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Electron field emission from room temperature grown carbon nanofibres

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Abstract

The observation of electron emission from room temperature deposited carbon nanofibres at low applied electric fields (~5 V/μm) is reported. The nanofibres were grown using methane as a source gas in conventional plasma enhanced chemical vapor deposition reactor over a Ni catalyst at room temperature. Scanning electron microscopy images of the nanofibres show them to possess an average diameter of 300 nm and that the nanofibres are radially dispersed over an area of 40 μm in diameter. A Fowler-Nordheim analysis of the field emission characteristics shows that for a work function of 5 eV a field enhancement factor of 4200 is measured. We believe that the electron emission from these nanostructures at low applied fields is due field enhancement at the tips rather than from the surrounding amorphous carbon film that has a much higher threshold field (> 20 V/μm) for emission.

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Since the identification of carbon nanotubes (CNTs) [1] in 1991, there has been considerable interest in their field emission (FE) properties with the observation of electron emission at low applied electric fields. [2] The ease of deposition over large areas has encouraged the belief that field emission displays (FEDs) utilising carbon nanotubes as emitters can be an alternative technology for the next generation of flat panel displays. [3] It has been shown that carbon nanotubes can now be easily deposited over areas only limited by the size of deposition reactor but that chemical vapour deposition is conventionally done at relatively high temperatures. Such nanotip based emitters possess a distinct advantage over current FED technology, such as Spindt tips, which require complex fabrication processing. Whilst electron emission is possible from a single nanotube, for practical applications needing suitable current densities, films or mats consisting of bundles of tubes are required. [4] It is also possible to observe electron emission from CNTs embedded in polymer matrix. [5] However, field emission from nanotip materials is not just confined to CNTs, but has been observed from a wide variety of material systems such as SiC nanowires [6], MoO_3 nanobelts [7], tungsten nanowires [8] and copper sulphide nanowire arrays [9]. These studies have shown that considerable effort is being placed into developing alternative nanotip based emitter materials. In this regard the recent report of the growth of carbon nanofibres (CNFs) at room temperature is significant. [10] This recent observation opens the possibility of the growth of an emitter material at *low temperatures* thereby allowing the potential use of plastic substrates. These CNFs were deposited using the standard and mature technique of plasma enhanced chemical vapour deposition. In this letter we report on the field emission measurements of room temperature deposited carbon nanofibres. A correlation between the FE characteristics and the structure of the material is

presented and demonstrate that CNFs may be an alternative flat cathode material for large area FEDs.

Glass slide substrates were cleaned using a standard three stage chemical bath process on to which a thin layer of Ni was evaporated. The Ni film was subsequently treated to an Ar ion plasma of 100 sccm for 30 minutes at room temperature in a Plasma Technology DP800 capacitively coupled rf plasma enhanced chemical vapour deposition (PECVD) reaction chamber. A process pressure of 200 mTorr and a rf power of 300 W was used. The surface of the film was examined using a Hitachi S4000 cold field emission scanning electron microscope (SEM) and shows the interaction of the Ni with the plasma causes a roughening of the film surface as shown by the circular features of Fig. 1(a). These features are of approximately 3 μm diameter and are surrounded by smaller circular islands of less than 500 nm in diameter as can be observed in the higher magnification image shown in Fig. 1(b). The roughened film possesses numerous round sites, but it is the smaller sites of Fig 1(b) which we believe act as growth sites for nanofibre growth. Nanofibre growth was performed in the same reactor chamber, in which CH_4 was introduced at a flow rate of 30 sccm and a pressure of 1 Torr. The reverse power of the plasma was continually adjusted to keep it as close to zero as possible in order to prevent substantial substrate heating. The water cooled substrate table temperature was monitored to be about 30^oC throughout the deposition. Both the Ar ion treatment and CH_4 growth were carried out on the earthed electrode.

An SEM image of the surface after CH_4 deposition shows the growth structure of the nanofibres, arranged radially in clusters forming star shaped objects, approximately 50 μm across as shown in Fig. 2(a). Towards the centre of the cluster a higher concentration of fibres with diameters of 100 – 400 nm are observed. Such small structures are referred to here as

carbon nanofibres rather than the related CNTs which often possess much smaller diameters. The carbon nanofibres are observed to have well defined features including a rounded tip and a cylindrical shape as evidenced from a high resolution SEM of a group of nanofibres on the outside edge of the star structure shown in Fig. 2(a). Due to the tilt of the sample when the SEM analysis was carried out and the fact that the emissive electrons are analogous to light, we see light and dark regions of the encircled fibre of Fig. 2(b), confirming a three dimensional cylindrical shape.

The field emission characteristics of the CNFs were examined using a sphere-to-plane electrode geometry with a 5 mm stainless steel ball bearing suspended above the sample with a high positive potential applied in a vacuum of around 10^{-6} Torr. Although a spherical anode is used it is assumed that the electric field between the anode and the surface of the sample can be modelled as a parallel plate due to the large radius of the anode with respect to the nanofibre structure size. The voltage is stepped up and down four times in 20 V increments and the macroscopic electric field is defined as the applied voltage divided by the anode-cathode separation. Further details about the experimental set-up can be found elsewhere. [11] The threshold field, E_{th}, is defined as the macroscopic electric field, which gives an emission current of 1 nA. The sample deposited at room temperature displayed excellent emission characteristics with a threshold field of 5 V/μm as shown in Fig. 3(a). The results show a uniform increase in emission current when the applied electric field is increased with a maximum current of 10^{-6} A observed at a field of 30 V/μm. The first two current-voltage characteristics are presented and no significant difference between the two I-E characteristics is apparent. This implies that there is no need for a "conditioning" required for the onset of stable and reproducible emission which is in contrast to what has been reported in amorphous carbon

(*a*-C) thin film. [12] In addition, there is no evidence of hysteresis behaviour between the upward and downward cycle of either I-E characteristic. This is an important result since any spread in the I-E characteristic could mean more complicated and expensive drive circuitry of a nanofibre based field emission display.

To exclude the possibility of emission from the roughened Ni film substrate, the emission characteristics prior to CH_4 deposition was also tested. The results of the measurements revealed only background noise (<20 pA) and confirms the emission observed in Fig. 3 is due to the carbon growth stage. To confirm that the observed emission is from the CNF rather than the surrounding amorphous carbon film, the FE characteristics of an area on the same sample that did not possess CNFs was tested by moving the probe anode.

The FE results, illustrated in Fig. 3(b), show the difference in field emission characteristics from that of Fig 3(a). Firstly, the threshold field for this part of the sample can be seen to be approximately 20 V/μm, higher than reported previously and has a peak emission current of 10^{-8} A, lower than the peak current of 10^{-6} A seen in Fig 3(a). Secondly it is apparent there is a definite hysteresis between the upward and downward cycle of the electric fields consistent with conditioning cycle, sometimes found in results from a-C films [12]. From these results we believe that the FE reported in Fig.3 (a) comes from the CNFs.

An analysis of the electron field emission I-E characteristics presented in Fig. 3(a) was performed using the standard Fowler-Nordheim (F-N) equation,

$$I = \frac{aA\beta^2 E^2}{\Phi} \exp\left(\frac{-b\Phi^{3/2}}{\beta E}\right), \qquad (1)$$

where *a* and *b* are constants, A is the emission area, Φ is the emission barrier and βE represents the *local* electric field. In this context β represents the field enhancement factor. [13] The inset in Fig. 3(a) shows the I-E characteristic of the first (upward) field cycle plotted in the usual F-N

coordinates. The slope of the line is $-\frac{b\Phi^{3/2}}{\beta}$ and for a work function (barrier height) of 5 eV, a value of 4200 is found for the field enhancement factor. Although some caution must be exercised in this analysis since there will be a distribution of field enhancement factors due to the different local work functions, a distribution in nanofibre lengths, radii and screening, we believe that the electron emission from the structure at the low applied field was primarily from the nanofibre structures as the surrounding amorphous carbon film has a much higher threshold field of approximately 20 V/μm. However, the high value of β obtained is consistent with a tip emission mechanism.

In conclusion carbon nanofibres were grown by plasma enhanced chemical vapour deposition of CH_4 at room temperature on Ni catalysed glass substrates. The observed structures displayed excellent electron field emission with a low threshold field of 5 V/μm. A Fowler-Nordheim analysis gives rise to a high field enhancement factor consistent with a tip controlled emission mechanism.

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Figure captions

Figure 1. (a) Scanning electron microscope image of the Ni film after Ar^+ treatment. A roughening of the film surface was observed with the formation of 3 m circular features. (b) Higher magnification image of that of part (a), smaller circular feature of diameter >500 nm are observed surrounding the larger features.

Figure 2. (a) SEM image of nanofibres grown at room temperature by plasma enhanced chemical vapour deposition. The structures grow out from a central point to form star shapes consisting of many fibres. (b) Higher magnification SEM image of a group of nanofibres, orientated with each other. The nanofibres have a diameter of about 0.3 μm with rounded tips

Figure 3. (a) First (○) and second (■) field emission I-E characteristics for the nanofibre sample. The threshold field (for 1 nA) can be seen as 5 V/μm. Inset: Fowler-Nordheim analysis of the field emission I-E data of that of the first upward cycle of the voltage (field) from part (a). (b) First (△) and second (◆) field emission I-E characteristics for the surrounding amorphous carbon area where hysteresis can be seen in both curves. The threshold field can be seen as 20 V/μm.

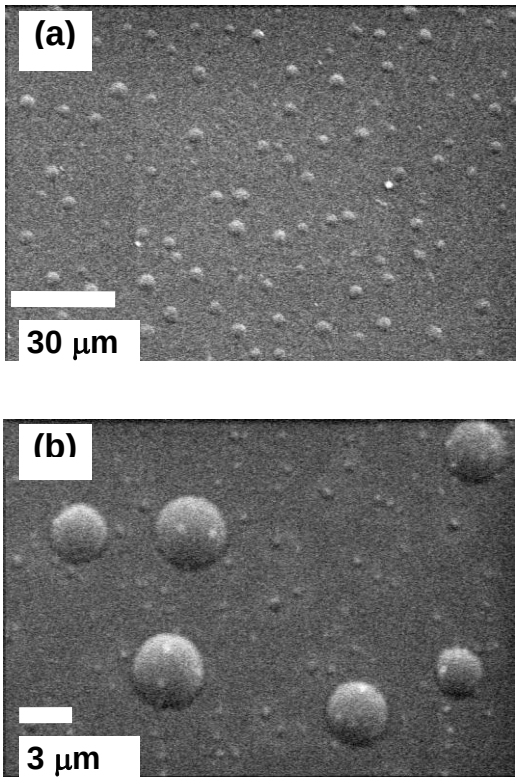

Figure 1 **Smith et al.**

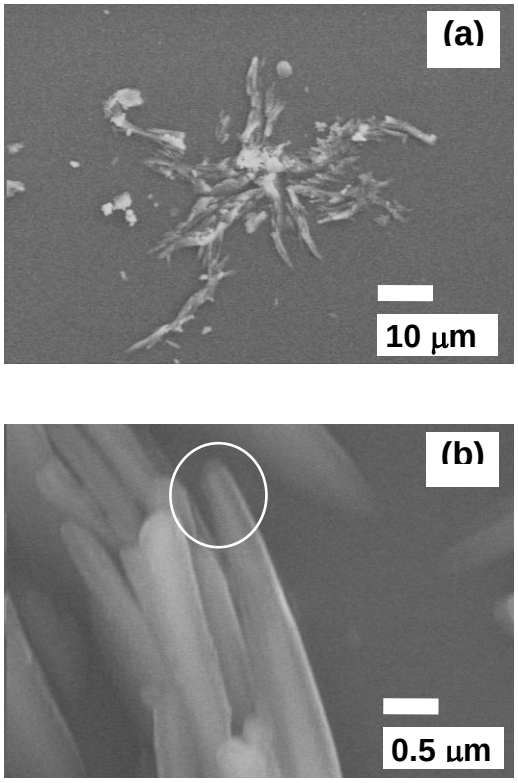

Figure 2 **Smith et al.**

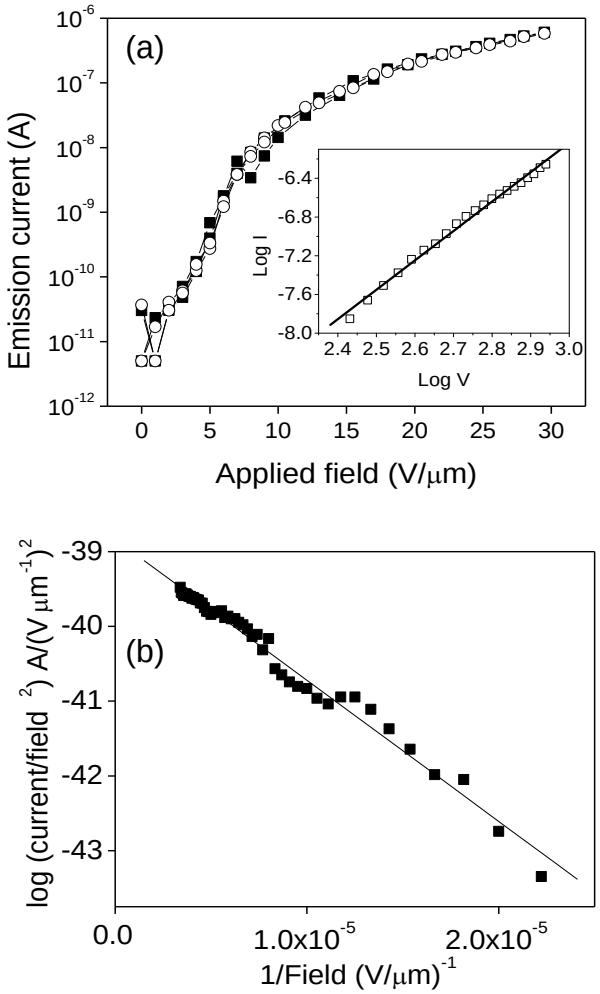

Figure 3 **Smith et al.**

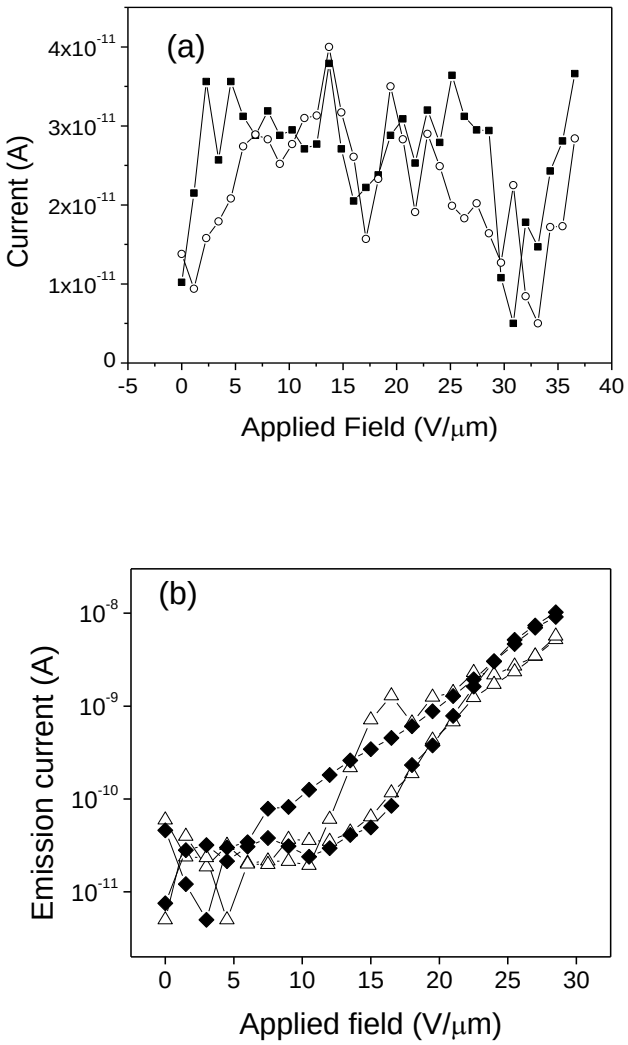

Figure 4 **Smith et al.**