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Freestanding vertically oriented single-walled carbon nanotubes synthesized using microwave plasma-enhanced CVD

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Abstract

Freestanding single-walled carbon nanotubes (SWCNTs) have been synthesized in a vertical direction, perpendicular to the growth substrate, using applied DC substrate bias in a microwave plasma-enhanced chemical vapor deposition (PECVD) synthesis process. The degree of alignment and spatial density of SWCNTs demonstrate a strong dependence on the magnitude of applied bias, with increased alignment and decreased density with increased bias. The unique synthesis environment created by the application of a negative substrate bias in PECVD aligns SWCNTs along electric field lines and decreases SWCNT density due to bombardment by positively charged hydrogen ions. Multi-excitation wavelength Raman spectroscopy reveals shifts in dominant RBM peaks with the application of dc bias. Use of this technique to orient SWCNTs in the vertical direction may allow for three-dimensional SWCNT-based device architectures. © 2006 Elsevier Ltd. All rights reserved.

Keywords: Carbon nanotubes; Plasma deposition; Raman spectroscopy

1. Introduction

Since their discovery in 1991 [1], single-walled carbon nanotubes (SWCNTs) have been extensively investigated due to their novel properties and nanoscale geometric features. The introduction of SWCNTs into applications, however, has been hindered by the challenge of controlled synthesis. For applications such as electrical interconnects and electron emission devices, among others, control of SWCNT alignment perpendicular to the growth substrate is necessary for optimal device performance and spatial efficiency. In situ directional control of SWCNT synthesis has been reported previously but has been limited to hori-

zontal configurations. Because of the highly anisotropic polarization of SWCNTs [2], the application of electric fields can orient SWCNTs [3–5] and multi-walled CNTs [6] along field lines during CVD synthesis as well as during post-synthesis processing [7,8]. Vertical orientation of freestanding SWCNTs by application of an electric field, however, is an additional challenge that has not been reported previously.

Plasma-enhanced chemical vapor deposition (PECVD) processes have been used to synthesize vertically aligned carbon nanotubes (CNTs) by means of the electric field present in the plasma sheath [9]. However, until recent reports of SWCNT synthesis using PECVD [10–15], CNT types grown by PECVD had been limited to multi-walled carbon nanotubes (MWCNTs), and vertical alignment of SWCNTs using this technique has not been clearly established. Oriented SWCNTs have been synthesized from zeolite structures by Kato et al. [13], but due to the small

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aspect ratio (length ~ 100 nm) the alignment can be attributed to directional growth determined by the zeolite pore structure. Additionally, the oriented SWCNTs were shown to convert into MWCNTs for synthesis times greater than 30 s. In addition to the PECVD syntheses stated above, thermal CVD syntheses of SWCNTs using supported catalysts similar to that used in this study show no vertical alignment [16–24]. We report the stable synthesis of high aspect ratio, freestanding, vertically oriented SWCNTs using microwave PECVD and the application of a negative dc bias to the growth substrate.

2. Experimental methods

SWCNT synthesis was conducted in a SEKI AX5200S microwave PECVD reactor shown schematically in Fig. 1. Substrate heating was supplied by a 3.5 kW radio frequency power supply acting on a graphite susceptor. A hollow stainless steel rod in contact with the center of the susceptor and connected to an external dc voltage supply (Sorensen DCS600-1.7E) provided a means to electrically bias the growth substrate with respect to the electrically grounded chamber walls. Temperature feedback control was facilitated with a K-type thermocouple embedded in the rod, while the substrate surface temperature was measured using a Williamson (model 90) dual wavelength. The growth substrate rested on a 5.08 cm diameter, 3.30 mm thick molybdenum puck used to concentrate the plasma directly above the sample.

The catalyst and support were prepared by a wet mechanical mixing and combustion synthesis procedure using a solution of molybdenum, cobalt nitrate hexahydrate, and magnesium nitrate according to a previously reported procedure [15] to produce bimetallic Mo/Co catalyst particles embedded in a nanoporous MgO support. This catalyst and support system has been shown to play a role in controlling SWCNT diameter, as suggested by Liu et al. [25]. The silicon sample with catalyst was loaded into the PECVD reactor, which was then evacuated to 100 mTorr by an external mechanical pump. The susceptor

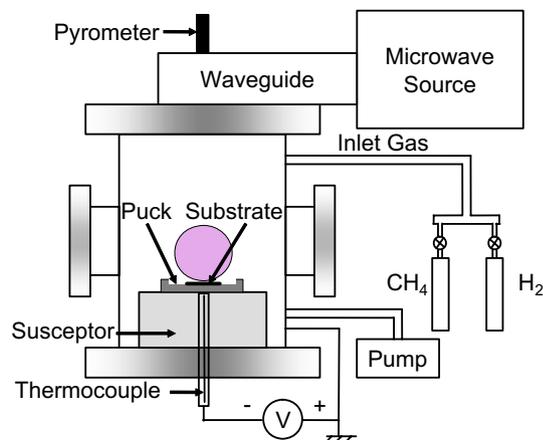


Fig. 1. Schematic of microwave PECVD chamber.

was heated to 900 °C in 50 sccm of flowing hydrogen at a pressure of 10 Torr. After a plasma was ignited at a power of 200 W, a dc bias between 0 and -250 V was applied to the substrate, and 5 sccm methane was introduced for 20 min. The surface temperature of the substrate recorded by the dual wavelength pyrometer was ≈ 770 °C for all levels of applied bias.

A Hitachi S-4800 field emission scanning electron microscope (FESEM) and Senterra micro-Raman system were used to characterize the resulting SWCNTs. Laser excitation wavelengths of 533 nm and 785 nm were used for recording Raman spectra over ten locations on each sample. The FESEM characterization allowed for length, density, and diameter estimates of individual SWCNTs and SWCNT bundles, while the Raman spectra allowed for confirmation of SWCNT products, their quality, and their diameters.

3. Results and discussion

The degree of SWCNT alignment in the vertical direction is a strong function of the magnitude of the bias applied to the substrate. Given an electric field above a critical minimum value, it is anticipated that SWCNTs will grow parallel to field lines. Fig. 2 shows both an illustration of the anticipated effect of SWCNTs synthesized at different orientations within a sufficiently strong electric field as well as FESEM images of SWCNTs synthesized at orientations similar to the illustration. Freestanding SWCNTs initiated at an angle with respect to the flat substrate (as shown in Fig. 2(b)) display curvature acting to align the tip vertically, reflecting the contours of the electric field lines around the MgO support particle. Fig. 3 shows SWCNTs synthesized under different magnitudes of applied bias ranging from 0 to -150 V in -50 V increments. The SWCNTs synthesized without bias (Fig. 3(a))

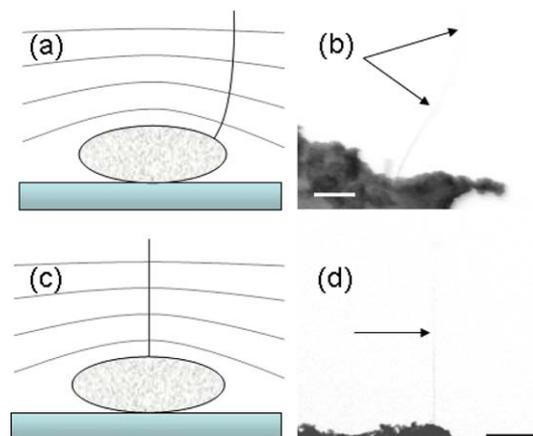


Fig. 2. Effect of applied substrate bias. (a) Schematic of and (b) cross-sectional image of SWCNT synthesized using -200 V substrate bias originating on side of support particle (scale bar = 50 nm) and growing perpendicularly to electric field lines. (c) Schematic of and (d) cross-sectional FESEM image of SWCNT synthesized at -200 V substrate bias originating from flat support particle surface (scale bar = 200 nm).

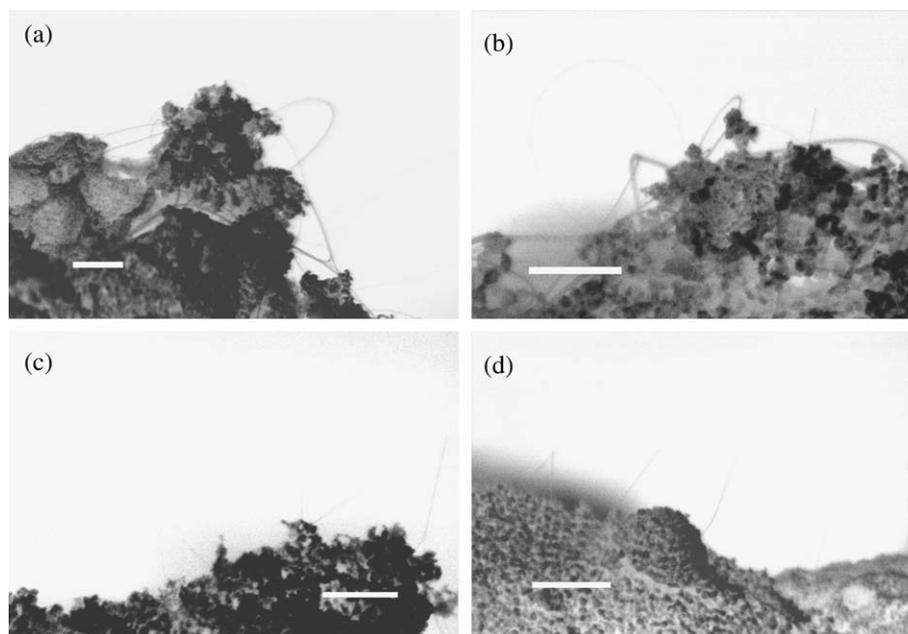


Fig. 3. Cross-sectional FESEM micrographs of SWCNTs grown under dc biases of (a) 0 V, (b) -50 V, (c) -100 V, (d) -150 V. Scale bar = 200 nm.

formed large bundles that follow the profile of the MgO support particles and silicon substrate, likely due to strong van der Waals forces. In contrast, SWCNTs grown under a -150 V bias were vertically aligned and largely free of bundles. SWCNTs grown without applied bias obtained a length of several microns [15], while the lengths of vertical freestanding SWCNTs grown under an applied bias of -250 V were generally less than 200 nm. Intermediate levels of bias (-100 V to -200 V) resulted in vertical SWCNTs with lengths of 500 nm and greater. Because of thermal vibration, resolving the precise length of freestanding SWCNTs greater than approximately one micron by FESEM was not possible.

Incremental enhancement in vertical alignment was observed with increasing bias from 0 to -50 V and between -50 and -100 V as seen in Fig. 3(b) and (c). For applied bias levels between -50 and -150 V, SWCNTs longer than one micron tended to form loops oriented in the vertical direction. In the presence of a relatively weak electric field, thermal vibrations of SWCNTs and SWCNT bundles

growing in the vertical direction may be large enough to create sufficient bowing that the tip touches or becomes attracted to the substrate or support particle, creating vertically oriented loops. Conversely, SWCNTs grown under applied bias levels of -200 and -250 V (Fig. 4) displayed strongest alignment with no such vertically oriented loops, suggesting that the electric field generated at these bias levels was of sufficient magnitude to counteract forces acting to draw the SWCNT tips toward the substrate. SWCNTs synthesized with an applied bias of -200 V obtained lengths of nearly one micron, while, as mentioned, those grown with a bias of -250 V were significantly shorter.

Figs. 3 and 4 also demonstrate that the spatial density of SWCNTs decreases dramatically with an increasing bias magnitude. The negatively biased substrate attracts and accelerates positively charged hydrogen and hydrocarbon ions generated in the plasma, and these species could serve as etchants, destroying SWCNTs. Selective etching of small-diameter SWCNTs by atomic hydrogen in a hydrocarbon plasma environment has been experimentally dem-

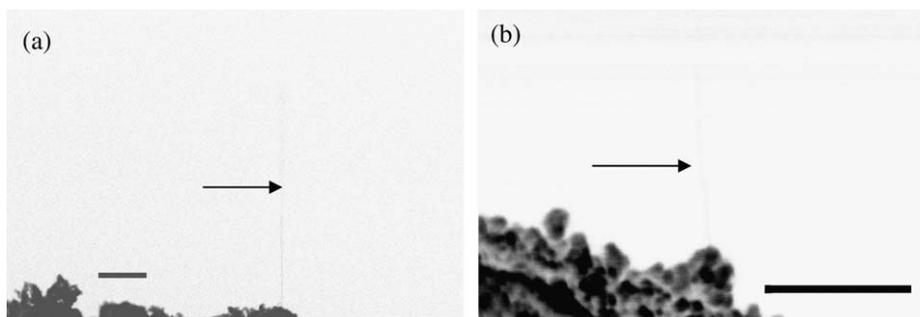


Fig. 4. Cross-sectional FESEM micrographs of SWCNTs grown under dc biases of (a) -200 V and (b) -250 V. Scale bar = 200 nm.

onstrated by utilizing oxygen gas as a scavenger to adjust levels of atomic hydrogen [26]. Additionally, SWCNTs growing in the direction of the electric field are expected to carry electrical current when the substrate is biased. If the current density exceeds a critical value, a SWCNT may be partially or completely destroyed. Typical burnout current for SWCNTs based on field emission experiments is anticipated to be on the order of microamps [27–29]. Using this criterion, metallic SWCNTs and long SWCNTs that protrude farther into the plasma sheath would be most susceptible for burnout, as they would potentially carry the largest current. Synthesis would thus favor SWCNTs carrying a lower current density such as short, larger-diameter, and/or semi-conducting SWCNTs. Indeed, previous experiments have shown that post processing of SWCNTs in hydrogen plasma preferentially etches metallic nanotubes, leaving mainly semi-conducting SWCNTs [30].

Raman spectra obtained at 533 nm and 785 nm excitation wavelengths, shown in Fig. 5, confirm the existence of SWCNTs. Radial breathing mode (RBM) peaks, generally found between 100 and 300 cm^{-1} , are characteristic of SWCNTs. Intense peaks are also found near 1320 and 1580 cm^{-1} , indicating disordered or nanocrystalline carbon and highly ordered graphite, respectively. Examination of the low frequency spectra (Fig. 5(a)) shows RBM peaks from 103 to 240 cm^{-1} depending on the Raman excitation wavelength and substrate bias condition. The RBM peaks obtained with both excitation wavelengths reveal a substantial shift in the distribution of RBMs, with lower frequency peaks favored with increasing substrate bias. SWCNT diameters may be determined from the frequency of the RBM peak using the relation $w_{\text{RBM}} (\text{cm}^{-1}) = 248/d(\text{nm})$ proposed by Dresselhaus et al. [31], where d is the SWCNT diameter and w_{RBM} is the Raman shift of the

RBM peak. The observed shift towards low frequency RBM peaks consequently corresponds to an increase in SWCNT diameter, with SWCNT diameters as large as 2.41 nm observed at the -250 V bias synthesis condition.

In addition, based on the incident laser wavelength and Raman shift of the RBM peaks, it is possible to classify the corresponding SWCNTs as metallic or semiconducting [31]. The distribution of semiconducting and metallic SWCNTs that are resonant at given Raman laser excitation wavelengths may be graphically described by a so-called Kataura plot [32] such as that found in Fig. 6 [33]. Using the Kataura plot as a guide, the most intense RBMs obtained using the 533 nm excitation wavelength (120–200 cm^{-1}) fall within the anticipated range of semiconducting SWCNTs for all bias levels, while the location of the most intense RBM peaks obtained using the 785 nm excitation wavelength vary from a mix of metallic and semiconducting SWCNTs at applied bias levels of -150 V or less (103–211 cm^{-1}) to strictly semiconducting at -250 V (103 and 143 cm^{-1}). These relations suggest that larger diameter and semiconducting SWCNTs are favored when applying negative substrate bias during PECVD synthesis.

The ratio of the G- to D-band intensities in a given Raman spectrum indicates the relative amount of highly ordered graphitic carbon as compared to amorphous carbon and sidewall defects, and this ratio has been used as an index to assess the purity of the SWCNTs [21,34,35]. A G- to D-band ratio much greater than unity indicates an abundance of highly ordered graphite and a low amount of undesired carbon content. As seen in Fig. 5(b), the G- to D- band ratio decreases from a value of 20 for SWCNTs grown with no applied bias to approximately 0.45 for SWCNTs grown under applied biases of -250 V. Such G- to D- band ratios are comparable to or better than

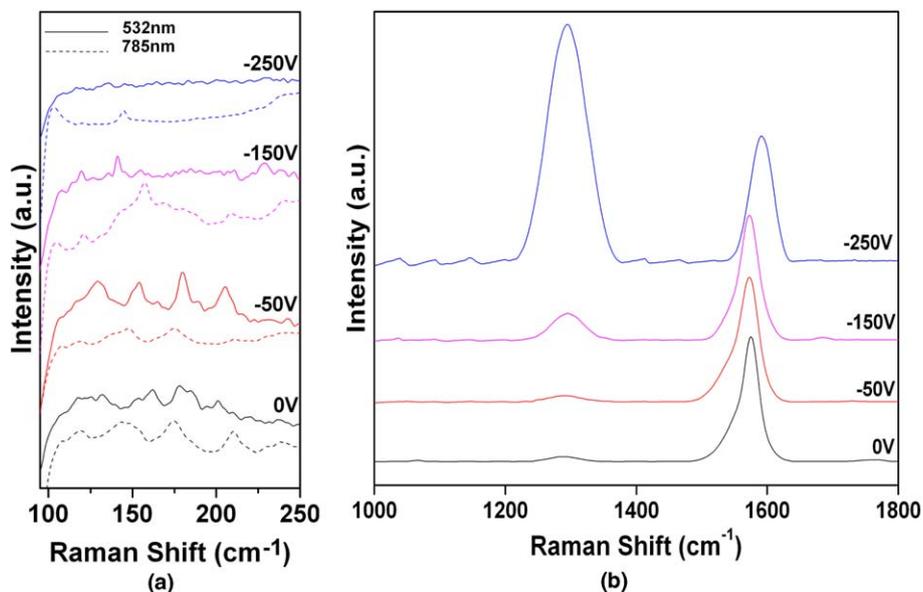


Fig. 5. (a) Low frequency Raman spectra for SWCNTs synthesized under dc bias obtained at 533 nm and 785 nm excitation wavelength. (b) G- and D-bands for SWCNTs synthesized under dc bias taken at 785 nm excitation wavelength.

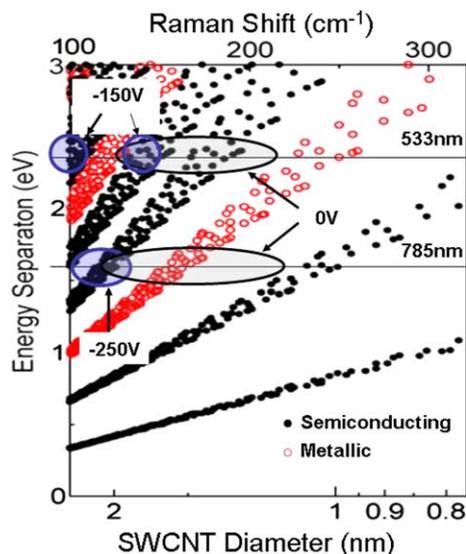


Fig. 6. Kataura plot [33] with 533 nm and 785 nm Raman excitation wavelengths indicated. RBM peaks from SWCNTs synthesized without bias and at -150 V (533 nm) or -250 V (785 nm) are indicated in the shaded oval regions.

those obtained for a similar catalytic system used for SWCNT synthesis by thermal CVD without applied bias [36]. The decrease in the ratio under applied bias is likely a result of decreasing graphitic content caused by lower SWCNT density and may indicate the presence of disordered carbon residue from SWCNTs that were fully or partially destroyed as a result of carrying high electrical currents or by bombardment of hydrogen ions, as previously discussed.

4. Conclusions

Synthesis of SWCNTs in the direction perpendicular to a substrate has been demonstrated using applied bias and plasma-enhanced CVD. The degree of alignment and spatial density of SWCNTs are strong functions of applied substrate bias, with greater alignment and decreased density observed with increased bias. Raman spectra obtained at 533 nm and 785 nm reveal that the RBM peaks are shifted towards lower frequencies with applied bias, indicating a shift towards larger diameter SWCNTs. Raman spectra also indicate that metallic SWCNTs synthesized with an applied substrate bias of greater than -150 V are selectively removed, leaving mainly semiconducting SWCNTs. It is hypothesized that energetic hydrogen ions attracted by the negatively charged substrate may significantly etch SWCNTs and that SWCNTs carrying sufficient electrical current may be fully or partially destroyed when sufficient substrate bias is applied to the substrate. Synthesis of vertically aligned freestanding SWCNTs, as described herein, is a technique that may allow for more complex physical structures for device applications that employ carbon nanotubes.

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