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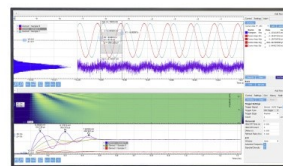
Fluorination of carbon nanotubes in CF_4 plasma

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The effect of CF_4 gaseous plasma exposure to single-wall carbon nanotubes (CNTs) has been studied. Raman spectroscopy results show that CNTs have gained more disordered sp^3 bonds associated with functionalization, as both the flow rates of gas in the plasma and exposure time in the plasma are increased. Scanning electron microscopy images indicate the CNTs have been preserved after CF_4 plasma exposure. X-ray photoelectron spectroscopy provides evidence of carbon to fluorine bonds (C–F) on the CNTs samples after CF_4 plasma exposure. Semi-ionic and covalent C–F bonds are prevalent on the CNTs after CF_4 exposure with the intensity ratio of the semi-ionic to covalent C–F bond decreasing as the flow rate of CF_4 and exposure time in the CF_4 plasma is increased. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1611621]

Since their discovery in 1991[1] great interest has been shown in carbon nanotubes (CNTs) both in the theoretical understanding and in practical applications,[2] due to the physical and electrical properties of the material.[3] The conduction properties of carbon nanotubes have been studied previously, as single conducting wires[4] and as more complex device structures such as field effect transistors.[5] An important step that will lead to more practical use of the naturally stable nanotubes is the process of functionalization. Functionalized nanotubes are chemically more reactive and can be employed for further processing such as thiolization[6] or for integration in nanocomposites.[7] Moreover, tuning of the electrical characteristics of nanotubes from metallic to semiconducting is possible depending on the degree and nature of functionalization.[8,9] However, functionalization of the CNTs is a complex step and has been carried out using a number of different techniques.[10–16] Recently, a glow discharge has been used to attach hydrogen to the sidewalls of carbon nanotubes.[17,18] Plasma processing is known to modify surfaces at an atomic scale.[19] For example, various types of C–F bonding have been found on silicon carbide surfaces after exposure to fluorinated plasma.[20] In this work, we demonstrate the fluorination of single wall CNTs using CF_4 plasma. The advantages of CNT functionalization using plasma exposure are the short duration of time needed and the room temperature processing ability in comparison to previous methods, which often require long process times and high temperature treatment.

Single wall CNTs, from Carbon Nanotechnologies Inc. were prepared by dispersion in isopropanol (IPA), at a concentration of 5 mg of CNTs to 15 ml of IPA, using a magnetic stirrer for 2 h at room temperature resulting in the formation of a thick black paste. The dispersion was then filtered through a 2 μm polytetrafluoroethylene (PTFE) filter membrane from Millipore under vacuum and left to dry for 24 h at room temperature, resulting in the formation of "bucky papers" on top of the PTFE membranes. Subsequently, the samples were exposed to CF_4 plasmas with 20

and 40 sccm flow rates for 30 s, 1, and 2 min in a Vacutech reactive ion etcher, with a chamber pressure of 0.15 Pa at 20 sccm and 0.196 Pa at 40 sccm. All samples were exposed to the plasmas with a dc bias of −300 V. The nonplasma-exposed sample is referred to as the control sample throughout the text. To characterize the effect of the plasma on the nanotubes, Raman spectroscopy, scanning electron microscopy (SEM), and x-ray photoelectron spectroscopy (XPS) have been used.

The Raman spectra of the control and CF_4 plasma exposed CNTs are shown in Fig. 1. The shape of the spectra remains unchanged after plasma treatment with the intensity of the lines being altered. Both the G line (at around 1580 cm^{-1}) corresponding to sp^2 bonded carbon, characteristic of the C–C bond in carbon nanotubes and the D line (at around 1375 cm^{-1}) corresponding to sp^3 bonding, relating to scattering defects in the CNT samples are evident in the spectra. Our Raman spectra are characteristic of CNTs when compared with the Raman spectra of amorphous carbon, glassy carbon, and carbon black[21] as well as other Raman studies of CNTs.[14,21]

The relative intensity ratios of the D–G bands shown in
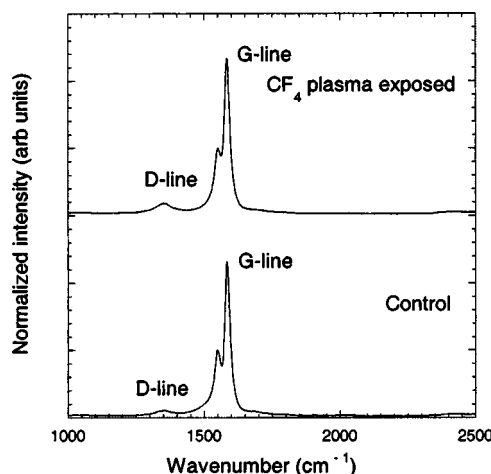

FIG. 1. Raman spectra of control and CF_4 plasma exposed single wall CNTs.

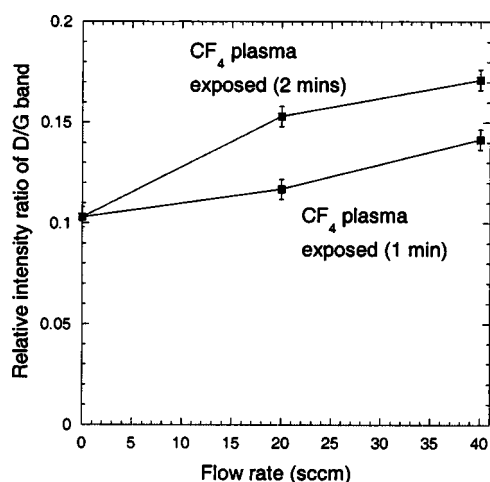[a)]Electronic mail: natalie.plank@ee.ed.ac.uk

FIG. 2. Relative intensity ratios of the $D-G$ bands of CF_4 plasma exposed CNTs as a function of flow rate of CF_4 in the plasma.

Fig. 2 give an indication of the degree of disorder in the carbon nanotubes. The weak D band at approximately 1300 cm^{-1} has previously been correlated to the extent of sidewall functionalization,[14] it is highly likely that the same effect occurs on our samples. The general trend is that as the flow rate of the gas increases, a larger degree of disorder, functionalization is observed. Moreover, exposing the carbon nanotubes to CF_4 plasma for 2 min results in a larger degree of disorder compared to exposure for 1 min. It should be noted here that the G band has stayed strong throughout indicating that a large proportion of ordered nanotubes remain. It is worth noting that the extreme treatments for fluorine or oxygen attachment in other works have often caused the significant broadening of the D and G peaks.[13–16] Additionally, energies up to 100 keV are reported to be necessary to damage nanotubes,[22] it is believed that at the typical energies involved in the plasma process ~ 300 eV, the nanotubes would not have been damaged although they may be slightly modified, as confirmed by the Raman study. Figure 3 shows the SEM images of the control and CF_4 plasma exposed bucky papers. Both surfaces look very similar suggesting that subtle changes have been introduced to the nanotubes after CF_4 plasma exposure.

XPS has been used as a means of detecting chemical species attached to the CNTs. Figure 4 shows the normalized F $1s$ spectra of the control and CF_4 plasma exposed tubes. The presence of fluorine on the bucky papers is detected only on the CF_4 plasma exposed tubes. The nature of the carbon to fluorine bonds (C–F) has been analyzed by deconvoluting the F $1s$ peak of the CF_4 plasma exposed CNTs with Gaussian peaks after subtraction of linear mode backgrounds. Both semi-ionic (685.5 eV) and covalent (687.5 eV) C–F bonds[20,23,24] have been clearly observed. There is also a third peak observed in the F $1s$ spectra of the CF_4 plasma exposed nanotubes at 689.2 eV, possibly due to the presence of $p-(CF_2=CF_2)$ bonds.[25] The occurrence of the fluorinated carbon bonds is believed to be due to the plasma chemistry.

The intensity ratios of semi-ionic and covalent C–F bonds ($I_{semi-ionic}/I_{covalent}$) from the CF_4 plasma exposed CNTs are shown in Table I. It is noticed that the presence of covalently bonded C–F increases as the CF_4 gas flow rate is increased during CF_4 plasma exposure and/or with increase
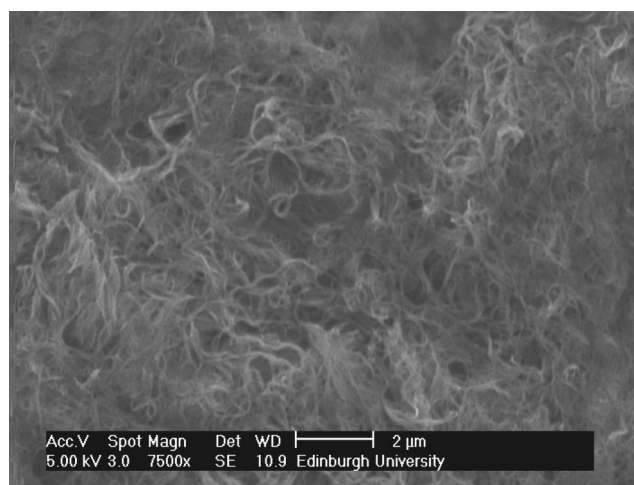
(a)
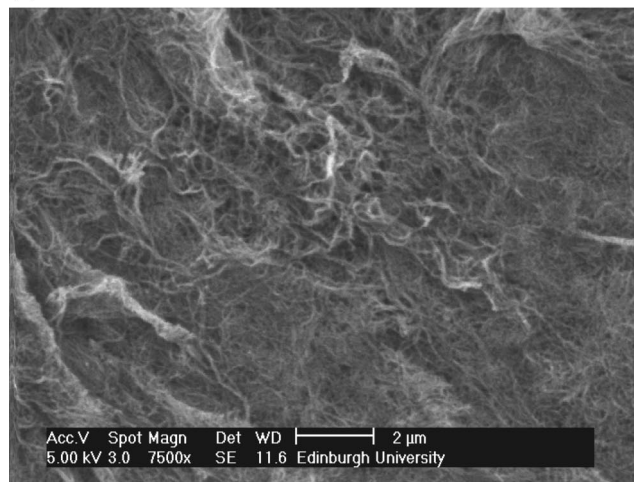
(b)

FIG. 3. Scanning electron micrographs for (a) control CNTs and (b) CNTs after CF_4 plasma exposure with 40 sccm flow rate for 1 min.

with exposure time. The smallest ratio is observed for the highest CF_4 flow rate and maximum exposure time under study. This observation is commensurate with the fact that covalently bonded C–F occurs when the localization of pi electrons of the C atoms increases strongly as a result of an increase in the F density, causing the F atoms to get closer to the C atoms.[15,23] It should be noted that the F $1s$ and C $1s$
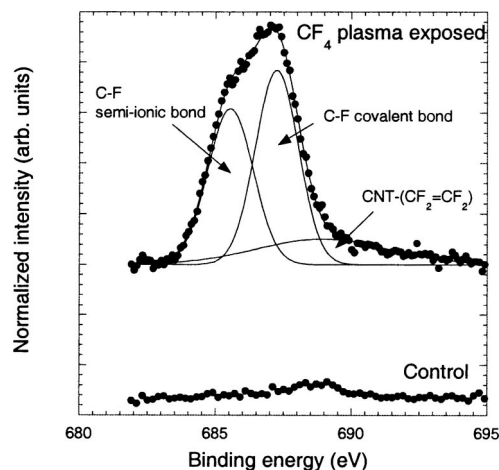

FIG. 4. X-ray photoelectron spectra of F $1s$ peak for control CNTs and CNTs after CF_4 plasma exposure with 40 sccm flow rate for 1 min.

TABLE I. $I_{semi-ionic}/I_{covalent}$ intensity ratio for C–F bonds, derived from the F $1s$ spectra as a function of CF_4 flow rate and plasma exposure time.

Flow rate	20 sccm	40 sccm
Time (min)		
1	0.888	0.848
2	0.810	0.639

peaks observed during this study are similar to those found during the fluorination of CNTs by An *et al.*[15] at low temperatures (150 °C) where the CNTs had a F/C ratio <0.5. The highest F/C ratio found in our CF_4 plasma exposed CNTs has been 0.22, which is less than the theoretical and experimental saturation stoichiometries of C_2F[13] or $CF_{0.5}$.[15] The low stoichiometry, coupled with the subtle Raman changes observed indicate the possibility that the F atoms are chemisorbed at the outer surface of the CNT wall.[15,23]

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