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Thin Solid Films 471 (2005) 140–144

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Root growth of multi-wall carbon nanotubes by MPCVD[1]

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Received 1 May 2003; received in revised form 31 July 2003; accepted 6 May 2004
Available online 15 June 2004

Abstract

This work examines the relationships among the growth and interlayer reactions of carbon nanotubes (CNTs) to develop an effective process for controlling the nanostructure, orientation and characteristics of CNTs. Vertically oriented CNTs were successfully synthesized by microwave plasma chemical vapor deposition (MPCVD) with CH_4/H_2 as source gases. Additionally, the Ti and SiO_2 barrier layers and the Co catalyst were used in an experiment on the growth of CNTs on the Si wafer. Then, the SiO_2 barrier layer was deposited by low-pressure chemical vapor deposition (LPCVD). The Ti barrier layer and Co catalyst films were deposited on the Si wafer by physical vapor deposition (PVD). The deposited nanostructures were characterized by scanning and transmission electron microscopy, the results of which reveal that the deposited MWCNTs were grown under the influence of a catalyst on Si substrates with or without a barrier layer, by MPCVD. Vertically grown, dense MWCNTs attached to a catalytic film demonstrate that various MWCNTs penetrated the root particles. The diameter of the root particles, of approximately in the order of 100 nm, is larger than those of the tube, 10–15 nm. The well-known model of the growth of CNTs includes base- and tip-root growth. The interaction between the catalytic film and the supporting barrier layer is suggested to determine whether the catalytic particles are driven up or pinned down on the substrate during the growth.

PACS: 81.05.Y
Keywords: Nanostructures; Growth mechanism; Carbon; Plasma processing and deposition

1. Introduction

In 1991, Iijima [1] observed carbon nanotubes (CNTs) that comprised of sheet(s) of graphite rolled into a cylinder. This novel material has attracted strong interest in the area of nanotechnology, because of its notable characteristics and promising technological applications. Understanding the mechanism growth of its growth is critical in the yield and quality of CNTs in various applications. However, the growth mechanisms of CNTs are very complex and remain controversial. They depend on the method of deposition, the catalyst used and the process parameters. Many mechanisms have been suggested proposed for the growth of CNTs. Several methods, including arc discharge [2], laser ablation [3], microwave plasma chemical vapor deposition (MPCVD) [4], thermal CVD [5] and others, have been used to synthesize the CNTs. Baker [6] adopted the concept of the vapor–liquid–solid (VLS) mechanism [7] to explain the growth of Si whiskers, and stated that the growth of CNTs was followed by the decomposition of hydrocarbon into carbon atoms on the surface of the catalyst and dissolution of these atoms in the catalyst. Then, carbon atoms diffused through the catalytic particles, and precipitated at the rear to generate the filament structure. The diffusion of carbon was the rate-determining step. Oberlin et al. [8] proposed that the surface diffusion of carbon around, rather than through, the catalyst particle, is essential to growth. Endo and Kroto [9] indicated that, in the arc-discharge method, the presence of a pentagonal lattice assisted the formation of tubes that involves the C_2 adsorption process for reconstructing cap morphology. Iijima et al. [10] proposed an open-ended growth mechanism, in which carbon atoms are added to the open ends of the tubes. The catalytic growth of single-walled carbon nanotubes (SWCNTs) remains a controversial debated issue. Dai et al. [11] proposed a yarmulke (Yiddish for skullcap) mechanism

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[1] This paper was presented at the ICMCTF Conference 2003, San Diego, California, 28 April–2 May 2003.

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doi:10.1016/j.tsf.2004.05.004

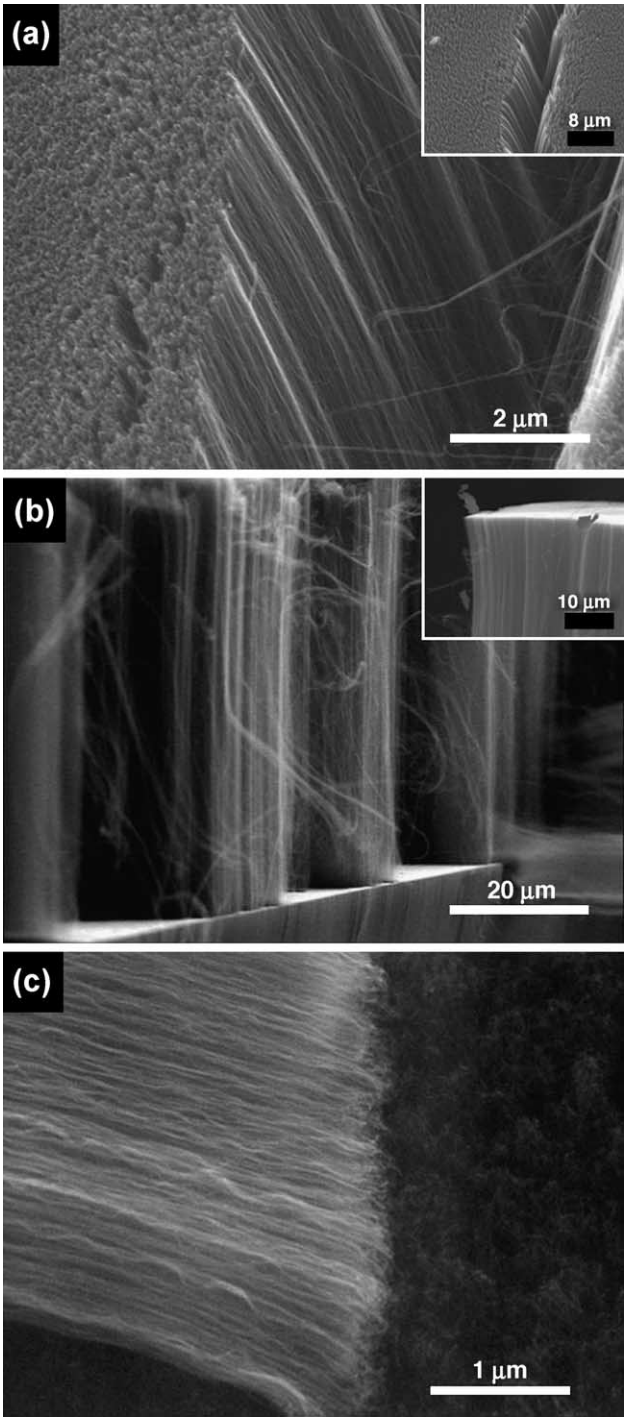

Fig. 1. SEM morphologies of vertically aligned CNTs under Ti barrier layer deposition conditions (CNT grown on Si/Ti); (a) top views at two magnifications; (b) cross-sectional views at two magnifications; (c) CNTs tips far from the substrate.

in which carbon forms a hemispherical graphite cap on the catalyst particle and the nanotubes grow to form the yarmulke. In the root growth mechanism for SWCNTs [12–16], various CNTs grow radially from the surface of single catalytic particles, whose diameters greatly exceed that of the CNTs.

Controlling a tube's diameter, density and length during growth is important to industry. This investigation presents method for growing dense vertically aligned multi-walled carbon nanotube (MWCNTs) bundles using the barrier layer (Ti,SiO_2). Moreover, mechanisms of the base- and the tip-root growth of MWCNTs are presented.

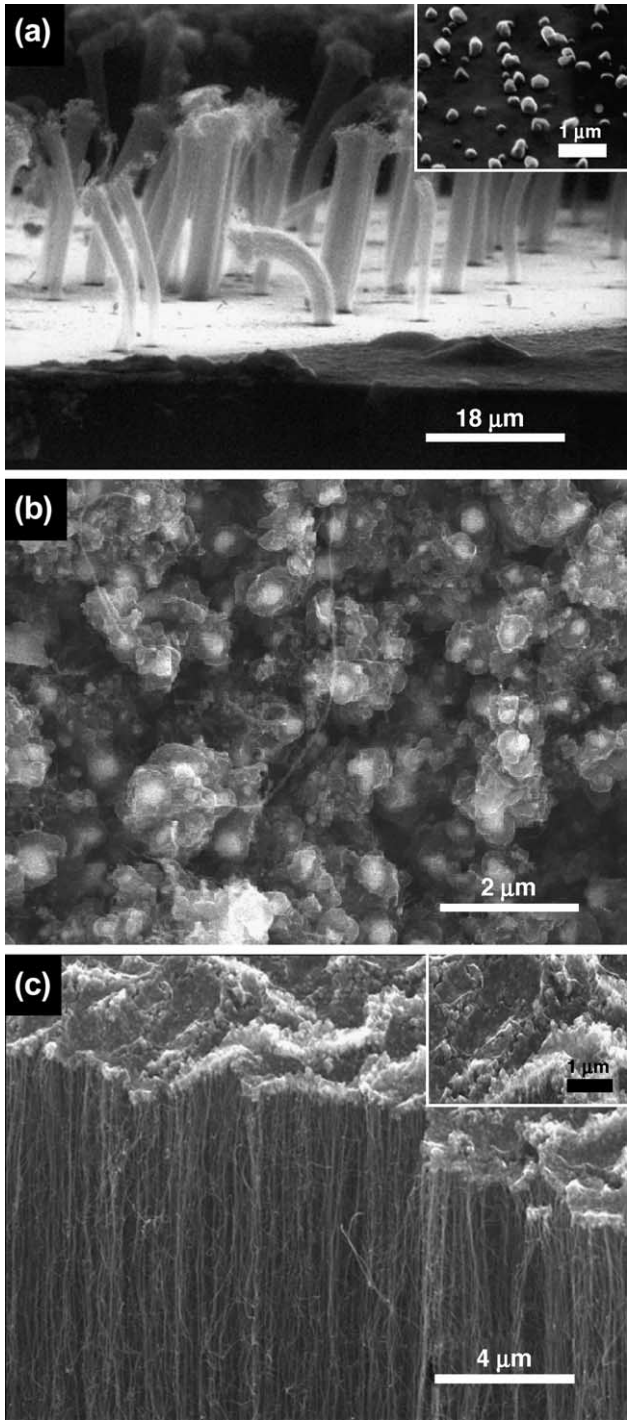

Fig. 2. SEM morphologies of vertically aligned CNTs under SiO_2 barrier layer deposition conditions (CNT grown on Si/SiO_2); (a) isolated CNTs bundles; (b) top view of catalyst that includes the carbon layer; (c) cross-section and top view of CNTs film.

2. Experimental details

Vertically oriented MWCNTs were catalytically grown on Si wafers by the MPCVD method with CH_4/H_2 as source gases. The SiO_2 (1 μm) and Ti (750 nm) barrier layers were deposited by low-pressure chemical vapor deposition (LPCVD) at a pressure of 10 Torr and physical vapor deposition (PVD) at a pressure of 5×10^{-3} Torr, respectively. The structures of the specimens thus formed were Si/SiO_2 and Si/Ti. Co was applied to catalyze the growth of CNTs on a Si wafer by the PVD method (Si/SiO_2/Co and Si/Ti/Co). CNTs were synthesized by the following procedure: (1) pretreatment with H_2 plasma for 10 min to yield well-distributed nano-sized catalysts, at a pressure of 20 Torr and a microwave power of 500 W, and (2) the introduction of CH_4/H_2 (10:100 sccm) process gases at a pressure of 2.13 kPa and a microwave power of 800 W. The substrate temperature was 650 °C during the growth of CNTs. The CNTs grown using the different barriers Ti and SiO_2, were called Si/Ti and Si/SiO_2, respectively.

The morphologies and microstructures of the deposited CNTs were characterized by field emission scanning electron microscopy (FESEM; HITACHI S-4000), transmission electron microscopy (TEM; JEOL 2000 FX) and high-resolution transmission electron microscopy (HRTEM; JEOL 4000 FX).

3. Results and discussion

3.1. Effect of the interlayer on the growth of vertically aligned CNTs

Fig. 1 depicts the SEM morphologies of the CNTs using a Ti_2-coated Si substrate (CNT grown on Si/Ti); Fig. 2 presents those obtained using the SiO_2-coated Si substrate (CNT grown on Si/SiO_2), indicating that they grew vertically and were dense. The SEM top and cross-section views of CNT grown on Si/Ti in Fig. 1(a) and (b), respectively, demonstrate that the CNTs have a high density. Fig. 1(c) shows the top layer of the CNT film, clearly without any catalyst at the tip of the CNTs. In contrast, CNTs covered with a top thin layer, and in which nanoparticles were embedded, were observed for CNT grown on Si/Ti, as presented in Fig. 2(a–c). Fig. 2(a) depicts the isolated CNT bundle grown from a single catalytic particle. Fig. 2(b) and (c) clearly shows the carbon film that is surrounded by catalytic particles on the tips of CNTs. The SiO_2 barrier layer effectively blocks the interaction between Co and the Si substrate; the Co catalysts are driven upwards during growth, indicating the tip growth of the CNTs (CNT grown on Si/SiO_2). However, increasing the deposition time can cause bonding between the Co and the Ti film and the further formation of silicide using a Si substrate, inducing base growth of the CNTs. Therefore, the use of a barrier layer may determine the position of the catalytic film (on top or bottom) in relation to the substrate. Different barrier materials are associated with different growth mechanisms of CNTs.

Fig. 3(a–c) presents the TEM microstructures of CNTs, for the SiO_2-coated CNT grown on Si/SiO_2. The samples of CNTs for TEM were prepared by ultrasonic dispersion on a carbon–copper grid. Notably, the basic results were the same for all samples with different barrier layers (Ti,SiO_2): the free vertex and the other vertices of the MWCNTs bundles are attached to the catalytic film, and embedded with nanoparticles in stem of tubes. Fig. 3(a) depicts the typical microstructure, as determined by TEM. The diameter of the nanoparticles (100–150 nm) exceeds the tube diameter of the CNTs (10–15 nm), and many CNTs grow out from individual nanoparticles. This phenomenon is similar to the root growth mechanism of SWCNTs, first presented by Saito et al. [8], to explain the sea-urchin-like structures.

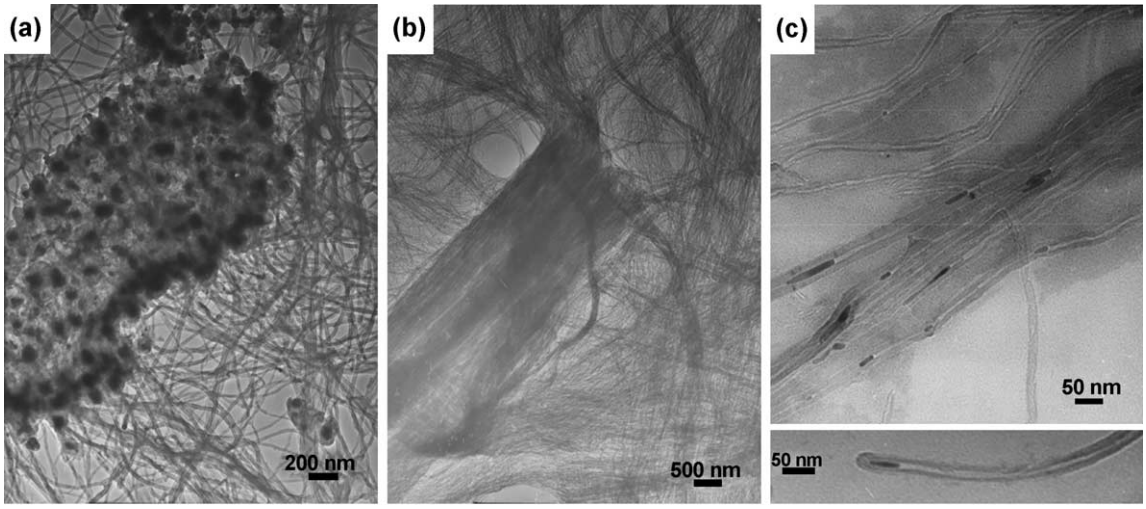

Fig. 3. TEM microstructures; (a) MWCNTs attached to the catalytic particles; (b) dense MWCNT bundles; (c) vertex and stems of CNTs, showing split particles.

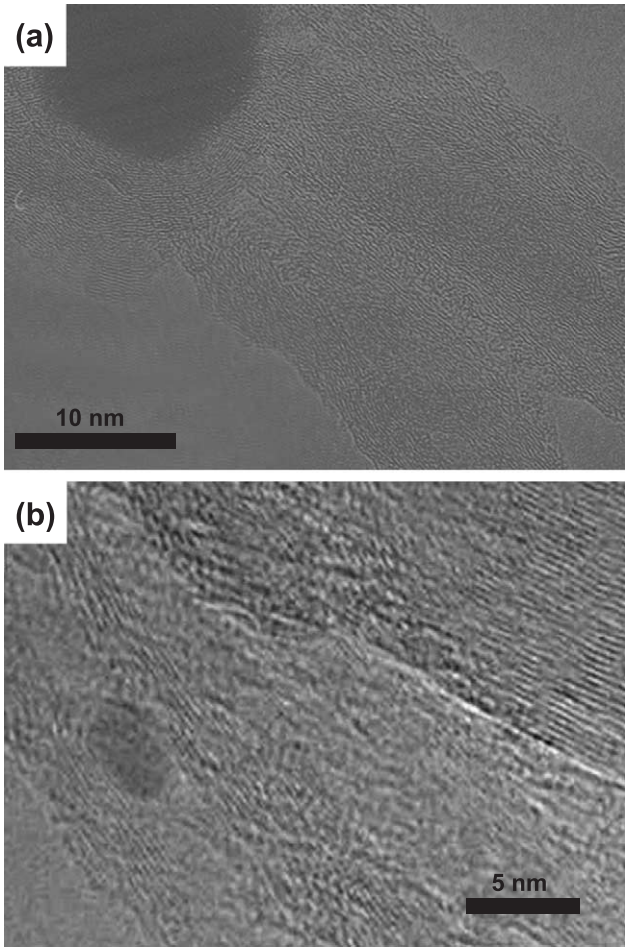

Fig. 4. HRTEM image of MWCNTS; (a) particles are surrounded by numerous graphite sheets, and MWCNTS penetrate the root particle; (b) a nanoparticles splits away form a root particle.

The process that results in the radial growth of several large numbers of nanotubes from a single catalytic particle is suggested to involve the segregation and nucleation of carbon on the metal surface. In this work, the presence of a catalyst on the base of the growth of CNTs on Si/Ti indicates base-root growth. In contrast, the growth of CNTs on Si/SiO_2 exhibits tip-root growth. Fig. 3(b) presents MWCNTs bundles. Large ropes of MWCNTs have similar diameters and lengths, suggesting that the tubes grow cooperatively. The splitting catalysts from the root particle are observed on the apex of CNTs, or remain in the tube stems, as shown in Fig. 3(c). Fig. 4 presents the HRTEM image of MWCNTs (CNT grown on Si/SiO_2), revealing that multi-shell graphite sheets surround the root particle and protrude from MWCNTs (Fig. 4(a)). Fig. 4(b) depicts the nanoparticles, encapsulated in the inner tube.

3.2. Tip- and base-root growth mechanism of CNTs

Fig. 5 schematically depict the proposed growth models of CNTs. The first stage is the formation of a "large" catalytic particle, originating from the catalytic film, at a low H_2 pretreatment temperature (~ 590 °C). Under such conditions, the system energy and surface energy for forming new particles favor the formation of large particles (100 ~ 150 nm). At a growth temperature of 650 °C, the liquid state of the catalytic particles enables carbon atoms to dissolve in the droplets, reaching supersaturation conditions. The introduction of various carbon atoms into nanoparticles, which are in the liquid state, may cause surface instabilities. These surface instabilities lead to the formation of small protrusions, which act as nucleation sites for the subsequent growth of MWCNTs. Notably, when CNTs grow perpendic-

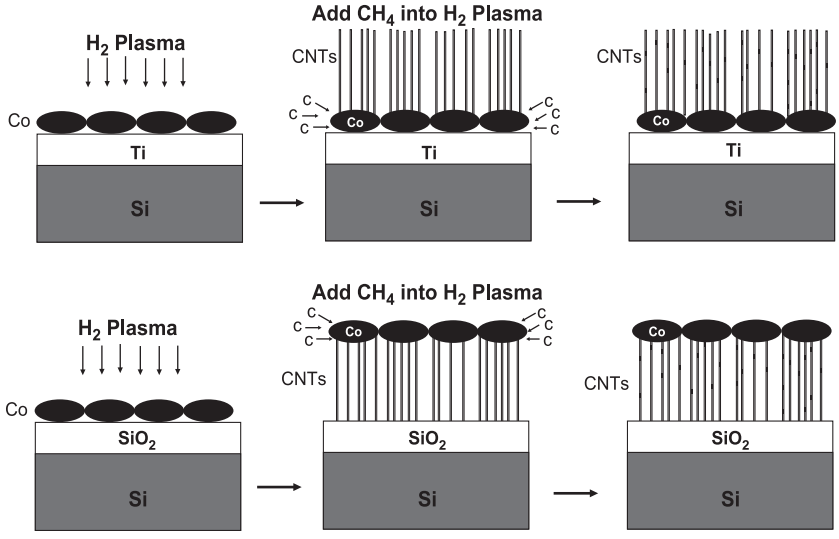

Fig. 5. Schematic diagrams of growth mechanisms of tip- and base-root growth of MWCNTs.

ular to the sample surface they grow, underneath, or above the catalytic film, suggesting that growth involves bulk and surface diffusion of carbon atoms through the catalytic liquid particles. When the carbon atoms are segregated from the catalytic particles and diffuse on their surface, the CNTs grow randomly rather than perpendicularly to the catalytic film and surface of the substrate. The growth of CNTs proceeds via the further incorporation of carbon atoms into the root particles. During the synthesis, part of liquefied nanoparticles split off from root particles due to capillary suction, as a results of the fuse state of the particles and surface instabilities; such behavior was illustrated in Fig. 3.

4. Conclusions

In conclusion, this study investigated the base- and tip-root growth mechanisms of MWCNTs. The attachment of several vertically grown, dense MWCNTs to a catalytic film reveals that various MWCNTs penetrate the root particles. This finding provides a different perspective on the catalyzed growth of MWCNTs that can support a comparison between the root growth of SWCNTs and that of MWCNTs. The presence of the catalytic film, on either the base or the top of CNTs, controlled by the barrier layer, suggests potential use in other applications.

Acknowledgements

The authors would like to thank the supports of the Industrial Technology Research Institute (Contract No.: A321XS9410, A311XS31E1), National Science Council (Contract No.: NSC90-2216-E-009-034, -035 and -040) and the Ministry of Education of Taiwan (Contract No.: 89-E-FA06-1-4).

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