Field electron emission of double walled carbon nanotube film prepared by drop casting method

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Abstract

Thick films of double walled carbon nanotubes (DWCN) were deposited on indium-tin-oxide (ITO) coated glass substrates by drop casting method and were studied for their field electron emission property in a parallel plate configuration using bare ITO coated glass as counter electrode. They show excellent field electron emission property with low turn-on-field of about 0.8 V/μm and threshold field of about 1.8 V/μm. Field enhancement factor calculated from the non-saturated region of the FN plot is about 1715. Field electron emission current was observed to be stable up to 3000 min, indicating thereby that DWCNs are excellent electron emitters with appreciable stable performance.

Keywords: Double walled carbon nanotubes; Field electron emission

1. Introduction

Carbon nanotubes (CN) and nanofibers (CNF) exhibit excellent field electron emission characteristics because of their unique properties such as high aspect ratio, small tip radius of curvature, high conductivity together with chemical inertness and mechanical strength and have potential applications in flat panel displays, X-ray sources etc. [1–9]. Much of the efforts have been concentrated on enhancing the field electron emission (FEE) efficiency and to decrease the threshold electric field (E_{th}). For practical use, it is required to satisfy both requirements of low E_{th} with good field electron emission uniformity and stability. Field electron emission current generally decreases with the operation time, mainly due to the damage of emitter tips induced by the bombardment of ionized residual gas molecules. Once, the emitting tips are damaged, they do not contribute any more to the intense electron emission. This is why, ultra-high vacuum (UHV), usually lower than 10^{-6} Pa, is required for stable and long term application. However, such UHV condition is unrealistic for the practical application view point and tough emitters with a long life time operation under lower vacuum condition should be developed. Single walled carbon nanotubes (SWCNs) are shown to have better field electron emission properties than multiwalled carbon nanotubes (MWCNs), because of their smaller tip size [8,9]. Double walled carbon nanotubes (DWCNs) are one of the important member of the carbon nanotubes family and is predicted to have superior properties than SWCNs and MWCNs [10]. Recent study of field

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electron emission of DWCNs have shown that DWCNs and SWCNs have similar threshold fields, but DWCNs have much longer lifetime than SWCNs [Refs. cited in 10]. This may be because of their better thermal stability which results from their high crystallinity. Moreover, to realize field electron emission displays (FEEDs) using carbon nanotubes, it is necessary to develop a low cost, simple process that is applicable to large area and amenable for mass production. In past, carbon nanotubes based field emitters have been fabricated by various methods such as screen printing [11–13], spray method [14], direct growth [15], suspension-filtering [8] and electrophoresis [16].

In the present work undertaken, we study the field electron emission and its stability (for a period of 3000 min) of DWCNs film deposited on indium-tin-oxide (ITO) coated glass substrates by drop casting method. Moreover, no binder has been used and the films deposited are only of pure DWCNs. Such films are observed to have good adhesion with the substrate. Stable and excellent field electron emission has been observed from such films with a field enhancement factor of about 1715. Our results indicate that the simple drop casting method is also promising for large area deposition of DWCN films for field electron emission application.

2. Experimental part

DWCNs are synthesised in gram-scale by catalytic chemical vapour deposition (CCVD) of a mixture of CH_4 in H_2 on a MgO-based catalyst at 1000°C. The main interest of MgO-based catalysts is to be easily removable after the CCVD step, by dissolution in HCl. The catalyst, which can be written as $Mg_{0.99}(Co_{0.0075}Mo_{0.0025})O$, was prepared by combustion synthesis. Magnesium and cobalt nitrates were dissolved in deionised water and the required amount of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ was added to the solution. Citric acid was used as the fuel, using the stoichiometric proportion. For each experiment, 1.5 g of the starting oxide was reduced in a H_2–CH_4 mixture (18 mol.% CH_4, heating and cooling rates 5 °C/min, maximum temperature 1000 °C, no dwell). This resulted in a mat of composite powder (which density depended on the composition of the catalyst), which was then treated with a concentrated aqueous HCl solution (12 M) to separate the DWCNs by dissolving all the remaining oxide material, as well as unprotected metal particles . The suspensions were filtered and washed on cellulose nitrate membranes (Whatman, 0.45 μm) with deionised water until neutrality [17,18].

DWCNs are studied by high resolution transmission electron microscopy (HR-TEM) using JEOL 2100F field emission–transmission electron microscope operated at 200 kV and by visible Raman spectroscopy using 488 nm excitation.

DWCNs are dispersed in chloroform and sonicated for several days. Thick film of DWCNs is deposited on ITO coated glass substrates (100 Ω/cm^2) from the chloroform dispersion by drop casting method. Field electron emission measurements were done in a parallel plate configuration at a typical working pressure of 1×10^{-5} Pa. Bare ITO coated glass is used as an anode which was separated by 100 μm from the sample by Teflon spacers. The total emission area was about 0.2 cm^2. Stability of the field electron emission is studied at an applied field of 3 V/μm over a period of 3000 min by measuring the current in the external circuit.

3. Results and discussion

Fig. 1a and b shows the HR-TEM images of DWCNs. Many DWCNs are clearly visible in the images. Two tubes – one inside another are observable. Inset of Fig. 1a and b shows the intensity pattern along the line marked in the respective figures. Outer and inner diameters of DWCNs can be calculated using these intensity patterns. Intensity pattern shown in Fig. 1a yields an outer diameter of about 3.35 nm while an inner diameter of about 2.5 nm. Similarly,

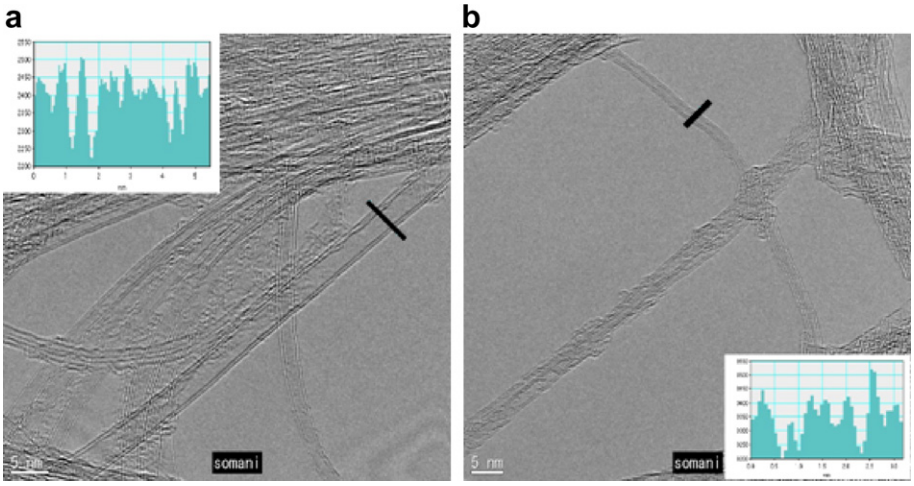

Fig. 1. HR-TEM images of DWCN. Inset shows intensity pattern along the line marked.

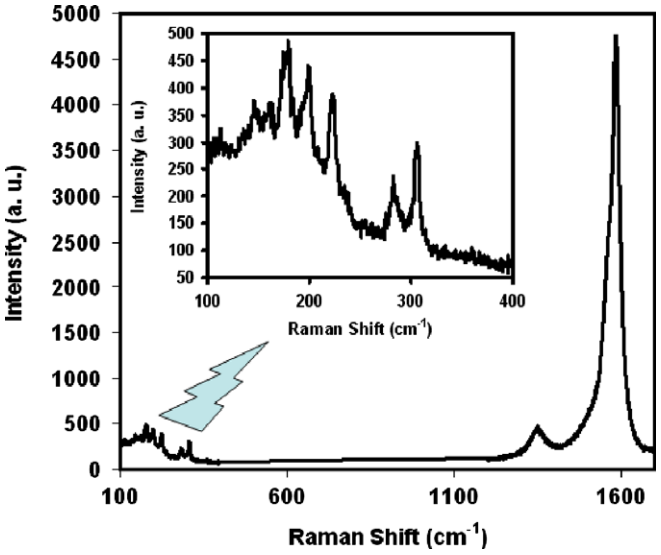

Fig. 2. Raman spectra of the DWCN. Inset shows the magnified view of the Raman spectra in the low frequency region (Radial breathing mode).

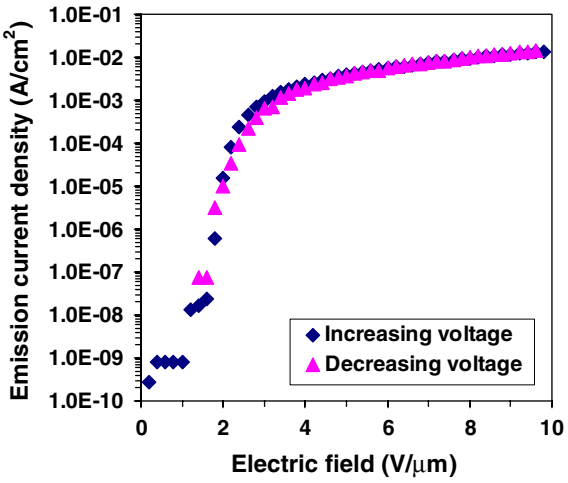

Fig. 4a. Variation of Emission current density (A/cm^2) vs. electric field (V/μm) for DWCN drop cast film on ITO with increasing and decreasing applied field.

from Fig. 1b, outer and inner diameters estimated are about 2.1 nm and 1.3 nm, respectively. Study of different TEM images of DWCNs indicates that the outer diameter is between 2.1 nm and 3.4 nm while the inner diameter ranges between 1.3 nm and 2.5 nm. Nevertheless, DWCNs are observed to be free from any metallic and other impurities. Fig. 2 shows the Raman spectra of the DWCN sample. Intense G-peak is centered at 1582.6 cm^{-1} while a weak D-peak is observable centered at about 1343 cm^{-1}; indicating their by that DWCNs have good graphitization and less amount of defects which may arise from the incorporation of pentagons, heptagons etc. Along with these, radial breathing mode peaks in the lower frequency region are also observable centered at 304.5 cm^{-1}, 283.2 cm^{-1}, 225.3 cm^{-1}, 199 cm^{-1}, 176.7 cm^{-1} and 146 cm^{-1} and are discussed in details earlier [17,18]. Fig. 3 shows the electron spin resonance (ESR) spectra of the DWCNs along with MgO:Mn^{2+} as a reference measured at room temperature (25 °C). It is observable that DWCNs are ESR silent at room temperature. This also indicates good graphitization in nanotubes with less defects and absence of dangling bonds; indicating their good quality.

Fig. 4a shows the emission current density (A/cm^2)–electric field (V/μm) characteristic of the DWCN film on ITO substrate, taken with increasing the applied field from zero to maximum and also while reducing the field from maximum to zero. It can be clearly seen that the two curves nearly matches and there is no hysteresis. The corresponding Fowler–Nordheim (FN) plot is shown in Fig. 4b. It is observable that the FN plot is not a single straight line but consists of at least two different regions with different slopes. The turn-on field and threshold field observed is about 0.8 V/μm and 1.8 V/μm, respectively. Here, the turn-on field and threshold field are defined as the fields

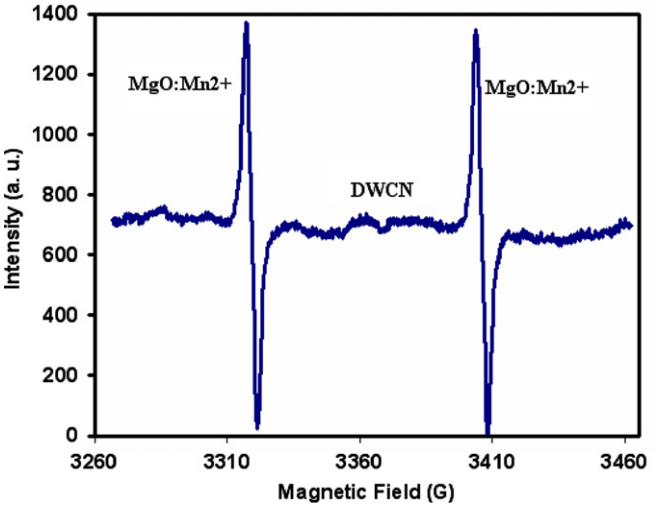

Fig. 3. ESR spectra of DWCNs at room temperature along with MgO:Mn^{2+} reference.

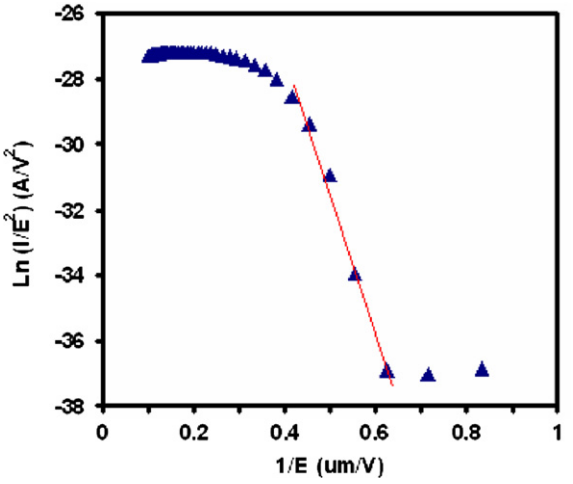

Fig. 4b. Corresponding FN plot for the DWCN film.

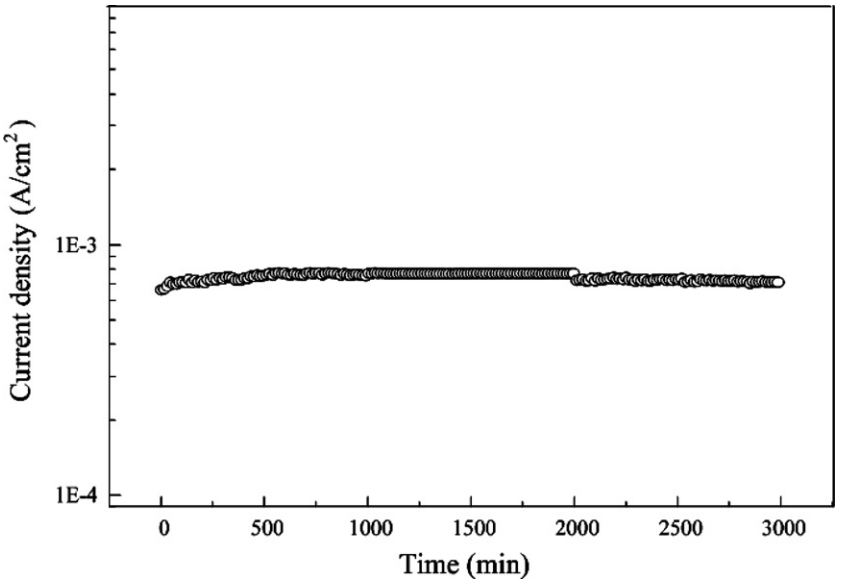

Fig. 5. Variation of field electron emitted current density (A/cm^2) with respect to time (min); indicating that DWCNs show stable performance.

at which the emission current density reaches 1 nA/cm^2 and 1 μA/cm^2, respectively. An effective field enhancement factor (β) calculated from the non-saturated FN region (using FN equation) is about 1715, assuming a work function of 5 eV and value of constant B as 6.83×10^9 eV$^{-3/2}$ V/m. In order to confirm the reproducibility of the field electron emission characteristic, current–voltage (I–V) measurements were performed at several locations. The observed I–V characteristic is almost independent of the locations, due to nearly uniform distribution of the DWCNs over the area of the sample.

Fig. 5 presents the field electron emitted current density measured over a period of 3000 min of continuous operation at an applied field of 3 V/μm. It is observable that the emission current was almost constant over this period indicating the excellent stability of DWCNs for field emission. The emission current of nanotubes decreases when the nanotubes tip attached with residual oxygen gases gets degraded by Joule heating under a high electric field. In fact the out-gassing from the electrodes is one of the main reasons of vacuum deterioration, resulting in degradation of emission currents. In the proposed approach, deposition of DWCN film by drop casting method is advantageous for high vacuum levels, since there is no organic vehicle as out gassing source, compared to conventional screen printing with paste. Also, it is shown by Machida et al. [11] that grinding time of the DWCN paste for screen printing increases the threshold voltage required to obtain a fixed amount of current and decreases field enhancement at the DWCN tip as a result that DWCNs are shortened in length by the grinding treatment. Reproducibility of the results of such a process is a question since a small change in grinding conditions can affect largely the emission properties. Also, the process involves high temperature treatment step of the screen printed DWCN paste in order to remove the organic binder. The advantage of the present proposed method of drop casting is that no such breaking of the carbon nanotubes is involved leading to reproducible emission characteristic. Almost any conducting substrate can be used to deposit the DWCN film. The present proposed method is the simplest, cost effective and can be completed within less time as compared to screen printing [11–13], spray method [14], direct growth [15], suspension-filtering [8] and electrophoresis [16] methods.

Turn-on field (corresponding to current density of 1 μA/cm^2) of screen printed DWCN film is observed to be between 1.33 V/μm and 1.78 V/μm by Lee and co-workers [12]. However, authors could not explain the difference observed in the turn-on field of different samples and speculate that the content of DWCN within the carbon nanotube paste (containing DWCN, glass frit and organic binder) and the surface morphology may play an important role in determining the field electron emission characteristic. In comparison, we observed a turn-on field (corresponding to current density of 1 μA/cm^2) of about 1.8 V/μm, which is comparable to the upper value observed by Lee and co-workers [12]. A direct comparison of results is rather difficult. Lee [19] reported the turn-on field of 1.7 V/μm which is comparable to our results.

The structural modification of the nanotubes tips by the ion bombardment of residual gases could reduce the emission current at the high electric field region. Hence, the emission current degradation rate of carbon nanotubes would depend on the physical strength of a particular carbon nanotube tip, and thus it could be concluded that the stable field electron emission of DWCNs is due to their chemical and physical stability [20].

4. Conclusion

In conclusion, we present a simple drop casting method to fabricate DWCN films. Although, in the present investi-

gations, films were deposited on ITO substrates; in principle, can be deposited on any substrate by the proposed method. These DWCN films show excellent field electron emission with low turn-on field (0.8 V/μm) and threshold field (1.8 V/μm). These values are much better than other carbon nanomaterials such as MWCNs, carbon nanofibers etc. Further, the emission current stability over a period of 3000 min indicates that DWCNs are quite stable materials. Present study suggests that DWCNs are one of the most promising materials for field electron emission applications.

Acknowledgements

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