

# Field emission properties of carbon nanohorn films

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Self-supporting carbon films were prepared from a carbonaceous material, nanohorns. Nanohorns are spherical particles built of sharp cones of a single graphene sheet. The films show good field emission characteristics due to the sharp horn-like structures, in particular a low turn-on field and good long-term stability. © 2002 American Institute of Physics. [DOI: 10.1063/1.1481200]

## I. INTRODUCTION

Since the discovery of the  $C_{60}$  molecule,<sup>1</sup> the family of carbon nanostructures has been steadily growing. After multi-<sup>2</sup> and single-walled nanotubes,<sup>3</sup> carbon onions<sup>4</sup> and carbon cones,<sup>5</sup> the latest members are carbon nanohorns.<sup>6</sup> There is an ever growing activity in the development of carbon-based field emitters (diamond-like carbon, *ta-C*,<sup>7</sup> nanostructured carbon,<sup>8</sup> and carbon nanotubes,<sup>9</sup> just to name a few). Of all of these materials, the application of carbon nanotubes has been the most successful, since prototypes of nanotube-based flat panel displays have been demonstrated.<sup>10</sup> Among the numerous tasks for optimization of the field emission, simplification of the fabrication procedure as well as the development of large scale/low price production methods remain open problems. Carbon nanohorns can be synthesized in large quantities (10 g/h), and the product, unlike nanotubes, does not need any further purification. These two key factors make them promising candidates for large scale applications. In this article, we report on the field emission properties of thick films of carbon nanohorns.

## II. EXPERIMENTAL DETAILS

Nanohorns were prepared by an intense  $CO_2$  laser ablation of graphite, as described in Ref. 6. The powder of highly dispersed carbon soot consists of spherical graphitic particles with an almost uniform size distribution peaking around 80 nm, as shown in the scanning electron microscopy (SEM) image in Fig. 1(a). The transmission electron microscopy (TEM) image of Fig. 1(b) reveals that irregular and horn-shaped graphene sheets assemble to form what resembles a dahlia flower at the nanoscale. In the interior of these balls,

graphene is surrounded by amorphous carbon. Sonication of the soot in ethanol breaks up the agglomerates and a dark suspension of dahlia particles is formed (these do not fragment up during sonication). A thick deposit of nanohorns can be prepared by drawing the suspension through a ceramic filter of 200 nm pore size. The thick film can be easily detached from the filter after drying overnight.

The field emission experiments were performed in an UHV chamber with a base pressure of  $10^{-7}$  mbar. The counterelectrode was a highly polished stainless steel sphere of 1 cm diameter, which corresponds to an emission area of  $\sim 0.007$  cm<sup>2</sup> according to electrostatic calculations. The nanohorn samples were mounted on a linear manipulator and the interelectrode distance  $d_0$  was fixed to 125  $\mu$ m. The emission current was measured with a Keithley 6517A electrometer capable of sourcing up to 1000 V and 1 mA.

## III. RESULTS AND DISCUSSION

Figure 2 shows a typical  $I$ - $V$  curve. The emission sets on at an applied field of 2.6 V/ $\mu$ m. The corresponding Fowler–Nordheim plot,<sup>11</sup> where the  $I$ - $V$  curve is displayed by plotting  $\ln(I/V^2)$  vs  $1/V$ , is given in the inset of Fig. 2. The plot shows a straight line up to emitted currents of 10  $\mu$ A/cm<sup>2</sup>, which indicates that the nanohorn films follow Fowler–Nordheim like behavior. The slope in a Fowler–Nordheim plot depends on the work function, the field amplification factor  $\beta$  and the interelectrode distance.<sup>11</sup> We can estimate  $\beta$  with the hypothesis that the work function is similar to that of graphite ( $\sim 5$  eV), and found  $\beta=930$  for the film shown in Fig. 2.

A marked flattening of the  $I$ - $V$  curve was observed at higher currents. Such behavior has been noted in nanotube and nanocarbon films by several authors.<sup>12–17</sup> The phenomena that underlie this deviation from the Fowler–Nordheim model are not clear but are probably linked to the presence of adsorbates such as water molecules on the emitter tip.<sup>16,17</sup>

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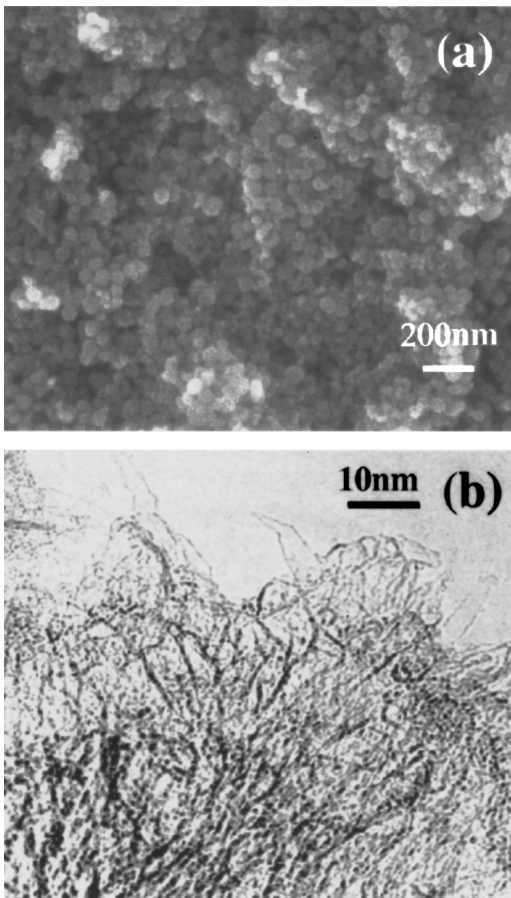


FIG. 1. (a) Scanning electron microscopy and (b) transmission electron microscopy images of carbon nanohorns characterized at different scales.

In Fig. 3 and Table I we compare the performance of nanohorns with other carbon-based emitters. The samples mentioned in the upper section of Table I and displayed in Fig. 3 are continuous films prepared by the same film transfer method as that used for nanohorns<sup>13</sup> from arc discharge multiwall nanotubes (MWNTs), single wall nanotubes (SWNTs) and 30 nm diam carbon fibers grown by chemical vapor deposition (CVD).<sup>13</sup> The field amplification factor  $\beta$  is

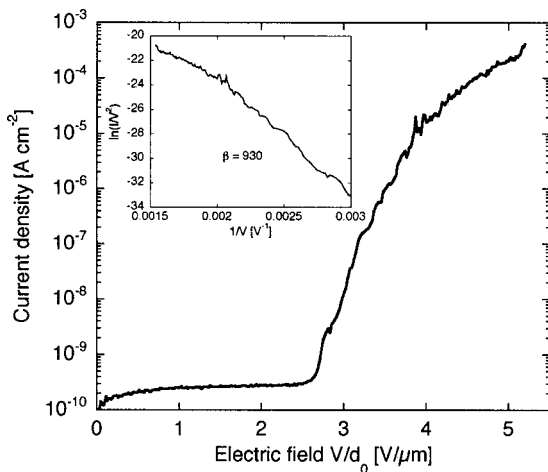


FIG. 2. Typical field emission characteristics of a carbon nanohorn film with a corresponding Fowler-Nordheim plot in the inset.

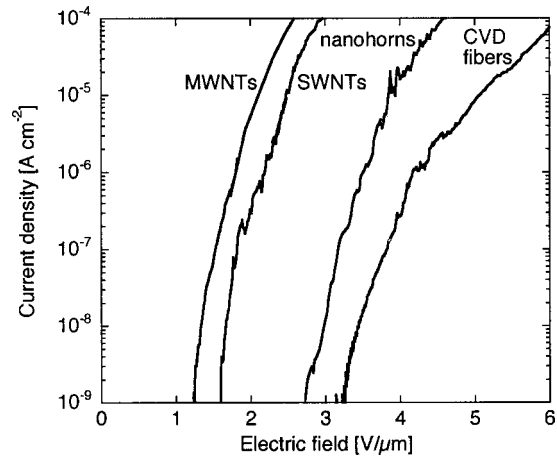


FIG. 3. Low current field emission of nanohorns compared with arc discharge single wall and multiwall nanotubes, as well as with CVD-grown fibers.

significantly higher for SWNT than for MWNT films, which is most probably due to the smaller tip radius of SWNTs. The tip radius is also responsible for the low field amplification and high emission fields obtained with the catalytic fibers. Interestingly, the small diameter of SWNTs should lead to very low emission fields, while the SWNT films show “only” comparable performance to that of MWNTs. We surmise that this is due to a low emitter density, since most SWNTs are bundled into ropes and only a few SWNTs tips are detected.

The values given in the second section of Table I were measured on patterned nanotube films.<sup>14</sup> These films were realized by CVD of acetylene over Si substrates with catalyst patterns deposited by microcontact printing.<sup>18</sup> This method allows one to produce films with a nanotube density that can

TABLE I. Emission characteristics of nanohorn, nanotube and nanocarbon films. MWNT and SWNT stand for multiwall and single wall carbon nanotubes, respectively, prepared by arc discharge or chemical vapor deposition (CVD). The interelectrode distance was 125  $\mu\text{m}$  for all samples.  $E_{to}$  and  $E_{thr}$  are the turn-on and threshold fields needed to produce current densities of 10  $\mu\text{A cm}^{-2}$  and 10  $\text{mA cm}^{-2}$ . An asterisk means that the value indicated was extrapolated.  $\beta$  is the field amplification factor extracted from the low current  $I-V$  characteristics.

Emitter	$E_{to}$ (V/ $\mu\text{m}$ )	$E_{thr}$ (V/ $\mu\text{m}$ )	$\beta$	Reference
Arc MWNT	2.6	4.6	1100	13
Arc SWNT	2.8	5.2	1600	13
CVD fibers	5.6	14	830	13
CVD MWNT (low density)	9.8	14.4	450	14
CVD MWNT (medium density)	2.3	3.3	1200	14
CVD MWNT (high density)	3.6	5.3	860	14
Nanohorns	3.9	7*	930	This work
O <sub>2</sub> -etched ta-C	5	20*	-	7
Nanostructured carbon	3	15	600-900	8

be varied from a low density of very short tubes, to a medium density of long nanotubes that protrude over the film surface, and to walls of densely packed nanotubes that grow perpendicular to the substrate. The emission fields of the low density films are high because only a few short emitters are available. The medium density films show the lowest emission fields and high  $\beta$ , because the nanotubes are long and screening effects are minimized due to the large distance between nanotubes. Conversely, the high density films have high emission fields and low  $\beta$  because of shielding between the densely packed nanotubes.

In the lowermost section we list parameters of other continuous nanocarbon films used for field emission, namely, nanostructured carbon deposited by *ta-C*,<sup>7</sup> as well as a cathodic arc.<sup>8</sup>

The nanohorns compare very well to the nanotube films and show much higher current capabilities than the emitters in the lowermost section. They are less efficient than the best emitters, but show a turn-on field below 4 V/ $\mu\text{m}$  that makes them good candidates for field emission applications. The field amplification factor  $\beta$  depends only on the geometrical shape and on the surroundings of the emitter, and a comparison with other nanocarbon emitters should allow us to draw conclusions on the actual emitting sites. In fact, we see that the field amplification of nanohorns is close to that of the high density CVD films, and that their performances are nearly identical.

TEM observations show that the nanohorns are quite similar in structure to SWNTs, but with the difference that they protrude a few nm only over the surface of the dahlias and that their shape is conical. It is therefore not surprising that the field amplification is far lower than for the continuous arc-discharge SWNT and MWNT films and the medium density CVD MWNT film where nanotubes project high above the surface. The high density CVD films, however, are composed of highly entangled nanotubes that form walls that rise perpendicular to the substrate. The length of the nanotubes is nearly identical, so that very few nanotubes rise above the tops of the walls. The surface density of nanotubes and nanohorns is comparable, as estimated from electron microscopy, and the smaller height of nanohorns is compensated for by their sharper tip, resulting in comparable field amplification and thus similar emission characteristics. This also means that the films may be far more homogeneous in

terms of spatial distribution of the emission and density of emitting sites than some nanotube and nanocarbon films.

The only marked difference with respect to nanotube films is that we were not able to extract current densities higher than 1 mA/cm<sup>2</sup> without inflicting permanent damage to the sample, whereas nanotubes can withstand densities that are higher by at least two orders of magnitude. This again may be due to the very peculiar structure and high resistivity of nanohorns. Since their long-term stability is comparable to that of nanotubes (not shown here), nanohorns could represent an enticing alternative for field emission applications that do not require high current densities.

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