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Electron field emission from single-walled carbon nanotube nonwoven*

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Field emission from single-walled carbon nanotube (SWNT) nonwoven has been investigated under high vacuum with different vacuum gaps. A low turn-on electric field of 1.05 V/μm is required to reach an emission current density of 10 μA/cm^2. An emission current density of 10 mA/cm^2 is obtained at an operating electric field of 1.88 V/μm. No current saturation is found even at an emission current of 5 mA. With the vacuum gap increasing from 1 to 10 mm, the turn-on field decreases monotonically from 1.21 to 0.68 V/μm, while the field amplification is augmented. The good field-emission behaviour is ascribed to the combined effects of the intrinsic field emission of SWNT and the waved topography of the nonwoven.

Keywords: single-walled carbon nanotubes, field
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1. Introduction

Since the discovery of carbon nanotubes (CNTs),[1] they have emerged as one of the most promising electron field emitters due to their high aspect ratio, high emission current and chemical stability.[2−4] In the last decade, much effort has been directed to investigate and apply the field emission properties of various carbon nanotube structures. Rinzler *et al* reported a field emission current up to 2 μA from individual carbon nanotubes.[5] Bonard *et al* reported electron field emission from random carbon nanotube films with different densities and found that current densities of 10 mA/cm^2 below 4 V/μm were reached from medium density nanotube films.[6] Fan *et al* reported that current density of 1 mA/cm^2 and 10 mA/cm^2 can be reached from regular nanotube arrays at the electric fields of about 3 V/μm and 5 V/μm, respectively.[7] Most recently, Ren and coworkers reported that a low electric field of less than 0.4 V/μm is required to reach emission current density of 1 mA/cm^2 from CNTs grown on carbon cloth.[8] In application, Samsung Electronics Co., Ltd. has developed a sealed full-colour CNT field emission display.[9] Luminescent tubes with both flat and cylindrical geometry fabricated using CNT cathode also show stable, adequate, and long-lifetime luminance.[10,11] However, the field emission of CNTs is still a key issue for their further applications in flat panel display, illumination, electron source, and other vacuum microelectronic devices.

In our previous works, a texture of SWNT nonwoven with high mechanical values was prepared by floating chemical vapour deposition method (CVD).[12] Here, we report electron-field-emission from these non-

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woven under high vacuum with different vacuum gaps. A low turn-on electric field of 1.05 V/μm is required to reach an emission current density of 10μA/cm^2. Meanwhile, an emission current density of 10 mA/cm^2 is obtained at an operating electric field of 1.88 V/μm. The emission behaviour agrees with Fowler–Nordheim (FN) theory with low turn-on field, and shows a good stability and a high emission current. It is attributed to the waved topography of the nonwoven and the good intrinsic emission property of SWNT. The low field operation of SWNT nonwoven emitters is attractive for many practical applications in displays and microelectronic fields.

2. Experimental

SWNT nonwovens were produced by optimal floating chemical vapour deposition (CVD) on two-stage furnace system at 1100°C. The detailed experimental condition was described previously.[12] For field emission measurements, SWNT films with area about 20 mm^2 were spread on the highly conductive aluminium substrates before being transferred into the vacuum chamber. Meanwhile, the setup for field-emission measurement contains the SWNTs covered aluminium substrate and a phosphorous glass plate coated with indium-tin oxide as cathode and anode, respectively. In order to avoid damage of the phosphorous glass anode, metal is used as another anode to obtain high emission current. The vacuum gap between them is variable as needed. A voltage ranging from 300V to 15kV is applied on the electrodes. A ballast resistor of 10MΩ is used and the emission current is measured by a picoammeter (Keithley 485). During the test, the pressure of the chamber is $\sim 10^{-7}$Pa. Herein, we use the threshold electric field needed to produce a current density of 10 mA/cm^2 (which is typically required for effectively exciting a phosphor pixel in displays) and the turn-on field (for a current density of 10μA/cm^2) as a figure of merit to compare various samples.

3. Results and discussion

Figure 1 shows atomic force microscope (AFM) image of a typical SWNT nonwoven grown by floating CVD. It appears that the textures are composed of highly entangled carbon nanotube bundles with compact structure. These bundles with diameter of 20–30 nm are mostly curved and are several hundred microns in length, which form random networks with pore sizes of 50–200 nm. The thickness of the nonwoven is several micrometers. It is worth noting that the surface of nonwoven is not flat while waved, having bulges of sizes of several nanometres. On the basis of the above observation, one sees that the SWNT nonwoven provides a novel membrane surface of pure carbon composition with dimensionally nanostructured topography.

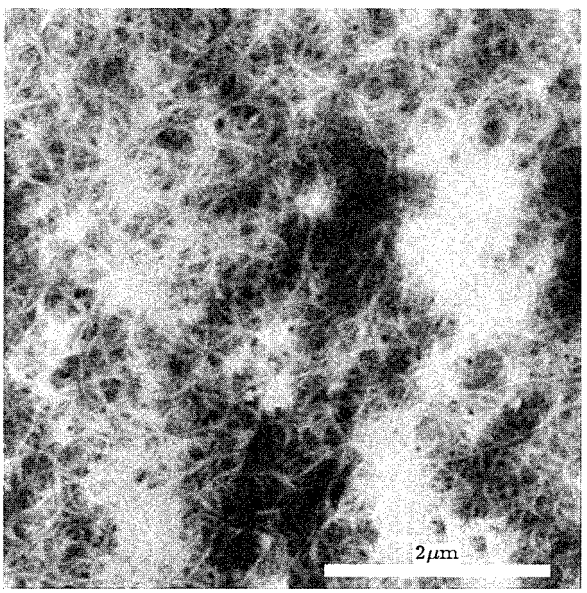


Fig.1. An AFM image of SWNTs nonwoven.

Figure 2 shows typical curves of emission from SWNT nonwoven. Fig.2(a) shows the measured field emission current of SWNT nonwoven as a function of the applied voltage (I-V curve) for three cycles. With a vacuum gap of 1140μm, obvious emission current is observed in the first cycle when the applied voltage increases to 300 V, indicating a turn-on field of 0.26 V/μm. With the increase of the applied voltage, the emission current is enhanced markedly. The current on the cathode approaches 2 mA (current density 10mA/cm^2) at a voltage of 1650 V. As a voltage of 2300 V is applied the corresponding emission current is as large as 5 mA. However, the emission current fluctuates in the first cycle during the increasing of applied voltage, at places labelled with "A" and "B" in Fig.2(a). Meanwhile, the vacuum decreases sharply with the degradation of the emission current. It is indicated that some primitive emission sites are destroyed by local high temperature due to the high emission current. Here, several cycles of increasing-decreasing voltage are performed on the sample in order to ensure the reliability of emission current. It is clear that subsequent measurements usually show stable and reproducible I-V characteristics after sev-

eral cycles. Hereby, the obvious emission current from the nonwoven is found when the applied voltage increases to about 1200 V, which indicated a turn-on field of 1.05 V/μm. Besides, the threshold field is about 1.88 V/μm with emission current density of 10 mA/cm^2, which is very stable without current decline during a long-time emission. The turn-on field of SWNT film reported previously ranges typically from 1.5 to 2.1 V/μm, while the threshold field is about 4–7 V/μm.[3,13]

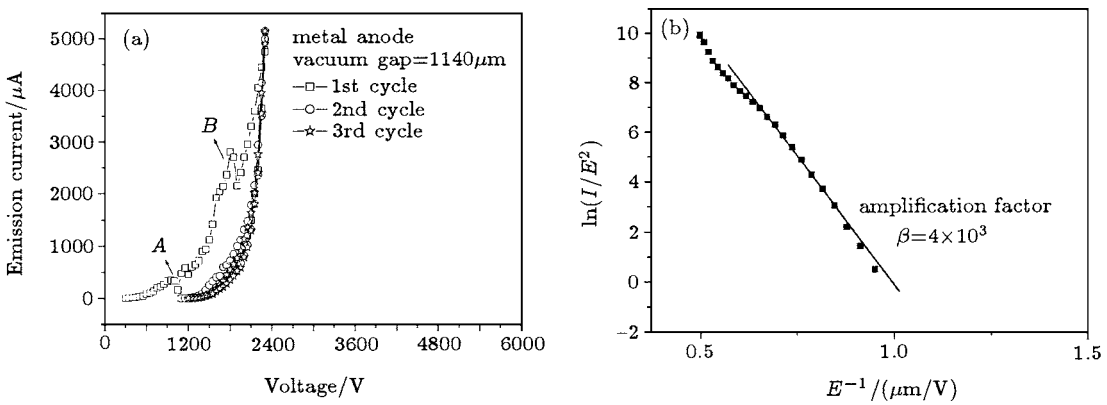


Fig.2. (a) Emission I-V curves from SWNTs nonwoven with vacuum gap 1140 μm for three cycles. (b) FN plot of electron-field-emission, indicating a conventional field-emission mechanism. The emission current significantly deviated from FN behaviour in the high-field region.

Although it is a very crude approximation, the Fowler–Nordheim theory is still frequently used as a mathematic interpretation of field emission from different materials. The total current I as a function of the local field at the emitter surface E is approximately given by $I = A(E^2/\Phi)\exp(-B\Phi^{3/2}/E)$, where A and B are constants (B= 6.83×10^9[V eV$^{-3/2}$m^{-1}]), and Φ the work function.[14] E is usually taken as $E = \beta E_0$, where β is the field amplification factor, and E_0 is the mean field between the cathode and anode. The plot ln(I/E^2) vs 1/E is expected to be a straight line. However, the field emission from SWNT nonwoven probably has a more complicated mechanism than that the FN theory is based on. The I-V behaviour of the SWNTs nonwoven under our investigation seems to follow the FN formula well in low current region, as suggest by Fig.2(b). The emission current significantly deviates from FN behaviour in the high-field region. Tentatively, we use the value of bulk graphite (5 eV) as the work function Φ of carbon nanotubes.[15] We would like to point out that by doing so we probably have exaggerated the work function of the SWNTs; thus the calculated β could be higher than the actual one. Under this assumption, β is calculated to be 4×10^3 from the slope of the straight line (Fig.2(b)), which is smaller than the values of CNTs films reported previously.[2,8]

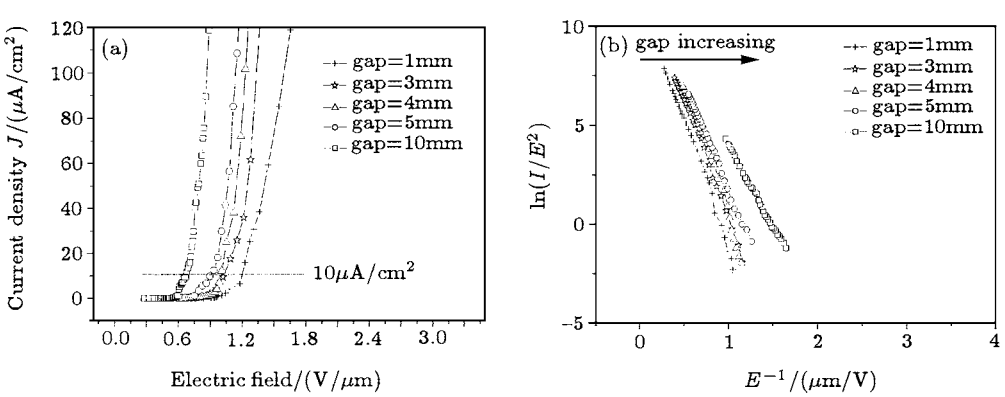


Fig.3. (a) J-E curves and (b) FN plots of electron-field-emission from SWNTs nonwoven with different vacuum gaps. A horizontal line at the emission current density of 10 mA/cm^2 is drawn to determine the turn-on electric field.

Furthermore, we investigated field-emission behaviour of SWNT nonwoven with different vacuum gaps. Based on our former discussion, the curves are taken from a series of 5 subsequent I-V cycles in order to obtain stable and reproducible emission behaviour. Fig.3 shows the measured field emission current density of nonwoven as a function of the macroscopic electric field (J-E) with vacuum gap between the cathode and anode varying from 1 to 10mm. It is noted that the turn-on field of field emission from SWNT nonwoven is decreased from 1.21 to 0.68 V/μm with the increase of vacuum gap. The FN plots with different vacuum gap are shown in Fig.3(b). Over the emission current density ranging from our detection limit of 1 μA/cm^2 to about 1 mA/cm^2, the FN plot is linear, indicating a conventional field-emission mechanism for the SWNT nonwoven in the low-field regime with different vacuum gaps. We also estimated the field amplification β from the constant FN slope in the low current regime with Φ=5eV. On average, the order of the field enhancement for SWNT nonwoven is about $\sim 10^3$. The turn-on field and amplification factors of field emission behaviours with various vacuum gaps are listed in Table 1. It is found that the enhancement factor is increasing obviously with the increase of vacuum gap between cathode and anode, which is similar to previous reports.[16]

Table 1. Emission characteristics of the SWNTs nonwoven with different vacuum gaps. $E_{\mathrm{turn-on}}$ is the turn-on field at current density of 10μA/cm^2. $\beta_{\mathrm{nonwoven}}$ is the field amplification factor extracted from the linear region of FN plot.

	Different Gap	Vacuum Gap=1mm	Vacuum Gap=3mm	Vacuum Gap=4mm	Vacuum Gap=5mm	Vacuum Gap=10mm
Field Emission	$E_{\mathrm{turn-on}}$/(V/μm)	1.20	1.02	0.99	0.91	0.67
	$\beta_{\mathrm{nonwoven}}$	5.2×10^3	6.8×10^3	6.9×10^3	7.2×10^3	8.7×10^3

The screen image on the anode plate can be used to characterize the special distribution of the emitting sites, as shown in Fig.4. At low voltage and small current density, the image of electron emission is located at some sites of the screen (Figs.4(a), (b)). At high voltage and large current density, the screen image expands dramatically, indicating that almost the whole SWNT nonwoven is emitting, as shown in Figs.4(c), (d). It is indicated that the electrons emitted from SWNTs nonwoven cathode excite all of the phosphor on the glass anode at high-applied voltage. Furthermore, some bright spots disappear with time during the increase of the applied electric field due to the destruction of emission sites on the SWNT nonwoven.

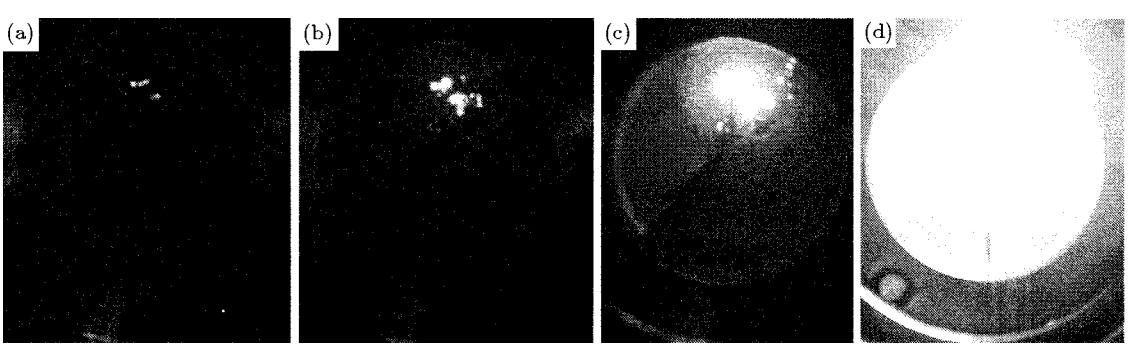


Fig.4. (a)–(d) Emission site distribution of the SWNTs nonwoven recorded with a CCD camera at the applied voltage of 1750 V, 2100 V, 2400 V and 4000 V, respectively.

Figure 5 shows SEM images of the SWNT nonwoven topography before and after emission test. It is clear that the density of nanotubes on nonwoven surface is decreased substantially, and amorphous carbon layer covers the surface after the field emission (Fig.5(b)). Furthermore, we observed some conglomerated black spots with a diameter of about several micrometers appearing on the surface of SWNT texture, as shown in Fig.5(c). During the observations in transmission electron microscope, SWNTs are very sensitive to electron bombardment, deforming and finally being rent in a matter of minutes. Based on

the above field emission test and the images of the emission sites, it is most probable that the tubes were gradually destroyed primarily through ion bombardment.

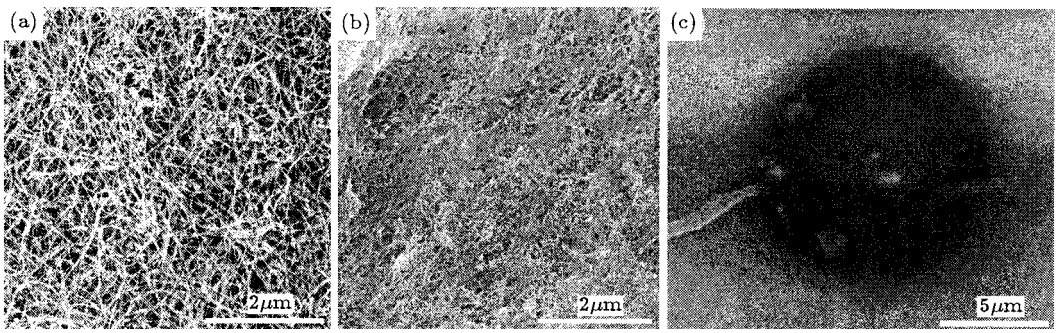


Fig.5. SEM images of the SWNTs nonwoven: (a) before and (b), (c) after the field emission experiment.

It is reported that there is a distinctive difference in the electronic properties between the tip and the cylindrical part of the tube.[5,8,17−20] According to these studies, electrons could emit from either the tip or the body of carbon nanotubes under enough high electric field. In our samples, neither graphite flakes nor open-top nanotubes tips can be detected. The possible mechanism is that the electrons emit from the sides of the nanotubes which are orientated not exactly parallel to the applied field. More precisely, it appears highly probable that the emission sites were the highly curved body of the nanotubes, which bring some defects on the sides of nanotubes and may change the electronic structure of the SWNTs. On the other hand, the emitters that contribute to the emitted current in large area measurements involve only a very small proportion of exceptionally long and narrow nanotubes. It is thought that the weaving of nanotube bundles is responsible for the emission of the nonwoven at lower field.

4. Conclusions

In summary, we reported the field emission behaviours of the SWNT nonwoven grown by floating CVD. The emission current densities of 10 μA/cm^2 and 10 mA/cm^2, corresponding to the turn-on and threshold fields, were observed at a field of 1.05 V/μm and 1.88 V/μm with the gap of 1140μm, respectively. No current saturation is found even at an emission current of 5 mA. The field-emission behaviours from SWNTs nonwoven with different vacuum gaps are discussed. When the vacuum gap is increase from 1 to 10mm, the threshold field decreases monotonically from 1.21 to 0.68 V/μm. It is found that the field amplification increases with the increase of vacuum gap. The emission behaviour is ascribed to the combined effects of the field enhancement from carbon nanotubes and rough topography of the nonwoven. The low field operation of SWNT nonwoven emitters is attractive for displays and microelectronic applications.

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