31 May 2002

ELSEVIER

Chemical Physics Letters 358 (2002) 187–191

CHEMICAL PHYSICS LETTERS

www.elsevier.com/locate/cplett

Uniform carbon nanoflake films and their field emissions

N.G. Shang, F.C.K. Au, X.M. Meng, C.S. Lee, I. Bello, S.T. Lee *

Department of Physics and Materials Science, Center Of Super-Diamond and Advanced Films (COSDAF),
City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong SAR, PR China

Received 28 January 2002

Abstract

Films of uniformly distributed carbon nanoflakes have been prepared by using hot filament chemical vapor deposition. A large amount of carbon flakes with a thickness of less than 20 nm interlaced together to form a layer of carbon nest-like film with their sharp edges almost perpendicular to the Si substrate. Raman spectroscopy showed that the films were characteristic of pyrolytic graphite and became more disordered with the increase of substrate temperature and acetylene concentration. The growth mechanism of the carbon nanoflake films was discussed. The field emission performance has been done, showing a turn-on field of about 17 V/μm. Considering the ease of large-area preparation, the carbon nanoflake films might have a potential application in vacuum electronic devices. © 2002 Elsevier Science B.V. All rights reserved.

Carbon has a unique state of affairs in nature, since it is capable of constructing a variety of novel materials such as diamond, graphite, fullerenes and nanotubes. The various structures have shown remarkable differences in properties and potential applications [1,2]. Moreover, carbon also constitutes many nanoscaled materials with novel properties not observed in the bulk materials due to the quantum size effect [3,4]. As a new carbon allotropy and nanoscaled material, the carbon nanoflake film, which consists of petal-like graphite flakes with a thickness of less than about 20 nm, is of much interest [5]. Each carbon nanoflake can be considered a quasi-two-dimensional structure with strong anisotropy in physical properties. It is interesting that almost all the carbon nanoflakes are vertical to the substrate. This can lead to a large surface-to-volume ratio for hydrogen adsorption, as in the case of carbon nanotubes and herringbone-like carbon nanofibers [6,7]. Their very sharp and thin edges perpendicular to substrates are potentially good electron field emission sites. In this Letter, the hot filament chemical vapor deposition (HFCVD) method is first used to prepare these carbon nanoflake films. As compared with the previously reported arc discharge techniques, the current deposition process has the advantages of low synthesis temperature, better controllability, large-area deposition, compatibility with current semiconductor techniques and neither catalyst nor special substrate treatment are needed.

The carbon nanoflake films were fabricated in a typical HFCVD system previously used for

---

* Corresponding author. Fax: +852-2784-4696.
E-mail address: apannale@cityu.edu.hk (S.T. Lee).

PII: S0009-2614(02)00430-X

growing diamond films [8]. Two parallel tungsten filaments of 0.75 mm in diameter were heated to 2100 °C to decompose a C_2H_2 (3–15%) and H_2 mixture fed at a rate of 200 sccm into the system. After a series of cleaning procedures using acetone, ethanol, HF acid and de-ionized water, Si(1 0 0) wafers were put at about 4–7 mm below the filaments, where the substrate temperature can be controlled between 400 and 700 °C as measured by a thermocouple under the substrate. The surface morphology, structure and chemical composition of the as-deposited samples were analyzed with scanning electron microscopy (SEM), Raman scattering spectroscopy and X-ray photoelectron spectroscopy (XPS).

Fig. 1 shows typical SEM images of the carbon nanoflake films deposited for 4 h at different substrate temperatures from 400 to 700 °C. It can be seen that all films consist of a large amount of small clusters with the shape of leaves or petals. They perpendicularly interlace together to construct a layer of the nest-like film with a large surface-to-volume ratio and very sharp edges. The carbon nanoflakes deposited at 400–600 °C have a thickness of less than about 10–20 nm and a size of 300–600 nm in the other two dimensions. In this temperature range, the size and the density of the nanoflake gradually decreases and increases respectively as the temperature increases. When the deposition temperature was increased to 700 °C, the size of the carbon flakes abruptly decreases to about 5 nm in thickness and 80 nm in width.

Fig. 2 shows the Raman spectra of the samples deposited at different temperatures. In these spectra, the two strong peaks at about 1350 (±5) and 1590 (±5) cm^{-1} are the typical D and G bands of microcrystalline graphite, which originate from the A_{1g} zone-edge phonon induced by the disorder due to the finite-crystallite size and the zone-center E_{2g} first-order mode, respectively. Another strong peak at 2700 (±8) cm^{-1} is the overtone of the D band, and the weak broad peak at about 2930 cm^1 is attributed to the sum of the D and G bands. A small peak at about 1625 cm^{-1} and its overtone (3250 cm^{-1}) were also observed. They correspond to a maximum in the density of state of the midzone phonon and they also reveal a disorder-induced behavior similar to that of the 1350 cm^{-1}. The Raman spectra are basically similar to that of carbon nanotubes and quite different from that of

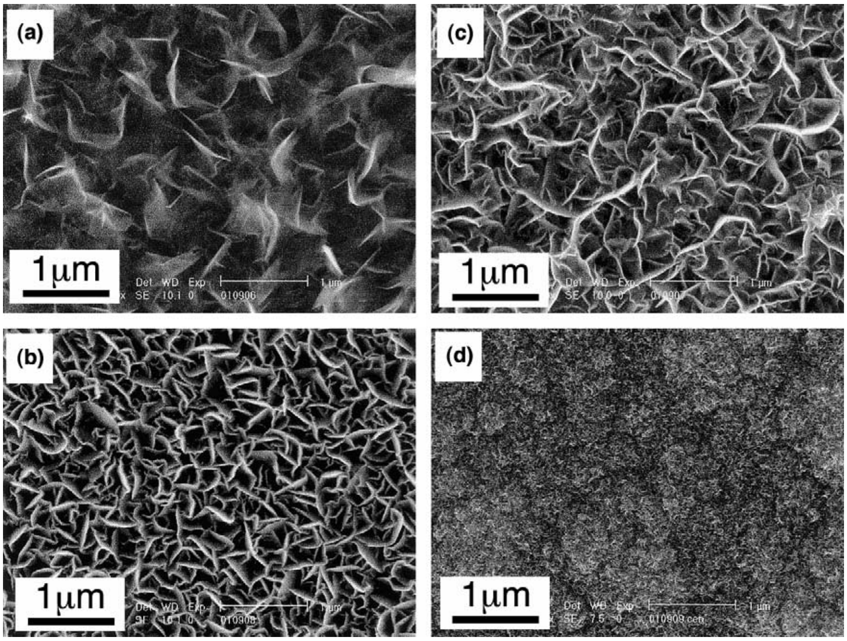

Fig. 1. SEM images of the carbon nanoflake films deposited at the substrate temperature of 400 (a), 500 (b), 600 (c) and 700 °C (d).

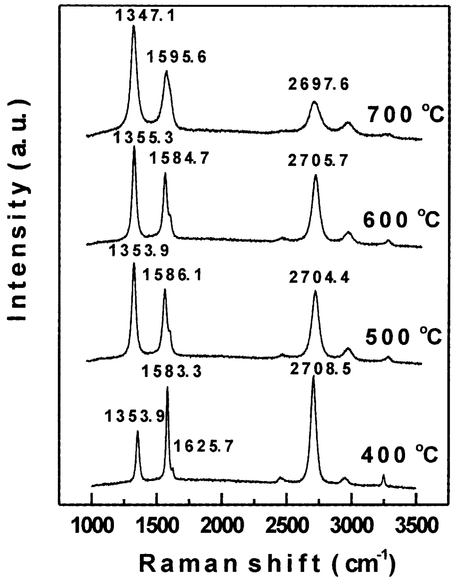

Fig. 2. Raman spectra of the carbon nanoflake films deposited at different substrate temperatures, revealing the carbon films becoming disordered with the increase of the substrate temperature.

high-oriented pyrolytic graphite [9,10]. As the substrate temperature increased, the distinct differences in these spectra were observed in the ratio of the integrated intensities of the D band to G band ($R = I_{1350}/I_{1590}$), the peak frequencies and full width at half maximum (FWHM) of the D and G bands, and the intensity and position of the peak at 1625 cm^{-1}. It was found that the ratio R, FWHM of the D and G bands as well as the intensity of the peak at 1625 cm^{-1} increased considerably with the substrate temperature. This suggests that the deposited graphitic carbon flakes become more disordered as the substrate temperature increases. This is consistent with the SEM observation that the size of the carbon flakes decreases as the substrate temperature decreases.

In addition to the substrate temperature, the acetylene concentration was also found to have a significant effect on the deposited films. Fig. 3 shows the relationship between the D to G band intensity ratio and the FWHM of D band versus the acetylene concentration from 3% to 15% at a substrate temperature of 600 °C. It is clear that both the intensity ratio and D band peak width increase as the acetylene concentration increases. This reveals that the films become more disordered as acetylene concentration increases.

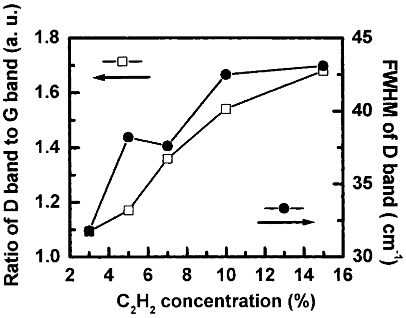

Fig. 3. Relationship between the intensity ratio of D band to G band and the FWHM of D band versus the acetylene concentration for the samples deposited at the substrate temperatures of 600 °C.

To investigate the growth mechanism of the carbon nanoflake films, chemical compositions of the deposited films were characterized by XPS. It was found that the films are composed mainly of carbon and with less than 3% of tungsten metal contamination from the hot filaments and 2% F originated from substrate cleaning processing with HF acid. The time evolution of the film deposited at 600 °C and 5% C_2H_2 is shown in Fig. 4. Fig. 4a–c show the images of the carbon nanoflake film after deposition for 7 min, 20 min and 24 h, respectively. The film deposited for 7 min consists of a large amount of worm-like short carbon rods or small carbon sheets with a uniform size estimated about 100 nm long and 5–10 nm wide. After 20 min of deposition, almost all the carbon nanoflakes (Fig. 4b) have approached a similar size and thickness to those in the sample after 24 h deposition (Fig. 4c).

From simple surface energy consideration, the formation of the nanorod and nanoflake rather than nanosphere structure suggests that an anisotropic process occurs during the growth of carbon nanoflake films in the current HFCVD system. The carbon clusters from the vapor could first condense along one direction to form a rod, and then grow along another direction almost normal to the substrate to form a sheet. On the other hand, the carbon nanoflakes may follow a two-dimensional growth model with a defined ratio of

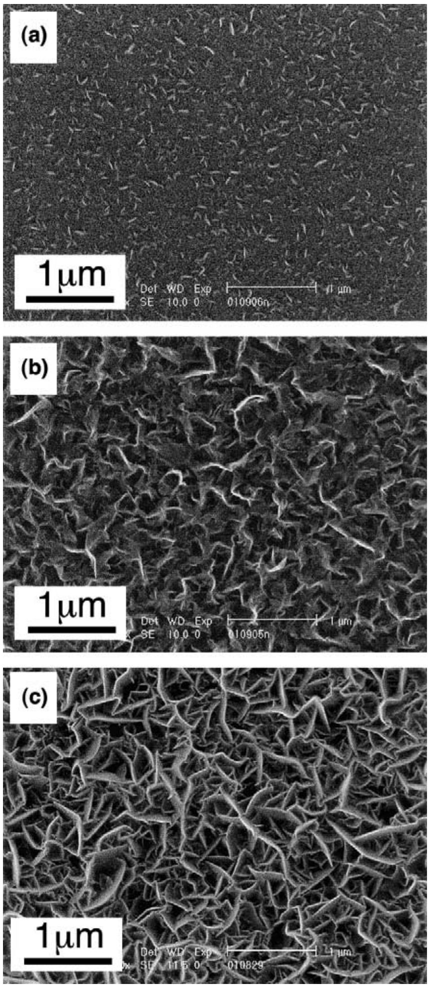

Fig. 4. SEM images of the samples deposited at the substrate temperature of 600 °C for 7 min (a), 20 min (b) and 24 h (c).

growth rate along two directions. During the growth of carbon nanotubes, the asymmetry factors are the directed flux of carbon (the ion current in arc discharge, or the flow of carbon vapor in vapor deposition methods) and the presence of a metal particle in the catalytic method, which acts as seed particles for precipitation of carbon from gas phase into the form of a hollow tube [11,12]. In the present synthesis, no bias voltage, metal catalysts or other auxiliary techniques that may produce asymmetric distribution of condensed carbon clusters were applied to our deposition system. Instead, just a Maxwellian distribution of carbon clusters was presented in the low temperature thermal plasma produced by heated filaments. However, a thin boundary layer of carbon clusters with a non-Maxwellian distribution could be formed just above the substrate surface due to the interaction between the reflected particles from the surface and the newly arrived ones. This is possibly favorable for the formation of large carbon clusters and subsequent asymmetric condensation. When the substrate temperature and acetylene concentration increase, condensed carbon clusters in the critical size and mobility on the surface will change, leading to the formation of more disordered carbon nanoflake film of a smaller size. In addition, at the temperature of several hundreds Kelvin, the space structure of the orbitals (or dangling bonds) of a free carbon atom could be considered asymmetric, with three in-plane sp^2 bonds and one p_z orbital that perpendicular to this plane. Such a configuration has the potential to form a plane structure and is native for the asymmetric surface energy of graphite. This asymmetric factor has proven to be important for the catalytic method of nanotube fabrication, and may play a similar role in the formation of carbon nanoflake films. In previous reports, carbon nanoflakes were produced outside the flame of arc discharge and on the graphite wall surrounding the anode and cathode as a byproduct of carbon nanotubes. In such a case, the growth radicals for the carbon nanotubes and carbon nanoflakes must be quite different, although their formation mechanisms are not yet clear. The arc discharge deposition method of carbon nanoflake films generally requires a higher substrate temperature (e.g. about 800 °C) and is less controllable compared with the present HFCVD method. Using the present approach, we can easily control the morphology, structure, and thickness of films on Si substrates. The present method also has the advantage that uniform films can be deposited over a relatively large area (about 30×50 mm^2 in the present system that uses two filaments) and can be further scaled-up, as in other HFCVD processes, with a filament array.

Since a high density of very sharp carbon nanoflakes in the film are perpendicular to the Si substrates and quiet uniform over the large area, they are expected to have a good field emission.

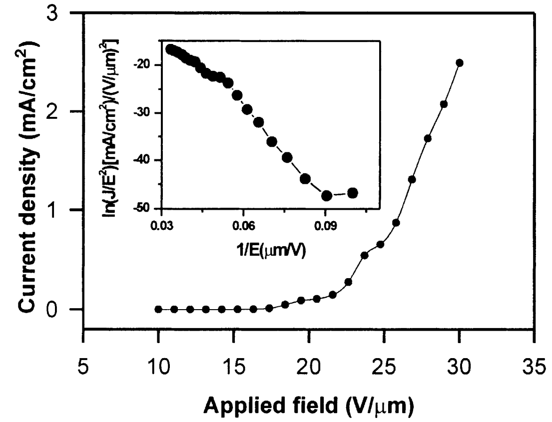

Fig. 5. Field emission *J–E* data taken from the carbon nanoflake films. The inset is the corresponding *F–N* plot.

The measurement process and apparatus has been described in detail in our previous paper [13]. The relations of emission current density (J) versus applied electric field (E) shown in Fig. 5 were taken from the sample deposited at the substrate of about 600 °C and acetylene concentration of 5%. The turn-on field defined as 0.01 mA/cm^2 were obtained to be about 17 V/μm. This value is smaller than that of curvy SiC nanorods our previously reported. For the other samples a turn-on field range from 20 to 35 V/μm were obtained. The curve of Fowler (F)–Nordheim (N) shown in the inset of Fig. 5 shows the emission process of the carbon nanoflake films followed the traditional mechanism of field emissions.

In summary, carbon nanoflake films have been prepared by conventional HFCVD without using any catalysts or surface pretreatment. The surface morphology and structure of carbon nanoflake films depended strongly on the acetylene concentration and substrate temperature. The growth mechanism of the carbon nanoflake films may be attributed to the asymmetric factor in the deposition system and the bonding nature of free carbon atoms. Considering the simple controllable deposition process for a large area and compatible with the current semiconductor industry, the carbon nanoflake films may be good candidates for large-scale applications as nanostructured templates and electron vacuum emitters.

Acknowledgements

This work was financially supported by the Research Grants Council of Hong Kong SAR, PR China (Project No. 9040637).

References

[1] S. Iijima, Nature 354 (1991) 56.
[2] H.W. Kroto, J.R. heath, S.C. O'Brien, R.F. Curl, R.E. Smalley, Nature 318 (1985) 162.
[3] J. Yu, E.G. Wang, X.D. Bai, Appl. Phys. Lett. 78 (2001) 2226.
[4] Y.H. Tang, N. Wang, Y.F. Zhang, C.S. Lee, I. Bello, S.T. Lee, Appl. Phys. Lett. 75 (1999) 2921.
[5] Y. Ando, X. Zhao, M. Ohkohchi, Carbon 35 (1997) 153.
[6] C. Liu, Y.Y. Fan, M. Liu, H.T. Cong, H.M. Cheng, M.S. Dresselhaus, Science 286 (1999) 1127.
[7] A. Chambers, C. Park, R.T.K. Baker, N.M. Rodriguez, J. Phys. Chem. B 122 (1998) 4253.
[8] N.G. Shang, C.S. lee, Z.D. Lin, I. Bello, S.T. Lee, Diamond Relat. Mater. 9 (2000) 1388.
[9] W.Z. Li, H. Zhang, C.Y. Wang, Y. Zhang, L.W. Xu, K. Zhu, S.S. Xie, Appl. Phys. Lett. 70 (1997) 2684.
[10] P.V. Huong, R. Cavagnat, P.M. Ajayan, O. Stephan, Phys. Rev. B 50 (1994) 15473.
[11] G.G. Tibbetts, J. Cryst. Growth 66 (1984) 632.
[12] A.A. Lucas, P.H. Lamblin, R.E. Smalley, J. Chem. Phys. Solids 54 (1993) 587.
[13] K.W. Wong, X.T. Zhou, F.C.K. Au, H.L. Lai, C.S. Lee, S.T. Lee, Appl. Phys. Lett. 75 (1999) 2918.