthesis route for these films.[2]

In early deposition methods of PLV and EA, the growth of single-wall carbon nanotubes (SWNTs) is typically supported by the metal catalysts.[2] For CVD growth the catalyst is typically incorporated on the supporting surface. In this approach a hydrocarbon (usually methane, acetylene, benzene, or CO) gas is passed over the catalyst bed (such as Fe, Ni, or CO), which is heated to relatively high temperatures of 800–1000 °C. This technique is termed as catalyst-assisted CVD (CCVD).[3,4] Nevertheless, the role of transition metals and the related growth mode (tip versus base, bamboo versus hollow tube) have long been debated and are still a subject of intense investigation.[2,5]

In prior studies, several research groups have shown that CVD growth results in multiwalled nanotubes irrespective of the catalyst.[6,7] For microwave plasma CVD, vertically aligned CNT films of multiwalled CNTs are usually observed. Less has been reported on the synthesis of vertically aligned single- and double-wall CNT films utilizing a microwave plasma CVD technique.[8,9] Besides the size of catalyst particles for microwave CVD, other critical factors controlling the diameter of the nanotubes include the nature of the support, the reaction conditions on their formation, and the catalytic activity (or surface properties). With these requirements in mind, we employed thin Fe catalyst layers, elevated growth temperatures (*circa* 900 °C) and relatively fast growth time (<40 s) with acetylene and ammonia gas mixtures to achieve well-crystallized nanotubes with less a-C and Fe impurity content.

The CNT films were grown in a 1.5 kW IPX3750 ASTEX microwave CVD reactor, which has been employed to grow poly- and nanocrystalline diamond films.[10] Initially, Si(001) (n^+-type with 0.001 ohm-cm) substrates were thermally oxidized (Tylan II furnace) and a very thin catalyst layer iron (~0.3 and 0.5 nm) was deposited using electron-beam evaporator. A relatively thick SiO_2 layer (~180 nm) was used as a diffusion barrier preventing reaction between Si and Fe and forming silicides. Basically two steps were used to synthesize aligned CNTs. In step 1, the as-prepared substrates ($Fe/SiO_2/Si$) were annealed in vacuum at ~850 °C for 10 min in order to promote the formation of discrete Fe droplets/islands (see Fig. 1). In step 2, these annealed substrates were introduced in the MPCVD reactor which was evacuated to a base pressure $<10^{-3}$ Torr, and the chamber pressure was increased to 20 Torr with hydrogen and maintained during the deposition. Before initiating the growth, a deposition temperature of ~850 °C through induction heating, combined with the MW power source of 600 W, was obtained and a single burst of hydrogen was employed to ignite the plasma and shut off. Then a gaseous mixture of ammonia and acetylene was introduced with a flow rate ratio of 4:1 at ~850 °C. Deposition continued for <30–40 s for all of the samples. The nanotube film growth was carried out in a configuration, where the substrates were partially covered with sections of a Si wafer screening the actual substrates from the plasma, and the deposition took place underneath the covering regions.

As-deposited CNT samples were characterized using scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), and Raman spectroscopy (RS). SEM images were obtained on a JEOL 6400 with a beam energy of 5 kV along energy dispersive x-ray spectra (EDX). HRTEM was performed on a JEM 200-cx microscope operating at 100 kV. The samples for HRTEM were prepared by sonicating a small amount of the peeled CNTs in methanol for 15 min and drying a few drops of the

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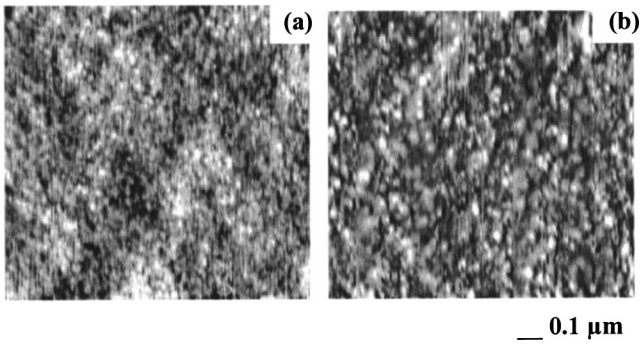

FIG. 1. Atomic force microscopy images ($0.5\times0.5\ \mu m^2$) of the annealed SiO_2/Si substrates coated with (a) 0.3 and (b) 0.5 nm Fe catalyst films exhibiting the variation in droplet microstructure.

suspension on a holey carbon or Cu grid. Visible RS analyses were carried out using 514.5 nm excitation and an ISA J-Y U-1000 spectrometer in a backscattering geometry. All spectra were measured with a beam-spot size of ($\sim2\ \mu$m with minimum power (~10 kw/cm^2) to avoid thermal degradation.

Two-dimensional AFM images of the annealed (0.3 nm and 0.5 nm) Fe catalyst layers were obtained with a Thermo Microscope M5 model in contact mode (Fig. 1). The images of the annealed films show structures at $\sim10-15$ nm with surface roughnesses of 0.4–0.5 nm. The 0.5 nm film was relatively homogeneous as compared to 0.3 nm film [Fig. 1(a)]. It was seen that after annealing at $\sim850\,^\circ$C Fe breaks into small islands due to surface tension. It was found that the droplet size depends upon the thickness of the initial Fe films, i.e., increasing with Fe thickness consistent with those reported by Bower *et al.*[4] Figure 2 shows a representative example of SEM images (cross sectional) of the as-grown CNT films on the annealed 0.3 and 0.5 nm Fe catalyst layers. The images show a high areal density of long fine tubes, which are well aligned perpendicular to the substrate, although somewhat wavy. Qualitatively, it is also apparent that the yield of CNTs is relatively higher, despite the short deposition times of <40 s, with an areal density of $\sim10^{12}$-10^{13}/cm^2. The estimated length of the nanotubes was $5-8\ \mu$m resulting a growth rate of about $0.12-0.20\ \mu$m/s, which is relatively higher than ($\sim0.08-0.10\ \mu$m/s) reported by other groups using plasma enhanced CVD techniques[11,12] and for multiwalled CNTs ($\sim0.01\ \mu$m/s) in our previous work.[13]

Through analyses of HRTEM and visible RS, the nature and type of the nanotubes (single-, double-, or multiwalled, and semiconducting or metallic) is revealed. HRTEM images shown in Fig. 3 exhibit the presence of single- and double-wall carbon nanotubes (as S/DWNT marked by arrows). The tubes were either isolated or weakly bundled, and could readily be dispersed. The diameters for most of the isolated nanotubes ranged between 0.8–1.25 and 4.0–5.0 nm for single- and double-walled nantubes, respectively [Fig. 3(a)]. A closed nanotube with no catalyst at the tip [Fig. 3(b)] indicates that the base growth model dominates in our system. We speculate that the relatively higher deposition temperature encourages anchoring of the catalyst and promotes root/base growth.

Raman spectroscopy (RS) is a nondestructive characterization tool that probes the structural bonding of carbon nanotubes.[14] As-deposited CNTs usually contain a mixture of

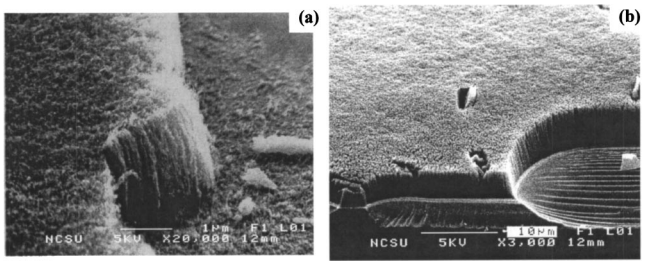

FIG. 2. Scanning electron microscopy (SEM) images of MWCVD carbon nanotube (CNT) films on (a) 0.3 nm Fe and (b) 0.5 nm Fe catalyst.

semiconducting and metallic nanotubes. However, due to resonance effects by utilizing an excitation wavelength of 514.5 nm (2.41 eV), we preferentially excite semiconducting nanotubes, while metallic nanotubes are analyzed using 632.8 nm (1.92 eV). Assignment of vibrational modes in the Raman spectrum is carried out following Refs. 14 and 15. Figure 4 displays first-order Raman spectra in the low-frequency ($100-300$ cm^{-1}) and high-frequency ($1000-1800$ cm^{-1}) regions for both of the representative CNT films. For a realistic comparison the spectra were normalized with respect to the intense high-frequency band.

The Raman spectra show signatures of single- and double-wall CNTs by the presence of the well-defined bands in the low-frequency region at ~187 and ~266 cm^{-1}, which correspond to the radial breathing mode (RBM). In the case of more than one wall nanotube, the primary and secondary RBMs are observed, which are related to outer- and inner-wall modes of the nanotubes, respectively [see Fig. 4(a)].[15] The presence of these bands is further evidence of the growth of small diameter or fewer shell CNTs, unlike multiwall (or a large number of shell) CNTs, where this band is invariably absent.[13] The RBM position (ω_{RBM}) can be scaled to the diameter of the nanotube (d_t) using the empirical relation, $d_t(\mathrm{nm})=234/\omega_{\mathrm{RBM}}$. We find $0.87<d_t<1.26$ nm range, which is in agreement with those estimate using HRTEM measurements.

The other pronounced feature of interest is the tangential displacement mode associated with the C-C stretching of SWNTs in the high-frequency region at $\sim1540, 1560$, and 1593 cm^{-1}. These narrow bands with full width at half maximum $\leqslant5-6$ cm^{-1} indicate high uniformity and primarily semiconducting nature of the tubes.[14] A relatively weak band ~1350 cm^{-1} (D band) arises due to disorder and is present in both spectra [see Fig. 4(b)]. The intensity ratio of the D to G band (I_D/I_G) is a qualitative measure of the phase purity

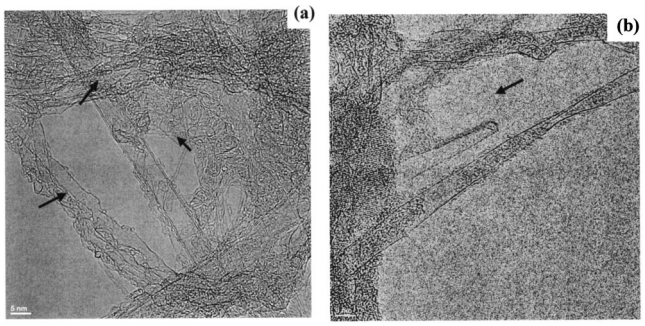

FIG. 3. High-resolution transmission electron microscopy (HRTEM) images of MWCVD CNTs. Well graphitized double- and single-wall CNTs are marked by arrows.

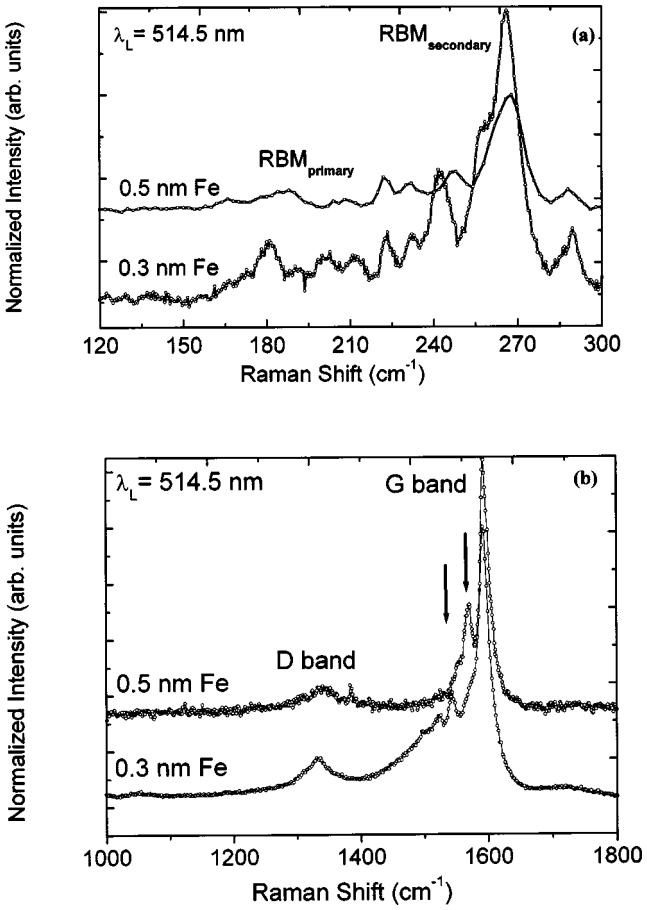

FIG. 4. Representative Raman spectra of CNT films grown on 0.3 and 0.5 nm Fe in (a) the low-frequency and (b) the high-frequency regions showing the radial breathing modes (RMMs), and disorder (*D*) and *G* bands, respectively, The spectra normalized with respect to the highest frequency band for a realistic comparison.

(alternatively degree of disorder) of the CNTs. Under the specific growth conditions considered in this study, $I_D/I_G \sim 0.10-0.12$.

Well-graphitized CNTs observed at relatively higher growth temperatures may be partly due to the presence of specific excited or ionized gaseous ($C_2H_2^{*/\pm}$ and $NH_3^{*/\pm}$) species, rather than the deposition temperature alone. One of the primary functions of ammonia is to etch competing graphitic or amorphous carbon phases which form during deposition. It also keeps the catalyst particles activated by allowing continuing access of gas. Various etching gases, such as ammonia and hydrogen, have been compared, but ammonia has been shown to be the more efficient.[6] The limitation of the supply of carbon species through C_2H_2 by utilizing thin Fe catalyst was also helpful to form S/DWNTs, because the low concentration of carbon (or flux of carbon containing species) in the catalyst suppresses the additional nucleation and forming multiwall structures, such as in the case of large catalyst particles.[13]

Moreover, similarities among the samples synthesized by different growth techniques and by different groups tempt us to adopt the classic VLS model proposed for filamentary carbon,[16,17] according to which the growth proceeds via solvation of carbon vapor (*dissolution*) into the metal islands, followed by *precipitation* of excess carbon into nanotubes (*supersaturation*). Nevertheless, the conditions necessary to achieve growth of small diameter nanotubes using CVD techniques are much more critical than those of large diameter multiwalled CNTs. Small island size catalyst causes the diffusion length of carbon atoms to be shortened (i.e., fast supersaturation due to limited C diffusion) and results in the acceleration of the growth rate of nanotubes.

In conclusion, we have elucidated a way of depositing aligned single- and the double-wall CNTs by microwave plasma-assisted CVD with C_2H_2/NH_3 gas mixture. By using elevated substrate temperatures and effective manipulation of the Fe catalyst thickness, and hence improving catalyst efficiency, the growth characteristics of nanotubes were considerably affected. As a result, we were able to grow well-graphitized vertically aligned CNTs. The production of small diameter CNTs is attributed to the coupling of relatively higher deposition temperatures and rapid growth and the controlled Fe microstructures (nanoislands) required to seed small diameter CNTs.

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