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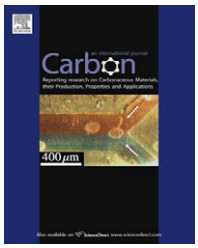

Electron field emission from transparent multiwalled carbon nanotube sheets for inverted field emission displays

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ABSTRACT

Strong, conducting, transparent carbon nanotube sheets were prepared by solid-state draw from well-ordered, aligned multiwalled carbon nanotube (MWCNT) forests [Zhang et al., 2005] [1]. Study of electron field emission from such transparent MWCNT sheets shows threshold fields of less than 0.5 V/μm with current densities high enough for display applications. Step-like field emission current increase and hysteresis behavior in *I*–*V* curves has been observed. The origin of such behavior is discussed in terms of mechanical rearrangement of the nanotube network in high electric field. Studied MWCNT transparent sheet field emission cathodes have several advantages when used as multi-functional electrodes. They are high current, high stability, transparent, and flexible field emission sources and can be used in an inverted geometry, with cathode being in front of the light emitting plate. At the same time transparent CNT sheets may serve as a transparent conducting electrode for electrical connection and pixel addressing in field emission displays (FEDs). Also, these sheets can be used as an optical polarizer in FEDs.

1. Introduction

Field emission displays (FEDs) are a very promising substitute for conventional liquid crystal displays (LCDs). While having the best available image quality of CRT displays, FEDs also offer a superior viewing angle (160°) and faster response time as compared to LCD.

It was realized in late 1990s that materials other than carbon cannot be used as stable field emitters (FEs). Among different forms of carbon, carbon nanotubes (CNTs) are the most promising material for use in FEDs [9].

For applications in displays and highly efficient luminescent lamps carbon nanotube FEs have several advantages over conventional field emission sources [2,3]. They have lower threshold fields for emitting high current densities as compared to existing FE sources. CNT field emitters have high chemical stability, large thermal conductivities, and high mechanical strength.

Most widespread technology uses CNT paste and requires physical surface treatment such as using sticky tape to expose vertically aligned CNT emitters [4]. However it is highly desirable to avoid any kind of binder in order to increase FE life-time and stability.

We present a study of the field emission properties of transparent and conducting carbon nanotube sheets [1]. Our unique method of MWCNT sheet preparation is binderless. Besides, MWCNT sheets can be mass produced and are much cheaper to fabricate as compared to conventional field emitter arrays. Resistance of a transparent MWCNT sheet is about 600 Ω/sq in aligned direction and about 15 KΩ/sq in transverse direction.

Transparent FEs can be interesting for such applications as smart windows, FEDs or 3D displays. Moreover, transparent FEs enables FEDs and field emission lamps in the inverse geometry, which have several benefits. First, in the inverse devices the phosphorus does not need to be thin. Second,

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thicker metallic layer can be used that enables improved discharge of the phosphorus. Also, the inverse geometry makes possible the use of organic light emitting layers which do not require a high energy electron beam.

2. Experimental details

A free-standing carbon nanotube sheet is drawn laterally from the side of a CNT forest (Fig. 1a) as earlier described [1]. It is then placed on a glass substrate or flexible plastic (polyethylene terephthalate (PET) or polyethylene naphthalate (PEN)). The sheet is weakly bound to the substrate by van der Waals forces. The CNT sheet is then densified using the surface tension effects of an imbibed liquid (for example, methanol). The rapid evaporation of the solvent absorbed in the sheet causes compression of the 20 μm thick MWCNT low density aerogel, its shrinkage to a 50–100 nm thick film, and densification. Fig. 1b shows the SEM image of a densified sheet of well-aligned MWCNT bundles. Each bundle consists of tens of 5–10 nm diameter multiwalled carbon nanotubes. The sheet is highly transparent (70% transmission for polarization parallel to nanotube orientation and 90% for perpendicular polarization at 450 nm) and has the ability to polarize transmitted light (Fig. 2). Before the field emission measurements the sample is heat treated in vacuum in order to remove adsorbates.

The field emission measurements have been performed in a vacuum chamber maintained at $\sim 10^{-7}$ Torr. The cathode and anode mounting stands are made of Al and are machine ground to ensure that they are perfectly parallel. The spacing between anode and cathode is controlled externally through a spring loaded micrometer gauge. The CNT sample is mounted on the cathode stand. *I–V* measurements are done with a tungsten plate mounted on the anode stand, while ITO-coated glass with phosphorous screen is used as the anode for the visualization of field emission sites distribution. High-voltage source-measure unit Keithley 237 and high-voltage pulse generator M25k-50N (HV Pulse Technology, Inc.) are used for measurements.

3. Results and discussion

Vertically oriented CNT bundles which raise from the sheet after the electron emission cycle are shown on Fig. 3a. Each bundle ends with a single multiwalled nanotube. The electrostatic force, applied to the nanotubes during field emission, pulls free ends of nanotubes towards the anode direction, parallel to the electric field direction and keeps them perpendicular to a substrate (Fig. 3b). As it has been shown [4], such flexing and alignment of nanotubes is reversible at low electric field (after switching off the field) and becomes permanent in a strong electric field when high field emission currents are observed. We observe similar phenomena of unbundling and the appearance of free ends for CNT twist-yarns cathodes [10].

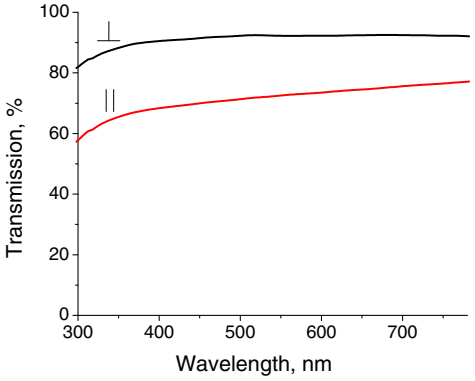

Fig. 2 – Optical transparency of MWCNT sheet for two different polarizations, parallel (||) and perpendicular (⊥) to nanotube orientation.

Photographs of phosphorescent screen due to electron emission are shown in Fig. 4. The images were taken in reverse geometry where the phosphorous screen was placed behind the sample, so the green light on the picture is coming through the transparent MWCNT sheet. In a typical CNT sheet there are about 100 emitting nanotubes per cm^2. However, this number can be adjusted by varying CNT forest height and density, as discussed later in the text.

Stability measurements were done by applying a constant potential difference between the electrodes. The temporal change of FE current was measured (Fig. 5). Usually, current decreases by a factor of about 2–2.5 during the first 2 h. The initial decrease in current is explained by a change in structure of CNT sheets, which is typical for nanotube FE. In the beginning, nanotubes that stick out of the substrate more than the others burn away due to high currents going through them [8].

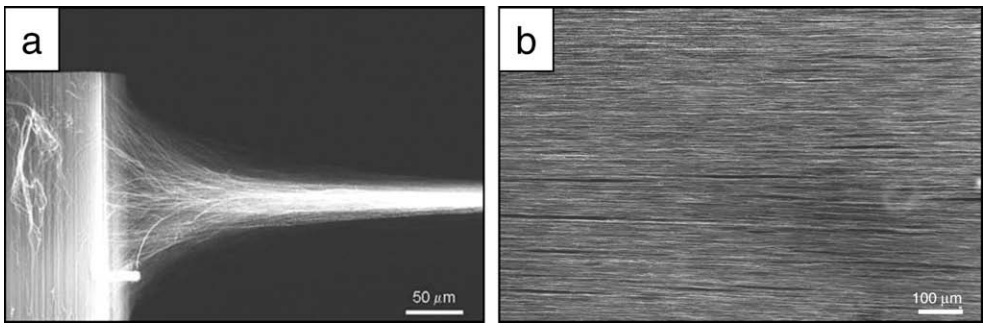

Fig. 1 – SEM images of (a) draw of a MWCNT sheet from a nanotube forest and (b) a densified MWCNT sheet on a glass substrate, top view.

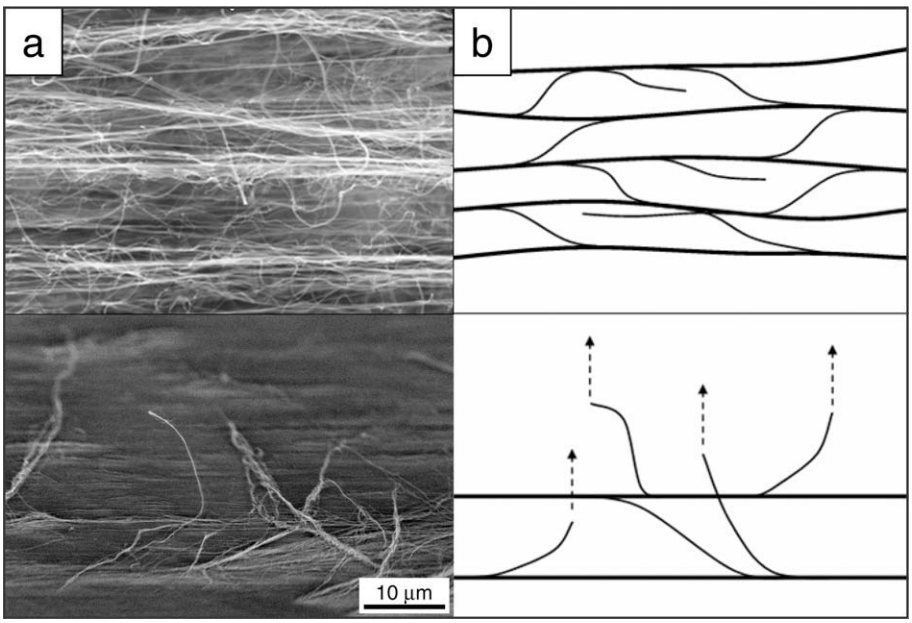

Fig. 3 – (a) SEM images of a MWCNT sheet showing raised CNT bundles which are responsible for enhanced field emission; top and side view and (b) schematics of raised nanotube bundles under the applied field; top and side view. Electrons are emitted from free ends of bundles, which are shown by arrows.

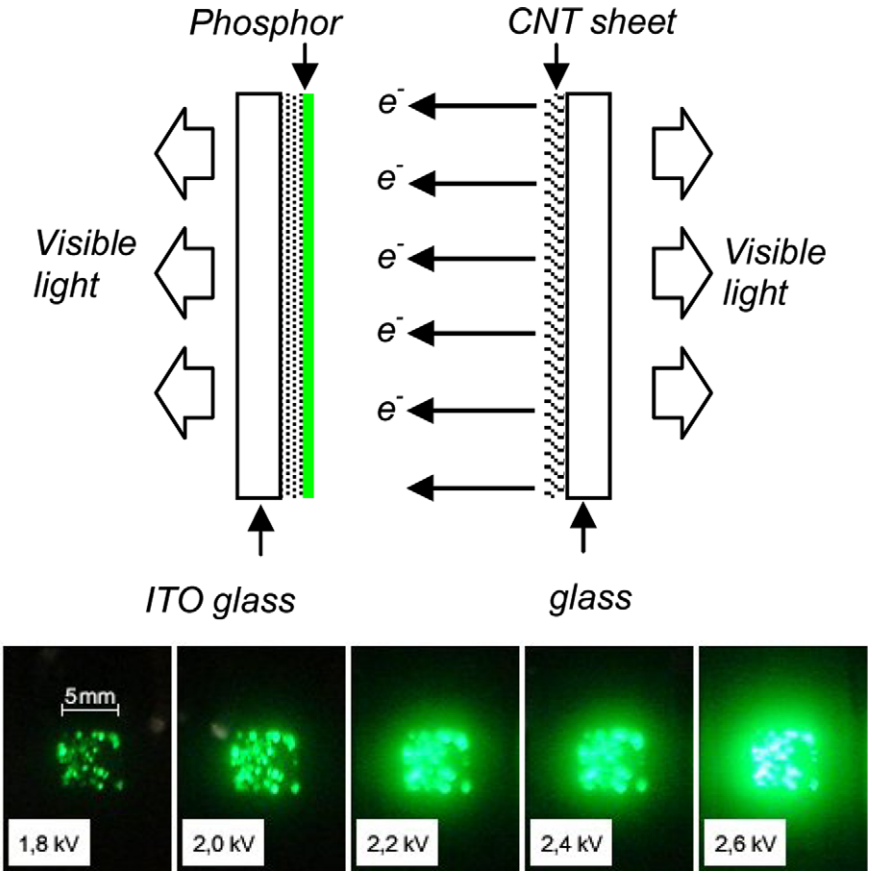

Fig. 4 – Schematic diagram of a MWCNT sheet placed in front of the phosphorous screen (top). Light patterns on the screen induced by emitted electrons (bottom). Applied voltage (with 2 mm anode–cathode distance) is indicated on each picture.

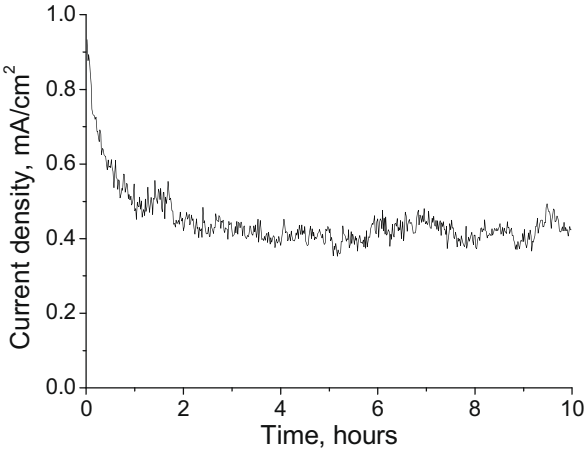

Fig. 5 – Field emission stability measurements for an applied voltage of 350 V and an inter-electrode distance of 150 μm.

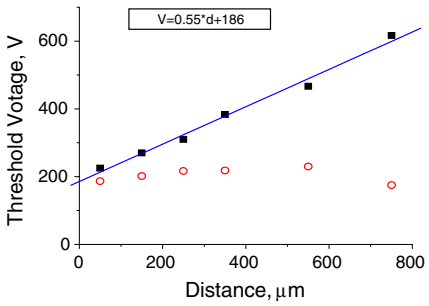

Fig. 7 – Threshold voltage vs. anode–cathode distance determined while increasing (black squares) and decreasing (red circles) applied voltage. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 6 shows the field emission current from a MWCNT sheet with an area of 0.5 cm^2 for two different anode–cathode distances, 150 μm and 350 μm. The field emission current from a transparent single-wall carbon nanotube (SWCNT) sheet produced by the floating catalyst CVD [12] method is also shown for comparison (Fig. 6b). SWCNT sheets are made of very long nanotubes (up to 1 cm) and so do not have free ends that are able to reorient in a strong field. A Fowler–Nordheim plot is shown in the inset (Fig. 6a). The field enhancement factor β calculated for the MWCNTs by assuming a work function of 5.2 eV is 3900. Furthermore, using this value and the length of a single emitting bundle (Fig. 3) one can estimate [7] the radius of the emitting tip to be approximately 5 nm, which corresponds to the radius of a single multiwalled nanotube.

MWCNT sheets exhibit hysteretic behavior and the area of hysteresis loop increases with increasing inter-electrode distance. Such behavior is not usually observed for stable field emission cathodes, unless there is degradation (see, for example, field emission from SWCNT sheet shown on Fig. 6b). However, we found that in MWCNT sheets hysteresis loops are reproducible and appear because of reversible structural changes. When applied voltage increases and electric field between cathode and anode reaches a certain "activation" value, free ends of some nanotubes get detached from the CNT bundles and rise. Because the threshold field for a nanotube tip is few times higher than for its side [6], a steep increase in the current is observed at this point. A step-like increase in the current at larger distances shows that in the beginning only a part of nanotubes rise and at increasing voltages other tubes do (Fig. 6b). For inter-electrode separations above 1 mm we have observed up to three "steps" before current saturation.

Fig. 7 shows the dependencies of the threshold voltage on the anode–cathode spacing. Threshold voltage is determined as the voltage where the FE current reaches a value of 100 nA. We used two different methods to measure *I–V* curves. In the first method we started from 0 V and increased voltage in steps of 5 V up to some maximum value (shown as black squares). In the second method we started at the maximum value and decreased the voltage to zero (shown as red circles). These two methods show very different results and help to explain the behavior of the studied sample during the emission. It is clearly seen that in the second case the threshold voltage is practically independent of the distance between

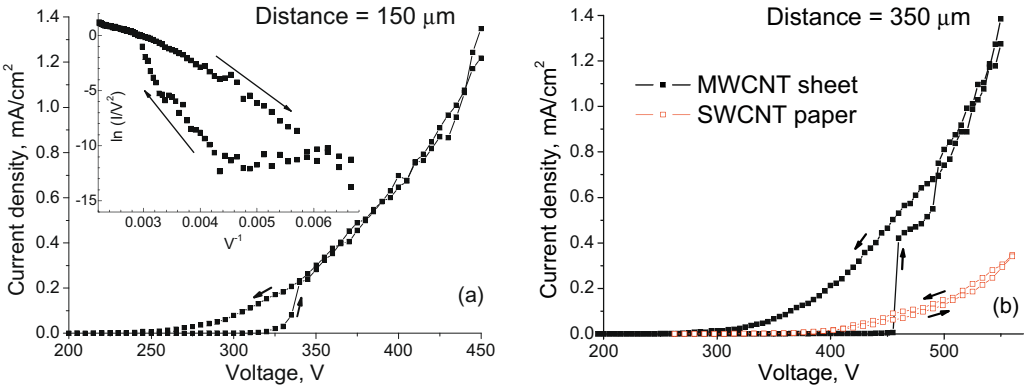

Fig. 6 – (a) Field emission from MWCNT sheet for 150 μm inter-electrode distance. The inset is a Nordheim–Fowler plot for this data. (b) Hysteretic and step-like field emission from MWCNT (solid squares) as compared to smooth field emission from SWCNT sheets (open circles) for 350 μm inter-electrode distance.

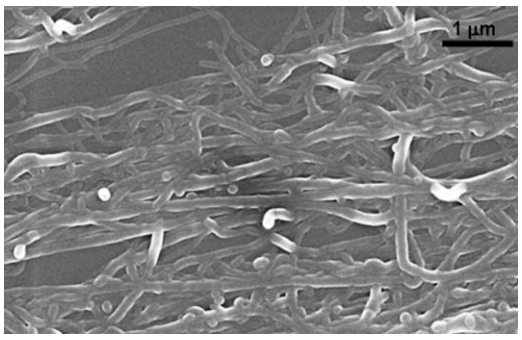

Fig. 8 – MWCNT sheet with amorphous carbon deposited on it.

the anode and the cathode. Contrary to this, the threshold voltage, measured by the first method (black dots), increases with the distance. It is described by the relationship

$$V_{thr} = E \cdot d + V_0,$$

where E determines the threshold field and V_0 is the initial voltage when electron emission occurs from the CNT sheet. The value of V_0 is approximately the same as the constant value obtained by the other method. For different samples the threshold field varies from 0.25 to 0.8 V/μm, depending on the properties of the given CNT sheet, such as its density and the length of the individual nanotubes.

When we start the experiment by applying high voltage, emitting nanotubes initially stand vertically and keep standing until the voltage is reduced to a certain value. From Fig. 7 we can see that this value does not depend on the anode–cathode spacing. Therefore, in the emitting state the MWCNT sheet is a transparent array of vertically aligned individual nanotubes. Since the emitting nanotubes are well separated from each other, the screening effect [5] is absent.

To show that bundles rise and fall under the applied electrical field, we deposited 10 nm thick amorphous carbon layer on top of the MWCNT sheet. The deposition was done by field emission induced carbon evaporation from single-wall carbon nanotube paper. The deposit welds together the bundles (Fig. 8), thus preventing them from rising. Samples with deposited carbon have several orders of magnitude lower emission currents than the original MWCNT sheets.

A schematic of the dry drawing process used to produce MWCNT sheets is shown on Fig. 9. When the MWCNT sheet is drawn from forest, vertically oriented bundles of the forest become horizontally oriented bundles in the sheet (as shown on Fig. 1a). During sheet draw smaller bundles that are present in initial forest redistribute themselves, interconnecting bigger bundles and providing a continuous drawing process. The detailed model of MWCNT sheets formation is described in [11].

MWCNT sheets can be drawn from forest of different densities and height (100–500 μm tall). These parameters influence the number of emitting nanotubes per unit area and the length of bundles. SEM images of high- and low-density sheets are shown in the Fig. 10. In general, the number of free ends of bundles is inversely proportional to the forest height, i.e., the shorter the forest the more free ends of bundles per unit area are in the drawn MWCNT sheet. Simple calculations based on the model of sheet formation [11] show that the number of free ends N per unit area is proportional to $(hL)^{-1}$, where h is forest height and L is an average distance between neighboring bundles. As a result, shorter forests have more free ends contributing to field emission, which makes field emission more uniform. Longer forests make longer bundles in sheets and ensure higher field enhance-

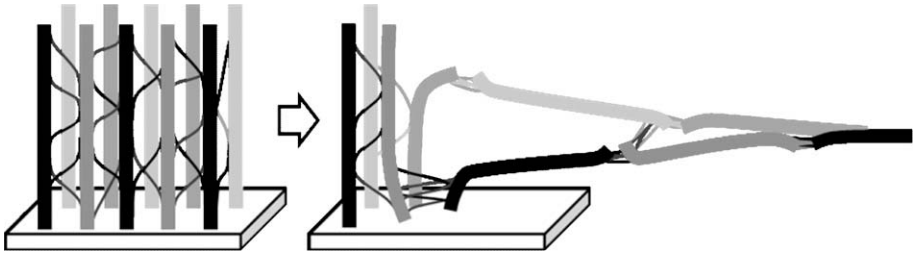

Fig. 9 – Schematic diagram of MWCNT sheets dry spinning process.

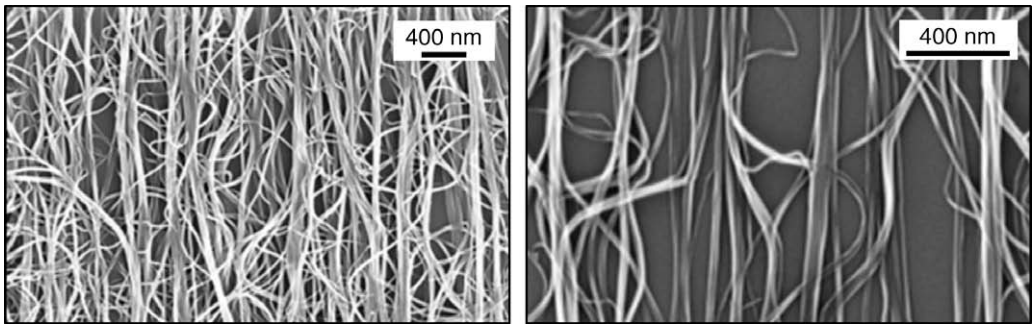

Fig. 10 – SEM images of high- and low-density MWCNT sheets.

ment factors. Therefore, by controlling the density and height of MWCNTs in the CVD-grown forest, the field emission properties of MWCNT sheets can be easily tuned during their preparation.

Conventional field emission displays comprise the plurality of separate elements: electron-emitting elements, a series of ballast resistors, conductive elements, and light-emitting elements on transparent conductive viewing screen. The transparent and conducting field-emitting MWCNT sheet combines many properties in one element and can significantly reduce the complexity of field-emissive display. Low threshold field values together with high enough field enhancement factors provide current densities up to 3 mA/cm^2, which is sufficient for display applications [9]. In addition, MWCNT sheets can be patterned by application of well known lithography methods or by laser ablation.

4. Conclusions

Electron field emission of MWCNT sheets made of well-ordered aligned arrays of multiwalled carbon nanotubes was studied. In some cases the MWCNT sheets have a very low threshold field of 0.25 V/μm. All of the studied samples have very high current densities and steep *I*–*V* curves.

If used as a cathode for phosphorescent screens, CNT sheets show rather bright and uniform light emission. Stability measurements demonstrate 2–2.5 times initial decrease in current and no significant changes later on. The proposed field emitter and the technique of its preparation overcome the problem of CNT emitter contamination in existing devices. Such multifunctional MWCNT transparent sheets can be used as a high current, high stability, transparent, flexible field emission sources that provide the additional benefits of optimal electrical connection and pixel addressing in displays with inverted geometry. Additionally, the light polarizing capabilities of the nanotube sheets can be utilized.

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