Low-macroscopic field emission from carbon fibers synthesized by direct current plasma enhanced chemical vapour deposition

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Received 10 April 2006; revised 3 July 2006; accepted 17 July 2006

Carbon fibers, in thin film form, have been synthesized on Si substrates via direct current plasma enhanced chemical vapour deposition with acetylene as a precursor using Ni as a catalyst at substrate temperature 750-850°C. X-ray diffraction studies confirmed the graphitic phase of the carbon fibers. Surface morphologies of the films have been studied by a scanning electron microscope and an atomic force microscope. The graphitic carbon fibers have showed good field emission properties with a turn-on field lying in the range 2.57-9.71 V/μm for films deposited with different substrate temperatures. The field enhancement factor and the approximate work function have also been calculated. The emission properties have been studied for different anode-sample spacing for the carbon fibers film deposited at 850°C.

Keywords: Carbon fibers, Thin film, Field emission, Plasma
IPC Code: C03C

1 Introduction
Field emission displays (FED) and vacuum microelectronic devices have recently attracted attention for low power panel applications because of their thin profile, high production efficiency, fast response, high brightness, wide operating temperature range, possible expansion of size and excellent picture quality at a lower cost. During the last decade, the advent of low-macroscopic field (LMF) emission from carbon based films, such as diamond, diamond like carbon (DLC), amorphous carbon (a:C), carbon nanotube/nanofibers etc., made them the candidate materials for FEDs. Since the discovery of carbon nanotubes and nanofibers by Iijima in 1991, there has been explosive growth in the field of synthesis and characterization of nanotubes and nanofibers due to their remarkable properties and potential applications, such as field emission electron guns, scanning microscope probe tips, electronic circuits etc. Carbon nanotubes and nanofibers emitters are suitable, in particular, for high current-density applications in low or medium-vacuum condition due to their high-physical strength, chemical stability and high electrical and thermal conductivity. Typical examples of such high current-density applications include microwave power-amplifier tube, X-ray tube, high-luminescence light source and micro machined mass spectrometer. Although field emission property of carbon nanotubes has been widely studied during the last one decade, there are not many reports on the studies of field emission from carbon fibrous thin films. In this paper, the field emission property from carbon fibers thin film synthesized by direct current plasma CVD technique has been reported. The emission properties have been studied for different anode-sample spacings. The threshold field, field enhancement factor and approximate effective work function are calculated.

2 Experimental Details
The Ni target has been sputtered on Si substrates via dc sputtering technique to produce thin film of Ni catalyst. The target used for sputtering was a Ni plate of thickness ~1 mm with a diameter 2.5 cm (with purity 99.99%, Aldrich). For sputtering, we maintained high voltage 2.5 kV and corresponding current density was 19.5 mA cm². The sputtering was performed for 5 min, which yielded a Ni film with a thickness ~10 nm, as measured by quartz crystal thickness monitor. After deposition of the Ni film, the sample was immediately transferred into the CVD chamber where nanofibers growth has been performed. The substrate (Si) with Ni catalyst was placed on a molybdenum substrate holder, which could be directly heated. When the chamber pressure...
attained $10^{-6}$ mbar, the Mo substrate holder was started heating by sending current through it. The substrate temperature could be varied by varying the current through the Mo substrate holder, which was connected to the secondary of a step down transformer. The temperature of the substrate was measured by a disappearing filament type pyrometer (PYROPTO, IT65). Acetylene ($\text{C}_2\text{H}_2$) gas was used in PECVD process as a precursor of carbon. Acetylene ($\text{C}_2\text{H}_2$) gas was allowed to flow maintaining the CVD chamber pressure 50 mbar. Deposition was performed at 2.0 kV $dc$ supply with corresponding current density 25 mA cm$^{-2}$ for 30 min. Substrate temperature was varied from 750 to 850°C for different sets of experiment.

3 Results and Discussion

The deposited films were characterized by X-ray diffraction (XRD) using a diffractometer (Bruker D8 Advance) by Cu K$_\alpha$ radiation ($\lambda = 0.15406$ nm) operating at 40 kV, 40 mA with a normal $\theta$ - 2$\theta$ scanning. The films deposited on Si substrates showed crystalline structure as shown in Fig. 1. The spectrum showed various peaks of carbon fibers due to diffraction from (002), (100), (004) and (110) planes$^{10}$. The inter-planar spacings (3.40, 2.12, 1.71 and 1.23 Å) obtained form XRD peaks are well matched with the standard reported data$^{11}$. From the X-ray diffraction of carbon fibers (as shown in Fig. 1), the (100) and (110) peaks have been observed at 42.62$^\circ$ and 77.45$^\circ$, respectively and the inter-planar spacing ($d_{100} = 2.12$ Å and $d_{110} = 1.23$ Å) is comparable with that of graphite ($d_{100} = 2.13$ Å and $d_{110} = 1.23$ Å), which indicates that the carbon fibers and graphite have similar structures$^{12}$.

The surface morphology of the films was studied by a scanning electron microscope (SEM, JEOL-JSM-6360), Fig. 2 showed the SEM micrographs of the deposited films, which showed the existence of carbon fibers in the films. The morphologies of the
films have been changed with the change of substrate temperature. At 750°C, oval shaped particles have also been grown. At 800°C substrate temperature, fiber like structure have been grown with length ~1000 nm and the corresponding diameter ~400 nm. Finally, at 850°C substrate temperature, the best quality carbon fibers have been grown with length ~2000 nm with corresponding diameter ~400 nm. It is clear from these studies of substrate temperature variations that the morphology changes and quasi-one dimensional growth takes place at a higher substrate temperature. The thickness of the films was measured by a cross-sectional SEM measurement (not shown here) and was found to be 1.2 μm.

AFM imaging was used to analyze the surface topography of the grown carbon fibrous films. The AFM images were recorded in semi-contact mode by (AFM-NT-MDT, Solver Pro.). Fig. 3 showed the AFM images of the films deposited at 850°C substrate temperature, the grown fibers are having an average diameter ~400 nm.

Electron field emission properties of the films were also studied. The field emission properties of the films deposited on Si substrates have been studied by our high vacuum (~10⁻⁷ Torr) field emission set-up. Field emission measurements were carried out by using a diode configuration consisting of a cathode (the film under test) and a stainless steel tip anode (conical shape with a 1mm tip diameter) mounted in a liquid nitrogen trapped rotary-diffusion high vacuum chamber with an appropriate chamber baking arrangement. The measurements were performed at a base pressure of ~4×10⁻⁷ mbar. The negative terminal of the high voltage dc power supply (range is 0 to 5 kV) was connected with the films by silver paint, at least 6 mm away from the position of the anode tip. The tip-sample distance was continuously adjustable to a few hundred micrometer by a spherometric arrangement with a screw-pitch of 10 μm. The anode-sample spacing was set at a particular value by rotating the micrometer screw which served as an anode electrode. The position of just touching the anode with the sample was determined by an optical microscope and then various spacings were obtained by rotating the micrometer screw as its screw-pitch is known. The current was measured by a Keithley Electrometer (model 6514). The whole surface of the film was visible through the chamber viewport, which enabled us to recognize the electron emission and discharge, if any. It was confirmed that there was no
discharge and the current observed due to cold field emission of electron from carbon nanofibers.

Fig. 4(a) shows the emission current \( I \) versus macroscopic field \( E \) curves of carbon nanofibers thin film deposited on Si substrate for anode-sample separation \( d \) of 60 \( \mu \)m. The macroscopic field is calculated from the external voltage applied \( V \), divided by the anode-sample spacing \( d \). Theoretically, the emission current \( I \) is related to the macroscopic electric field \( E \) by:

\[
I = A a t_F^{-2} \phi^{-1} (\beta E)^2 \exp\left\{ -\frac{b v_F \phi^{3/2}}{\beta E} \right\} \quad \text{(1)}
\]

where, \( \phi \) is the local work-function, \( \beta \) the field enhancement factor, \( A \) the effective emission area, \( a \) the first Fowler-Nordheim Constant \((1.541434 \times 10^{-6} \text{ A eV V}^{-2})\), \( b \) the second F-N Constant \((6.830890 \times 10^9 \text{ eV}^{-3/2} \text{ V m}^{-1})\), and \( v_F \) and \( t_F \) are the values of the special field emission elliptic functions \( 14 \) \( v \) and \( t \), evaluated for a barrier height \( \phi \).

In so-called Fowler-Nordheim coordinates, this equation takes the form:

\[
\ln\left\{ \frac{I}{E^2} \right\} = \ln\left\{ a t_F^{-2} A a \phi^{-1} \beta^{-2} \right\} - \frac{b v_F \phi^{3/2}}{\beta E} \quad \text{(2)}
\]

An experimental F-N plot is modeled by the tangent to this curve, taken in the mid-range of the experimental data. This tangent can be written in the form \( 15 \):

\[
\ln\left\{ \frac{I}{E^2} \right\} = \ln\left\{ r A a \phi^{-1} \beta^{-2} \right\} - \frac{s b \phi^{3/2} \beta^{-1}}{E} \quad \text{(3)}
\]

where \( r \) and \( s \) are appropriate values of the intercept and slope correction factors, respectively. Typically, \( s \) is of the order of unity, but \( r \) may be of order 100 or greater. Both \( r \) and \( s \) are relatively slowly varying functions of \( I/E \), so a F-N plot (plotted as a function of \( I/E \)) is expected to be a straight line. The F-N plot of our sample is shown in Fig. 4(b). It has been observed that the \( I-E \) curve in the present work is closely fitted with straight line. This suggests that the electrons are emitted by cold field emission process. The turn-on field, which we define as the macroscopic field needed to get an emission current \( I = 0.09 \mu \text{A} \), (which corresponds to an estimated macroscopic current density, \( J_{\text{est}} = 14.5 \mu \text{A/cm}^2 \), where \( J_{\text{est}} = I/A, A = \text{anode-tip area} \) were lying in the range 2.57 to 9.71 \( \text{V/\mu m} \) for variation substrate temperature of the films. This value is quite lower than that of nanocrystalline carbon\( 16 \) (6.4 \( \text{V/\mu m} \)) and carbon nanofiber arrays (~3
V/μm) reported by Cao et al.\(^{17}\). The plots of emission current versus electric field are shown in Fig. 5(a) and the corresponding F-N plot shown in Fig. 5(b) for different electrode distance. The turn-on field was found to vary in the range 2.87 to 6.87 V/μm for a variation of anode sample spacing 80-120 μm for the carbon fibrous film deposited at 850°C.

According to the F-N plot (Fig. 4(b)), the slope \(m\) (given by Eq.\((4)\)) would represent the combined effect of work function and enhancement of local electric field and is given by

\[
m = - \frac{b \phi^{3/2}}{\beta} \quad \ldots (4)
\]

The effective work function \(\phi_C\) is related with the true work function \(\phi\) through the relation\(^{19}\) \(\phi_C = \phi / \beta^{2/3}\). Using \(\phi = 5\) eV is the work function\(^{18}\) CNF; the field enhancement factor was calculated from the slope of the F-N plot, lies in the range 8090-1945 and the corresponding effective work function \(\phi_C\) lies in the range 0.0124-0.0321 eV for films deposited with different substrate temperatures, which is comparable with CNT films\(^{19}\).

4 Conclusion

Carbon fibers in thin film form have been successfully synthesized on Si substrates via PECVD using Ni as a catalyst. The deposition temperature has been varied from 750-850°C. X-ray diffraction patterns have confirmed the graphitic phase of carbon fibers. Surface morphologies of the films have been studied by using SEM and AFM. The diameter of the carbon fibers lies in the range 400-500 nm. Carbon fibrous film has showed good electron field emission properties with a low turn-on field. The turn-on field lying in the range 2.57-9.71 V/μm for films deposited with different substrate temperature (750-850°C) and for an anode-sample separation (\(d\)) of 60 μm. The turn-on field was found to vary in the range 2.87-6.87 V/μm for a variation of anode sample spacing 80-120 μm for the carbon fibrous film deposited at 850°C. Approximately calculated effective work function lies in the range 0.0124-0.0321 eV and field enhancement factor becomes 8090. This study shows that carbon fibrous films might become good candidates for low-threshold field emitter, among other applications.

Acknowledgement

The authors wish to acknowledge the financial support by the University Grants Commission (UGC), New Delhi, Govt. of India, under the University with Potential for Excellence Scheme during the execution of the work.

References

12. JCPDS data file no. 00-013-0148.