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Field electron emission from bunchy flake-like nano-carbon films*

Wang Xiao-Ping(王小平)†, Wang Li-Jun(王丽军), Duan Xin-Chao(段新超),
Wang Long-Yang(王隆洋), Zhang Lei(张 雷), Lv Cheng-Rui (吕承瑞), and Lei Tong(雷 通)

College of Science, University of Shanghai for Science and Technology, Shanghai 200093, *China*

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This paper reports that bunchy flake-like nano-graphite crystallite films (BNGCFs) were deposited on Si substrates by using the microwave chemical vapour deposition technique. Furthermore the BNGCFs were characterized by x-ray diffraction spectra, scanning electron microscopy, Raman spectra and field emission (FE) I–V measurements, and a lowest turn-on field of 1.5 V/μm, and a high average emission current density of 30 mA/cm^2 at a macroscopic electric field of 8.0 V/μm were obtained. The J–E data did not follow the original Fowler–Nordheim (F–N) relation since they were not well represented in the F–N plot by a straight line. A model considering the F–N mechanism, and the statistic effects of FE tip structures has been applied successfully to explain all the FE data observed for $E < 8.8$ V/μm.

Keywords: bunchy flake-like nano-graphite crystallites films, chemical vapour deposition, electron field emission

PACC: 7970, 8115H, 8120V,7340C

1. Introduction

Electron emission from carbon-based materials has received increased interest recently due to their low voltage operation and high current density; various carbon films (include a:C, DLC, CNT and nano-structured carbon etc.) have been investigated accordingly.[1−19] Most field emission (FE) characteristics obtained from various carbon films were analysed commonly using the standard Fowler–Nordheim (F–N) theory. The standard F–N theory, however, adapted to plate cathode surfaces of metals or materials with sufficiently high electrical conductivities.[13] Such an ideal situation may not be applicable for the various carbon films having complex structures and irregular shapes where the emission sites and electrical conductivities significantly differ from those of pure metal plates. Moreover the number of effective FE sites and the field enhancement factor β of such films may not be constant when the electrical field applied, E, is varied in a wide range, which may result in a contradiction between theoretical calculations and experiment results.[13−16]

In this paper, we have fabricated a series of nano-structured carbon (nC) films using a microwave-plasma chemical vapour deposition (CVD) apparatus and have investigated the surface morphology, film structure and FE characteristics. A nano-carbon film, which was composed of bunchy flake-like nano-graphite crystallites (BNGC), was synthesized, and a lowest turn-on field of 1.5 V/μm, and a high average emission current density of 30 mA/cm^2 at a macroscopic electric field of 8.0 V/μm were obtained. The macroscopic FE areas of the measured samples were $\approx$30 mm^2. Moreover the experimental result indicates that the J–E data do not follow the original F–N relation; meanwhile the effective field enhancement factor β reduces with the increase of the macroscopic electric field E.

2. Experiment and discussion

2.1. Carbon film cathode fabrication

The nC films were deposited on Si substrates by using the microwave CVD technique at 1100°C in a gas mixture of H_2/CH_4 = 100/13 and 10.0×10^3 Pa pressure for 9h. The nC film morphology and composition were tested by using x-ray diffraction (XRD) spectra, Raman spectra, scanning electron microscopy (SEM) and optical microscopy. A Raman spectrum of the sample is shown in Fig.1, the peak position of the

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†Corresponding author. E-mail: wxpchina64@yahoo.com.cn

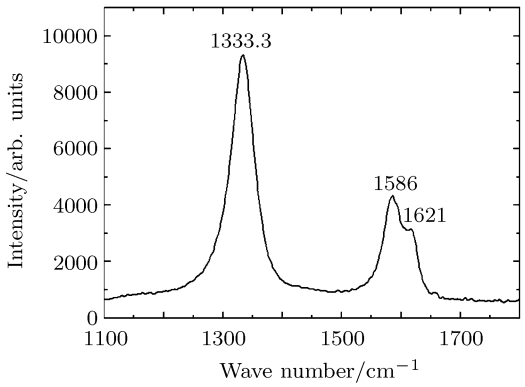


Fig.1. Raman spectrum of a BNGCF.

D band and G band are around 1333.3 and 1586 cm^{-1}, respectively, where the $I_\mathrm{D}/I_\mathrm{G}$ ratio is ∼1.78. Huang's group proposed that a shift of the $\mathrm{E_{2g}G}$ mode from its normal value of 1580 to 1598 cm^{-1} is an indication of the existence of nanocrystalline graphite of sp^2 clusters.[20−22] The XRD spectrum indicates that the films are polycrystalline graphite, and no diamond peaks are presented in the XRD spectrum, as shown in Fig.2, which further testifies that the peak at 1333.4 cm^{-1} is assigned as the $\mathrm{A_{1g}}$ mode due to the presence of aromatic rings in disordered graphite rather than a diamond peak at 1332 cm^{-1}. A typical SEM image of the nC films is shown in Figs.3(a), 3(b) and 3(c). It indicates that our nC films are composed of many BNGC, which are called BNGC films (BNGCFs). The characteristic sizes of the sharp edges of BNGC are in the range of 10–60 nm. The surface resistance of the film is 500 kΩ/□.

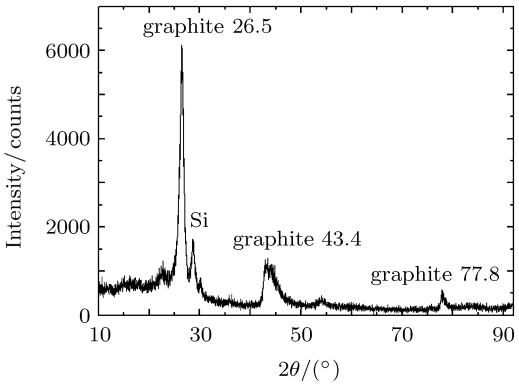


Fig.2. XRD spectrum of a BNGCF.

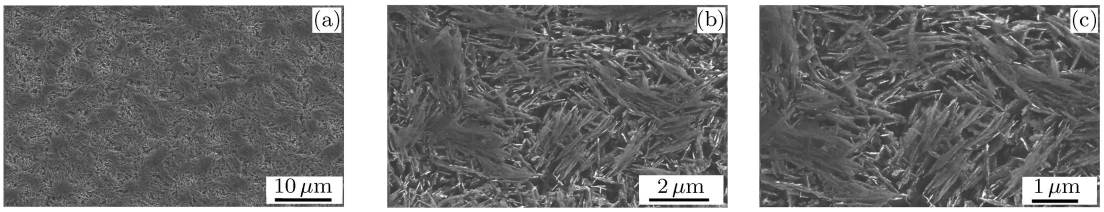


Fig.3. SEM image for BNGCFs.

2.2. Field electron emission result and discussion

Finally, a functional FE device was made by using BNGCFs/high doped-silicon as a cold cathode, glass/indium-tin oxide film with fluorescent coat as an anode, and keeping the cathode and anode apart by a 270 μm insulating sheet of mica film. This nC film field emitter was placed in a vacuum system with a Hyvac pump operating at a base pressure of about 3.0×10^{-5} Pa. The typical images of distribution of FE sites taken at macroscopic electric field $E = 4.0\,\mathrm{V}/\mu\mathrm{m}$ and $7.0\,\mathrm{V}/\mu\mathrm{m}$ are shown in Fig.4, and uniform FE from the whole BNGCF area of 30 mm^2 were obtained.

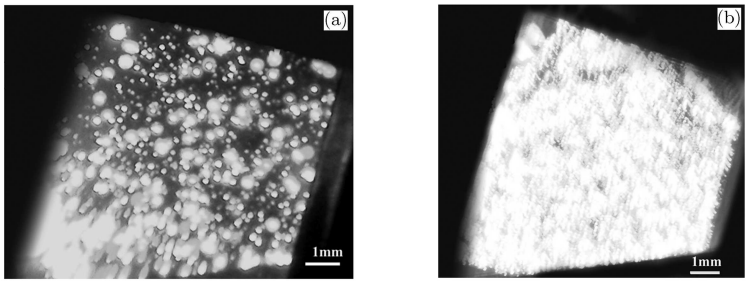


Fig.4. Image of FE site distribution obtained for the BNGCF cathode with macroscopic field (E) 4.0 V/μm (a) and 7.0 V/μm (b).

Current density (J)-electric field (E) characteristics were measured for our as-grown samples. The threshold microscopic field, $E_{\rm th}$ defined as the one yielding $J = 10\,\mu{\rm A/cm^2}$, was as low as $1.5\,{\rm V}/\mu{\rm m}$. The observed J rapidly increased with increasing E and exceeded $30\,{\rm mA/cm^2}$, at $E = 8\,{\rm V}/\mu{\rm m}$. Figure 5(a) shows a series of J–E data including the 1st, 2nd and 5th measurements, indicating that the present sample yielded a reasonable reproducibility of the J–E characteristics only after several supplies of sufficiently high electric fields. These J–E data did not follow the original Fowler–Nordheim (F–N) relation since they were not well represented in the F–N plot by a straight line, as shown in Fig.5(b). Similar features were often observed for the various types of nC films.[13−16]

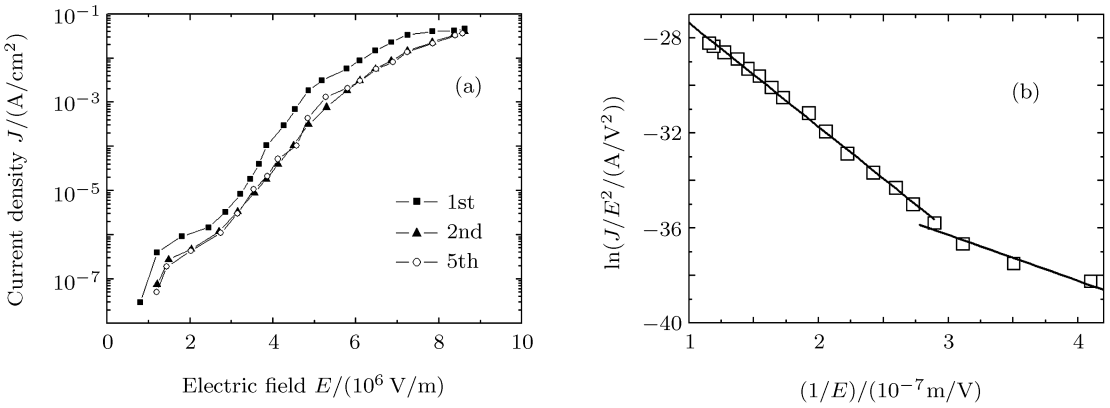


Fig.5. (a) Emission current density (J) versus electric field (E) plots of the 1st, 2nd and 5th measurements for a typical BNGCF sample; (b) Fowler–Nordheim (F–N) plots from BNGC films for the 3rd measurement.

Thus, in order to analyse the well-reproduced FE characteristics observed for the large-numbered cycles in more detail, one should consider some modified F–N scheme such as a statistical analysis model,[13] and furthermore as a field-dependent parameter model previously proposed by Obraztsov *et al.*[13,14] The modified F–N equation can be expressed as[16]

$$J = 0.95^2 \frac{AN\pi r_0^2}{\phi S_{\rm a}} \exp(10.1/\sqrt{\phi})\beta_0^2 E^2 \times \exp\left[-\frac{B\phi^{3/2}}{E\beta}\right], \qquad (1)$$

where J is the FE current density in the unit of ${\rm A/m^2}$, E is electric field in the unit of ${\rm V/m}$, N is the number of FE sites, r_0 in m is the average radius distribution of the FE tips. An effective field enhancement factor β, is defined by the relation that $\dfrac{1}{\beta} = \dfrac{1}{\beta_0} - \dfrac{0.09^2}{2}\dfrac{B\phi^{3/2}}{\beta_0^2 E}$, where $\beta_0 = \dfrac{H}{0.95 r_0}$ is the geometric field enhancement factor. The ϕ is the work function in the unit of eV, then $A = 1.541434 \times 10^{-10}\,{\rm A\cdot V^{-2}\cdot eV}$ and $B = 6.830888 \times 10^9\,{\rm V\cdot eV^{-3/2}\cdot m^{-1}}$.

If N represents the total number of FE sites on the cathode, the total effective FE areas of the emitter, S, may be represented by $S = \pi r_0^2 N$ while the apparent (nominal) FE area of the emitter, $S_{\rm a}$, was $3.0\times10^{-5}\,{\rm m^2}$. Then, the following relation is deduced with $a = A/\phi$, $b = B\phi^{3/2}$ and $S_{\rm r} = 0.95^2(S/S_{\rm a})\exp(10.1/\sqrt{\phi})$ (where $S_{\rm r}$ is an effective relative emission area)

$$\ln\frac{J}{E^2} = \ln(S_{\rm r} a \beta_0^2) - \frac{b}{\beta}\left(\frac{1}{E}\right). \qquad (2)$$

Here, $S_{\rm r}$ and β are now treated as the E-dependent fitting parameters. Assuming the work function ϕ of the BNGCFs to be 5.0 eV, the values of β were estimated to be 3900 ($E < 3\,{\rm V}/\mu{\rm m}$) and 1740 ($3\,{\rm V}/\mu{\rm m} < E < 8.8\,{\rm V}/\mu{\rm m}$) in the low and high E range respectively. According to the modified F–N scheme, the reduction of the effective field enhancement factor β in the high E range can be understood as follows. When a rather low E was applied to the sample, the emission behaviour was governed by a small quantity of FE sites with larger β whereas the contribution to J from large numbers of FE sites with relatively small β was practically negligible. When E was further increased to relatively large values, the effective emission area S will increase as the number of FE sites increases, and such FE sites with the relatively small β began to substantially contribute to J. The number of such tips with smaller β tips should be significantly larger than that of the tips with larger β tips. A similar feature was previously reported for FE tips whose diameters and orientations were randomly distributed.[23]

Finally, the short-team stability of the FE characteristics was measured for samples after an aging process. It indicates that the sample had a good stability of 4%, as was defined at the average FE current of $0.2\,\mathrm{mA/cm^2}$.

This specificity of nC emitters, in fact, originates from the possibility of carbon atoms being arranged with sp^3 (diamond-like) and sp^2(graphite-like) hybridization. These two different carbon-phases may be combined with a very narrow interface providing immediately high electrical conductivity and reduction of the potential barrier to electrons escaping into vacuum. Furthermore by having the sharpness edge size of about 60–10 nm, these nano-sheets carbon structures correspond to a higher geometrical field enhancement factor. In a word, the higher emission current density and uniformity were attributed to the unique geometry structure of the BNGCFs.

3. Conclusion

BNGCFs were successfully deposited on Si wafers by means of a 1.7 kW microwave-plasma CVD process. An emission current density as large as $30\,\mathrm{mA/cm^2}$ was attained at a macroscopic field of $8.0\,\mathrm{V}/\mu\mathrm{m}$ from the BNGCFs. The macroscopic FE areas of the measured samples were $\approx 30\,\mathrm{mm^2}$. The high emission current density is considered to be a unique geometrical structure of BNGCFs.

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