Available online at www.sciencedirect.com
SCIENCE DIRECT®
Chemical Physics Letters 412 (2005) 269–273
CHEMICAL PHYSICS LETTERS
www.elsevier.com/locate/cplett

Growth, nitrogen doping and characterization of isolated single-wall carbon nanotubes using liquid precursors

Gayatri Keskar [a], Rahul Rao [b], Jian Luo [a], Joan Hudson [c], Jia Chen [d], Apparao M. Rao [b,*]

[a] School of Materials Science and Engineering, Clemson University, Clemson, SC 29634, USA
[b] Department of Physics and Astronomy, Clemson University, 107 Kinard Laboratory of Physics, Clemson, SC 29634, USA
[c] Advanced Materials Research Laboratories, Clemson University, Clemson, SC 29634, USA
[d] IBM Research Division, T.J. Watson Research Center, Yorktown Heights, NY 10598, USA

Received 25 May 2005; in final form 29 June 2005
Available online 21 July 2005

Abstract

Isolated single wall carbon nanotubes (SWNTs) were prepared on bare quartz and SiO_2/Si substrates using a chemical vapor deposition process in which xylene was used as the carbon source. Controlled doping of isolated SWNTs with nitrogen was achieved by mixing appropriate amounts of acetonitrile with xylene. As the nitrogen concentration in the feed was increased from 0 to 33 at.%, the radial breathing mode intensity decreased dramatically while the intensity of the D-band increased gradually relative to that of the G-band. The D′-band at ~1620 cm^{-1} was observed in the Raman spectrum when the nitrogen concentration reached ~2–3 at.%.

1. Introduction

Single-walled carbon nanotubes (SWNTs) have been used as the 'building blocks' in the fabrication of room temperature field effect transistors [1–4], diodes [5] and inverters [6]. For developing nanotube-based complementary logic circuits, we need both p- as well as n-type carbon nanotube field effect transistors (CNTFETs). Current devices based on as-grown isolated SWNTs are invariably p-type in behavior and degassing them leads to n-type characteristics [7]. However, the p-type characteristics are recovered upon exposing the device to ambient conditions. Thus, CNTFETs that will exhibit permanently p- or n-characteristics are needed. Recently, we have shown that boron-doped SWNT bundles exhibit permanently p-type characteristics, which suggests that nitrogen-doped isolated SWNTs may lead to permanently n-type devices [8]. In this Letter, we report a simple liquid injection chemical vapor deposition (CVD) method for synthesizing nitrogen-doped isolated SWNTs. The nitrogen concentration in the nanotubes is varied by changing the concentration of acetonitrile in the feed, and micro-Raman spectroscopy is used to study the effect of doped nitrogen in the SWNTs.

Raman scattering is an excellent probe for investigating the electronic and phonon structure in pristine and doped SWNT materials due to the resonant coupling of the laser excitation energy to the transition energies between the van Hove singularities in the electronic density of states (DOS) [9]. There are three basic groups of Raman-active bands in SWNTs that reveal distinctive structural and electronic properties. The in-phase vibration of carbon atoms in the direction perpendicular to the nanotube axis, called the radial breathing mode (RBM), is usually observed between 100 and 300 cm^{-1}

* Corresponding author. Fax: +1 864 656 0805.
E-mail address: arao@clemson.edu (A.M. Rao).

0009-2614/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cplett.2005.07.007

in the Raman spectra. The diameter of individual SWNTs is inversely proportional to the RBM frequency [10]. The next important vibrational mode is the disorder-induced D-band which provides a measure of crystallinity in an individual nanotube. Finally, the tangential C–C bond stretching vibrations of SWNTs are found in the frequencies range between 1520 and 1600 cm^{-1}. Distinct line shapes for the tangential bands have been observed in semiconducting and metal nanotubes [11].

2. Experimental details

Pristine isolated SWNTs were synthesized by a liquid injection CVD process with xylene as the carbon source. Substrate preparation was similar to the procedure described in [12]. Briefly, about 1.5 mg of iron (III) nitrate non-ahydrate powder (Aldrich) was dissolved in 10 ml of 2-propanol. Then the substrates (quartz, SiO_2/Si) were dip-coated in this solution for 10 s followed by a quick rinse in *n*-hexane for 1 s. Finally, the substrates were dried in air at room temperature [12]. The catalyst coated substrates were inserted into the quartz tube reactor and xylene was introduced inside the reactor using a syringe pump at a flow rate of 1 ml/h for 2.5 h after the reactor had reached 750 °C. The xylene vapors are carried by the carrier gas (argon–hydrogen mixture: 600 sccm Ar, 400 sccm H_2) into the reactor. In a similar process, nitrogen-doped isolated SWNTs were prepared by co-injecting controlled amounts of acetonitrile (1–33 at.% nitrogen) with xylene. The as-grown pristine and nitrogen-doped isolated SWNTs were characterized by scanning electron microscopy (SEM, Hitachi, S-3500N), scanning transmission electron microscopy (STEM, Hitachi, HD-2000) and micro-Raman spectroscopy. The as-grown pristine and nitrogen-doped SWNTs on silicon substrates were excited by the 514.5 nm line from an Ar ion laser using the 50× objective of a Leica microscope. Back-scattered Raman spectra were collected by a ISA Triax 550 single grating spectrometer equipped with a liquid nitrogen cooled CCD detector. The laser power at the sample was kept below 5 mW to avoid excess sample heating. Lorentzian lineshape analysis was performed on the collected spectra and all spectra were normalized with respect to the G-band at $\sim$1592 cm^{-1} so that meaningful comparisons could be made between pristine and doped tubes.

3. Results and discussion

SEM images obtained from the as-grown pristine and nitrogen-doped SWNTs prepared on silicon substrates are shown in Fig. 1a,b, respectively. The coverage of the isolated nanotubes on the substrates was controlled by varying the amount of iron nitrate catalyst particles. As expected, when the catalyst containing solution was diluted in 30 ml isopropanol, the nanotube coverage on the substrate decreased drastically as compared to the coverage obtained with 10 ml isopropanol solution. The images reveal the presence of isolated SWNTs on the substrates which enabled us to measure their resonant Raman spectra. The scale bar in Fig. 1 should be used with caution since the residual charging effects make isolated SWNTs appear thicker than its true diameter. As discussed below, from the position of the radial breathing mode frequency (RBM), we estimate the tube diameters to be in the range from 1.33 to 1.75 nm.

The room temperature micro-Raman spectra of isolated pristine SWNTs are presented in Fig. 2a. A single peak corresponding to the radial breathing modes can be seen in the figure signifying the presence of pristine isolated SWNTs on the substrates. The RBM mode

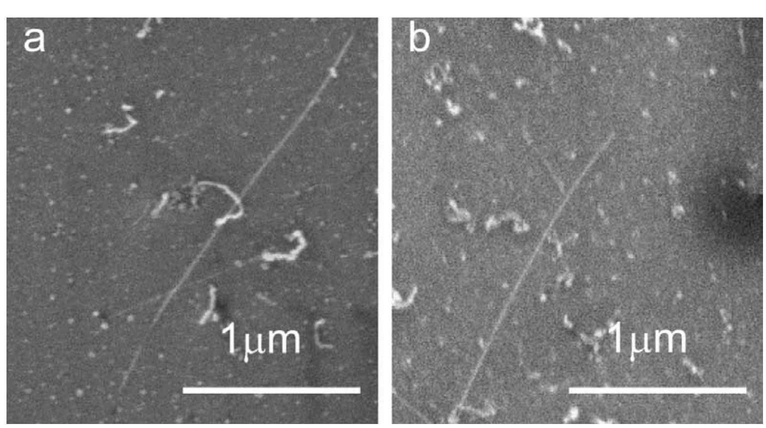

Fig. 1. SEM images of (a) pristine and (b) nitrogen-doped SWNTs prepared on the quartz substrates from a thermal CVD decomposition of xylene and xylene–acetonitrile in the presence of iron catalyst nanoparticles, respectively. Approximately, 1.5 mg of iron (III) nitrate non-ahydrate powder was dissolved in 30 ml of 2-propanol.