Electron field emission from cluster-assembled carbon thin films

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Abstract. – Cluster-assembled carbon films deposited at room temperature from a supersonic cluster beam are found to be good electron field emitters. The films have been characterized by Raman spectroscopy showing a largely sp^2 bonded character. Scanning Electron Microscopy shows that the films have a low-density granular structure, characterized by voids on the nanoscale. We have observed a threshold field of 0.75 V/μm for an emission current density of 1 μA/cm^2, among the lowest values reported for a carbon phase. The observed field emission characteristics suggest that this nanostructured material may be interesting for flat panel display applications.

The realization of high-performance vacuum microelectronic devices and flat panel displays requires cold cathode emitters providing intense and stable electron beams. Electron field emission (FE), on which cold cathode are based, consists of the injection of electrons from a solid into vacuum through a potential barrier at its surface. By applying an accelerating electric field, this barrier can be decreased in height and width, enhancing the electron emission. To achieve FE at macroscopic electric fields reasonably low for practical applications, arrays of sharp tips of Mo or Si are used [1]. Since reliable fabrication of microtip arrays over large area is difficult, films of materials with low electron affinity have been proposed as a viable solution for the production of FE displays [1].

Field emission occurs relatively easily from various carbon-based films, such as diamond [2, 3], nanocrystalline diamond [4-6], diamond-like carbon [7], and hydrocarbon polymers [8]. It

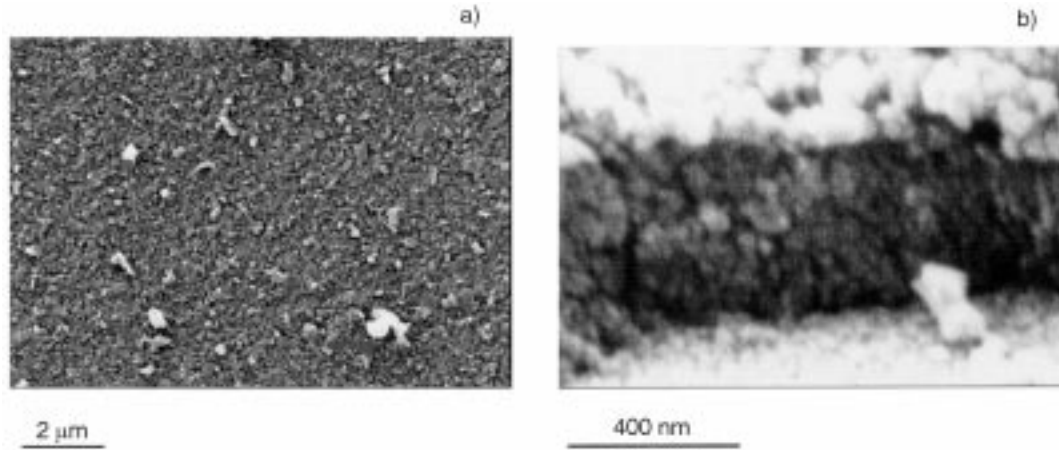_____

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Fig. 1. – Scanning Electron Microscope cross-section of cluster-assembled carbon films. a) Surface; b) cross-section.

has been recently shown that carbon nanotubes are also good field emission materials [9-13]. Although the emission mechanism of carbon-based materials is still under debate [14], these experimental results suggest that better field emission comes from more complex forms of carbon, with both sp^3 and sp^2 bonding and often having structure at the nanoscale [15].

This paper reports the first field emission studies of nanostructured carbon films produced by depositing supersonic carbon cluster beams generated by a pulsed plasma cluster source [16]. This method produces low-density, porous films with a grain size of a few nanometers. The films are mainly sp^2 and retain the structure of the precursor clusters.

Nanostructured films with an area of 0.5 cm^2 and thicknesses ranging from 40 to 80 nm were prepared by depositing a supersonic beam of clusters onto n^{++}-type Si(100) substrates at room temperature. The cluster beam is produced by a pulsed cluster source which consists of a discharge between two graphite electrodes fired into a pulse of helium delivered by a solenoid valve [16,17]. The carbon plasma mixes with the helium and is thermalized in a condensation cavity. The He-C cluster mixture then expands in the vacuum through a nozzle to form a supersonic beam with a velocity of about 1800 m/s and a Mach number of ~ 10. The high sputtering efficiency of the source coupled with the high degree of beam collimation attainable in a supersonic regime gives deposition rates of up to 1 nm/s on the beam axis.

In typical discharge conditions, the beam has a log-normal cluster mass distribution in the range 1–1500 atoms/cluster, with a maximum at ~ 400 atoms/cluster and a mean of ~ 950 atoms/cluster. The clusters have a kinetic energy of under 0.2 eV/atom, well below the binding energy of atoms in the cluster. Consequently, there is little fragmentation when the cluster hits the surface, and the clusters in the films largely retain their original structure [17].

Figure 1 shows a SEM micrograph of the surface and the cross-section of a cluster-assembled carbon film. The film has voids on a nanoscale, consistent with the low density of $\sim 1 \, \mathrm{g\,cm^{-3}}$ found by X-Ray Reflectivity [18,19]. The roughness evolution, characterised with Scanning Electron Microscopy and Atomic Force Microscopy, indicates that the surface is self-affine [19].

Experimental and theoretical investigations find that small carbon clusters (< 40 atoms) have chain or ring structures [20,21], whereas larger clusters as used here tend to form three-dimensional, cage-like structures with sp^2 bonding. We have performed Raman spectroscopy in order to characterize the nanostructure of the films (fig. 2). Unpolarized Raman spectra
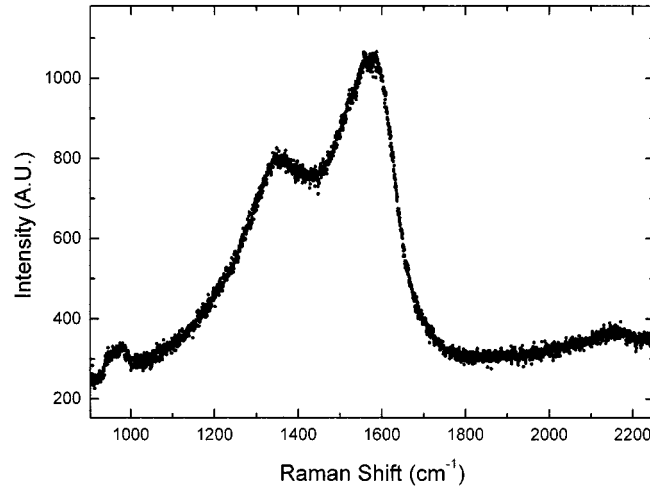
Fig. 2. – Raman spectrum of cluster-assembled carbon films.

were recorded *ex situ* at room temperature in backscattering geometry for 514.5 excitation, using a Jobin-Yvon T64000 spectrometer coupled with a notch filter. Care was taken to avoid damaging the sample by the laser excitation. No significant difference is found for the Raman spectra of films deposited in the same condition but with different thicknesses. The prominent D band and the position of the G peak (1573 cm^{-1}) of the film show an ordering of the sp^2 phase towards microcrystalline graphite. However, the G and D Raman bands are rather broad, so the cluster size can no longer be safely derived by the Tuinstra and Koenig [22] relationship. Instead, the sizeable $I(D)/I(G)$ ratio, the G peak position and its width all suggest that the clusters have a size of about 1–2 nm, which is comparable to their gas phase size. Previous studies found an optical Tauc gap of 0.6 eV [16], which is consistent with a cluster size around 2 nm for weakly disordered sp^2 bonded layers [23]. The Raman peak at ~ 2160 cm^{-1} indicates the presence of some sp^1 sites [17]. The sp^3 content of the films is estimated at $\sim 10\%$ from X-ray photoemission and electron energy loss spectroscopy [19, 24].

Our films are expected to have a disordered graphitic structure reminiscent of the fullerene-like character of the clusters. The films are found to contain closed graphitic particles distorted nanotubes and graphene sheets when viewed by transmission electron microscopy [25].

Field emission tests were carried out in the parallel plate configuration with an anode of indium-tin oxide coated glass, a plate spacing of 50 μm, defined by Macor spacers and in a chamber maintained by a liquid N$_2$ trapped diffusion pump at below 5×10^{-7} Torr pressure [7]. No forming process was needed to obtain emission from these films. No macroscopic surface damage was found on the films after emission testing, which is expected as the applied field was kept under 20 V/μm and the films are moderately conducting.

The emission current density is shown as a function of applied field in fig. 3 for films deposited under the same conditions but with different thicknesses. It is seen that the best film, A, requires an applied field of 0.75 V/μm to provide a current density of 1 μA/cm^2 and the current density rises further to 1 mA/cm^2. This threshold field is amongst the values found for a carbon solid [5, 8]. No optimisation of the deposition process has been made in order to enhance the field emitting properties. A similar value was recently found for polymer films [8], but it is likely that emission from pure carbon films will show better long-term stability.

The current density J (A/cm^2) for field emission is analysed according to the Fowler-
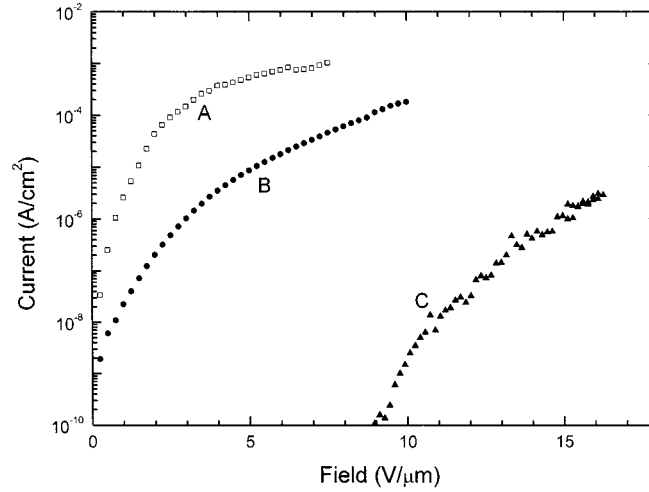
Fig. 3. – Field emission current density *vs.* applied electric field for films of different thickness: $A \approx 40$ nm, $B \approx 60$ nm, $C \approx 80$ nm.

Nordheim equation:

$$J = aE^2 \exp\left[-\frac{b\phi^{3/2}}{\beta E}\right] , \tag{1}$$

where ϕ (eV) is the barrier height, E is the field (V/m), β is a dimensionless field enhancement factor and a and b are constants with $b = 6.8 \times 10^9$ in these units. Figure 4 shows the current density plotted according to the Fowler-Nordheim relation. If we define an effective barrier $\phi^* = \phi/\beta^{2/3}$, the slopes of the Fowler-Nordheim plots correspond to ϕ^* of 0.1 eV,
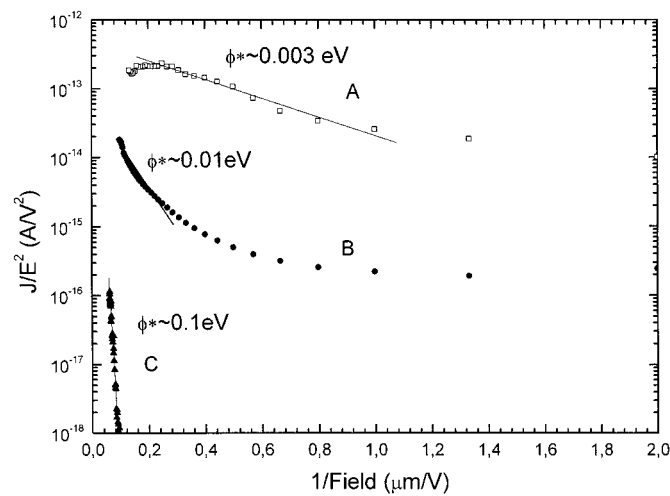

Fig. 4. – Fowler-Nordheim plot of the field emission current density. The lines and barrier heights are indicative values.
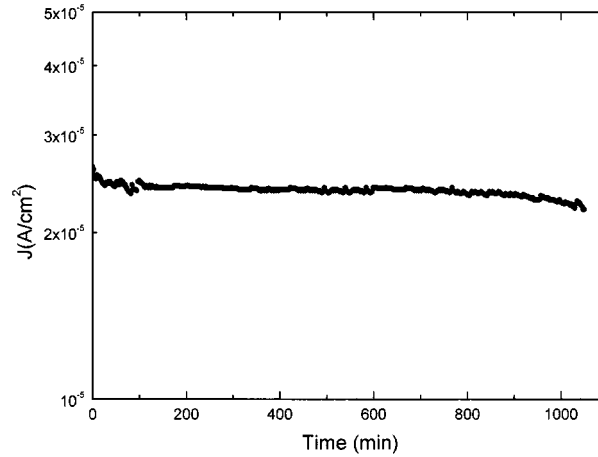
Fig. 5. – The stability of emission current density from film B of fig. 3, measured at 10 V/μm.

0.01 eV and 0.003. If we take a work function of 5 eV, typical of graphitic bonding, then the Fowler-Nordheim slopes correspond to field enhancement factors of 350 and over. Indeed, the most emitting film shows a positive slope on the Fowler-Nordheim plot at field higher than 3 V/μm, indicating that the emission may be limited by space charge effects rather than a barrier [8]. Moreover, the rather non-linear shape of the Fowler-Nordheim plots of samples B and C shows that (1) is just an approximation of a more complex emitting behaviour. The source of the field enhancement factors observed for different forms of carbon is still under debate [26, 14]. It presumably arises here from the roughness and internal structure of the films.

Figure 5 shows the stability of the emission current from the film B. Only a slight decrease in the current density was observed over 17 hours at 10 V/μm of applied electric field. A current density of 0.5 mA/cm^2 can be achieved at applied fields of 4.75 V/μm for film A. This value exceeds that needed for a field emission display.

In conclusion we have shown that nanostructured carbon films, produced by cluster beam deposition, are interesting electron field emitters. The use of supersonic beams allows deposition at very high rates over sizeable areas at room temperature. This is a considerable advantage since it allows to overcome the limitations for thermal sensitivity of many substrates. Compared to other emissive carbon films, the present films can be deposited, for example, onto glass substrates. In contrast, nanotubes can so far only be formed by plasma deposition at 700–1000 °C [11-13] or by extracting from a post-discharge deposit [10]. The low threshold field, good current stability and low-temperature processing make these nanostructured carbon films very suitable for display applications. There are many issues of the field emission behaviour of these cluster-assembled carbon films which are presently being studied, such as the influence of different precursor clusters or film thickness.

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