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Effects of CF_4 plasma on the field emission properties of aligned multi-wall carbon nanotube films

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Abstract

We present a simple method to functionalize the surface and to modify the structures of aligned multi-wall carbon nanotube (CNT) arrays grown on silicon substrates using CF_4 plasma produced by reactive ion etching (RIE). Field emission (FE) measurements showed that after 2 min of plasma treatment, the emission currents were enhanced compared with as-grown CNTs; however, extended treatment over 2 min was found to degrade the FE properties of the film. Scanning electron microscopy, transmission electron microscopy, X-ray photoelectron spectroscopy and Raman spectroscopy have been employed to investigate the mechanism behind the modified FE properties of the CNT film. The FE enhancement after 2 min of etching could be attributed to favorable surface morphologies, open-ended structures and a large number of defects in the aligned CNT films. On the other hand, deposition of an amorphous layer comprising carbon and fluorine during extended CF_4 plasma treatment may hamper the field emission of CNT films.

Keywords: A. Carbon nanotubes; B. Etching; D. Field emission

1. Introduction

In recent years carbon nanotubes (CNTs) have been of great interest to researchers due to their remarkable structural, electronic and mechanical properties [1]. They have also been identified as potentially useful materials for a broad range of useful devices, especially in the area of cold-cathode emission for flat panel displays [2]. Their excellent electron emission properties can be attributed to their high aspect ratio and high chemical stabilities [3]. Furthermore, the electron emission properties of carbon-based materials can be altered with chemical functionalization [4] or with plasma treatment [5]. On the other hand, using tetrafluoromethane (CF_4) plasma to fluorinate diamond films [6], amorphous carbon nanoparticle films [7] and single-wall carbon nanotubes [8] has also been recently studied, showing that the morphologies and field emission (FE) properties of carbon-based materials can be improved by CF_4 plasma [6,7]. Moreover, improved FE current of multi-wall CNTs (MWCNTs) after CF_4 plasma treatment during growth has been reported [9]. However, a systematic study of the fluorination of aligned MWCNTs is needed to investigate its effects on the FE properties. In this work, we exposed aligned MWCNT

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films to CF_4 plasma from a reactive ion etching (RIE) system and studied the corresponding dependence of the FE properties of the films on the time of exposure.

2. Experimental methods

In this work, our samples consisted of aligned CNTs that were grown perpendicularly onto iron-coated silicon substrates. The details of growth have been reported elsewhere [10]. In brief, aligned multi-wall CNTs were grown on silicon substrates using plasma-enhanced chemical vapor deposition (PECVD) under a reactant gas flow (C_2H_2/H_2, 15 sccm/60 sccm) at around 750 °C, 1.2 Torr and a DC plasma of 100 W, and the iron nanoparticle catalyst was sputtered onto the substrate with radio frequency (RF) sputtering. As-grown CNT films were placed inside the chamber of a SAMCO RIE-10N Reactive Ion Etching Unit and pumped down to a base pressure of 4×10^{-6} Torr. CF_4 gas at about 30 sccm was utilized during the treatment. A RF glow discharge was used to generate the reactive CF_4 plasma. The samples were placed on a RF driven capacitatively coupled electrode. RF power was set at 20 W and reflected power was about 1 W. Work pressure was about 0.05 Torr in the chamber and temperature was kept at 20 °C.

Using as-grown and treated CNTs as the cathode, measurements of their FE properties were carried out by a diode-type structure in a vacuum chamber with a pressure of about 8×10^{-7} Torr. An indium tin oxide (ITO) glass covered with a layer of phosphor was employed as the anode. The distance between electrodes was kept at 260 μm by polymer films which were used as spacers. A Keithley 237 high voltage source measurement unit was used to apply a voltage and to measure emission current at the same time. All the measurements were performed at room temperature. Scanning electron microscopy (SEM, JEOL JSM-6400F; voltage and current are 5 kV and 10 μA, respectively), X-ray photoelectron spectroscopy (XPS, ESCA MK II; Al source, operating at a voltage of 15 kV a current of 20 μA), Micro Raman (Jobin Yvon T6400) and transmission electron microscopy (TEM, JEOL JEM-2010F; operating at 30 kV) with energy dispersive spectroscopy (EDS) were used to explore the differences in the surface morphologies, chemical components and microstructures of CNT films under various stages of CF_4 plasma treatment.

3. Results and discussion

Fig. 1(a) shows the typical current density versus applied voltage (J–V) curves of the same aligned CNT film before and after 2 min of CF_4 plasma treatment. We can see that after 2 min of plasma treatment, the emission current density of the sample under an applied voltage of 500 V was enhanced to about 1.6 mA/cm^2 from the original value of about 0.5 mA/cm^2. The inset in Fig. 1(a) shows that the corresponding Fowler–Nordheim (FN) plots have a feature of two different slopes, which are typical FE characteristics of CNT films [11] possibly caused by space charge effect [12], resonance tunneling of adsorbate states [13] and so on. Fig. 1(b) shows the field emission current density at an applied voltage of 500 V as a function of treatment time. We can see the increase in the current density with treatment time up to 2 min, followed by degradation after 4 min of CF_4 plasma treatment. Repeated experiments revealed that for the aligned CNT arrays with a uniform length of about 60 μm used in our experiments, the FE current mostly peaked after about 2 min of CF_4 plasma treatment, provided other parameters are kept unaltered during the RIE process. Generally speaking, enhancements of FE properties of CNTs after plasma treatment are attributed to open-ended edges [14,15] and a large number of defects [5]. In our experiments, SEM, TEM, XPS and Raman spectroscopy were used to investigate the changes in morphologies, chemical composition and microstructures of the CNTs as a result of exposure to CF_4 plasma.

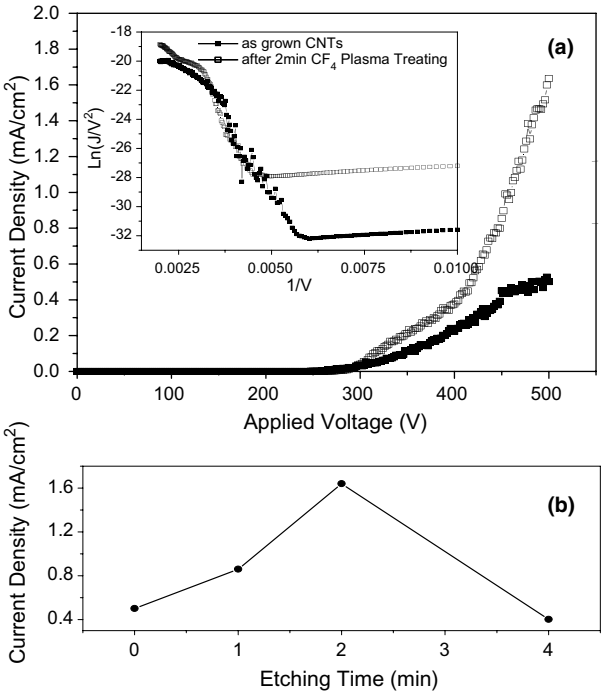

Fig. 1. (a) Field emission data of CNT film before and after 2 min of CF_4 plasma treatment. Inset is the corresponding Fowler–Nordheim plots. (b) Field emission current density dependence of aligned multi-wall CNTs on CF_4 treatment time under an applied voltage of 500 V.

First of all, changes in surface morphologies of CNTs have been carefully examined by SEM. Fig. 2 shows the typical top view SEM images of aligned CNT films be-

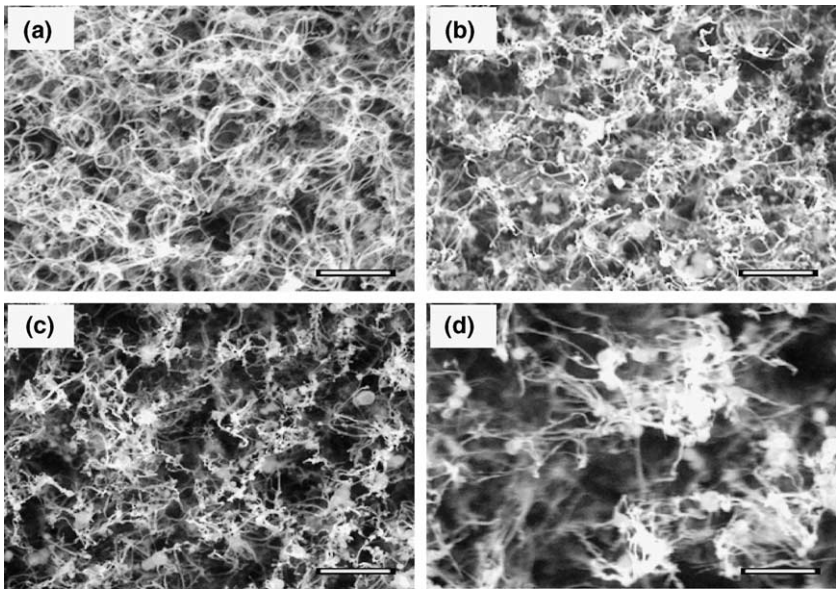

Fig. 2. Top view SEM images of CNT films of (a) as grown and after (b) 1 min, (c) 2 min and (d) 4 min CF_4 plasma treatment. Scale bars: 1 μm.

fore and after CF_4 plasma treatment. From Fig. 2(a) it can be seen that the typical diameter of as-grown CNTs is about 20–40 nm and CNTs are randomly distributed on the surface. Fig. 2(b)–(d) show that after CF_4 plasma treatments, the originally random CNTs on the surface tend to cluster together to form bundles, which become larger with increasing CF_4 treatment time. At the same time, many particles were found to attach on the side walls of CNTs (Fig. 2(b)–(d)) or appear on the top as joints of CNT bundles (Fig. 2(c) and (d)). To further clarify what happened during sequential exposure to CF_4 plasma, the morphologies of a specific region near the tips on the same sample were monitored by cross-sectional SEM imaging. The results are shown in Fig. 3, from which, we can see that:

(i) With CF_4 treatment, the surface density of aligned CNTs becomes reduced due to the formation of CNT bundles, which helps to reduce screening effects between adjacent emission sites leading to larger emission currents [16].

(ii) Original winding CNTs on the surface tend to straighten. It should be noted that after 1 min of CF_4 treatment, there are already some signs of CNTs being shortened; after 2 min of CF_4 treatment, the average length of the CNTs shortened by about 1 μm, and it becomes further shortened by another 0.8 μm with another 2 min of plasma treatment. Moreover, after 1 min and 2 min of treatment, the CNT diameters appear to be slightly reduced (Fig. 3(b) and (c), respectively). On the other hand, the diameters of 4 min treated CNTs are obviously larger (Fig. 3(d)), even when compared with as-grown samples. Since the previous study shows that the tips of aligned CNTs are more reactive and more easily removed by plasma [17], it is possible that plasma etching occurs on the tips and the cylindrical walls of the CNTs near the tips when treatment time is less than 2 min; after that, plasma deposition becomes more significant. Such a deposition process could lower the etching rate and make CNTs thicker.

(iii) From the beginning of CF_4 plasma treatment, it is observed that a few particles were found to attach to the cylindrical body of CNTs (Fig. 3(b)). TEM and EDS with the electron beam solely focused onto the bare particles (not shown) demonstrate that the average diameter of the particles is about 25 nm and their chemical composition comprises mainly of Fe and C. It is believed that this is derived from Fe particles shed from inside the CNTs. Thus, in the subsequent treatment, more particles would come out from CNTs and attach on the cylindrical walls (Fig. 3(c)). On the other hand, because of the deposition process, the previously shed particles would be covered, resulting in an increase in size, up to several hundred nanometers (Fig. 3(d)). With longer treatment, the deposition process would dominate and form a thick layer on the top of CNTs (Figs. 3(d) and 2(d)), which could result in the degradation of FE current.

Fig. 4(a) shows a TEM image of an as-grown multi-wall CNT, from which we can see the Fe particle enclosed within the graphite layers. After 10 min of CF_4 plasma treatment, the structures of CNTs are shown in Fig. 4(b) and (c). From Fig. 4(b) it can be seen that the end has been opened by plasma treatment and the Fe particle is not observed. This is very similar with that in CNTs treated by other plasma [14,15,17,18] or oxidization processes [19]. The open-ended structure is

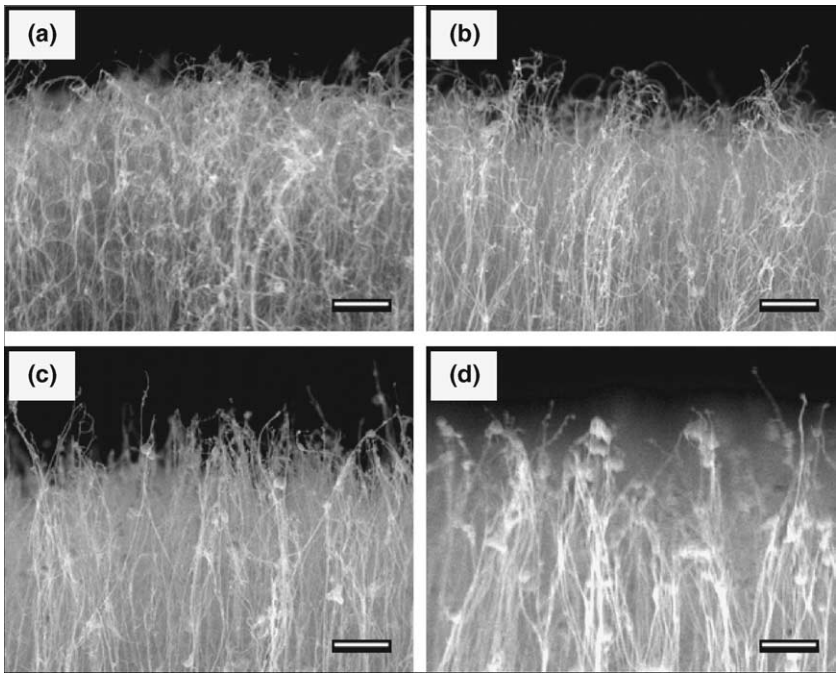

Fig. 3. Side view SEM images of tip regions for (a) as grown, (b) 1 min treated, (c) 2 min treated, (d) 4 min treated CNTs. Scale bars: 1 μm.

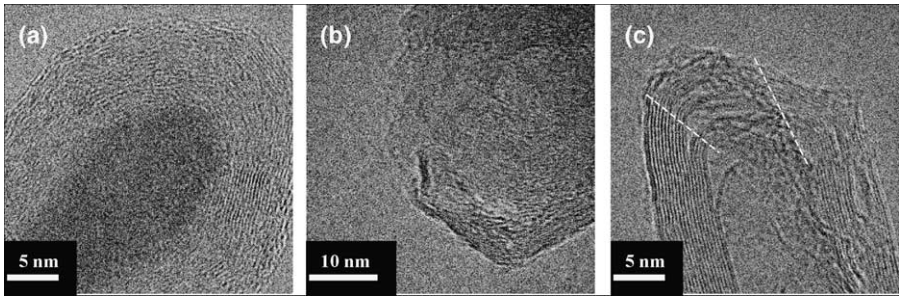

Fig. 4. (a) Typical TEM image of one end of an as-grown multi-wall CNT, (b) and (c) TEM images of ends of CNTs after 10 min of CF_4 plasma treatment.

regarded as one of the possible factors for the observed enhancement in the FE of CNTs [14,15,18]. Fig. 4(c) demonstrates a more typical TEM image of the CNTs after 10 min of CF_4 plasma treatment, in which the tip end shows an amorphous structure and the amorphous-crystalline interfaces are observable, as shown by dashed lines. Such structures could be caused by filling of the open end due to the deposition process mentioned above.

XPS was carried out to investigate the chemical states on the surface of the CNT films. XPS spectra obtained from our samples are shown in Fig. 5(a), which highlights the C 1s and F 1s peaks. Since for AlK_α X-ray source used in the measurements, the escape depth of photoelectrons is about 4 nm [20], these spectra reflect the chemical properties on a scale of several nanometers into the surface. From Fig. 5(a) we can see that after CF_4 plasma treatment, the intensity of the C 1s peak reduces significantly and two other peaks near 288.7 eV and 291.2 eV are observed in the C 1s spectra; at the same time a strong F 1s peak appears near 688 eV from original noise spectra of as-grown CNTs. All these demonstrate that fluorine has chemically bonded into CNTs. In previous reports, the peaks at 288.7 eV and 291.2 eV in the C 1s spectra were attributed to C–F and C–F_2 binding, respectively [7], and in the F 1s spectra, the semi-ionic fluorine peaks at 687 eV and covalent fluorine peak at 689 eV were observed [7,8]. However, it is difficult to unambiguously and uniquely identify the bonds in the C 1s and F 1s spectra as the peaks are relatively broad and the sample has mixed amorphous and crystalline phases [21]. Nevertheless, from the XPS spectra in Fig. 5(a), the fluorine to carbon ratios (F/C) are plotted as a function of plasma treatment time and presented as Fig. 5(b). It can be seen that the F/C ratios are almost about the same for both 1 min and 2 min treatments,

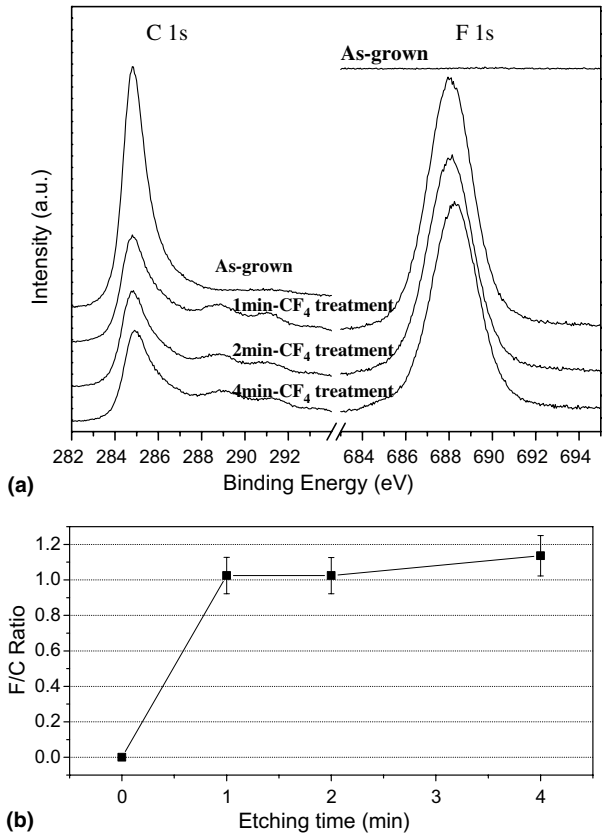

Fig. 5. (a) XPS spectra of C 1s and F 1s peaks for as-grown CNTs and CNTs after 1 min, 2 min, 4 min of CF_4 plasma treatment, (b) dependence of fluorine/carbon ratio on CF_4 plasma treatment time, from XPS measurements.

which suggests that here the CF_4 plasma only destroys the tip structures or some side walls exposed on the surface; thus, fluorine could only exit in some defects or saturates plasma-induced dangling carbon bonds. However, in the next 2 min of treatment, the deposition process helps to form a layer of fluorocarbon materials, which causes the ratio to increase again. Although the increase at 4 min of treatment is not so significant, the deposited layer is probably the cause of the degradation of FE current density of the CNT films (Fig. 1(b)).

Finally, we used micro Raman scattering to explore the microstructure changes induced by CF_4 plasma treatment. Fig. 6 shows the dependence of the ratio of D-band to G-band intensity (I_D/I_G) and the line width of D-band on the treatment time. We can see that with treatment both values increase except for a minimum at 2 min of treatment. Previous studies show that in multi-wall CNTs, the D-band indicates disordered or amorphous carbon, while the G-band corresponds to graphite or ordered carbon [22]. In addition, the line width of D-band is related to the amount of amorphous carbon [23]. Previous work [17,24] reported more disorder or amorphous carbon in the top-layer of CNTs compared with CNTs underneath. Thus, after 2 min etching, not

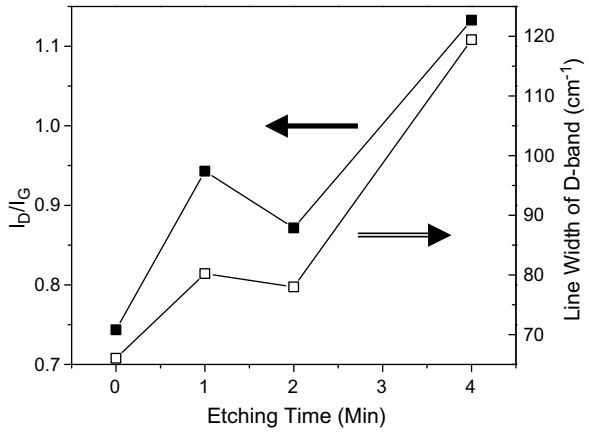

Fig. 6. CF_4 plasma treatment time dependence of the ratio of D-band to G-band intensity (I_D/I_G) and line width of D-band.

only are tip structures opened but some disordered top layers could be removed so that more ordered CNTs contribute to the Raman signal, resulting in the decrease of I_D/I_G and D-band line width. Furthermore, for aligned multi-wall CNTs whose top layer is trimmed by laser, a similar reduction of I_D/I_G has been observed [24]. After 4 min of CF_4 plasma treatment, the formation of an amorphous layer on the top (seen in SEM, TEM and XPS results) results in a Raman signal characteristic of increased disorder.

4. Concluding remarks

We have demonstrated a simple technique that allows the functionalization of multi-wall carbon nanotubes in a fast and controlled manner. Two minutes of CF_4 plasma modified CNTs were found to give higher field emission currents compared with the unmodified samples. SEM studies reveal changes in surface morphology and the clustering of nanotubes exposed to the CF_4 plasma. TEM images show the opening of the nanotube caps. Raman spectra of CF_4 plasma treated CNTs show an increase in defect density. Such increase in the number of defects and optimized surface morphologies are believed to play a significant role in the improvement in the field emission properties observed. Furthermore, XPS data reveals fluorination in the CF_4 treated CNTs. This work demonstrates a simple process for improving the FE properties of CNT FE display devices, and provides an insight into the changes to the physical and chemical properties of CNTs during plasma processing.

Acknowledgments

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