Available online at www.sciencedirect.com
SCIENCE DIRECT®
Carbon 43 (2005) 2530–2535
CARBON
www.elsevier.com/locate/carbon

Field emission properties of N_2 and Ar plasma-treated multi-wall carbon nanotubes

A. Gohel [a], K.C. Chin [b], Y.W. Zhu [a], C.H. Sow [a,b], A.T.S. Wee [a,b,*]

[a] Department of Physics, National University of Singapore, 2 Science Drive 3, Singapore 117542, Singapore
[b] NUS Nanoscience and Nanotechnology Initiative, 2 Science Drive 3, Singapore 117542, Singapore

Received 8 November 2004; accepted 6 May 2005
Available online 24 June 2005

Abstract

We modify multi-wall carbon nanotubes (MWCNTs) by plasma treatment with N_2 and Ar for varying durations and measure their field emission characteristics. The N_2 treated MWCNTs showed significant improvement in field emission properties, while the Ar treated MWCNTs displayed poorer field emission characteristics compared to untreated MWCNTs. X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), Raman spectroscopy and work function measurements are used to investigate the field emission mechanisms after plasma treatments.

Keywords: Carbon nanotubes; Plasma treatment; X-ray photoelectron spectroscopy; Scanning electron microscopy; Raman spectroscopy

1. Introduction

With conventional cathode ray tubes gradually being replaced by flat panel displays [1], there is an intense interest in electron field emitters. This can be attributed to the recent development of cheap and robust field emitting materials, and carbon nanotubes in particular have received much attention. Field emission is the process whereby electrons are emitted under high field conditions from the surface of a solid by tunnelling through the surface potential barrier. Early into its discovery, the potential of carbon nanotubes as excellent field emitters was evident as the early papers reported extremely low-turn on fields and high current densities in 1995 [2,3]. Moreover, with the development of the catalytic chemical vapor deposition method, the controlled deposition of carbon nanotubes can take place via catalyst patterning. The breakthrough for this technology came in 1998 when a crude display using nanotubes as emitters was first announced [4]. In this paper, we report the enhanced field emission characteristics of carbon nanotubes by nitrogen plasma treatment.

2. Experiment

Random multi-walled carbon nanotubes (MWCNTs) were grown on Fe coated Si substrates by hot filament plasma-enhanced chemical vapor deposition (PECVD) using acetylene (C_2H_2) and hydrogen (H_2) as inlet gases [5]. To synthesize random nanotubes, the process temperature was set at 630 °C and the deposition time limited to 3 min. We subsequently exposed the MWCNT film to 10 min of N_2 plasma treatment in a Denton radio frequency magnetron sputtering machine set at 100 W power and 2 mTorr pressure. After treatment, we measured the field emission characteristics before treating

* Corresponding author. Address: Department of Physics, National University of Singapore, 2 Science Drive 3, Singapore 117542, Singapore. Tel.: +65 68746362; fax: +65 67776126.
E-mail address: phyweets@nus.edu.sg (A.T.S. Wee).

0008-6223/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbon.2005.05.003

the same set of samples for a further 10 min. The samples were labelled CNT-N10min and CNT-N20min, respectively.

The anode to cathode distance in the field emission system is fixed at 150 μm, which is the thickness of the micro-glass spacer used to isolate the cathode from the anode. The height of the random MWCNT is negligible compared to the thickness of the spacer. The role of the cathode is performed by the MWCNT film on the Fe/Si substrate, while the anode is a commercially available ITO glass slide. The applied voltage during the field emission measurement is swept to a maximum of 450 V (3 V/μm), and increased in 5 V steps at 1 s intervals. The field emission measurements were repeated. We also measured the field emission characteristics of pure MWCNTs as control, as well as MWCNTs after 10 and 20 min of Ar plasma treatment (referred to as CNT-Ar10min and CNT-Ar20min, respectively) at pressure 10^{-7} Torr.

3. Results and discussion

The plasma-treated MWCNTs were imaged using a JEOL JSM 6700F field emission scanning electron microscope (SEM). Fig. 1 shows a series of SEM images of the as-grown MWCNTs as well as the MWCNTs after 10 and 20 min N_2 and Ar plasma treatments, respectively. We observe that the plasma treatment process causes morphological changes to the random MWCNTs. In general, the nanotubes become increasingly shorter with increasing process time. The nanotube density decreases and the random MWCNTs bundle together to form arrays of vertically aligned nanotube bundles, consistent with a recent report [6]. Each bundle consists of several nanotubes that are joined at their tips. Several large particles cap the top of each bundle, which can be identified as the bright particles in the SEM images. These particles have been identified as iron catalyst particles using transmission electron microscope

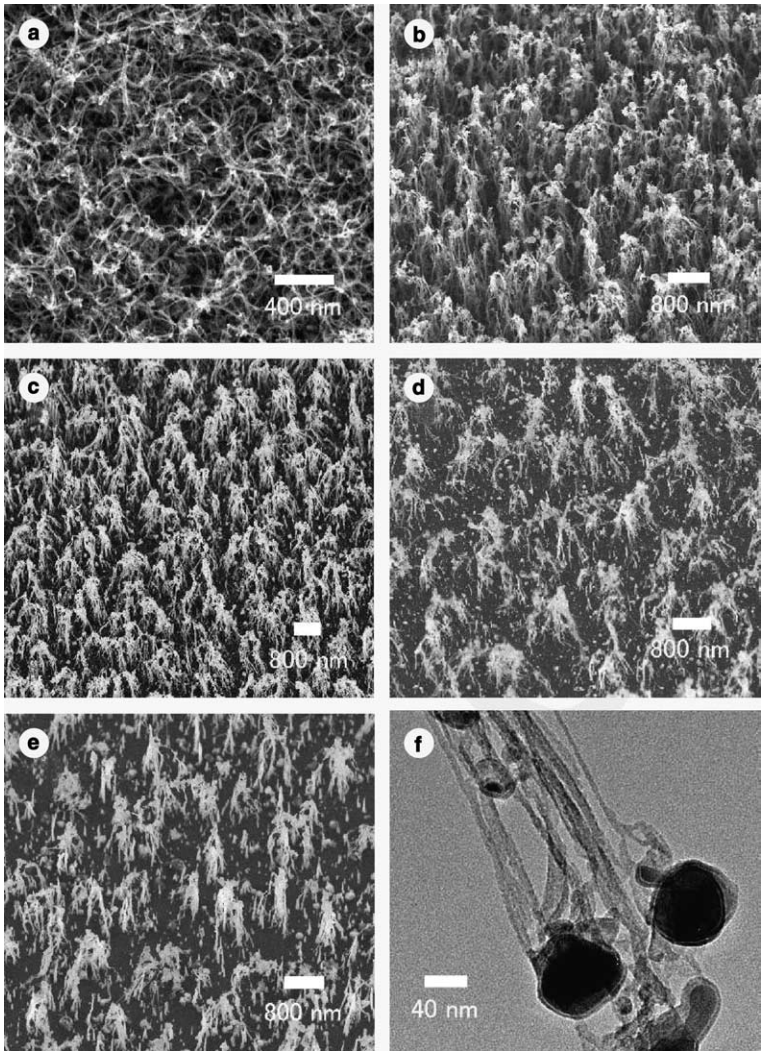

Fig. 1. SEM images of (a) as-grown random MWCNTs; (b) MWCNTs after 10 min N_2 etching (CNT-N10min); (c) MWCNTs after 20 min N_2 etching (CNT-N20min); (d) MWCNTs after 10 min Ar etching (CNT-Ar10min); (e) MWCNTs after 20 min Ar etching (CNT-Ar20min) and (f) TEM image of CNT-Ar10min.

(TEM) with EDX capability. It is clear that the rate of etching is greater for Ar than N_2 as the MWCNTs treated with Ar plasma has lower density and are shorter in length compared to that treated with N_2 after equivalent treatment times.

Fig. 2a shows the results of the field emission measurements made on pure MWCNTs, CNT-N10min, CNT-N20min, CNT-Ar10min and CNT-Ar20min to the maximum applied voltage of 450 V. Fig. 2b shows the Fowler–Nordheim plot for the field emissions of pure MWCNT, CNT-N10min and CNT-N20min. Both N_2 treated MWCNTs samples show improved field emission compared to the unmodified MWCNTs, with CNT-N20min showing the best characteristics. CNT-N20min displays the lowest turn-on voltage (1.73 V/μm) and highest emission currents (450 μA/cm^2) at 450 V applied voltage. On the other hand, both CNT-Ar10min and CNT-Ar20min show poorer field emission characteristics compared to the untreated MWCNTs. In fact, both Ar treated MWCNTs show only negligible field emission currents at 450 V.

The enhancement of field emission after N_2 treatment is attributed to both physical and chemical changes that occur during the etching process. In terms of physical changes, the N_2 plasma causes the nanotube density to decrease and the nanotube length to be shortened. There have been several reports that show that the density and orientation of the nanotubes affect the emission characteristics [7,8]. A high-density film shows poorer emission quality compared to one that has medium density due to screening effects. Electrostatic calculations have shown that the field amplification factor optimizes once the intertube distance is twice the height of the carbon nanotubes and drops rapidly with decreasing distances [4]. However, the nanotubes cannot be too far apart as well since the number density of emitters decrease with increasing intertube distance. If there are too few emitters then the nanotube film becomes an ineffective cathode. Following this argument, field emission can be enhanced by properly reducing the surface density of the nanotubes. This partially explains why CNT-N20min shows better emission than CNT-N10min since the density and length of CNT-N20min are both less than for CNT-N10min.

However, the optimal surface morphology is not the only reason for the enhanced field emission since the Ar plasma-treated MWCNTs gave poorer results. Thus, micro-structural effects due to plasma treatment were also studied by Raman spectroscopy. Fig. 3 shows the Raman spectra for the five samples under study. In this study, we utilized a Renishaw Raman Scope 2000 System with an attached Olympus microscope. The excitation source used was the 514 nm line of an argon-ion laser. The G peak (1593 cm^{-1}) indicates crystalline

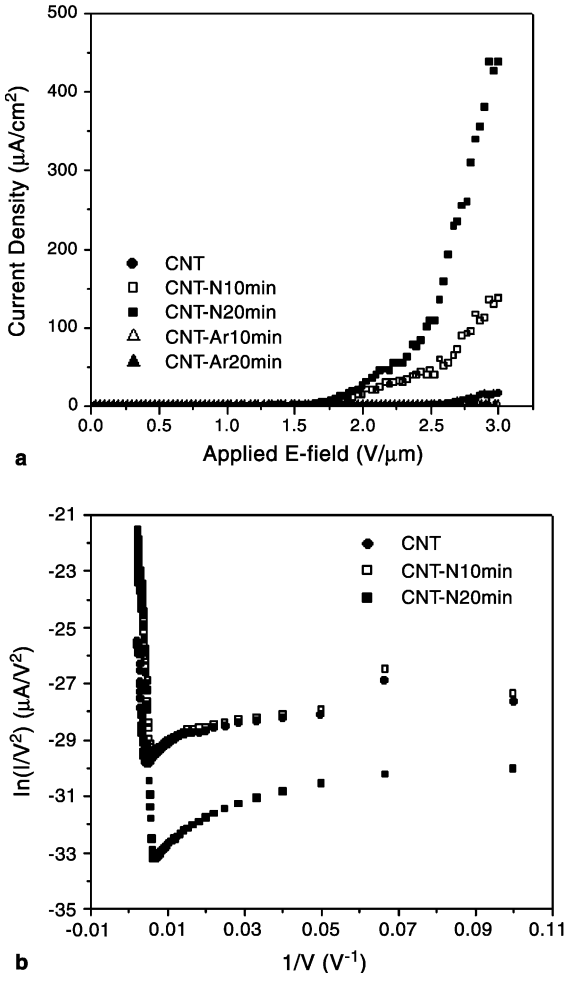

Fig. 2. (a) Field emission of random MWCNTs, CNT-N10min, CNT-N20min, CNT-Ar10min and CNT-Ar20min. CNT-N20min shows the best field emission properties. (b) F–N plots of field emission of MWCNT, CNT-N10min and CNT-N20min.

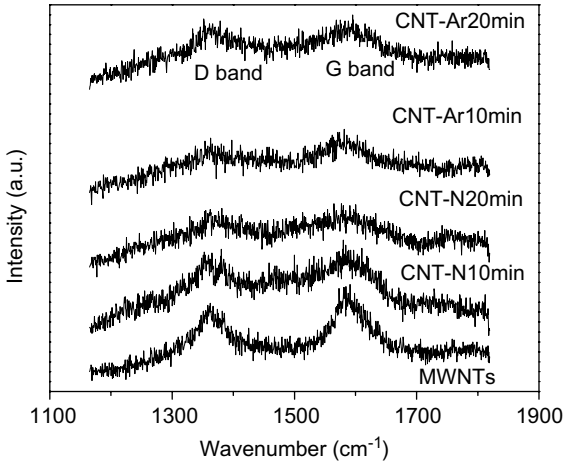

Fig. 3. Raman spectra for MWCNTs, CNT-N10min, CNT-N20min, CNT-Ar10min and CNT-Ar20min.

graphite while the D band (1368 cm^{-1}) is associated with disordered carbon [9]. Hence, an increase in the ratio of the intensity of the D peak (I_D) to the intensity of the G peak (I_G) indicates an increase in the density of structural defects. Moreover, the ratio is related to the size of disordered graphite clusters during the amorphization process of MWCNTs induced by ion bombardment during plasma treatment [10]. Table 1 shows the I_D/I_G values for all five samples. Obviously, after the treatment with chemically inert Ar plasma, the I_D/I_G values increase, indicating the higher concentration of disordered graphite clusters. Since the graphite clustering suggests a shorter correlation length [11], the electron scattering by such disorder would increase, resulting in reduced conductivity and field emission properties, even though screening effects are reduced. Previous reports also show that excessive exposure to Ar plasma results in the degradation of nanotube field emission [11]. In contrast, the N_2 plasma treatment

Table 1
Relative intensities of the D and G bands from Raman spectroscopy

Sample	I_D/counts	I_G/counts	I_D/I_G
MWCNT	139	158	0.880
CNT-N10min	190	203	0.936
CNT-N20min	235	239	0.983
CNT-Ar10min	291	292	0.996
CNT-Ar20min	346	345	1.002

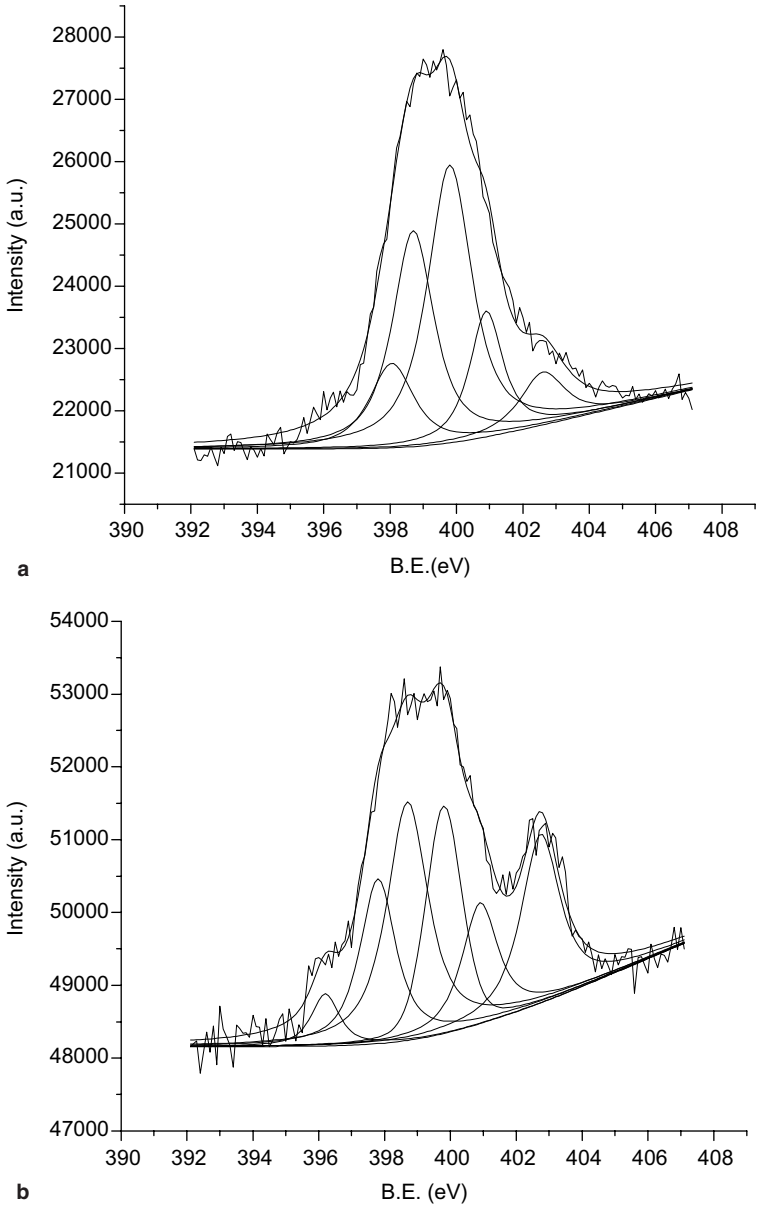

Fig. 4. XPS N 1s spectrum for (a) CNT-N10min and (b) CNT-N20min.

would have more complicated effects on MWCNTs since plasma treatment not only induces structural defects [12] but creates chemical doping sites, which will be discussed in the following XPS study.

The XPS measurements of CNT-N10min and CNT-N20min are shown in Fig. 4a and b, respectively. The experiments were performed at the soft X-ray beamline at the Singapore Synchrotron Light Source (SSLS). The energy of the incident X-rays used is 700 eV. The N 1s spectra of both samples can be fitted with component peaks at 398.2, 398.6, 399.7 and 400.8 eV, which correspond to C—N, C≡N (sp^3 bonding), C=N (sp^2 bonding) and NO [13]. There is also a high binding energy peak at 402.5 eV in both spectra, which we attribute to interstitial N. This peak has been observed in previous reports of nitrogenated carbon but not identified [14]. The XPS spectrum for CNT-N20min has an additional low binding energy peak that corresponds to nitrided Fe at 396.1 eV. From the XPS spectra, we observe that nitrogen has been doped into the MWCNTs during the N_2 plasma treatment process. It is believed that nitrogen doping can effectively improve the field emission properties of carbon nanotubes and diamond films [15,16] which is also consistent with our field emission measurements.

Using the same synchrotron beamline, we performed photoelectron spectroscopy (PES) measurements with 0.02 eV step-size to investigate the work function Φ of MWCNTs, CNT-N10min, CNT-N20min and CNT-Ar10min. The photon energy used is 45.12 eV. A thin gold reference film deposited on a Si(100) wafer was used to calibrate the Fermi level, which is clearly evident in a pure metal PES spectrum. Since all samples were in electrical contact, their Fermi levels would be aligned. The work function of MWCNT and CNT-N10min were measured to be 4.20 ± 0.02 and 4.14 ± 0.02 eV, respectively. The work function of CNT-N20min, however, was measured to be slightly higher than MWCNT, which is unexpected. A possible explanation could be that the PES measurement also picked up signals from the Fe particles at the tips of the nanotube bundles and the exposed Fe/Si substrate. Signal from the treated MWCNTs is correspondingly reduced as the density of the MWCNTs decreased. The work function of CNT-Ar10min was 4.20 ± 0.02 eV, which is the same value as for MWCNT, indicating that there is no chemical change in the MWCNT after Ar plasma treatment.

4. Conclusion

We have successfully demonstrated that nitrogen plasma treatment can be an effective process for enhancing the field emission characteristics of carbon nanotubes. Using N_2 plasma, we observe lower turn-on fields of up to 1 V/μm and increase in emission current density by almost 30 times compared to untreated MWCNTs. This is attributed not only to the shortening of the nanotube length and reduction in nanotube density, but also to nitrogen doping in the treated MWCNTs. The reduction of work function by nitrogen doping contributes to better field emission properties. However, the same improvement is not observed when using Ar plasma under the same conditions. This is due to the much higher etching rate of Ar compared to N_2, which resulted in more defects being formed.

Acknowledgments

The authors thank Dr. Gao Xingyu for his assistance in the use of the synchrotron radiation facilities, Mr. Chen Gin Seng for his assistance in the PECVD work and Mr. Ho Kok Wen of the Surface Science Laboratory, Department of Physics for his support in the SEM operation.

References

[1] Talin AA, Dean KA, Jaskie JE. Field emission displays: a critical review. Solid-State Electron 2001;45:963–76.
[2] Chernozatonskii LA, Gulyeav YV, Kosakovskaya ZY, Sinitsyn NI, Torgashov GV, Zakharchenko YF, et al. Electron field emission from nanofilament carbon films. Chem Phys Lett 1995;233:63–8.
[3] De Heer WA, Chatelain A, Ugarte D. A carbon nanotube field-emission source. Science 1995;270:1179–80.
[4] Bonard J-M, Kind H, Stockli T, Nilsson L-O. Field emission from carbon nanotubes: the first five years. Solid-State Electron 2001;45:893–914.
[5] Chin KC, Gohel A, Elim HI, Ji W, Chong GL, Lim KY, et al. Optical limiting properties of amorphous Si_xN_y and SiC coated carbon nanotubes. Chem Phys Lett 2004;383:72–5.
[6] Liu Y, Liu L, Liu P, Sheng L, Fan S. Plasma etching carbon nanotube arrays and field emission properties. Diamond Relat Mat 2004;13:1609–13.
[7] de Pablo PJ, Howell S, Crittenden S, Walsh B, Graugnard E, Reifenberger R. Correlating the location of structural defects with electrical failure of multiwalled carbon nanotubes. Appl Phys Lett 1999;75:3941–3.
[8] Davydov DN, Sattari PA, AlMawlawi D, Osika A, Haslett L, Moskovits M. Field emitters based on porous aluminium oxide templates. J Appl Phys 1999;86(7):3983–7.
[9] Yu K, Zhu Z, Xu M, Li Q, Lu W. Electron field emission from soluble carbon nanotube films treated by hydrogen plasma. Chem Phys Lett 2003;373:109–14.
[10] Ferrari AC, Robertson J. Interpretation of Raman spectra of disordered and amorphous carbon. Phys Rev B 2000;61:14095–107.
[11] Kyung SA, June SK, Chae OK, Jin PH. Non-reactive rf treatment of multiwall carbon nanotube with inert argon plasma for enhanced field emission. Carbon 2003;41:2481–5.
[12] Zhu SB, Sun SX, Zhou WW, Xu JJ, Li Y. The preparation of nitrogen-doped carbon nanotubes from pyridine. Acta Phys-Chim Sinica 2004;20:1320–3.

[13] Bhattacharyya S, Cardinaud C, Turban G. Spectroscopic determination of the structure of amorphous nitrogenated carbon films. J Appl Phys 1998;83(8):4491–500.

[14] Laskarakis A, Logothetidis S, Charitidis C, Gioti M, Panayiotatos Y, Handrea M, et al. A study on the bonding structure and mechanical properties of magnetron sputtered CN_x thin films. Diamond Relat Mat 2001;10:1179–84.

[15] Doytcheva M, Kaiser M, Verheijen MA, Reyes-Reyes M, Terrones M, de Jonge N. Electron emission from individual nitrogen-doped multi-walled carbon nanotubes. Chem Phys Lett 2004;396:126–30.

[16] Che RC, Peng LM, Wang MS. Electron side-emission from corrugated CN_x nanotubes. Appl Phys Lett 2004;85:4753–5.