Field Emission from Multi-Walled Carbon Nanotubes

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Abstract. Films of multi-walled carbon nanotubes are very efficient cathodes for field emission devices. Films are grown by thermal chemical vapour deposition on silicon substrates with iron as a catalyst particle. Different types of films are investigated: vertically aligned MWNT with clean and coated nanotube sidewalls. SEM, TEM and Raman spectroscopy has been used in order to determine the structure of the different films. The results show that the aligned MWNT films have excellent field emission properties with high emission current densities and low turn-on and threshold fields. They also show that the presence of a surface coating with amorphous carbon has no impact on the efficiency of the field emission.

The current density as a function of applied electric field (on multiple cycles) is reproducible up to a value of 1 mA/cm^2. Exceeding this value leads to light emission from the carbon nanotube film at the investigated spot. Spectral measurements of this light shows a purely blackbody radiation effect with a temperature around 1550 K for the onset current density but temperatures over 2000 K are also seen for higher current densities. In addition, there is a strong correlation between the light intensity and the current density.

INTRODUCTION

Among all interesting properties of carbon nanotubes their very high efficiency for electron field emission is of high technological relevance [1]. Producing carbon nanotubes using a thermal CVD method gives the possibility to make larger areas of aligned and non-aligned films with different quality depending on the production parameters such as the temperature, flow rate etc. [2]. This has been used in order to produce prototype flat panel displays [3]. In this report films of aligned MWNT are grown with different quality and later on compared with their efficiency for field emission. For high field emission current densities we have also observed light emission from the film of carbon nanotubes. The spectral measurements of this light report results that correlates very well with what other groups recently have reported [4]. But our spectral measurements are on the other hand, very different from what the first observations from other groups showed [5, 6].

EXPERIMENTAL

Films of aligned MWNT are grown on silicon substrates at a temperature of 750 °C with iron as catalyst particle and using acetylene as the carbon feedstock. The growth time for the two different films of aligned carbon nanotubes was 30 min for the clean and 3 hours for the coated film [7]. The characterisation of the films was made by electron microscope techniques and Raman spectroscopy. Field emission measurements were carried out using a stainless steel anode with a hemispherical tip with a radius of 2 mm at a distance of 100 µm from the nanotube film and a negative bias on the nanotube film. The emitted light that was observed for high current densities was imaged onto a spectrograph slit and analysed by an optical multichannel analyser.

RESULT AND DISCUSSION

Combining the information from the electron microscope pictures, Raman spectroscopy and the field emission properties we can see that the presence of a surface coating has no effect on the field emission current density, fig. 1 (left). A closer investigation of the same films of aligned carbon nanotubes shows that the current density as a function of the applied electric field is reproducible up to a value of 1 mA/cm^2 and can be cycled many times. However, as soon as the applied field is increased to induce an emission current density $J > 1$ mA/cm^2 the emission characteristics are no longer reversible and higher applied fields are required to produce the same emission current on subsequent cycles. This behaviour has been reported before [7]. The change in the field emission behaviour at approx. 1 mA/cm^2 is accompanied by the onset of visible light emission from the nanotube film. This value corresponds also to the point where there is a noticeable change in the slope of the Fowler-Nordheim plot [8] indicating that the local field conditions at the top of the

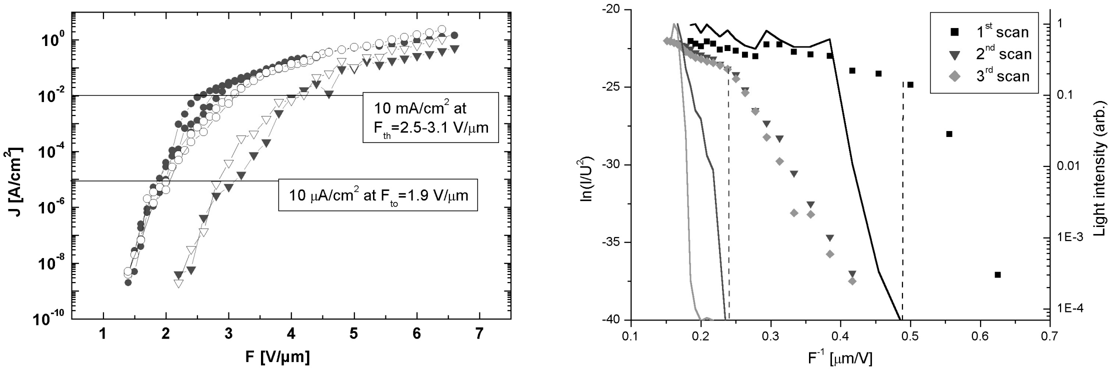

FIGURE 1. Left: Field emission current density as a function of the applied electric field for the clean (open symbols) and coated (closed symbols) films. Triangles: voltage scans after high current density operations. Right: Fowler-Nordheim plot. Full lines correspond to data from the light intensity. The threshold for light emission correlates well with the change in the slope of the F-N plot.

nanotube film have changed. This is seen in fig. 1 (right) where a Fowler-Nordheim plot for three voltage scans is plotted. In the same figure the logarithm of the integrated light intensity is shown versus the applied electric field. One can see here that the light intensity correlates very well with the current density and that the onset of the light intensity corresponds to the point where a drastic change in the slope of the F-N plot occurs.

Light emission during field emission from carbon nanotubes has been reported before [5, 6] and these results shows broad luminescence peaks in the visible range. More recently, electron energy distributions from individual multi-walled nanotubes have provided evidence for Joule heating [4], with light being emitted under conditions for which the electron energy distributions imply temperatures of 1500 K and above, however the spectral distribution of the emitted light was not studied. Spectral measurements of the emitted light from our sample are shown in fig. 2. The data provide very strong evidence for a thermal mechanism for light emission with no evidence of the luminescence peaks reported by others [5, 6]. The spectra closely follow black-body distributions and the temperatures obtained from the fit of the data to the Planck black-body formula are given in the figure. The results are in good agreement with the observations of Purcell [4].

Further evidence for the role of resistive heating can be obtained from considering the relationship between the total emitted light intensity and the field emission current

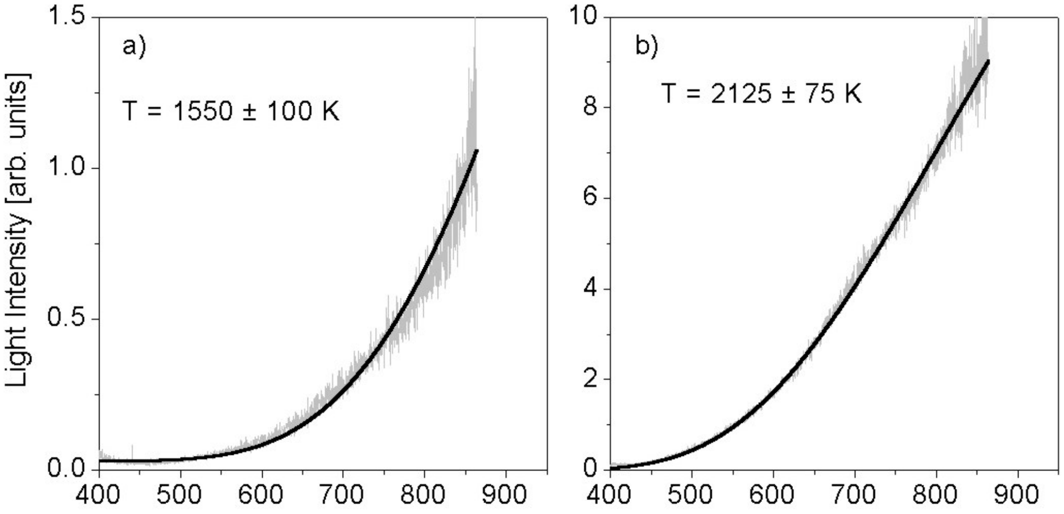

FIGURE 2. (a) shows the spectrum in the range 400-900 nm obtained at the threshold for visible light emission (1 mA/cm^2) which corresponds to a temperature of 1550 ± 100 K. This is in excellent agreement with the observations of Purcell et al concerning the electron temperature at which light is first observed from individual multi-walled nanotubes in their experiments (1500 K). Spectra b) is taken at a current density of 10 mA/cm^2 demonstrating a temperature around 2100 K.

density [9]. The total integrated intensity of Planck black-body radiation scales as T^4. In our experimental set-up we are only able to detect light in the wavelength range 350-900 nm. For a temperature range of ca. 1000 – 2800 K, relevant for the present studies, the detectable black-body intensity in our experimentally accessible wavelength range actually scales to a good approximation as T^8. Thus, the temperature of our emitters should scale with $I_{Light}^{1/8}$. On the other hand, the temperature (power) due to Joule heating scales as J^2. If our observed light emission has its origins in Joule heating, then a plot of $I_{Light}^{1/8}$ vs. J^2 should show straight-line behaviour. The first voltage scan does not show the expected correlation. This can be explained due to the fact that we have desorption of adsorbates combined with thermal annealing and/or thermal destruction of some tubes. However subsequent scans do indeed show linear behaviour providing conclusive evidence that the light emission is due to Joule heating and confirming the conclusions drawn by Purcell et al. from their electron energy measurements on individual multi-walled nanotubes.

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