

Available online at www.sciencedirect.com





C. R. Physique 4 (2003) 1021-1033

Carbon nanotubes: state of the art and applications/Les nanotubes de carbone : état de l'art et applications

Electron field emission from carbon nanotubes

Yuan Cheng, Otto Zhou*

Department of Physics and Astronomy and Curriculum in Applied and Materials Sciences, University of North Carolina, Chapel Hill, NC 27514, USA

Presented by Guy Laval

Abstract

Carbon nanotubes (CNT) have recently emerged as a promising class of electron field emitters. They have a low threshold electric field for emission and a high emission current density which make them attractive for technological applications. In this article we review recent progress on understanding of CNT field emitters and discuss issues related to applications of CNT-based cold cathodes in vacuum microelectronic devices. The emphasis is on the emission characteristics of macroscopic CNT cathodes and their relations with the underlying materials properties. *To cite this article: Y. Cheng, O. Zhou, C. R. Physique 4 (2003).*

© 2003 Published by Elsevier SAS on behalf of Académie des sciences.

Résumé

Emission sous champ des nanotubes de carbone. Les nanotubes de carbone se sont récemment avérés être d'excellents systèmes pour l'émission de champ. Leur bas seuil de champ électrique pour l'émission et leur forte densité de courant d'émission les rendent intéressants pour des applications technologiques. Dans cette revue, nous présentons les récents développements sur la compréhension des nanotubes de carbone en tant qu'émetteurs sous champ ainsi que les problèmes reliés à leur utilisation comme cathodes froides dans les composants microélectroniques sous vide. L'accent est mis sur les caractéristiques de l'émission de cathodes macroscopiques et leurs relations avec les propriétés des nanotubes de carbone sous-jacentes. *Pour citer cet article : Y. Cheng, O. Zhou, C. R. Physique 4 (2003)*.

© 2003 Published by Elsevier SAS on behalf of Académie des sciences.

Keywords: Carbon nanotubes; Electron field emission

Mots-clés : Nanotubes de carbone ; Emission sous champ

1. Introduction

Electron sources play an essential role in information display. They mostly use the thermionic emission mechanism, where electrons are emitted from heated filaments (hot cathodes) [1]. Field emission is an alternative mechanism to extract electrons. It is a quantum effect where under a sufficiently high external electric field, electrons near the Fermi level can tunnel through the energy barrier and escape to the vacuum level (Fig. 1) [2]. Compared to thermionic emission, this is a preferred mechanism for certain applications because no heating is required and the emission current is almost solely controlled by the external field.

The basic physics of field emission is well understood. The emission current from a metal surface is determined by the Fowler–Nordheim (F–N) equation: $I = aV^2 \exp(-b\phi^{3/2}/\beta V)$, where I, V, ϕ , β are the emission current, applied voltage, work function, and field enhancement factor, respectively. For metal, with typical work function and a flat surface the threshold field is typically around 10⁴ V/ µm which is impractically high. The work function is a basic material property that cannot be

* Corresponding author.

E-mail addresses: cheng@physics.unc.edu (Y. Cheng), zhou@physics.unc.edu (O. Zhou).

^{1631-0705/\$ –} see front matter $\,$ © 2003 Published by Elsevier SAS on behalf of Académie des sciences. doi:10.1016/S1631-0705(03)00103-8



Fig. 1. Potential-energy diagram illustrating the effect of an external electric field on the energy barrier for electrons at a metal surface.



Fig. 2. Schematic of a Spindt-type cathode array.

varied significantly. All the field emission sources rely on field enhancement due to sharp tips/protrusions, so they tend to have smaller virtual source sizes because of the primary role of the β factor. The larger the β , the higher the field concentration, and therefore the lower the effective threshold voltage for emission. The field of vacuum microelectronics was born with the fabrication of Spindt-type emitters by lithography [3]. As illustrated in Fig. 2, a Spindt-type emitter has cone geometry with a sub-micron apex radius. By placing the extraction electrode a few microns away from the emitter, electrons can be extracted at a very low operating voltage. In the last twenty years emission from nanostructured diamond has also been studied systematically [4]. The potential of utilizing electron field emitters as the cold electron sources in a variety of devices such as field emission display (FED) and microwave amplifier is being actively investigated in research laboratories worldwide. The Spindt type emitters, however, suffer from high manufacturing cost and limited lifetime. Failure is often caused by ion bombardment from the residual gas species that blunt the emitter cones. Diamond structures are unstable at high current densities [4]. These conventional cold field emission sources usually have comparatively poor current stability due to the variation of β and ϕ in the presence of strong adsorption at reduced temperatures.

A Carbon nanotube (CNT) is a new carbon allotrope that was discovered in 1991 [5]. Electron field emission from CNTs was first demonstrated in 1995 [6,7], and has since been studied extensively. CNTs have the right combination of properties: nanometer-size diameter, structural integrity, high electrical and thermal conductivity, and chemical stability [8], which makes them excellent electron emitters. In this article, we provide a brief review of the basic field emission characteristics of CNTs and their applications in vacuum electronics. It is based primarily on our own research at UNC Chapel Hill.

2. Electron field emission characteristics of CNTs

2.1. Single CNT emitter

Experiments carried out on individual nanotubes are valuable in providing a fundamental understanding of the emission mechanism. In the first report of electron emission from CNTs, Rinzler et al. studied field emission from an individual multiwalled nanotube (MWNT) attached to a graphite fiber along the field direction [6]. With a bias voltage of less than 80 volts,

1022

emission currents of 0.1 to 1 μ A were obtained at room temperature. They also reported that emission could be enhanced by opening the tips of the nanotubes. Electron holography experiment determining the magnitude and spatial distribution of the electric field surrounding individual emitting CNT showed that electrical field concentrates at the tips of the CNTs and not at defects such as sidewall imperfections [9], which is consistent with the experimental observation of emission from the CNT tips.

Field emission microscopy images from an atomically clean SWNT showed field emission patterns with a high degree of spatial symmetry [10]. Recently it was demonstrated that through repetitive field evaporation cycles, a variety of cap states can be produced on an individual SWNT. Changes in the electronic structure of the nanotube cap can bring significant differences in the field emission current and its temperature dependence [11]. Density-functional theory calculations showed that under emission conditions large electric field present at the tube tip could stabilize the adsorbates and lower the ionization potential, thereby making it easier to extract electrons [12].

The CNTs can emit very large electron current. Experiments from a single MWNT tip revealed that it is capable of emitting stably for more than 100 hours at $\sim 2 \mu A$ current [13]. Catastrophic failure of the CNT was not observed until the current reached 0.2 mA. Under the applied electric field, the CNTs can align along the field direction due to the electrostatic force [14, 15]. SWNTs generally have a smaller diameter and higher degree of structural perfection than MWNTs hence a capability for achieving higher current densities and a longer life time [16]. The current–voltage characteristics of an individual clean SWNT showed no sign of current limiting for an emission current reaching 2 μA , corresponding to a current density of 10^8 A/cm^2 [17]. However, current saturation around 100 nA was observed before removing the adsorbates. A theoretical study predicted that an open-ended SWNT has much better field-emission properties than a closed SWNT [18], due to the electronic effects that alter the bonding mode and decrease the work function. No experiments yet have been reported on the comparison of open and closed SWNTs.

2.2. Macroscopic CNT structures

Recent experiments have clearly shown that individual CNTs are excellent electron field emitters with a low turn-on field for emission and a high emission current density. These emission characteristics are directly related to the unique structure and chemical bonding of the CNTs. The situation however becomes complicated for macroscopic cathodes comprising ensembles of CNTs (Fig. 3). Understanding the relation between the structure of individual CNTs, their higher-level architecture and the macroscopic emission properties remains scientifically challenging and is important for technological applications. To design and fabricate cathodes with optimized performances, several important materials parameters need to be considered including: the type of CNTs, i.e., MWNTs versus SWNTs; the orientation, aspect ratio, and density of the CNTs; the interaction of the CNTs with the supporting surface; and the uniformity. Below we describe some experiments we have performed recently to understand the effects of these materials parameters on the emission properties of macroscopic CNT structures.

2.2.1. Structure of the carbon nanotubes

Today CNTs can be fabricated in laboratory quantities by several techniques including arc-discharge, laser ablation and chemical vapor deposition (CVD) [8]. The structure and morphology of the CNTs fabricated by each technique vary significantly. The arc-discharge and laser-ablation methods use extremely high temperatures – the temperature of the plasma/plume is 3000–4000 °C. As a result the CNTs produced tend to have a higher degree of graphitization than those produced by the CVD process which normally operates at 800–1200 °C. The defect density affects the thermal and electrical conductivity, the mechanical strength of the CNTs and therefore their emission characteristics due to stable CNT heating and subsequent destruction during field emission. The diameter of the SWNTs is usually in the range of 1–2 nm while the diameter of the MWNTs is 20–100 nm. This suggests that the SWNTs have a higher field amplification factor. However, they form close-packed bundles comprising 10^1-10^2 of SWNTs with a bundle diameter of 10–100 nm.

We have investigated the electron field emission characteristics of different types of CNTs fabricated by our group at UNC, our collaborators at Bell Labs, Duke Univ., Japan, and CNTs from commercial sources. These include SWNTs by the laser ablation [19], arc-discharge [20], and thermal CVD process [21]; MWNTs by the CVD [22] and arc-discharge [23] processes; and double-walled carbon nanotubes (DWNTs). The results are summarized in Fig. 4 which shows the emission current density versus applied electric field plotted for a variety of CNT emitters and nanostructured diamond [24]. The results show the emission threshold fields of these CNTs differ only by a factor of 2–3. They are all significantly lower than the reported values for other field emitters such as the Spindt tips and diamond materials [24]. The similarity between the SWNTs and MWNTs is not surprising considering the fact that the diameter of a SWNT bundle is comparable to that of a MWNT. The SWNTs, however, are more stable than the MWNTs at high current densities, which is attributed to their higher degree of structural perfection. It is important to note the exact value of the threshold field depends on how the macroscopic cathode is prepared and how the measurement is performed. The data shown in the figure were collected using scanning probe geometry with a small hemispherical current collector [24].



Fig. 3. Schematics illustrating the different geometries of macroscopic CNT field emission cathodes and images of the actual CNT structures fabricated. In the ideal case (top), the CNTs are aligned in the field direction and well-spaced (S/H > 1) so that there is less electrical screening. The SEM image of the isolated CNTs was taken from [50], with the authors' permission; originally published by the Materials Research Society.



Fig. 4. Measured emission current density vs. applied electric field plotted for a variety of CNT emitters and nanostructured diamond. (Data taken from [24], originally published by the Materials Research Society.)

Table 1

Threshold electric field required for a 10 mA/cm² emission current density for different materials

Cathode material	Threshold field $(V/\mu m)$ for a		
	current density of 10 mA/cm ²		
Mo tips	50-100		
Si tips	50-100		
p-type diamond	160		
Defective CVD diamond	30-120		
Amorphic diamond	20-40		
Cesium-coated diamond	20-30		
Graphite powders	10-20		
Nano-diamond	$3-5$ (unstable > 30 mA/cm^2)		
Assorted carbon nanotubes	$1-2 \text{ (stable >4000 mA/cm}^2)$		

Table 2
Effect of bundle length on the field emission properties of SWNTs

Average length (µm)	>10	>10	4.0	1.5	0.5
Field enhancement factor β	2423	2345	1021	623	602
Field for 10 µA/cm ² (V/µm)	1.2	0.9	2.0	3.6	4.0

2.2.2. Orientation of the CNTs

Because the electrons are emitted from the tips of the CNTs, intuitively one expects that the vertically aligned CNTs are better emitters than the random films. This is however complicated by the effect of electrical screening. Calculations have shown that to minimize the screening effect the individual emitters/CNTs should be evenly separated such that their spacing is greater than their height (Fig. 3). Most of the vertically aligned MWNTs fabricated by CVD process comprise densely packed CNTs. As a result they do not show enhanced emission properties as expected. As shown in Fig. 4, the emission characteristic of the aligned MWNTs is not significantly different from that of the random MWNT film. By lithographically patterning the location of the catalysts on the substrates, several groups have recently reported aligned CNTs and carbon nano-fibers with controlled spacing to minimize the screening effects. One concern of this approach is whether the lifetime of the cathode is affected because of the significant reduction in the density of the CNTs.

For cathodes with randomly oriented CNTs, the emitters come from two sources. One is the small fraction of the CNTs that point to the current collector due to simple statistical distribution. The second group comes from field induced alignment. Several experiments [14,15] have shown the CNTs can be easily bent and aligned to the electrical field direction under a moderate electrical field. One advantage of this type of cathode is the large number of CNTs available for emission which can lead to a longer lifetime.

2.2.3. Aspect ratio of the CNTs

We have investigated the effect of nanotube length on field emission properties of randomly oriented SWNT films. SWNT bundles synthesized by the laser ablation method were purified then chemically etched to different aspect ratios using a previously reported procedure [19]. The averaged bundle length was determined by transmission electron microscopy (TEM) measurements. The shortest SWNT bundles produced in this study were 0.5 μ m. The SWNTs with different bundle length were processed into thin membranes with random tube orientation and were annealed at 500 °C at 10⁻⁶ Torr vacuum before use. The experimental results showed that the emission threshold field increases with decreasing CNT bundle length. The measured threshold fields and the estimated enhancement factors are listed in Table 2. We attributed this to the dependence of field enhancement factor β on the average bundle length: β is reduced due to shortened CNT bundles.

2.2.4. Electronic work function

The electronic work function is the parameter of materials that determines the emission characteristics. The work function of the CNTs has been investigated by several techniques. Ultraviolet photoelectron spectroscopy (UPS) measurement shows that the work function of the SWNTs is 4.8 eV which is very close to the value of graphite [25]. The aligned MWNTs were found to have a larger density of states at the Fermi level and a slightly lower work function than the random MWNTs which is attributed to the difference in the electronic state between the tip and the sidewall of the CNT [26]. Similar to the other carbon allotropes, the electronic properties of the CNTs can be modified and tuned by chemical doping. Experimentally, it has been shown that the work function of the SWNTs can be reduced to as low as 2.5 eV by intercalation with Cs [25]. The in-situ Cs

Fig. 5. Photoemission spectra around the secondary electron threshold regions of graphite and pristine SWNTs (a) and Cs-intercalated SWNT bundles (b). Photoemission measurements were carried out at room temperature using a He discharge lamp (He I: hv = 21.22 eV) and an angle-integrated-type electron energy analyzer. (Data taken from [25], originally published by the American Institute of Physics.)

intercalation and UPS results are shown in Fig. 5. Each alkali metal atom can donate one electron to the SWNTs which results in the reduction of the work function. A recent theoretical calculation shows the same trend as the experimental result [27]. The effect of Cs intercalation on the field emission properties has also been studied. The result showed that Cs deposition on SWNTs can decrease the turn-on field by a factor of 2–3 and increase the emission current [28], consistent with reduction of the electronic work function due to Cs intercalation. The intercalated CNTs however are air-sensitive and can easily de-intercalate when the emission current is high.

2.3. Field emission characteristics of macroscopic CNT cathodes

In this section we present the basic electron field emission characteristics of macroscopic CNT cathodes fabricated in our laboratory. All the cathodes discussed here are produced by liquid-phase post-deposition methods using SWNTs [19]. Two types of systems are used to carry out these measurements. One uses a small hemispherical probe that can scan across the surface of the cathode to obtain the local properties. The second uses parallel-plate geometry where the overall properties of the entire sample are measured. The SWNTs are produced by either the laser ablation or arc-discharge method. They are purified and processed to the desired aspect ratio and chemical functionality such that they can be suspended in a suitable solvent such as water or ethanol without the use of surfactant. They are then deposited on a support surface by either the electrophoresis [29] or the self-assembly [30,31] method we developed. The readers are referred to these references for details on sample preparation.

2.3.1. Emission current-voltage characteristics

Fig. 6 shows the emission current–voltage (I-V) characteristics of the SWNT film measured using a hemispherical current collector of 1 mm diameter (anode) at 5×10^{-8} Torr base pressure at different anode–cathode gap distances. As shown in the figure and the inset, the SWNT film shows the classic Fowler–Nordheim behavior with a threshold field of 2 V/µm for 1 mA/cm² current density (the effective emission area is calculated using a previously described method [16]). Emission current density over 1 A/cm² can be readily achieved. The threshold fields are substantially lower than those reported for other electron field emissive materials [4].

2.3.2. Emission stability

The stability of emission performance can be readily evaluated by monitoring the evolution of total emission current at a fixed electric field. Fig. 7 shows the result from a macroscopic sample measured using the parallel-plate geometry. After the initial 'burn-in', under a constant DC voltage without feedback, no overall decay in the emission current is observed over 10 hours period. Recently we have demonstrated stable emission at comparable current level for over 300 hours at 100% duty cycle.





Fig. 6. Electron emission current versus applied voltage of a SWNT film measured at different anode–cathode distances using a hemispherical anode (1.0 mm in dia.). The effective emission area was calculated using a previously published formula [16]. The threshold field for 1 mA/cm² is 2 V/ μ m. Inset is the same set of data plotted as $\ln(I/V^2)$ versus 1/V (Fowler–Nordheim plot) which shows linear dependence. (Data taken from [34], originally published by the American Institute of Physics.)

The standard deviation of the current fluctuation is 2–4%. The emission stability can be improved significantly by incorporation of a simple feedback loop, as demonstrated in Fig. 7(b). The threshold field measured from the macroscopic sample is larger than the value obtained using the small probe which is related to the sample uniformity.

The origin of emission current decay is not very clear. Field evaporation of carbon was found to result in reduction of the length of the CNTs without catastrophic arcing events [17]; local Joule heating along the tube length due to the flow of emission current may 'burn' the CNTs. A field emission electron spectroscopy study from an individual MWNT revealed that the temperature at the tip was up to 2000 K induced by an emission current of 1 μ A [32,33]. On the other hand, Joule heating of CNTs may help to remove adsorbates during field emission. Besides, the bombardment of gas molecules ionized by the emitted electrons may also gradually modify the tubes. For macroscopic cathodes, the adhesion of the CNTs to the substrate is also critical for the stability. The strong electrostatic force exerted on the CNTs during emission can peel off the CNTs from substrate, causing current decay and arcing.

Because the field emission current is controlled by the applied voltage rather than temperature as in the case of thermionic emission, pulsed emission with variable pulse width and repetition rate can be readily obtained by programming the applied electrical field. Fig. 7(c) shows the pulsed emission current generated using a 100 Hz and 2 ms width square wave. A peak emission current of ~ 25 mA is obtained from a 0.2 cm² SWNT film (140 mA/cm²) [34]. There is a clear one-to-one correspondence between the applied voltage and the emission current. The instantaneous response is attractive for device applications.

2.3.3. Emission uniformity

One of the most challenging issues with macroscopic CNT cathodes is the emission uniformity. Due to problems with screening effect, variations in CNT structure and overall sample uniformity, only a very small fraction of the CNTs emit at a given time. The low emission site density means low resolution in field emission displays, low current density, and short lifetime. For flat-panel displays, an emission site density of $\sim 10^5$ cm⁻² is often required which is not easy to accomplish. Emission from poorly made CNT cathodes is often dominated by edge emission and hot spots. Edge emission is due to concentration of the electrical field at edges of the cathode which can be eliminated by modifying the electrical field distribution. Removing hot spots is also critical for achieving high emission uniformity. Several activation processes have been developed to eliminate these protrusions that dominate the emission process. These include plasma and mechanical treatments and aging. Fig. 8 illustrates the emission uniformity from a homogeneous SWNT film deposited on a metal substrate. The image was taken using 100 Hz



Fig. 7. (a) The stability of the emission current measured under a constant applied electric field from a 0.2 cm^2 area SWNT film using parallel plate geometry at 100% duty cycle; (b) variation of the emission current and the control voltage vs. time measured under the constant current mode. The applied field is automatically adjusted to maintain the set current via a feedback system; (c) pulsed emission current induced by a pulsed control voltage.

and 1% duty cycle applied field. A phosphor coated ITO glass was used as the anode which was placed in parallel to the anode. A uniform and bright image was obtained after activation. Using a liquid-phase deposition process we have fabricated patterned CNT cathodes on glass substrates at room temperature [30,31]. These cathodes show relatively uniform emission, as demonstrated in Fig. 8. The image was collected from a SWNT structure with a 100 µm line width patterned on an ITO glass.

3. Applications

Since the initial report of electron field emission from CNTs, there have been growing interests on new vacuum electronic devices based on these novel emitters in both academic and industrial laboratories [35]. Several prototype devices and device



Fig. 8. Phosphor screen images showing the emission uniformity of CNT cathodes. Left: a homogeneous 2×2 cm SWNT cathode. The image was collected at 4.4 V/µm applied field at 100 Hz, 1% duty cycle. Right: a patterned SWNT structure deposited on ITO glass at room temperature. The CNT line width is 100 µm. The data was collected using 5% duty cycle.

concepts have been reported. These include field emission displays (FEDs) [36], field emission x-ray tubes [34], plasma ignition [37] and lighting [38]. In this section we briefly describe the working mechanism of FEDs and field emission x-ray tubes.

3.1. Field emission displays

One of the first CNT-based display devices reported is a cathode ray lighting element using CNT field emitters as the electron source [39]. The device has a triode-type design. CNTs are used as the cathodes. The electrons are extracted by applying an electrical field between the cathode and a metal mesh used as the gate electrode. The field emitted electrons are accelerated towards the phosphor screen which acts as the anode. Different colors are obtained by using different fluorescent materials. The luminance of the phosphor screens measured on the tube axis is 6.4×10^4 cd/cm² for green light at an anode current of 200 μ A, which is two times more intense than that of conventional thermionic cathode ray tube (CRT) lighting elements operated under similar conditions.

Matrix-addressable diode-type field emission displays (FEDs) usually consist of CNT stripes on the cathode glass plate and phosphor-coated indium-tin-oxide (ITO) stripes on the anode plate. Pixels are formed at the intersection of cathode and anode stripes. A 32×32 prototype was first realized using carbon nanotubes as the electron source with a pixel size of $200 \times 200 \,\mu\text{m}^2$ [40]. Later a 4.5-inch three color display using SWNT emitters was fabricated [36]. The fully sealed diode display has 128 addressable lines and demonstrates a brightness of 1800 cd/m² at 3.7 V/µm [41]. Recently, Samsung introduced a 9-inch full-color FED with 576 × 240 lines [42].

A diode type FED has a limitation in individually controlling each pixel on the same stripe; a triode structure is needed for the practical applications of FEDs. Triode-type structure inserts a gate electrode between the CNT cathode and phosphor anode, while the gate gap is small (usually less than 10 μ m), so that the electrons can be extracted by applying a very low voltage on the gate. A prototype FED using gated CNT field emitters was demonstrated [43], which can address a 100 × 100 matrix over a 1 cm × 1 cm area and the gate voltage is about 50 V. A fully sealed 5-inch SWNT-based triode FED exhibited a luminance of 510 cd/m² with 240 × 120 lines. There is also an under-gate type triode structure, in which gate electrode is under the cathode, on the opposite side of the anode. Fig. 9 shows a color image produced by a 9 inch carbon nanotube based FED [36]. Comparing to the commercial LCD and plasma displays, the current CNT based FEDs require further improvement in pixel uniformity and stability.

3.2. X-ray tube

X-ray radiation is widely used in medical and industrial applications. A conventional x-ray tube comprises a metal filament (cathode) which emits electrons when resistively heated to over 1000 °C and a metal target (anode) that emits x-rays when bombarded by the accelerated electrons [44]. The use of thermionic cathodes results in several limitations. Field emission is a more attractive mechanism to extract electrons compared to thermionic emission because electrons are emitted at room temperature and emission is voltage controllable. The concept of field emission x-ray tube has been discussed in the past and



Fig. 9. A color image from a 9-inch CNT-based field emission display reported by Samsung Co. (Data taken from [36]; published with permission of Elsevier.)



Fig. 10. Schematic drawing of the CNT based field emission x-ray sources. SWNTs coated on a metal substrate are used as the cathode. The gate electrode is a W mesh 50–200 μ m away from the cathode. Electron emission is triggered by the voltage applied between the gate and the cathode. X-ray is produced when the emitted electrons are accelerated and bombarded on the copper target.

devices with low x-ray flux have been demonstrated [45–49]. However, most diagnostic applications require tube current in the order of 10–100 mA and operating voltage in the range of 30–150 KV which was difficult to accomplish for the field emission x-ray tubes.

We have recently demonstrated a CNT-based x-ray tube which can generate sufficient x-ray flux for diagnostic imaging applications [34]. The device, illustrated in Fig. 10, comprises a field emission cathode, a gate electrode, and a metal target in a vacuum chamber with a Be window. The cathode is a SWNT film deposited on a metal substrate. A relatively low voltage is applied between the gate and the cathode to extract electrons from the cathode. The field emitted electrons are accelerated by a high voltage applied between the anode and the gate. A total emission current as high as 30 mA is obtained from a small CNT cathode. The device can readily produce x-ray wave forms with programmable pulse width and repetition rate. Pulsed x-rays with a repetition rate up to 30 KHz have been generated by applying an external triggering voltage on the gate (Fig. 11). The x-ray flux is sufficient to image human extremity, as demonstrated in Fig. 11.

The CNT-based x-ray sources have several advantages compared to the thermionic x-ray tubes. The life span of the xray tubes can potentially be prolonged by eliminating the thermionic cathode. The size of the x-ray source can be reduced significantly. It also has the ability to produce focused electron beams with very small energy spread and programmable pulse





Fig. 11. X-ray generation by CNT-based field emission source developed at UNC. Left: 1 KHz and 50% duty cycle pulsed x-ray signals recorded using an oscilloscope by applying pulsed gate voltage with the same wave form. (The height of the signal is proportional to the photon energy.) Right: X-ray image of a humanoid hand taken using the CNT source on a Polaroid[™] film. The x-ray energy is 40 KVp and the image was taken at 40 cm away from the x-ray source without using an image intensifier.

width and repetition rate. This CNT-based cold-cathode x-ray technology can potentially lead to portable and miniature x-ray sources for industrial and medical applications.

4. Summary

Because of their unique structure and morphology CNT field emitters are shown to have excellent emission characteristics such as a low threshold field for emission and a high current density. These properties make them attractive as potential coldcathode electron sources for a variety of vacuum electronic devices. There are still important materials issues that need to be resolved before they can be utilized in practical devices. These include emission uniformity, lifetime, and efficient bottom-up processes for materials assembly and integration. Tremendous progress has been made in all these areas in the last few years. We are confident that CNT based field emission devices with enhanced performances will be commercially available in the near future.

Acknowledgements

We thank our colleagues at UNC and Applied Nanotechnologies Inc. for discussion and collaboration. O.Z. thanks current and former students, postdocs and visitors for their contribution and is grateful for financial supports from U.S. Office of Naval Research through a MURI program and NASA.

References

- [1] A. Modinos, Field, Thermionic and Secondary Electronemission Spectroscopy, Plenum, 1984.
- [2] R. Gomer, Field Emission and Field Ionization, Harvard University Press, Cambridge, MA, 1961.
- [3] I. Brodie, C.A. Spindt, Vacuum microelectronics, Adv. Electron. Electron Phys. 83 (1992) 1–106.
- [4] W. Zhu (Ed.), Vacuum Micro-Electronics, Wiley, 2001.
- [5] S. Iijima, Helical microtubules of graphitic carbon, Nature 354 (1991) 56-58.

- [6] A.G. Rinzler, J.H. Hafner, P. Nikolaev, L. Lou, S.G. Kim, D. Tomanek, D. Colbert, R.E. Smalley, Unraveling nanotubes: field emission from an atomic wire, Science 269 (1995) 1550–1553.
- [7] W.A.D. Heer, A. Chatelain, D. Ugarte, A carbon nanotube field-emission electron source, Science 270 (1995) 1179–1180.
- [8] M.S. Dresselhaus, G. Dresselhaus, P. Avouris (Eds.), Carbon Nanotubes: Synthesis, Structure, Properties, and Applications, in: Topics in Appl. Phys., Vol. 80, Springer-Verlag, Heidelberg, 2000.
- [9] J. Cumings, A. Zettl, M.R. McCartney, J.C.H. Spence, Electron holography of field-emitting carbon nanotubes, Phys. Rev. Lett. 88 (2002) 056804.
- [10] K.A. Dean, P. von Allmen, B.R. Chalamala, Three behavioral states observed in field emission from single-walled carbon nanotubes, J. Vac. Sci. Technol. B 17 (1999) 1959.
- [11] K.A. Dean, B.R. Chalamala, Experimental studies of the cap structure of single-walled carbon nanotubes, J. Vac. Sci. Technol. B 21 (2003) 868.
- [12] A. Maiti, J. Andzelm, N. Tanpipat, P.V. Allmen, Effect of adsorbates on field emission from carbon nanotubes, Phys. Rev. Lett. 87 (2001) 155502.
- [13] J.M. Bonard, F. Maier, T. Stökli, A. Chäelain, W.A. de Heer, J.-P. Salvetat, L. Forr, Field emission properties of multiwalled carbon nanotubes, Ultramicroscopy 73 (7) (1998).
- [14] Y. Wei, C. Xie, K.A. Dean, B.F. Coll, Stability of carbon nanotubes under electric field studied by scanning electron microscopy, Appl. Phys. Lett. 79 (27) (2001) 4527–4529.
- [15] Z.L. Wang, R.P. Gao, W.A.D. Heer, P. Poncharal, In-situ imaging of field emission from individual carbon nanotubes and their structural damage, Appl. Phys. Lett. 80 (5) (2002) 856–858.
- [16] W. Zhu, C. Bower, O. Zhou, G.P. Kochanski, S. Jin, Very high current density from carbon nanotube field emitters, Appl. Phys. Lett. 75 (6) (1999) 873–875.
- [17] K.A. Dean, B.R. Chalamala, Appl. Phys. Lett. 76 (2000) 375.
- [18] G. Zhou, W. Duan, B. Gu, Phys. Rev. Lett. 87 (2001) 095504.
- [19] O. Zhou, H. Shimoda, B. Gao, S.J. Oh, L. Fleming, G.Z. Yue, Materials science of carbon nanotubes: fabrication, integration, and properties of macroscopic structures of carbon nanotubes, Acc. Chem. Res. 35 (2002) 1045–1053.
- [20] C. Journet, W.K. Maser, P. Bernier, A. Loiseau, M.L.D.L. Chapelle, S. Lefrant, P. Deniard, R. Lee, J.E. Fischer, Large scale production of single wall carbon nanotubes by the electric arc technique, Nature 388 (1997) 756–758.
- [21] M. Su, B. Zheng, J. Liu, A scalable CVD method for the synthesis of single-walled carbon nanotubes with high catalyst productivity, Chem. Phys. Lett. 322 (2000) 321–326.
- [22] C. Bower, O. Zhou, W. Zhu, D.J. Werder, S. Jin, Nucleation and growth of carbon nanotubes by microwave plasma chemical vapor deposition, Appl. Phys. Lett. 77 (17) (2000).
- [23] T.W. Ebbesen, P.M. Ajayan, Large-scale synthesis of carbon nanotubes, Nature 358 (1992) 16.
- [24] C. Bower, O. Zhou, W. Zhu, A.G. Ramirez, G.P. Kochanski, S. Jin, Fabrication and field emission properties of carbon nanotube cathodes, in: Amorphous and Nanostructured Carbon, Mat. Res. Soc. Symp. Proc., 2000.
- [25] S. Suzuki, C. Bower, Y. Watanabe, O. Zhou, Work functions and valence band states of pristine and Cs-intercalated single-walled carbon nanotube bundles, Appl. Phys. Lett. 76 (26) (2000) 4007–4009.
- [26] S. Suzuki, T. Watanabe, T. Kiyokura, K.N. Nath, T. Ogino, S. Heun, W. Zhu, C. Bower, O. Zhou, Electronic structure at carbon nanotube tips studied by photoemission spectroscopy, Phys. Rev. B 63 (2001) 2454181.
- [27] J. Zhao, J. Han, J. Lu, Work functions of pristine and alkali metal intercalated nanotubes and bundles, Phys. Rev. B 65 (2002) 193401.
- [28] A. Wadhawan, R.E. Stallcup, J.M. Perez, Effects of Cs deposition on the field-emission properties of single-walled carbon nanotube bundles, Appl. Phys. Lett. 78 (1) (2001) 108–110.
- [29] B. Gao, G.Z. Yue, Q. Qiu, Y. Cheng, H. Shimoda, L. Fleming, O. Zhou, Fabrication and electron field emission properties of carbon nanotube films by electrophoretic deposition, Adv. Mater. 13 (23) (2001) 1770–1774.
- [30] H. Shimoda, S.J. Oh, H.Z. Geng, R.J. Walker, X.B. Zhang, L.E. McNeil, O. Zhou, Self-assembly of carbon nanotubes, Adv. Mater. 14 (12) (2002) 899–901.
- [31] S.J. Oh, Y. Cheng, J. Zhang, H. Shimoda, O. Zhou, Room-temperature fabrication of high-resolution carbon nanotube field-emission cathodes by self-assembly, Appl. Phys. Lett. 82 (2003) 2521.
- [32] S.T. Purcell, P. Vincent, C. Journet, V.T. Binh, Hot nanotubes: Stable heating of individual multiwall carbon nanotubes to 2000 K induced by the field-emission current, Phys. Rev. Lett. 88 (10) (2002) 105502.
- [33] P. Vincent, S.T. Purcell, C. Journet, V.T. Binh, Modelization of resistive heating of carbon nanotubes during field emission, Phys. Rev. B 66 (7) (2002) 075406.
- [34] G.Z. Yue, Q. Qiu, B. Gao, Y. Cheng, J. Zhang, H. Shimoda, S. Chang, J.P. Lu, O. Zhou, Generation of continuous and pulsed diagnostic imaging x-ray radiation using a carbon-nanotube-based field-emission cathode, Appl. Phys. Lett. 81 (2) (2002) 355.
- [35] P.M. Ajayan, O. Zhou, Applications of carbon nanotubes, in: M.S. Dresselhaus, G. Dresselhaus, P. Avouris (Eds.), Carbon Nanotubes: Synthesis, Structure, Properties, and Applications (Topics in Applied Physics, 80), Springer-Verlag, Heidelberg, 2000, pp. 391–425.
- [36] N.S. Lee, D.S. Chung, I.T. Han, J.H. Kang, Y.S. Choi, H.Y. Kim, S.H. Park, Y.W. Jin, W.K. Yi, M.J. Yun, J.E. Jung, C.J. Lee, Y.J. H, S.H. Jo, C.G. Lee, J.M. Kim, Application of carbon nanotubes to field emission displays, Diamond and Related Mater. 10 (2001) 265.
- [37] R. Rosen, W. Simendinger, C. Debbault, H. Shimoda, L. Fleming, B. Stoner, O. Zhou, Application of carbon nanotubes as electrodes in gas discharge tubes, Appl. Phys. Lett. 76 (13) (2000) 1197–1199.
- [38] J.M. Bonard, T. Stockli, O. Noury, A. Catelain, Field emission from cylindrical carbon nanotube cathodes: possibilities for luminescent tubes, Appl. Phys. Lett. 78 (18) (2001) 2775.

- [39] Y. Saito, S. Uemura, K. Hamaguchi, Cathode ray tube lighting elements with carbon nanotube field emitters, Jpn. J. Appl. Phys. 37 (1998) L346–L348.
- [40] Q.H. Wang, A.A. Setlur, J.M. Lauerhaas, J.Y. Dai, E.W. Seelig, R.H. Chang, Appl. Phys. Lett. 72 (1998) 2912.
- [41] W.B. Choi, D.S. Chung, J.H. Kang, H.Y. Kim, Y.W. Jin, I.T. Han, Y.H. Lee, J.E. Jung, N.S. Lee, G.S. Park, J.M. Kim, Appl. Phys. Lett. 75 (1999) 3129.
- [42] W.B. Choi, N.S. Lee, W.K. Yi, Y.W. Jin, Y.S. Choi, I.T. Han, D.S. Chung, H.Y. Kim, J.H. Kang, Y.J. Lee, M.J. Yun, S.H. Park, S. Yu, J.E. Jang, J.H. You, J.M. Kim, Technol. Dig. SID. (2000).
- [43] Q.H. Wang, M. Yan, R.P.H. Chang, Appl. Phys. Lett. 78 (2001) 1294.
- [44] S.C. Bushong, Radiologic Science for Technologist, Mosby, 1997.
- [45] R.R. Whitlock, M.I. Bell, D.V. Kerns, S. Kerns, J.L. Davidson, W.P. Kang, Transmission cathodes for x-ray production, U.S. Patent 6,333,968, 2001.
- [46] R. Baptist, X-ray tube comprising an electron source with microtips and magnetic guiding means, U.S. Patent 6,259,765, 2001.
- [47] P. Rangstein, C. Ribbing, C. Strandman, R. Hok, L. Smith, Field-emitting structures intended for a miniature x-ray source, Sensors and Actuators 82 (2000) 24–29.
- [48] O. Zhou, J.P. Lu, New x-ray generating mechanism using electron field emission cathode, U.S. Patent Application, S/N 09/679,303, 2000.
- [49] H. Sugie, M. Tanemura, V. Filip, K. Iwata, K. Takahashi, F. Okuyama, Carbon nanotubes as electron source in an x-ray tube, Appl. Phys. Lett. 78 (2001) 2578.
- [50] J.G. Wen, Z.P. Huang, D.Z. Wang, J.H. Chen, S.X. Yang, Z.F. Ren, J.H. Wang, L.E. Calvet, J. Chen, J.F. Klemic, M.A. Reed, Growth and characterization of aligned carbon nanotubes from patterned nickel nanodots and uniform thin films, J. Mater. Res. 16 (2001) 3246–3253.