Study of field emission of multiwalled C nanotubes synthesized by arc discharge

2007 J. Phys.: Condens. Matter 19 395014

(http://iopscience.iop.org/0953-8984/19/39/395014)

IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **19** (2007) 395014 (7pp) doi:10.1088/0953-8984/19/39/395014

Study of field emission of multiwalled C nanotubes synthesized by arc discharge

S Bellucci[1], **C Balasubramanian**[1,2], **F Micciulla**[1,3] **and A Tiberia**[1,3]

[1] INFN-Laboratori Nazionali di Frascati, Via E Fermi 40, 00044 Frascati, Italy
[2] Department of Environmental, Occupational and Social Medicine, University of Rome Tor Vergata, Via Montpellier 1, I-00133 Rome, Italy
[3] Department of Aeronautics and Astronautics Engineering, University of Rome 'La Sapienza', Via Eudossiana 18, 00184 Roma, Italy

Received 14 June 2007, in final form 22 June 2007
Published 30 August 2007
Online at stacks.iop.org/JPhysCM/19/395014

Abstract

Carbon nanotubes (CNTs) were synthesized by a DC thermal plasma method. After optimizing the synthesis parameters such as the pressure, current etc, the synthesized products, and the anodic deposit in particular, were characterized by scanning electron and transmission electron microscopy. The morphology of the product was ascertained to be multiwalled carbon nanotubes in a large ratio. The diameters of these nanotubes were of the order of 30–50 nm with lengths extending up to a micron and sometimes even 2 or 3 μm.

The field emission properties of these nanotubes were then studied. The CNTs were deposited on a metal stub which acted as the cathode. Care was taken to ensure complete coverage of the stub to remove any possibility of emission from the metallic stub itself. The emission studies were performed in a stainless steel chamber under a dynamic vacuum in the range of 10^{-8} Torr. The field emitted current was detected using a phosphorus coated indium tin oxide (ITO) glass. The phosphorus coating also helped in imaging the tips of the nanotubes. This was crucial in estimating accurately the emitting area and thus the field enhancement factor. The I–V curves for the field emission were recorded for various distances between the electrodes. The results are shown here.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Since their discovery in 1991 [1] carbon nanotubes have attracted increasing scientific and technological attention. This is basically due to their significant advantages over most existing materials [2]. One-dimensional nanostructures like nanotubes and nanowires are considered to be ideal field emission electron sources due to their nanosize, high aspect ratio, low extracting field, high current density and probable long operating time [3]. In fact, carbon nanotube based

electron field emitters are being proposed as the next generation cold cathode materials for a variety of vacuum electronic devices [4]. Carbon nanotubes of various shapes and sizes have been used as field emission sources in several different devices, including flat-panel displays. The current emitted by a nanotube depends on the field strength at its free end which is stronger than the applied macroscopic field [5]. It is important that the field emission source has a low turn-on voltage as well as a durable emission current [6]. In the recent past the field emission properties of various materials like diamond [7], Si [8], GaN [9], ZnO [10] and AlN [11] as well as carbon nanotubes have been studied. AIN nanotubes attracted a lot of attention also in connection with different properties and characterizations [12–15].

There are many reports on the field emission properties of carbon nanotubes, e.g. [16–20] including the above references. However, we are reporting here a quantitative study of the dependence of the turn-on field, as well as the emitted current density, on the distance between the CNT and the anode.

2. Experiment

Carbon nanotubes (CNTs) were synthesized by DC arc discharge between two graphite electrodes. A current of 120 A was applied under a DC voltage of ∼24 V. The base pressure of the chamber was typically 4×10^{-4} mbar. The operating pressure was increased to 700 mbar after filling the chamber with He gas. The arc was run for duration of ∼3 min and the chamber as well as the electrode holder was cooled by flowing water (for a comparison with carbon nanotube samples synthesized in previous work, see [21, 22]).

After allowing the chamber to cool, the cathode was removed from its holder and the deposit at the edge of the cathode consisting of nanotubes was used as the sample for analysis as well as field emission studies. These samples were analysed by scanning electron microscopy for study of the morphology.

The sample was then loaded into the field emission chamber and evacuated to a pressure typically in the range 6–7 $\times$ 10^{-8} Torr using a turbo pump with rotary pump backing. The field emission current was recorded for various applied voltages ranging from 0 V to 5 kV. An indium tin oxide (ITO) coated glass plate served as the anode/current collector. The coated glass plate has an intrinsic resistivity of 25 Ω cm.

Carbon nanotubes were studied for their field emission properties in two different modes. Namely, directly inserting the cathodic deposit of diameter 6 mm (of which the CNT covered an area of approximately 4 mm diameter) and length of 5 mm affixed on an aluminium stub which was loaded into the chamber. In the second mode a tungsten wire of diameter 0.2 mm, electrochemically etched to obtain a tip of approximately 10 μm radius, was coated with the CNT and used as the emitting source (cathode).

The distance between the electrodes (CNT cathode and ITO coated conducting glass plate anode) were varied in the millimetre range (typically from 0.5 to 2.0 mm) and the corresponding emission current recorded. Experiments were performed to check the variation of the turn-on voltage against various distances between the electrodes. The emitted current was measured with a Keithley 6485 picoammeter. The fluorescent image formed on the phosphorus coated ITO glass plate anode was captured.

3. Results and discussion

The SEM images, shown in figure 1, indicate that the CNT formed are quite dense with an average of >85% nanotubes (and the rest amorphous carbon). These nanotubes are found to have typical diameter of 30–50 nm and lengths varying between a few hundred nanometres

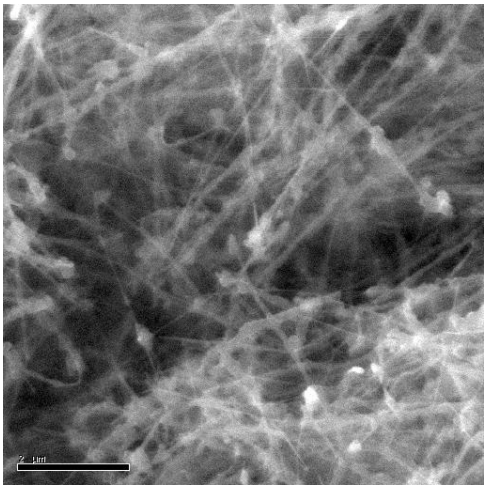

Figure 1. SEM image of the CNT synthesized by DC arc discharge; the scale bar corresponds to 2 μm.

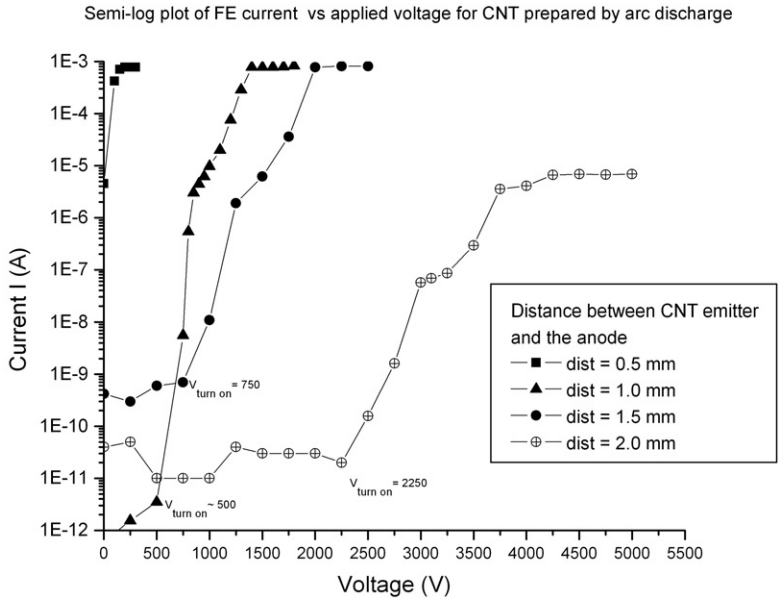

Figure 2. Semi-log plot of field emission current versus applied DC voltage for various electrode distances.

to even a few microns. These are in fact found to consist mostly of multiwalled nanotubes (MWNT) and some quantity of single-walled nanotube (SWNT) bundles.

For the directly loaded cathodic deposit the field emission current is seen to increase drastically (by more than six orders of magnitude) from a fraction of nanoamperes to milliamperes for applied voltages of up to a few kilovolts. As can be seen in the semi-log plot of figure 2, the turn-on voltage also varies as the distance between the electrodes is increased. The turn-on voltage for an electrode distance of 0.5 mm is just a few tens of volts and this value increases to 2250 V for a distance of 2 mm. The increase in the electrode distance raises the

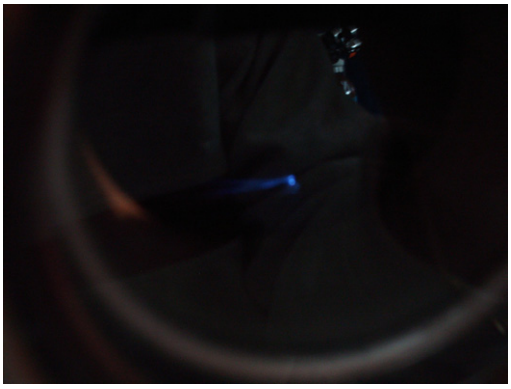

Figure 3. Fluorescent image of the field emission electrons on the phosphorus coated anode when the emitted current was ∼12 μA.

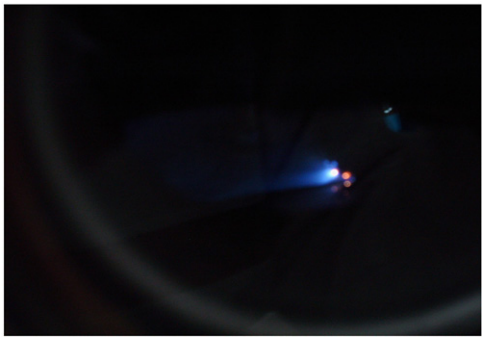

Figure 4. Fluorescent image for higher applied voltage; the emitted current was recorded to be ∼45 μA.

value of the turn-on field systematically. These results will help in estimating the ideal distances (for a specified electric field) of the CNT based field emitters for various applications.

The turn-on field was estimated to be 500 V mm^{-1} (for an applied electric field of 1350 V mm^{-1} and assuming an emitting surface of 4 mm diameter) and a typical current density of 6.4 mA cm^{-2} (under the same experimental conditions).

The phosphorescence glow of the anode due to the field emitted electrons is shown in figures 3 and 4. The emission glow threshold was observed to be in microamperes (the glow was seen for emitted currents of microamperes or more). Above the glow threshold it was noticed to be in pulses for lower applied voltages, indicating possible charging and discharging of the nanotubes. This could be due to the nanotubes being semiconducting.

Also, when the applied voltage was increased to higher values (and the emitted current increased to tens of microamperes) the emission glow was continuous. The image in figure 3 was captured at an emitted current of ∼12 μA and the glow at this juncture occurred in pulses. The image in figure 4 was obtained when the emitted current was >40 μA and the glow was continuous.

The sample was analysed by SEM again after the field emission experiment had been completed. Comparing the SEM images of figure 5 with figure 1, it can be seen that the density of the nanotubes remains the same both before and after the field emission studies, indicating

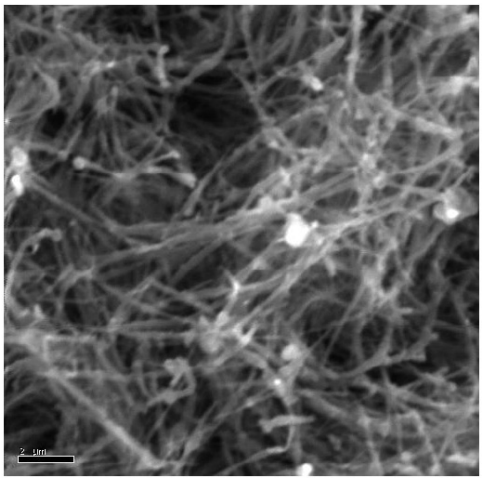

Figure 5. SEM image of the same sample (as in figure 1) after its use in the field emission studies; the scale bar corresponds to 2 μm.

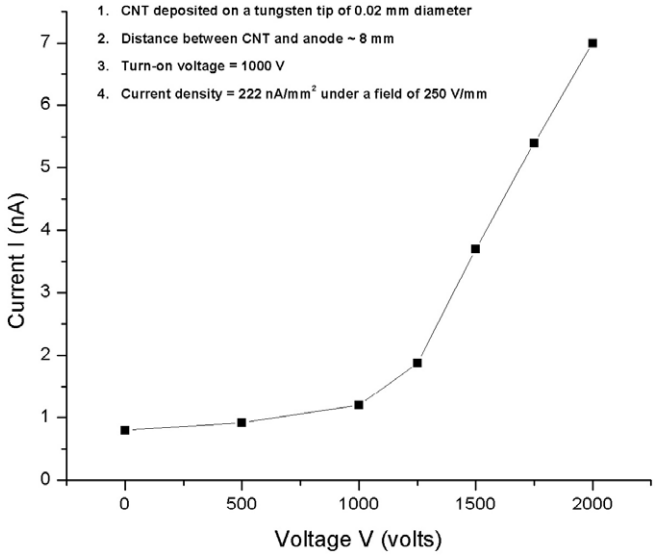

Figure 6. Plot of field emission current versus applied voltage from CNT deposited on a tungsten wire tip of diameter 0.02 mm.

that the nanotubes remain strongly attached to the graphite surface. However, a change in the dimensions of the nanotube was noticed. It was found that the diameter of the nanotube was much larger than it was before being used for the field emission experiment. It could be that single strands of the nanotubes become stuck together to form bundles of MWNT under the influence of the electric field.

Notice that the use of tungsten wire yields an advantage for the measurement, since an emission current can be observed even at large electrode distances (up to 1 cm) for a smaller applied voltage. This in turn helps us to obtain a large magnification of the image formed on the phosphorus coated glass plate.

Table 1. Results from recent publications on field emission from CNT.

Nanotube type	Turn on field/voltage	Max. current density	Inter electrode distance	Authors	Reference
Functionalized SWNT deposited on a patterned substrate by electrophoresis	∼850 V	10 mA cm^{-2} at 8 V μm^{-1}	0.15 mm	Oh *et al*	[4]
MWNT grown by thermal CVD (with Fe_2SO_4 or SS catalyst) on a carbon cloth	<0.5 V μm^{-1}	1 mA cm^{-2} at 0.4 V μm^{-1}	2.2 mm	Jo *et al*	[23]
20–30 nm dia. CNT made by microwave plasma CVD with Ni & Ti catalyst	12–9 V μm^{-1} (for 1 μA cm^{-2})	0.3–0.9 mA cm^{-2}	Data not available	Wong *et al*	[24]
MWCNT with catalyst made by thermal and PE CVD	1–10 V μm^{-1}	∼0.5 mA cm^{-2}	1 mm	Kayastha *et al*	[25]
Emission studies from bent single strand of MWNT	25 V (for 1 pA)	Few μA for anode voltage of 40–50 V	Data not available	Kim *et al*	[26]
Vertically aligned SWNT grown by CVD with Co catalyst	0.7 V μm^{-1} (for current density of 10 μA cm^{-2})	∼25 mA cm^{-2} (for a field of 5 V μm^{-1})	0.1 mm	Yeh *et al*	[27]
Arc deposited NTs treated by oxygen plasma for 120 min	0.8 V μm^{-1} (for current <10 μA cm^{-2})	1 mA cm^{-2} (for a field of 3 V μm^{-1})	80 μm	Wang *et al*	[28]
MWNT by arc deposition; no catalyst and no post synthesis treatment. Experiment done in 2 parts: direct cathodic deposit and second on a tungsten tip	(a) 1000 V for 8 mm (i.e. 0.125 V μm^{-1}) for W tip (b) cathodic deposit: 0.5 V μm^{-1} at a distance of 1 mm	(a) 2.22 mA cm^{-2} at 8 mm distance and 2000 V (b) 6.4 mA cm^{-2} at a distance of 1 mm and for a field 1.40 V μm^{-1}	Varying distance from 0.5 to 8 mm	Bellucci *et al*	Present work

The emission occurs even at an electrode distance of 8 mm (whereas in the previous case of CNT on an aluminium stub there was no emission at a distance beyond 2 mm for applied voltages of up to 4 kV). This is because the effective field is larger in a small wire as compared to the field from a large area cathodic deposit. The emitted current is low—a few nanoamperes (see figure 6). This is because the total number of nanotubes on the wire tip is much less than the number of nanotubes on the large surface of the cathodic deposit. However, this emitted current can be increased to some extent by increasing the applied voltage.

The current density was estimated to be 2.22 mA cm^{-2} under a field as low as 250 V mm^{-1}.

4. Conclusion

Multiwalled carbon nanotubes along with bundles of single-walled nanotubes were synthesized by DC arc discharge. These were found to be of a few microns in length with diameters of 30–50 nm. Field emission studies were performed on these samples both by directly introducing the large area cathodic deposit as well as a small area tungsten wire coated with the nanotubes. The emission studies gave a quantitative idea of the dependence of the emission current and the turn-on voltage as a function of CNT–current collector distance. The turn-on voltage increased from a few tens of volts at 0.5 mm electrode distance to 2250 V at 2.0 mm distance. It was also found that the nanotubes became bundled together under the influence of the electric field during the field emission experiment. The field emission from a carbon coated small area wire resulted in a lower turn-on voltage at larger distances of up to 8 mm.

Table 1 shows the results from recent publications on field emission from carbon nanotubes. It should be noted that field emission reported in the present paper stems from pristine (as-prepared) nanotubes without any post-synthesis treatment and with no catalyst, as compared to other works where catalysts and post-synthesis treatment were widely used. It has been shown here that large current density values, as well as low turn-on fields, are possible from nanotubes without any chemical treatment.

References

[1] Iijima S 1991 *Nature* **354** 56
[2] Tu J P, Jiang C X, Guo S Y and Fu M F 2004 *Mater. Lett.* **58** 1646
[3] Xinghui L, Changchun Z and Yukui Li 2004 *Physica* B **344** 243
[4] Oh S J, Zhang J, Cheng Y, Shimoda H and Zhou O 2004 *Appl. Phys. Lett.* **84** 3738
[5] Read F H and Bowring N J 2004 *Nucl. Instrum. Methods Phys. Res.* A **519** 305
[6] Tang Y B, Cong H T, Zhao Z G and Cheng H M 2005 *Appl. Phys. Lett.* **86** 153104
[7] Okano K, Koizumi S, Silva S R P and Amaratunga G A J 1996 *Nature* **381** 140
[8] Ng K L, Yuan J, Cheung J T and Cheah K W 2002 *Solid State Commun.* **123** 205
[9] Sugino T, Hori T, Kimura C and Yamamoto T 2001 *Appl. Phys. Lett.* **78** 3229
[10] Xu C X, Sun X W and Chen B J 2004 *Appl. Phys. Lett.* **84** 1540
[11] Tondare V N, Balasubramanian C, Shende S V, Joag D S, Godbole V P, Bhadbhade M and Bhoraskar S V 2002 *Appl. Phys. Lett.* **80** 4813
[12] Soldatov A *et al* 2007 *Nucl. Instrum. Methods Phys. Res.* A **575** 85
[13] Bellucci S *et al* 2006 *J. Neutron Res.* **14** 287–91
[14] Balasubramanian C *et al* 2006 *J. Phys.: Condens. Matter* **18** S2045
[15] Balasubramanian C *et al* 2004 *Chem. Phys. Lett.* **383** 188
[16] De Heer W A, Chatelain A and Ugarte D 1995 *Science* **270** 1179
[17] Kung S C, Hwang K C and Lin I N 2002 *Appl. Phys. Lett.* **80** 4819
[18] Bellucci S 2005 *Nucl. Instrum. Methods* B **234** 57
[19] Bellucci S 2005 *Atti XVII Congresso AIV* Ed Compositori, p 61, ISBN 88-7794-495-1
[20] Bellucci S *et al* 2006 *Nanotechnology* **3** 129–32
[21] Bellucci S 2005 *Phys. Status Solidi* c **2** 34
[22] Bellucci S 2004 *CANEUS 2004-Conf. on Micro-Nano-Technologies (Monterey, CA, Nov. 2004)* AIAA paper, 6752
[23] Jo S H *et al* 2005 *J. Vac. Sci. Technol.* B **23** 2363
[24] Wong Y M *et al* 2006 *J. Vac. Sci. Technol.* B **24** 1008
[25] Kayastha V K *et al* 2007 *Nanotechnology* **18** 035206
[26] Kim C D *et al* 2006 *Nanotechnology* **17** 5180
[27] Yeh C M *et al* 2006 *Nanotechnology* **17** 5930
[28] Wang Q H *et al* 1997 *Appl. Phys. Lett.* **70** 3308