Diamond & Related Materials 34 (2013) 1–8

Contents lists available at SciVerse ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Thermionic emission properties and the work function determination of arrays of conical carbon nanotubes

Andriy Sherehiy [a,c], Santoshrupa Dumpala [b], Abdelilah Safir [c], David Mudd [b], Ivan Arnold [a], Robert W. Cohn [c], Mahendra K. Sunkara [b,d], Gamini U. Sumanasekera [a,c,d,*]

[a] Department of Physics and Astronomy, University of Louisville, Louisville, KY, United States
[b] Department of Chemical Engineering, University of Louisville, Louisville, KY, United States
[c] Electro-Optics Research Institute & Nanotechnology Center, University of Louisville, Louisville, KY, United States
[d] Conn Center for Renewable Energy Research, University of Louisville, Louisville, KY, United States

ARTICLE INFO

Article history:
Received 25 October 2012
Received in revised form 19 December 2012
Accepted 4 January 2013
Available online 23 January 2013

Keywords:
Thermionic emission
Conical carbon nanotubes (CCNT)
Field penetration effect

ABSTRACT

Thermionic emission properties of conical carbon nanotubes (CCNTs) grown on platinum wires and planar graphite foils were investigated. The work function (Φ) values extracted from the thermionic emission data range from 4.1 to 4.7 eV. The range of Φ values is attributed to the morphological characteristics, such as tip radius, aspect ratio, density, and wall structure of CCNTs. The observed lower values for Φ are significantly smaller than that of multi-walled carbon nanotubes (MWNTs). The reduced Φ values are attributed to field penetration effect as a result of the local field enhancement from these structures having high aspect ratio and an excellent field enhancement factor. The high amplification of the external field at the apex of the nanostructures is capable of reducing both the barrier height and the width, in turn contributing to the improved emission current at lower temperatures. The ultraviolet photoemission spectroscopy data of CCNTs grown on Pt wires are in reasonable agreement with the thermionic emission data. The conical carbon nanotubes may be potential candidates for thermionic cathodes with superior performance over conventional cathodes.

1. Introduction

Their superior structural, mechanical, electrical, and thermal properties make carbon nanostructures suitable for many applications, including effective field emitters and thermionic emitters. Carbon nanotubes have especially been proven to be a promising material for field emission cathodes. Various configurations based on these materials have been shown to produce high current densities and low turn on voltages [1,2]. Carbon nanotubes are known to be mechanically, chemically and electrically robust. In contrast, metal oxides are not suitable for high current emission because they have too-high electrical resistivity and cause serious joule heating, which quickly damages the emitter when operating at high current density. It has been shown that poor vacuum conditions do not destroy carbon nanotube emitters, though it lowers their performance [3]. The geometrical properties, such as the small tip size and the high aspect ratio of carbon nanotubes, are believed to be responsible for the advantage of carbon nanotubes over other conventional materials. As a result, carbon nanotubes are considered to have great potential for field emission and thermionic emission applications.

More importantly, the fundamental parameter that governs the field emission and thermionic emission is the work function Φ, since the current density increases exponentially as the work functions decreases. There have been a wealth of results on experimental measurements and theoretical calculations of the work function of carbon nanotubes [4–20] (Table 1). The main advantages of the thermionic emission-based method of obtaining work function of CNT are the (i) accuracy of the measurement and (ii) elimination of the adsorbents [4]. It was shown by Peng Liu et al. that values obtained by thermionic emission method [4,5] are consistent with the theoretical prediction [17–19] and roughly agree with photoelectron emission (PEES) measurements (Table 1). Results of the study by Peng Liu et al. showed that values of the work function vary slightly from sample to sample, and there is no clear evidence of the dependence on the number of walls in the case of MWNT sidewalls. The value of work function for tips obtained from measurements was smaller than in the case of the sidewalls [5] of the CNT, which is in agreement with theoretical predictions [19]. It is clear that for sidewalls of the carbon nanotubes with a diameter larger than 1 nm, independent of the number of walls, the work functions lie in the range of 4.6 eV–5 eV.

Field emission properties of various carbon nanotubes, including single-walled carbon nanotubes (SWNTs), multi-walled carbon nanotubes (MWNTs) [1–3,20,21] and conical carbon nanotubes

* Corresponding author at: Department of Physics and Astronomy, University of Louisville, Louisville, KY, United States.
E-mail address: gusuma01@louisville.edu (G.U. Sumanasekera).

0925-9635/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.diamond.2013.01.007

Table 1
Values of CNT's work function obtained by different groups and using different techniques.

Method	Material		Work function, Φ [eV]	Reference
Thermionic emission	a) Sidewalls			
		SWNT	4.70–4.92	[4,5]
		DWNT	4.85–4.87	
		MWNT	4.80–4.91	
	b) Tips			
		MWNT	4.41	
		MWNT yarns	4.54–4.64	[5]
		CNT	4.2	[6]
		BaO/SrO coated CNT	2.1	
PEES		HOPG	4.80	[9,10]
		SWNT	~4.73–5.05	
		MWNT	4.95	
CPD[a]		SWNT	4.6–4.8	[11,12]
			4.7	

[a] Contact potential difference.

(CCNTs) [22–25] have been extensively studied. There has been limited work on the thermionic emission of carbon nanotubes [4,6,7] and carbon nanotube yarns [5].

Here we report thermionic emission properties of conical carbon nanotubes directly grown on platinum wires and graphite foils. Previously we reported enhanced field emission properties of such structures [24]. These structures consist of a central carbon nanotube surrounded by helical graphene sheets. The thermionic emission results were used to extract the work function values of CCNTs and further confirmed from ultra-violet emission spectroscopy.

2. Experimental

CCNT samples studied in this paper were grown by microwave plasma assisted chemical vapor deposition (MWCVD) on two different substrates: (i) platinum wire (Alfa Aesar, 300 μm diameter, 99.9% (metals basis)) [22–24] and (ii) graphite foil (Alfa Aesar, 130 μm thick, 99.8% (metals basis)) [25]. Total length of the Pt wire samples were ~3–4 cm and average area of deposition was 0.02 cm^2 (~2 mm section of Pt wire on one end). For graphite foils, average area of deposition was 0.5 cm^2 and total area of the sample ~1 cm^2. Samples grown on Pt wire are labeled 1, 2 and 3 while samples on graphite foil are labeled 4, 5 and 6 (Table 2). The experimental procedure of the growth has been described in detail elsewhere [22–25]. However, we changed the growth process for samples with CCNTs grown on graphite foil. The experimental procedure is still similar to that of previous work [25], except for the addition of a two-step process with a change in the gas phase composition to vary the structural characteristics of CCNTs. Step 1 consists of carbon deposition using 2.5 vol.% methane in 200 sccm of hydrogen followed by a deposition and etching with 2 vol.% methane in step 2. These changes include only samples with CCNTs grown on graphite foil.

Table 2
Characteristics of the CCNTs grown on graphite foil.

	CCNT sample	Length[a], l [μm]	Base diameter[a], D [μm]	Tip diameter[a] d [nm]	Aspect ratio, l/D
Pt wire	1–3	5–10	0.1–0.5	10–20	50–100
Graphite foil	4	15–30	2–4	30–50	10–30
	5	2–15	0.5–1	50–100	4–30
	6 (CCNT)	15–25	1–2.5	60–100	15–25
	("microhorns")	0.5–50	3–4	500–2000	1.7–10

[a] Length and diameter of CCNT are averaged values obtained from characterization of several different areas of each sample.

Thermionic emission and field emission measurements were performed on each sample in a vacuum chamber at a base pressure about 10^{-7} Torr. Two different arrangements of measurements were used for the CCNTs grown on (i) platinum wire and (ii) graphite foil (Fig. 2).

In the case of the platinum wire, the sample was placed in a V-groove of a molybdenum plate (Fig. 2(a)). A flat molybdenum anode was slowly moved toward the CCNTs by means of a micromanipulator. In the second case, conducting graphite foil with synthesized CCNTs was placed on a thin ceramic plate (Boron Nitride) supported on a Pyrolitic Boron Nitride (PBN) heater (Fig. 2(b)). A conducting molybdenum wire was attached mechanically to the graphite foil so that wire and foil act as the cathode. A molybdenum anode was arranged over the sample and attached to the micromanipulator (Fig. 2(b)). Zero distance ($d=0$) between cathode (sample) and anode was established by observing a sudden electrical short when the anode just touched the sample. Measurements were performed at a set distance (d) for different temperatures by sweeping the voltage U from 0 to 500 V while recording the current I using a pico-ammeter (Keithley 6487) equipped with a built-in variable voltage source. PBN heater was connected to a separate power supply. Temperatures were measured using an infrared pyrometer (Raytek MA2SCCF; Infrared; single color; Spectral response: 1.6 μm).

After loading the samples into the chamber and reaching desired pressure, field emission measurements were performed. I–U characteristics of the CCNTs were studied at room temperature for varying separations between the cold cathode and the anode. This was done in order to define conditions for which field enhanced thermionic emission will be the dominating mechanism of the electron emission to the vacuum and to obtain information about field emission properties of our samples. Separation distances between anode and cathode for thermionic emission measurements were typically 1000–2000 μm.

UPS measurements were performed using multi-chamber ultra-high vacuum (UHV) surface science facility (VG Scientific/RHK Technology) comprising of a 150 mm radius CLAM 4 hemispherical analyzer. CCNT arrays on platinum wire were studied using He-I (21.23 eV) and He-II (40.81 eV) UV excitations. A stable bias was provided to avoid the instrumental cutoff in the lens system of the analyzer at low kinetic energy (KE) for all the UPS spectra measurements. The external bias and the spectra were shifted back to zero-bias position through data post-processing. The calibration of the UPS spectrometer was performed by measuring and validating the absolute position of the Fermi level of a standard gold sample.

3. Results and discussion

As a result of the MWCVD growth, samples were obtained with an array of randomly scattered Conical Carbon Nanotubes (CCNTs) on the substrates. Fig. 1 shows the SEM images of the four CCNTs samples under investigation. There are visible variations in density, morphology, and aspect ratio. The insets show the enlarged view of the individual CCNT tip. The close-up view of sample 6 as shown in Fig. 1(e) shows the presence of "horn-like" structures with blunt tips along with CCNTs. The characteristics for the CCNT samples are summarized in Table 2.

CCNTs grown on platinum wire are usually smaller in size with aspect ratio higher than in the case of graphite foil. The density of the growth of the CCNTs for Pt wire is on average significantly larger ($10^7/cm^2$) in comparison with graphite foil samples: sample (4) — $10^4/cm^2$; sample (6) — $10^2/cm^2$ for both CCNTs and microhorns, respectively. However, these density values are rough estimates, as it is considered as an array of randomly grown CCNTs.

The thermionic Current–voltage characteristics measured at various temperatures are shown in Fig. 3a,b.

Field enhanced thermionic emission (FETE) was used to determine the work function value of the as-grown conical carbon nanotubes. FETE is also known in the literature as a Schottky effect, and dependence