

Synthesis of carbon nanotube peapods directly on Si substrates

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(Received 2 July 2004; accepted 10 November 2004; published online 5 January 2005)

Carbon nanotubes encapsulating fullerenes, peapods, have been synthesized directly on Si substrates. High-density and high-quality single-walled carbon nanotubes (SWNTs) were grown on a SiO₂/Si substrate by dip-coating of metal acetate solution and alcohol chemical vapor deposition technique. The caps of SWNTs were opened by annealing in dry air. Then, fullerene doping into the SWNTs was performed by vapor phase doping technique. Encapsulations of C₆₀ and Gd@C₈₂ were confirmed by transmission electron microscopy. Raman scattering spectroscopy was performed for synthesized peapods. From Raman scattering spectroscopy of synthesized peapods, the smallest diameters of the SWNTs capable of fullerene encapsulation were estimated to be 1.28 nm for C₆₀ and 1.43 nm for Gd@C₈₂. © 2005 American Institute of Physics. [DOI: 10.1063/1.1849835]

Single-walled carbon nanotubes (SWNTs) encapsulating fullerenes, so-called “peapods,”¹ are attracting materials for electronics applications because of the interesting electronic property. It has been predicted from the calculations using the local-density approximation that the band structure of a SWNT is modulated by encapsulating fullerenes.² Lee *et al.* have shown the local band gap modulation in Gd@C₈₂ peapod due to the existence of Gd@C₈₂ fullerenes by scanning tunneling spectroscopy.³ Recently, we have reported fabrication and characterization of field-effect transistors (FETs) of various types of peapods encapsulated with such fullerenes as C₆₀, C₉₀, and metallo-fullerenes as Gd@C₈₂, Dy@C₈₂, and so on.^{4,5} The devices showed ambipolar characteristics, and the gate voltage width of the off-state region of the transfer characteristics was varied with the kinds of encapsulated fullerenes. The results suggest that it is possible to control the energy gap by choosing the metallofullerenes because the off-state width of the gate voltage has close correlation with the band gap. These characteristics, so-called band gap engineering, is expected to open new horizons to the electronics device engineers.

In previous studies on peapod FETs, the devices were fabricated by dropping peapods on a SiO₂/Si substrate with electrodes. In this method, peapods were obtained as soot, dispersed in organic chemical solution, and then dropped on a SiO₂/Si substrate with electrodes. In this case, the yield of

peapod FETs was quite low. In order to characterize peapod FETs in detail and to apply them to nano-electronics, it is important to develop a reliable fabrication process, in which the peapods are synthesized directly on a substrate similar to SWNT FETs.^{6,7}

In this letter, we have synthesized C₆₀ peapods and Gd@C₈₂ peapods directly on SiO₂/Si substrates. The proposed procedure for the synthesis of peapods is as follows: (1) catalytic metal deposition on a SiO₂/Si substrate, (2) thermal chemical vapor deposition (CVD) of pod SWNTs, (3) cap opening of the pod SWNTs by annealing in dry air, and (4) doping of pea fullerenes in vapor phase. Transmission electron microscopy (TEM) and Raman scattering spectroscopy were performed to characterize the synthesized peapods.

In the present work, in order to obtain sufficient amount of peapods for characterizations such as TEM observation and Raman scattering, we employed the dip-coating method for catalytic metal deposition on the substrate and the alcohol catalytic CVD for the synthesis of pod SWNTs.⁸ A metal acetate solution was prepared by dissolving molybdenum acetate (CH₃COOH)₂Mo and cobalt acetate (CH₃COOH)₂Co·4H₂O into ethanol so that the concentration of each metallic species was 0.01 wt %. The mixture of ethanol and H₂ was used as the source gas for the CVD. The growth temperature, time, and total pressure in the CVD furnace were 800 °C, 10 min, and 20 Torr, respectively. The details have been described in Ref. 8.

Figure 1 shows the Raman scattering spectrum of synthesized SWNTs. A SEM image of the sample is also shown in the inset. High-density bundles of SWNTs were synthe-

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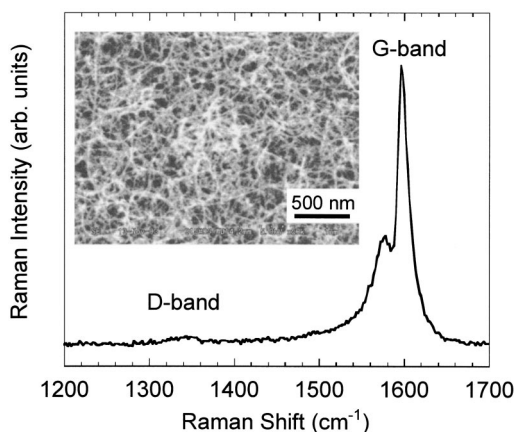


FIG. 1. Raman scattering spectrum and SEM image (inset) of SWNTs synthesized on SiO₂/Si substrate.

sized on the substrate. For the Raman measurement, the excitation wavelength was 515 nm of Ar⁺ laser. The scattered light was dispersed by a 1 m double monochromator and detected by a liquid-nitrogen-cooled charge-coupled device. The large *G* band/*D* band intensity ratio (*G*/*D* ratio) of the Raman scattering spectrum suggests that synthesized SWNTs are of high quality. The combination of the dip-coating of catalysts and the alcohol CVD yielded high-density and high-quality SWNTs on the SiO₂/Si substrate.

In the conventional method to synthesize peapods, the end caps of pod SWNTs were opened by the purification process using H₂O₂ reflux and subsequent HCl oxidation.^{4,9,10} In the present sample, these processes would remove SWNTs away from the substrates. Therefore, we have employed the method in which the cap opening was performed by annealing in a mixture of N₂/O₂(4/1) for 30 min. The caps of SWNTs have pentagonal rings which are easily oxidized compared with hexagonal rings of graphene sheet. Then, only caps of SWNTs would be eliminated without any damages in the nanotube wall. The condition of the cap opening was determined by Raman scattering spectroscopy measurement. The *G*-band intensity and *G*/*D* ratio, which are indices of the amount and the quality of SWNTs respectively, are summarized in Fig. 2 as a function of annealing temperature of the cap-opening process. The changes

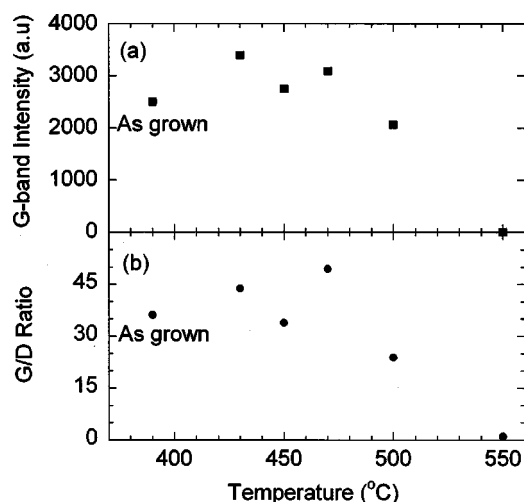


FIG. 2. (a) Intensity of *G* band and (b) intensity ratio of *G* band and *D* band of Raman scattering spectra as a function of anneal temperature.

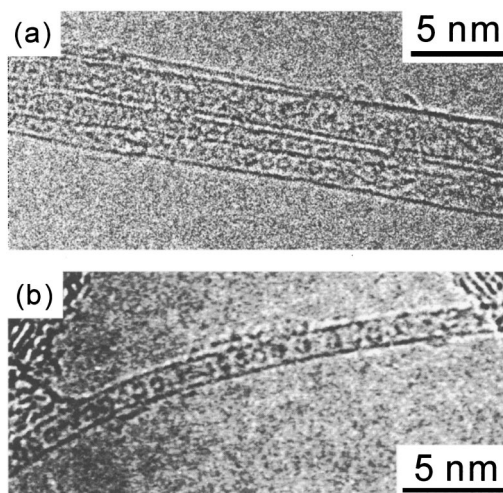


FIG. 3. TEM images of synthesized peapods, (a) C₆₀ peapods and (b) Gd@C₈₂ peapods.

in the *G*-band intensity and the *G*/*D* ratio were small after annealing at temperatures below 470 °C, whereas significant decrease in them was observed after annealing at temperatures above 500 °C. The annealing below 470 °C did not cause any detectable damages in the SWNTs. These results agree with that of thermo-gravimetric analysis.¹¹

The insertion of fullerenes into the cap-opened SWNTs was carried out by vapor phase method.^{9,10} The substrate with the SWNTs was put into a sealed glass ampoule with fullerenes, and then heated at 500 °C for 2 days. Figure 3 shows TEM images of synthesized (a) C₆₀ peapods and (b) Gd@C₈₂ peapods. In both samples, one-dimensional arrays of fullerenes were observed. The encapsulation of fullerenes into SWNTs was confirmed by TEM for the samples annealed at temperatures above 450 °C.

Raman scattering spectroscopy was performed for the peapods synthesized on a SiO₂/Si substrate. Here, the samples were mounted on a copper finger of a cryostat and cooled at 80 K in order to prevent polymerization of encapsulated fullerenes due to the laser irradiation.⁹ Figure 4 shows Raman spectra of radial breathing modes (RBM) for as-synthesized SWNTs, C₆₀ peapods, and Gd@C₈₂ peapods for two excitation wavelengths of 515 nm (lower curves) and

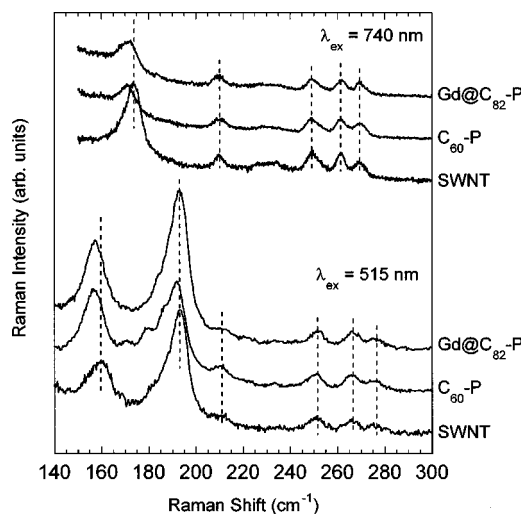


FIG. 4. Radial breathing mode of synthesized SWNTs, C₆₀ peapods, and Gd@C₈₂ peapods.

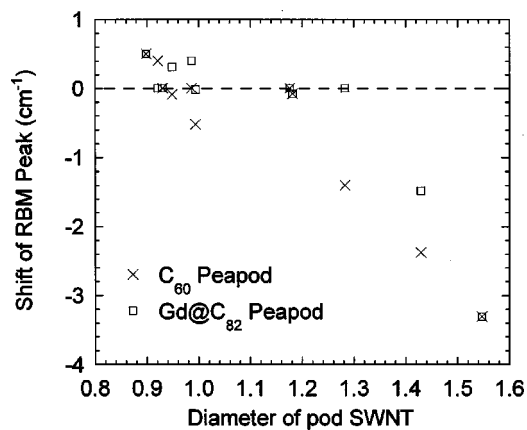


FIG. 5. Shift of RBM peaks caused by encapsulating fullerenes as a function of the diameter of pod SWNT.

740 nm (upper curves). The vertical dotted lines in the figure indicate the Raman frequencies of RBM peaks of as-synthesized SWNTs. Since the present CVD sample contains various SWNTs with different diameters, several RBM peaks were observed from 160 to 280 cm^{-1} . Some RBM peaks of C_{60} and Gd@C_{82} peapods shifted to lower frequency compared to those of SWNTs in the low frequency region, whereas the peaks in the high frequency region did not shift by the fullerene doping. The downshift of RBM peaks caused by encapsulation of fullerenes are thought to be caused by an increase in diameter of pod SWNT or a change of the intertube interaction.¹² Therefore, the observation of the downshift of RBM peaks suggests the encapsulation of fullerenes into the SWNTs. The high-frequency peaks which did not shift probably correspond to empty SWNTs because of the small diameter.

To show clearly the small shift of RBM peaks, the amount of shifts is plotted in Fig. 5 as a function of the diameter of as-synthesized SWNTs. Here, we assumed that the diameter of a SWNT (d) is given by the Raman frequency of the RBM (ω_{RBM}) as $d = 248/\omega_{\text{RBM}}$.¹³ The shift of RBM peaks was observed for the diameter larger than $d = 1.28$ nm for C_{60} peapods and $d = 1.43$ nm for Gd@C_{82} peapods. These values of d probably represent the smallest diameters of pod SWNTs for the fullerene encapsulation. The smallest diameters of pod SWNTs for the fullerene encapsulation were slightly larger than the diameter of pea fullerenes, 0.71 nm for C_{60} and 0.83 nm for Gd@C_{82} . According to the theoretical study on reaction energy for C_{60}

encapsulation by Okada *et al.*, the smallest diameter of the SWNT which is capable of encapsulating C_{60} is about 1.28 nm.² The present results agree with the theoretical prediction.

In summary, C_{60} and Gd@C_{82} peapods have been successfully synthesized directly on SiO_2/Si substrates. High-density and high-quality SWNTs were grown on a SiO_2/Si substrate by dip-coating of catalysts and alcohol catalytic CVD. The caps of SWNTs were opened by annealing in dry air at 450–470 °C without any detectable damages in Raman measurement. Fullerene doping into the SWNTs was performed by vapor phase doping technique. Encapsulations of C_{60} and Gd@C_{82} were confirmed using transmission electron microscopy. A downshift of the RBM peaks of Raman scattering spectra was caused by the fullerene doping. The smallest diameters of the SWNTs capable of fullerene encapsulation were estimated from the existence of the downshifts to be 1.28 nm for C_{60} and 1.43 nm for Gd@C_{82} .

This work was supported in part by the Special Coordination Funds of the Ministry of Education, Culture, Sports, Science, and Technology of the Japanese Government.

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