Raman Characterization of Nitrogen Doped Multiwalled Carbon Nanotubes

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ABSTRACT

N-type multi-walled nanotubes were synthesized by nitrogen doping using pyridine and pyridine-melamine mixtures in chemical vapor deposition, and their donor states were verified by Scanning Tunneling Spectroscopy. Tunneling Electron Microscopy reveals small amounts of residual catalyst and Scanning Electron Microscopy show well aligned mats of the Nitrogen doped nanotubes. Nitrogen is present in the lattice of these MWNTs as pyridine structures and CNₓ structures. Raman scattering measurements were performed as a function of increasing growth temperature and the results compared to previously studied boron doped multiwalled nanotubes.

INTRODUCTION

Doping of carbon nanotubes can greatly modify their electronic and optical properties paving the way to the creation of novel nanoscale devices. Nitrogen doping of carbon nanotubes (N-MWNTs) creates an electron donor state in the conduction band near the Fermi level.[1] Tailoring the electronic and optical properties by incorporation of dopants will lead to new applications in nano-electronics and photonics. Additionally, introducing defect states in the nanotubes by doping allows us to probe fundamental properties of carbon nanotubes. Previously, boron doping of multiwalled nanotubes (B-MWNTs) was used to investigate the defect induced double resonant process.[2] In this manuscript, Raman spectroscopy of the N-MWNT is used for experimental investigation of the doping level.

EXPERIMENTAL DETAILS

Multiwalled carbon nanotubes, both pure (MWNTs) and Nitrogen doped, were grown by chemical vapor deposition (CVD). For comparison, the doped tubes were grown as a function of temperature using melamine and pyridine as different nitrogen sources. Using a growth process similar to Andrews et al. [3] pristine nanotubes were formed. N-MWNTs grown from pyridine-melamine mixtures were synthesized by sublimating melamine (nitrogen source) in a preheater. Additionally, a mechanically injected solution of ferrocene (catalyst), xylene (carbon source) and pyridine (second nitrogen source and additional carbon source) was introduced into the furnace while using hydrogen as a scavenging and carrier gas. Pyridine N-MWNTs were grown with ferrocene as the catalyst and pyridine functioning as both the nitrogen and carbon source. Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM) were performed on a Hitachi HD2000 and a Hitachi 4700 respectively. Scanning Tunneling Microscopy (STM) and Spectroscopy (STS) were carried out in ultra high vacuum using a RHK low current STM with a Pt-Ir tip. The support substrate used was freshly cleaved highly
orientated pyrolitic graphite (HOPG) with the sample dispersed in tetrahydrofuran and drop cast onto the substrate. Raman spectroscopy was performed using J.Y. Horiba’s LabRam system with a 50X collection objective. All measurements were done at room temperature on “as produced” samples with an excitation of 632 nm at constant power and integration times.

DISCUSSION

Figure 1 a) is a typical TEM micrograph of the N-MWNTs grown at 750˚C showing very little catalyst after the growth process and an average diameter of approximately 20 nm. The previously identified “bamboo-like” structure is also evident in these N-MWNTs.[1] Shown in Figure 1 b) is the corresponding SEM micrograph revealing highly aligned mats of nanotubes with a length on the order of 30 µm.

Figure 1. a) TEM of N-MWNTs grown at 750˚C showing “bamboo-like” structures. b) SEM of corresponding N-MWNTs revealing highly aligned mats of N-MWNTs.

To verify nitrogen doping, STS of the N-MWNTs grown at 750˚C is shown in Figure 2. The local density of states (LDOS) was recorded using fixed gap spectroscopy and normalized to V/I
As with most MWNTs, a finite density of states exists at the Fermi level indicating a metallic tube. Nitrogen doping in MWNTs results in an electron donor state near the Fermi level in the conduction band evidenced by the feature at 0.18 eV. The donor state was verified for all growth temperatures in this study. To further confirm nitrogen doping in the lattice, electron energy loss spectroscopy (EELS) were performed (spectra not shown). The typical K-shell carbon feature was seen at 285 eV and the N-K edge at approximately 400 eV. The EELS investigation of the structure of the nitrogen edge, whether pyridine or CNₓ like, is ongoing.

![Graph showing LDOS of N-MWNTs grown at 750°C](image)

**Figure 2.** LDOS of N-MWNTs grown at 750°C showing the nitrogen electron donor state at 0.18 eV.

Significant progress has been made on the understanding of the Raman processes in carbon materials. The Raman spectra of carbon nanotubes result from a double-resonant process, where one resonance comes from the excitation energy matching an electronic transition and the second resonance from phonon or defect mediated scattering of the excited electron to a real state. Particular interest has been given to the excitation energy dependence of the D-band in graphite and carbon nanotubes. Thomsen and Reich [7] showed that the electronic dispersion leads to a double resonant condition in graphite. Maultzsch, Reich, and Thomsen [8] theoretically and experimentally demonstrated a shift of approximately 50 cm⁻¹/eV in the D-band of single-walled nanotubes and attributed this shift to a defect induced double resonant process. More recently in 2002, Maultzsch, Reich, and Thomsen. [9] determined that not only does the D-band originate from a defect induced double resonant process but also the high energy modes, namely the G-band.

Control of doping in carbon nanotubes has its obvious advantages as described in the literature, but also allows for systematic study of the origins of phonon modes in these materials.
In a previous study done by Maultzsch et al. [2] on the Raman characterization of B-MWNTs an increasing boron concentration was introduced into the lattice. The boron dopant behaved as a defect state and allowed for the study of the defect induced double resonant process. In the case for the B-MWNTs, both the D- and G-bands were enhanced with respect to the D*-band consistent with increasing boron concentration while the ratio of the D/G bands remained almost constant.[2] This showed that not only is the D-band a defect induced double resonant process but also the G-band. [9]

Figure 3 shows the Raman spectra of undoped MWNTs compared with N-MWNTs normalized to the D*-band at 2660 cm\(^{-1}\). Both the D- and G-bands of the N-MWNTs show an enhancement compared to the undoped MWNTs. Also seen in these spectra are overtone modes labeled by combinations of the peaks 1-3 at 1130, 1330 and 1581-1612 cm\(^{-1}\) respectively.

![Raman spectra comparing pure MWNTs with N-MWNTs normalized to the D*-band. A clear enhancement of the D- and G- bands is observed in the case of N-MWNTs.](image)

The Raman spectra of the normalized phonon modes of N-MWNTs grown from pyridine and pyridine and melamine as a function of growth temperatures are shown in Figure 4 a) and b) respectively. As seen here and with the B-MWNTs the ratio of the D/G-bands remains fairly constant of a function of growth temperature. This is expected since both phonon modes are influenced by defects in the samples. Of particular interest is the decreasing ratio of both D/D*...
and G/D* as a function of increasing growth temperature in both growth conditions indicating a
decrease in defects in the N-doped tube’s lattice with increasing temperature.

Figure 4. Normalized phonon modes of the N-MWNTs varied by growth temperature. a) N-
MWNTs grown with pyridine as the nitrogen source. b) N-MWNTs grown with pyridine and
melamine as the nitrogen sources.

CONCLUSIONS

N-MWNTs were grown by chemical vapor deposition as a function of growth
temperature with two sources of nitrogen; pyridine and pyridine + melamine. From STS,
nitrogen electron donor states were verified in the N-MWNTs for all combinations of growth
temperatures and nitrogen sources. Raman spectroscopy was performed as a function of growth
temperature on the N-MWNTs indicating a decrease in defects as the growth temperature was
increased. This may be due to less nitrogen (defect states) being substituted into the lattice as a
dopant. EELS and XPS measurements are in progress to confirm the dopant concentrations for
varying growth temperatures.

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