

Total energy distribution of field emission electrons from a film of carbon nanopearls

R. Mouton, V. Semet, D. Guillot, and Vu Thien Binh^{a)}

Equipe Emission Electronique, LPMC-N-UMR CNRS, Université Claude Bernard Lyon 1, Villeurbanne 69622, France

(Received 14 October 2005; accepted 23 January 2006)

Compared to other graphic nanostructures, in particular, the tubular geometry of carbon nanotubes, the nanopearls forming a three-dimensional foamlike material have the advantage of presenting statistically a high density of apex areas with a small radius of curvature (~ 75 nm) when deposited at the end of a tip. This structure is suitable for a self-repairing cathode working at high currents. The field emission study was performed in a conventional field emission microscope equipped with an energy analyzer. After a conditioning process, currents up to $50 \mu\text{A}$ can be obtained under continuous emission, and the variation of the field emission current with the applied voltage strictly followed the conventional Fowler-Nordheim behavior, i.e., a linear variation of $\ln(I/V^2)$ vs $(1/V)$. A systematic analysis of the total energy distribution spectra under different conditions has been done. For current emitted from a single nanopearl at the end of one string, the full width at half maximum (FWHM) of the single peak total energy distribution spectra is ~ 0.2 eV and it is position dependent on the string resistance. From the convolution of independent sources, associated to the foamlike structure of the carbon nanopearls, the total energy distribution spectra present a multiple peak structure with a global FWHM values from 0.5 to 1 eV. © 2006 American Vacuum Society. [DOI: 10.1116/1.2177232]

I. INTRODUCTION

Field emission (FE) of carbon nanotubes (CNTs) has been intensively studied due to their high aspect ratio and their chemical and crystallographic stabilities, related to the graphene surface of the apex region.^{1,2} They are used either in a spaghettilike deposition³ as represented in Fig. 1(a) or, recently, as isolated and vertically aligned CNT arrays.^{4,5} However, the use of CNTs for FE encountered two drawbacks. For layered films of CNTs, like the mats which are obtained with a paste deposition,⁶ the overall field amplification factor is drastically reduced due to the mutual screening effect within the spaghettilike structure, resulting in sparsely distributed emission sites then a nonuniformity of the emission area. For the vertically aligned CNT arrays, the drawback is the fixed number of emitting CNTs. In bad vacuum, the gradual destruction of the CNTs by retro-ion bombardment, sputtering, leads to an irreversible decrease of the emission sites. The lifetime of those cathodes is then limited because it is dependent on the density of the emission sites, which has an upper limit to avoid the mutual electrostatic screening between the CNTs.⁷

We have recently reported the synthesis, the characterization, and FE studies of carbon nanopearls.⁸ These nanopearls consist in monodisperse solid nanospheres of 150 nm diameter composed of nanocrystalline carbon flakes. The nanospheres form two-dimensional (2D) chains analogous to strings of pearls and the strings are assembled together to form finally a three-dimensional (3D) foamlike material [Figs. 1(b) and 1(c)]. The surface of such a structure is well

fitted for field emission and, in particular, it will provide a self-replacement of the emission sites⁹ as long as the material is present. This means that, unlike CNTs, when an arc occurred at high currents in the nanopearls, any structural breakdown was self-repairing and the same cathode returned to stable emission after a conditioning process.

In this article, we report further on the FE properties of these carbon nanopearls. We first recall the synthesis process to obtain reproducible and uniform layer of nanopearls at the apex of metallic tips. In Sec. II, we present the FE characteristics and their evolutions with discussion about the potentialities of these cathodes in relation to its foamlike structure. Then the total energy distribution of the emitted electrons will be presented and discussed within the context of multiple FE site cathodes.

II. CARBON NANOPEARL CATHODES

A catalytic chemical vapor deposition (CVD) process at ambient pressure was used to produce the carbon nanopearls,⁸ as follows. We first covered W tips having apex radius in the range of $5\text{--}10 \mu\text{m}$ with Ni clusters (diameter ~ 100 nm) as catalysts, before putting them in the CVD reactor for the growth of a carbon nanopearl film. The conditions for the CVD growth process were the following: the feed gas was C_2H_2 with a ratio $\text{C}_2\text{H}_2:\text{N}_2$ kept constant at 80:400 SCCM, (SCCM denotes cubic centimeter per minute at STP) the temperature is 700°C , and the deposition time was in the range of 10 s. The nanopearls grew directly on the metallic tips, as a uniform layer with a thickness of about $20 \mu\text{m}$ (Fig. 2). This constituted our carbon nanopearl cathodes.

^{a)}Electronic mail: vuthien.binh@lmpmcn.univ-lyon1.fr

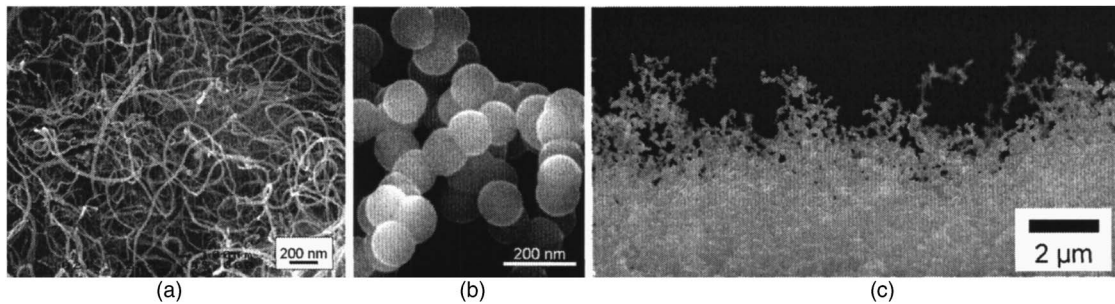


FIG. 1. Scanning electron microscopy of deposited films of carbon nanocompounds obtained by chemical vapor deposition processes. (a) Mat of carbon nanotubes under a spaghetti-like structure. (b) Top view (b) and (c) side view of a layer of nanopearls having a diameter in the range of 100 nm and for two different magnifications.

The field emission properties of the nanopearl tips were first analyzed in a conventional FE microscope. Initially the newly grown cathodes exhibited unstable FE currents. However, an *in situ* conditioning process⁸ consisting of a stepped increase of the FE current eliminated these instabilities.⁸ During the conditioning process, we observed a decrease of the needed voltage for a fixed current and the pattern evolved toward a unique emitting spot. This behavior suggested that some nanopearl strings or bunches of them became the predominant emitter sites after a modification of the apex geometry by a straining of the nanopearl strings at the surface, probably under the electrostatic forces from the applied electric field. By coupling the evolution of the FE patterns during this conditioning process and scanning electron microscopy (SEM) observations of the apex before and after the FE we noticed a stretching of the nanopearl strings after the conditioning process. This phenomenon induced an increase of the local field enhancement factor, therefore a decrease in the applied voltage to extract the same FE current during the conditioning process, as observed experimentally.

Figure 3 represents the typical current-voltage character-

istics after the conditioning process. They follow the expected metallic behavior, i.e., a linear variation of $\ln(I/V^2)$ vs $(1/V)$ (shown in the inset), as observed for the carbon nanotubes, even if the total current I results from the contribution of multiple FE sites. The nanopearls' surface is constituted of graphene: these field emission sites exhibit the same quality for current stability as observed with the carbon nanotubes, and currents in the range of microamperes were maintained stable for hours. At high currents over few tens of microamperes, bright spots appeared at the surface of the cathode, indicating that Joule heating of some nanopearl strings was occurring due to the high currents through the strings, a phenomenon that we have also observed with nanotubes.²

III. FIELD EMISSION ELECTRON ENERGY SPECTROSCOPY OF THE NANOEPEARLS

The experimental procedure for measurements of the total energy distribution (TED) of carbon nanopearl tips was as follows: (i) from the as-grown tip a conditioning process of the cathode until a stable emission was done prior to field emission electron spectroscopy (FEES) measurements, (ii) the FEES measurements were made at different locations of the FE spot and for different applied voltages, and (iii) all FEES measurements were done in a vacuum of about 10^{-10} Torr with a commercial hemispherical energy analyzer

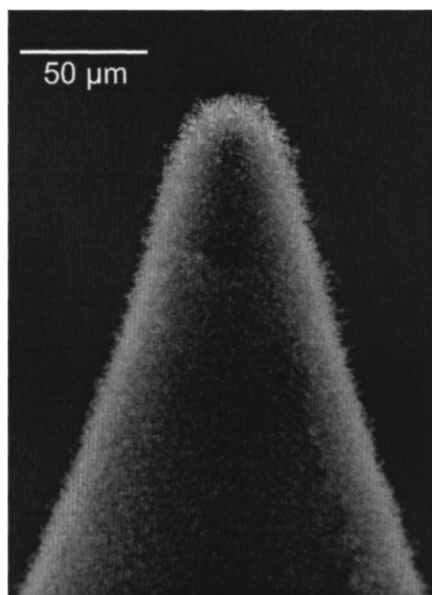


FIG. 2. Scanning electron micrograph of a metallic tip covered with a layer of nanopearls (thickness $\sim 2 \mu\text{m}$) obtained directly from a CVD growth.

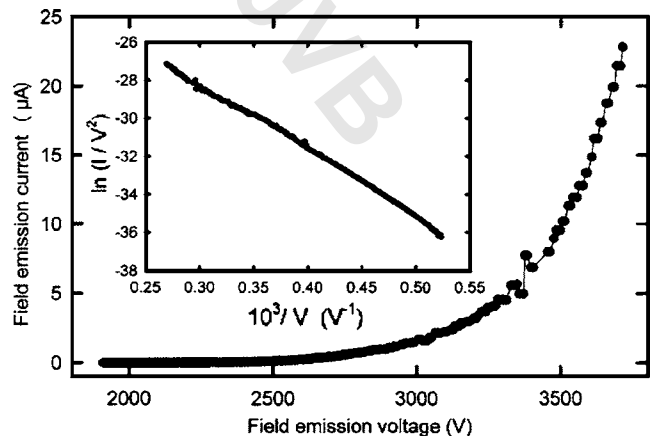


FIG. 3. Field emission characteristics from a carbon nanopearl tip after a conditioning process. The inset is the Fowler-Nordheim plot of the same I - V characteristics.

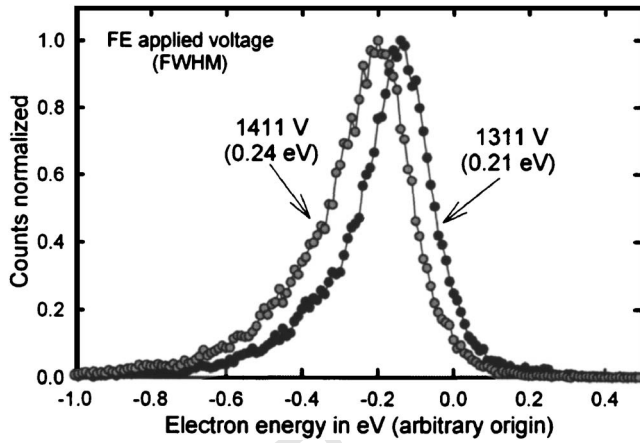


FIG. 4. Characteristic TED from a single nanopearl string indicating an energy distribution of ~ 0.2 eV and a shift towards the lower energy side for increasing applied voltage.

in which the entrance electrostatic lenses had been adapted for the FEES measurements. A fluorescent screen was placed at ~ 2 cm from the tip, with a 1 mm diameter probe hole in its center. Any region of the FE pattern could be studied by the electron energy analyzer, positioned behind the probe hole, by using the tip displacement movement and the visual control of the pattern on the screen. The TEDs were measured with a nominal resolution of 10 meV.

A. TED from a single nanopearl string

By a specific conditioning process, we can choose a FEES area that is limited to the FE from a single string of nanopearls. Figure 4 shows a characteristic TED spectrum obtained and its evolution for higher applied voltage. The main points that can be highlighted are as follows. (i) The TED is a single peak structure with a conventional metallic shape.¹⁰ The full width at half maximum (FWHM) of the TED spectra is in the range of 0.20 eV and it increases with the applied voltage. For the example presented in Fig. 4, the FWHM increases by 0.03 eV for an increase of the applied FE voltage $\Delta V_{\text{applied}} = 100$ V. This value is comparable with the TEDs from clean metallic surface tips.¹¹ (ii) A shift of the spectrum is observed as a function of the applied voltage. In this example, we notice a shift to the lower energy side of ~ 0.7 eV for a 100 V increase of the applied voltage. This shift to the lower energy side is systematically observed and it is linearly dependent on the FE current. We attributed this shift to a voltage drop along the string, ΔV_{string} , induced by the FE current I passing through it; $\Delta V_{\text{string}} = R_{\text{string}} I$, where R_{string} is the electrical resistance along the string. Such behavior was already observed for long nanotubes;² for nanopearls it will be exalted due to the string geometry and its amplitude will depend strongly on the string resistance.

B. TED from a convolution of independent field emission sites

After a severe conditioning process, the FE pattern from a carbon nanopearl tip is obtained from the contribution of

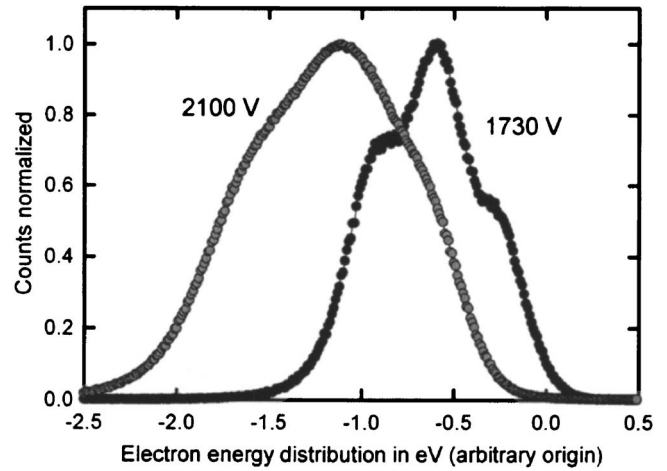


FIG. 5. TED spectra from a carbon nanopearl tip for two values of the FE applied voltage.

multiple independent sites, each of them is an individual string of carbon nanopearls. Figure 5 shows characteristic TED spectra measured under such conditions. They are very different from the ones obtained with the FE from a single string. We can point out the following main characteristics (all of them were systematically observed for different samples and for different locations). (i) The spectra do not have a simple feature as in Fig. 4. They present a multiple peak structure, which is completely different from one probe area to another. In the example presented in Fig. 5, the TED at 1730 V is a three-peak spectrum. (ii) The FWHM (ΔE) of the resulting spectrum is very large (in Fig. 5 $\Delta E \sim 0.8$ eV). (iii) By increasing the FE voltage we noticed a shift of the whole TED spectrum associated with a rapid enlargement of its shape. This rapid enlargement of the FWHM is the result of different values of the shifts associated to the individual peaks which constitute the whole spectrum. In the example presented in Fig. 5 the first peak at the high energy side, the middle, and the third peak have a shift, respectively, of 0.42, 0.50, and 0.70 eV, resulting in $\Delta E = 0.42$ eV for $\Delta V_{\text{applied}} = 370$ V.

At a first look, the multipeak TED spectrum can be related to some resonant tunneling through adsorbed species on the apex of the emitting nanopearls. However, by carefully checking the TED evolution in function of the conditioning process, thermal heating, and for different applied voltages, it appeared to us that it is highly improbable to hold this idea. We then propose to analyze these experimental results by taking into account the foamlike structure of the emitting surface of the carbon nanopearl tips, as illustrated in Fig. 1(c). Each individual strings are potentially a FE site. After a severe conditioning process, some height standardization of the strings occurred, resulting in a concomitant FE of different strings to the FE pattern. Each of these strings must present a metalliclike TED similar to the one presented in Fig. 4. However, even after the conditioning process the length of each string is not standardized due to the intrinsic structure of each string. This means that the resistance R_{string} related to each string is not the same, so the position of each

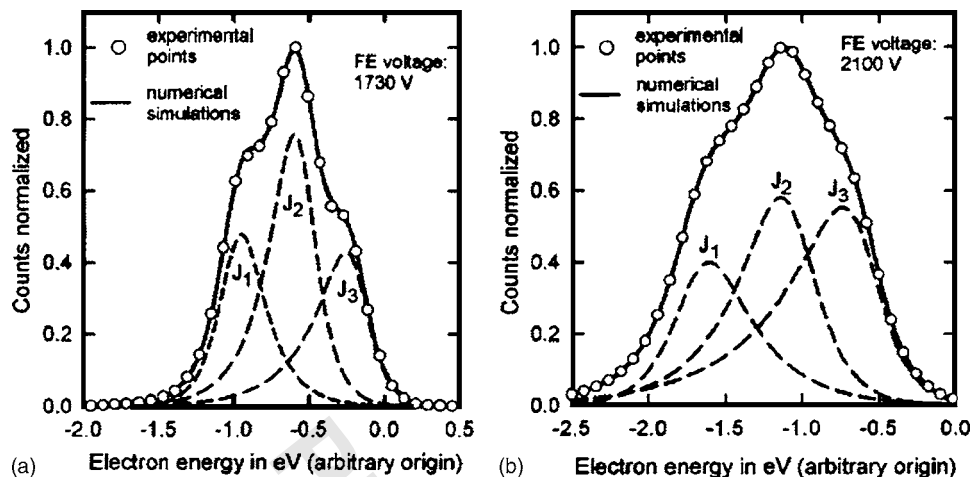


FIG. 6. Analysis of the multippeak TED spectra from carbon nanopearls (of Fig. 5) by the convolution of independent FE sites (J_1 , J_2 , and J_3). The results are the solid line plots which fit the experimental data (open circle points) of Fig. 5. (a) FE current $0.53 \mu\text{A}$ and (b) $8.55 \mu\text{A}$.

peak is different as a consequence of the different values for ΔV_{string} . The convolution of all these individual TED results in a multiple peak spectrum. By increasing the applied FE voltage V_{applied} , each of these peaks will experience a shift to the lower energy side due to the increase of ΔV associated with each string. As the values of the respective ΔV_{string} were not the same, the result is a shape modification of the TED peak and an important increase of ΔE .

In order to assess this analysis, numerical simulations have been performed to mimic the experimental TED spectra. The methodology used is the convolution of independent TED peaks from Fowler-Nordheim relations (J_1 , J_2 , and J_3 for the example presented in Figs. 5 and 6), each of them is associated to one peak making up the multippeak TED spectrum. The parameters used for fitting with the experimental data are the following: the position of the Fermi level related to one FE string, the local FE field, and the FE temperature. To illustrate this, the analysis of the experimental TED measured at 1730 and 2100 V is presented in Fig. 6. The three individual TED peaks are named J_1 , J_2 , and J_3 (dotted line plots) and their convolution results in the TED spectra plotted in solid line. The open circles are some of the experimental data of Fig. 5. Comparing the different plots of Figs. 6 allows following the evolution of each individual TED spectrum, in particular, its energy shift and relative intensity. In other words, we can go back to the FE behavior of each active string of the carbon nanopearl tip. At first approximation and for this example, we can estimate the “total effective resistance” of the nanopearl cathode to $60 \text{ k}\Omega$ with FE temperatures of 770 and 1230 K, respectively, for emission at 1730 and 2100 V, due to Joule heating. As a comparison, the measured resistance of one individual vertically aligned carbon nanotube is between 6 and $16 \text{ k}\Omega/\mu\text{m}$.¹² A systematic study is in progress and will be reported in detail elsewhere.

The number of individual emitting sites can be extracted from this analysis. We found, from different observations, a value between 3 and 5. By taking into account the size of the probe hole, the radius of the tip, and the distance between the tip and the probe hole we can then estimate for the carbon nanopearl surface a mean density for active FE sites of $1/\mu\text{m}^2$ or $2/\mu\text{m}^2$.

IV. CONCLUSIONS

FEES from single carbon nanopearls showed a metallic-like behavior for the TEDs of the emitted electrons. This means a conventional single peak shape TED, as described in Ref. 13, with a FWHM in the range of 0.2 eV. However, as the resistance of the string is not negligible, the position of the peak is then dependent on the potential drop along the string which is a function of the FE current, as shown by the shift of the TED peaks towards the lower energy side for increasing FE voltage.

After a severe conditioning process, more than one string contribute to the FE pattern. The resulting TED is then the convolution of different TED peaks related to independent FE sites. The TED spectrum is then a multiple peak spectrum with values of the FWHM in the range of 0.5–1 eV, behavior specific to the foamlke structure of the carbon nanopearl film. The density of FE sites from this structure is $1\text{--}2 \text{ sites}/\mu\text{m}^2$.

¹V. Semet *et al.*, Appl. Phys. Lett. **81**, 343 (2002).

²S. T. Purcell, P. Vincent, C. Journet, and V. T. Binh, Phys. Rev. Lett. **88**, 105502 (2002).

³W. A. D. Heer, A. Chatelin, and D. Ugarte, Science **270**, 1179 (1995).

⁴K. B. K. Teo *et al.*, J. Vac. Sci. Technol. B **21**, 693 (2003).

⁵M. Mauger, V. T. Binh, A. Levesque, and D. Guillot, Appl. Phys. Lett. (2004).

⁶D. S. Chung *et al.*, J. Vac. Sci. Technol. B **18**, 1054 (2000).

⁷L. Nilsson *et al.*, Appl. Phys. Lett. **76**, 2071 (2000).

⁸A. Levesque, V. T. Binh, V. Semet, D. Guillot, R. Y. Fillit, M. D. Brookes, and T. P. Nguyen, Thin Solid Films **464–465**, 308 (2004).

⁹A. Levesque, P. Vincent, V. T. Binh, D. Guillot, and M. D. Brookes, J. Vac. Sci. Technol. B **23**, 665 (2005).

¹⁰L. W. Swanson and A. E. Bell, in *Advances in Electronics and Electron Physics*, edited by L. Marto (Academic, New York, 1973), Vol. 32, pp. 193–309.

¹¹V. T. Binh, N. Garcia, and S. Purcell, in *Advances in Imaging and Electron Physics*, edited by P. W. Hawkes (Academic, San Diego, 1996), Vol. 95, pp. 63–153.

¹²V. Semet *et al.*, Appl. Phys. Lett. **87**, 223103 (2005).

¹³R. Gomer, *Field emission and Field Ionization* (Harvard University Press, Cambridge, MA, 1961).