OPTOELECTRONICS LETTERS Vol.5 No.2, 1 March 2009

Effect of nitrogen pressure on optical properties and microstructure of diamond-like carbon films grown by pulsed laser deposition*

DING Xu-Li (丁旭丽) 1, LI Qing-Shan (李清山) 1,2, and KONG Xiang-he (孔祥和) 1**

1. College of Physics and Engineering, Qufu Normal University, Qufu 273165, China

2. Department of Physics, Ludong University, Yantai 264025, China

(Received 10 November 2008)

The effect of nitrogen pressure on optical properties of hydrogen-free diamond-like carbon (DLC) films deposited by pulsed laser ablation graphite in different background pressures of nitrogen is reported. By varying nitrogen pressures from 0.05 to 15.00 Pa, the photoluminescence is gradually increased and optical transmittance is gradually decreased. Atomic force microscopy (AFM) is used to observe the surface morphology of the DLC films. The results indicate that the surface becomes unsmoothed and there are some globose particles on the films surface with the rise of nitrogen pressures. The microstructure of the films is characterized using Raman spectroscopy.

Document code: A **Article ID:** 1673-1905(2009)02-0117-3

DOI 10.1007/s11801-009-8158-z

Diamond-like carbon (DLC) is a very attractive material due to its unique properties, which resembles diamond while the synthetic conditions are easier compared with diamond[1-4]. Many physical and chemical methods have been adopted to synthesize DLC[4-8]. But most chemical vapor deposition (CVD) methods generate hydrogenated amorphous carbon which is not stable when temperature is high [9,10]. In addition, CVD techniques usually need high substrate temperature (⩾800°C) which is not favorable when the substrate is thermally sensitive. The pulsed laser deposition (PLD) has the unique ability to synthesize hydrogen-free DLC films at low deposition temperature. The deposition parameters (e.g. temperature, ambient gas pressure, laser intensity, etc) are important for PLD system. A wide range of DLC films growth conditions has been reported in the literature for the past several decades but there are few reports of nitrogen circumstances. In this letter, we report DLC films grown at different background pressures of nitrogen by PLD.

DLC films are deposited by pulsed laser ablation of a high pure (99.999%) graphite target using a Tuilaser Thin-Films Star 20 excimer laser operating at 248 nm. The laser beam with energy of 120 mJ is focused with a spherical lens onto rotating target at an incidence angle of 45°. The repetition rate of laser pulses is set to 10 Hz. Before depositting the films, the quartz substrates are ultrasonically cleaned with acetone and alcohol for 10 minutes separately, then rinsed repeatedly in de-ionized water and blew dry and then placed in growth chamber immediately. The growth chamber is evacuated using a turbomolecular pump to 5.0×10^{-6} Pa, and then backfilled with nitrogen to the required pressure. The DLC films are grown at different background nitrogen pressure ranging from 0.05 Pa to 15.00 Pa. The pulsed laser shots are maintained in the range of 10000-20000, in order to maintain the same film thickness for each deposition. The target to substrate distance is fixed at 60 mm. The films are deposited onto a rotating substrate which is wheeled by a motor in order to obtain uniform thin films. In order to avoid target drilling, the target is also rotated to provide each laser pulse a fresh target surface. Before deposition, the substrates are argon ion etched for residual impurities for 10 minutes.

The microstructure properties of DLC films are characterized by Raman spectroscopy using (Renishaw Ramanscope) 514.5 nm argon ion laser excitation and the resolving power of this spectrum is 1-2 cm^{-1}. The room-temperature PL measurements are performed by Shimadzu RF-5301 PC fluorescence spectrophotometer using the 488 nm laser excitation. The optical transmittance spectrum is measured using Shimadzu UV-3101 ultraviolet spectrophotometer in the range of 200-1300 nm. The surface morphology of the DLC films is also investigated by AFM Veeco DISPM and the measurements are performed in tapping mode using V-shaped ultra sharp Si cantilever tip.

---

* This work has been supported by the Natural Science Foundation of Shandong Province (Grant No. Y2002A09).

** Email: xuli.rende@163.com

Fig.1 shows the Raman spectra corresponding to the films deposited at different nitrogen pressures.

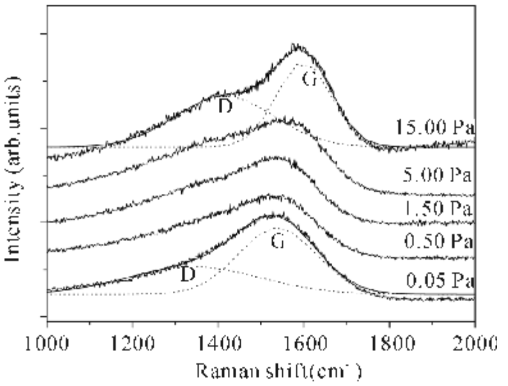


Fig.1 Plots of Raman spectra for DLC films deposited at different nitrogen pressures: (a) 0.05 Pa, (b) 0.50 Pa, (c) 1.50 Pa, (d) 5.00 Pa and (e) 15.00 Pa

All the Raman spectra for our samples show a broad and asymmetry band in the range from 1000 to 2000 cm^{-1} which shows the amorphous nature of the films. In order to analyze the Raman spectra, we adopte Gaussians function to fit these spectra which were all subtracted with baseline before fitting. In general, The D- and G-bands shown in the spectra are due to the inelastic scattering of sp^2 sites[11-13]. The variation in the position and the shape of the two peaks are due to the structural changes, formation of disorder, aromatic rings, micrographite, etc [11-14]. The G peak is a bond stretching of all pairs of sp^2 sites arranged in olefin chains or aromatic rings[15-17]. The D peak is a breathing vibration of a six-fold aromatic ring, associated with disorder [11,12,15]. Low sp^2 contents in the films are expressed by a low intensity ratio I_D/I_G, whereas a higher ratio points to a larger clustering of sp^2 sites in volume or number[11-16]. As the nitrogen pressure is increased, the D peak is becoming apparent and the ratio I_D/I_G is also increased and simultaneously the G peak position is up-shift. The result indicates that higher nitrogen pressure stimulates more sp^2 structure formation in the films. For comparison, the I_D/I_G ratio and the G peak positions are plotted as a function of nitrogen pressure in Fig.2.

After analyzing the microstructure of the films, the PL intensity over the same pressure range is also plotted in Fig.3. It can be seen that the majority of the detected PL intensity appears to come from the broad band centered approximately at 700 nm. For comparison, all these spectra have been normalized to the intensity of the Raman peak. As the increase of nitrogen pressure, the PL intensity is clearly enhanced, accompanied by the red-shift of the main PL band. The result in our group agrees with the result in the literature[17]. This result may be caused possibly by the increasing number of collision between carbon species and nitrogen when the pressure is increased; as a result, the energy of the C ions is decreased[17]. Thus more sp^2 structure is formed in the films. At the same time the scattering of C atoms or ions by collision is also increased which can be observed through the expansible plasma plume during deposition, and the film thickness measured by surface profile measuring system is thinner with the increase of nitrogen pressure at the same pulsed laser shots number.

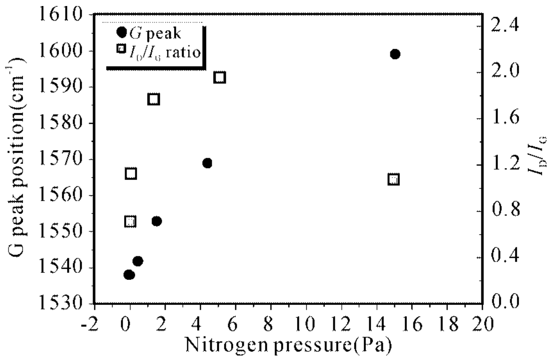


Fig.2 Plots of I_D/I_G ratio and G peak positions as a function of different nitrogen pressures during deposition.

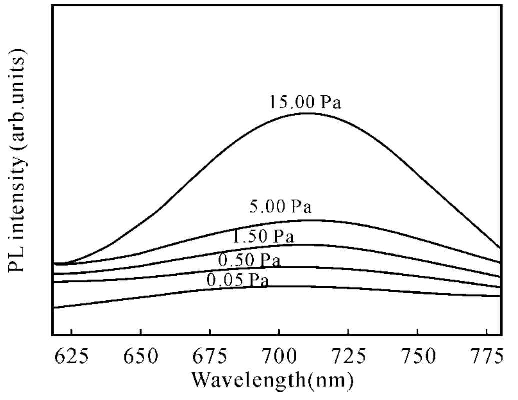


Fig.3 Plots of PL spectra using 488 nm excitation for DLC films deposited at different nitrogen pressures: (a) 0.05 Pa, (b) 0.50 Pa, (c) 1.50 Pa, (d) 5.00 Pa and (e) 15.00 Pa.

Fig.4 shows the optical transmittance spectra of the DLC thin films deposited at different nitrogen pressure. As can be seen from the spectra, the optical transmittance is gradually decreased with the increase of nitrogen pressure.

The surface of the films becomes rougher when the nitrogen pressure is increased. Fig.5 shows 5 μm × 5 μm AFM images of the surface morphology of the DLC films deposited at different nitrogen pressures. The surface of the film deposited at 0.05 Pa is smooth and compact. Inversely, there are a lot of mussy particles on the surface of the films deposited at 15.00 Pa, and the surface becomes rougher and not flat. This may be caused by the increasing number of collisions in the plasma.

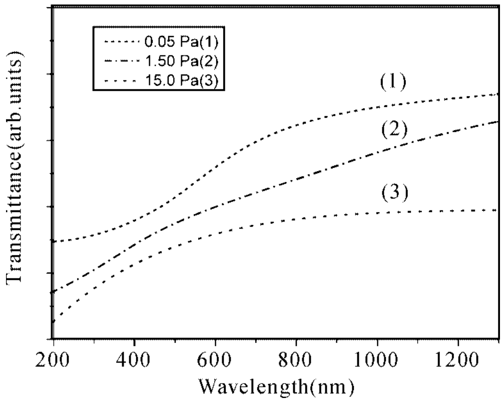
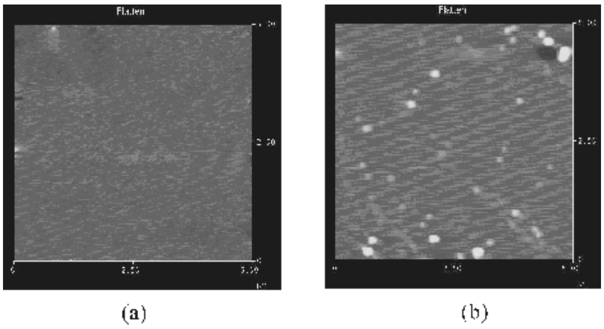


Fig.4 Plots of optical transmittance spectra of DLC films deposited at different nitrogen pressures: (1) 0.05 Pa, (2) 1.50 Pa and (3) 15.00 Pa.


(a) (b)

(a) and (b) Digital Instrument Nanoscope: Scan size: 5.000 μm; Scan rate: 1.969 Hz; Data scale: 20.00 nm; Engage *X* Pos: -19783.4 μm; Engage *Y* Pos: -42151.3 μm.

Fig.5 Surface 5 μm × 5 μm AFM images of the DLC films deposited. (a) 0.05 Pa, (b) 15.00 Pa.

In summary, we have prepared DLC films at different nitrogen pressures by pulsed laser deposition technique. All the samples exhibit amorphous nature with broad Raman peak at 1000-1900 cm^{-1}. The degree of graphitization becomes apparent when the nitrogen pressure arises from 0.05 Pa to 15.00 Pa. The room-temperature photoluminescence is gradually enhanced with the increase of nitrogen pressure. The optical transmittance is gradually decreased and the surface morphology of the films becomes rougher with the rise of nitrogen pressure.

References

[1] X. Xiao, B. W. Sheldon, Y. Qi, and A. K. Kothari, Appl.Phys. Lett., **92** (2008), 131908.

[2] J. David Carey, Simon J. Henley, Diamond Relat.Mater, **16** (2007), 1782.

[3] WU Xiao-guo, XIONG Ying, YANG Bao-he, Journal of Optoelectronics • Laser, **18** (2007), 963.(in Chinese).

[4] C. Vasiraghi, A.C. Ferrari, R. Ohr, D. Chu, R. Robertson, Diamond Relat. Mater., **13** (2004), 1416.

[5] C. Corbella, M. Vives, G. Oncins, C. Canal, J.L. Andujar, E. Bertran, Diamond Relat. Mater., **13** (2004), 1494.

[6] N. Maitre, T. Girardeau, S. Camelio, A. Barranco, D. Vouagner, E. Breelle, Diamond Relat. Mater., **12** (2003), 988.

[7] C. Sánchez Aké, H. Sobral , M. Villagrán-Muniz, Thin Solid Films, **516** (2007), 8.

[8] YANG Bao-he, CUI Jian, XIONG Ying, Journal of Opltoelectronics • Laser, 19 (2008), 0625.(in Chinese)

[9] A.M. Wu, J. Sun, X.K. Shen, N. Xu, Z.F. Ying, Z.B. Dong, J. D. Wu, Diamond Relat Mater., **15** (2006), 1235.

[10] CHEN Da, LI Qing-shan, WANG Jing-jing, ZHENG Xuegang. Optoelectronics Lett., **2** (2006), 1673.

[11] M.v. Gradowski , A.C. , Ferrarib, R. Ohr, B. Jacoby, H. Hilgers, H.-H. Schneider, Surf. Coat. Technol., **174 –175** (2003), 246.

[12] C. Sánchez Aké, H. Sobral , M. Villagrán-Muniz, Thin Solid Films, **516** (2007), 8.

[13] A. C. Y. Liu, R. Arenal, D. J. Miller, and Xidong Chen, Phys. Rev.B, **75** (2007), 205402.

[14] M. RUSOP, T. SOGA, T. JIMBO, M. UMENO, and M. SHARON, Surf. Rev.Letters., **12** (2005), 691.

[15] R. Sanginés, C. Sánchez Aké, H. Sobral, M. Villagrán-Muniz, Phys. Lett. A, **367** (2007), 351-355.

[16] A.C. Ferrari, J. Robertson, Phys. Rev. B, **61** (2000), 14095.

[17] S. J. Henley,J. D. Carey, and S. R. P. Silva, Appl.Phys.Lett., **25** (2004), 6236.