Transactions of the Materials Research Society of Japan 27 [4] 787-790 (2002)

Preparation of Carbon Nano-Structure by Pulsed Laser Deposition

Masaaki Yamazato, Masamitsu Nagano and Kenji Ebihara*
Department of Chemistry and Applied Chemistry, Saga University
1 Honjo-machi, Saga, 840-8502, Japan
Fax: 81-952-28-8591, e-mail: yamazato@cc.saga-u.ac.jp
*Department of Electrical and Computer Engineering, Kumamoto University
Fax: 81-96-342-3630, e-mail: ebihara@eecs.kumamoto-u.ac.jp

Carbon nano-structures were deposited on Si(100) and on sapphire (α-Al_2O_3) substrates in an oxygen atmosphere by KrF pulsed laser deposition (PLD) method. The structures were grown at a substrate temperature of 550 °C and in an oxygen pressure of 5×10^{-3} to 0.2 Torr. Atomic force microscope (AFM) and X-ray diffraction (XRD) were used to characterize the structure of deposited films. Carbon nano particles were grown under oxygen pressures ranging from 0.05 to 0.15 Torr, while graphite phase was grown below 0.05 Torr. The nucleation densities of nano particles on Si and on sapphire substrates were $3\times10^9/cm^2$ and $6\times10^8/cm^2$, respectively. The carbon nano structures deposited on Si(100) substrates under 0.1 Torr oxygen pressure exhibit the X-ray diffraction from diamond (111) plane and contain grains with an estimated size of 15 nm. Raman spectra of such nano structures on Si substrate showed a small broad peak at 1150 cm^{-1}.

Keywords: pulsed laser deposition, nanocrystalline diamond, carbon nano structure, oxygen atmosphere

1. INTRODUCTION

In recent years, novel carbon materials such as carbyne, fullerene, nanocrystalline diamond, diamond like carbon (DLC) and carbon nanotube (CNT) have been intensively investigated because of their potential utilization in electronic, magnetic, optical and micromechanical applications [1-4]. For example, diamond or DLC coated tool inserts, diamond space windows, X-ray masks, etc., are already available on the market and extensive research is ongoing to use them as a cold cathode material [5-6]. Cold cathode material is important element of field emission displays in order to obtain an image quality similar to a cathode ray tube. We have reported that the DLC films are promising surface coating candidate for preventing degradation of $YBa_2Cu_3O_{7-x}$ superconducting and $PbZr_xTi_{1-x}O_3$ ferroelectric films [7]. On the other hand, nanocrystalline diamond has several unique properties compared with the conventionally microcrystalline diamond films [8, 9]. The lower friction coefficients and the higher hardness make nanometric diamonds better candidates as coating material for mechanical tools, and also it has been presented that the electron emission efficiency of the nanocrystalline diamond films is much higher than that of the ordinarily microcrystalline diamond films [10]. The typical threshold electric field for nanocrystalline diamond is one order lower than that of microcrystalline diamond [11, 12].

Thus far, many attempts have been made to synthesize nanocrystalline diamond, such as plasma CVD [13], magnetoactive CVD [14], and sol-gel technique [15]. However, it is still difficult to prepare diamond films using physical vapor deposition method. Pulsed laser deposition is very attractive process for DLC, nanotubes and oxide thin film preparation [2, 7]. High initial rate of heating and energetic plasma beam result in high kinetic and internal excitation energies of ablated species assist film growth and promote surface solid state reactions. Recently, Yoshimoto et al. have reported the diamond growth in oxygen atmosphere by a PLD method. They prepared the diamond nucleation on ultra smooth single crystal sapphire (0001) substrate [16]. Chen et al. have reported the nanocrystalline diamond on sapphire by a PLD method. However, as far as our best knowledge, it has not been reported that the synthesis of nanocrystalline diamond on Si substrate by a PLD method. In this paper, we report on a preparation of nanocrystalline diamond grains on Si substrate by PLD method.

2. EXPERIMENTAL

A schematic diagram of the pulsed laser deposition system is shown in Figure 1. The carbon nano structures were prepared by KrF excimer laser deposition. Lambda Physik LPX205 KrF excimer laser (λ = 248 nm, pulse duration of 25 ns, max. output of 850 mJ) beam was focused on a rotating graphite target (99.9%, ϕ = 30 mm). The laser fluence and pulse repetition rate were 6 J/cm^2 and 5 Hz, respectively. The resulting plume of ablated material is caught on Si(100) and sapphire (α-Al_2O_3) substrates placed in front of the target. The distance between the substrate and the target was 30 mm. The Si and sapphire substrates were heated from room temperature to 550 °C by resistance heater (Neocera Flat Plate Heater SH2). The background pressure was less than 5×10^{-6} Torr. The operating pressure of O_2 gas was varied from 10 to 200 mTorr. The deposited films were characterized using X-ray diffraction (XRD, Rigaku RINT2100/PC),

atomic force microscopy (AFM, Seiko Instruments Inc. SII SPI-3800N) and Raman spectroscopy (OBIN-YVON T-64000). The main experimental conditions were listed in Table I.

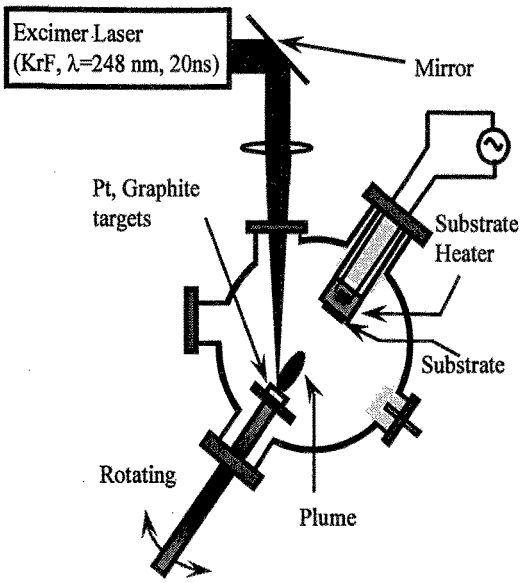


Fig. 1. Schematic diagram of pulsed laser deposition system.

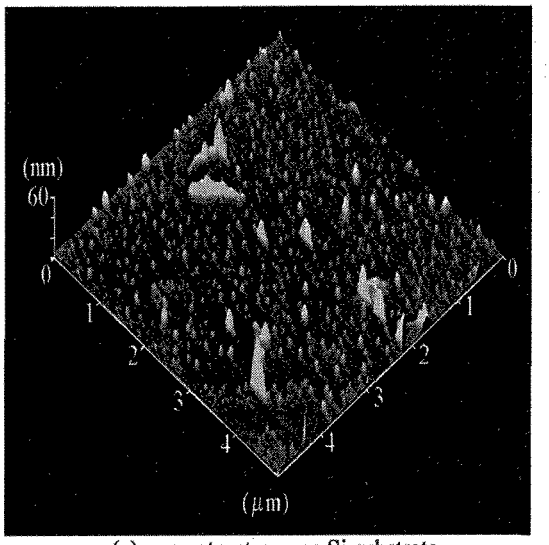
Table I. Preparation conditions

Targets	Graphite (99.9 %)
Laser fluence (J/cm^2)	6
Repetition rate (Hz)	5
Laser shots (shots)	72,000
Temperature (°C)	550
Substrate	Si and Sapphire
Distance of Target and substrate (mm)	30
Pressure (mTorr)	O_2 10, 30, 50, 75, 100, 200

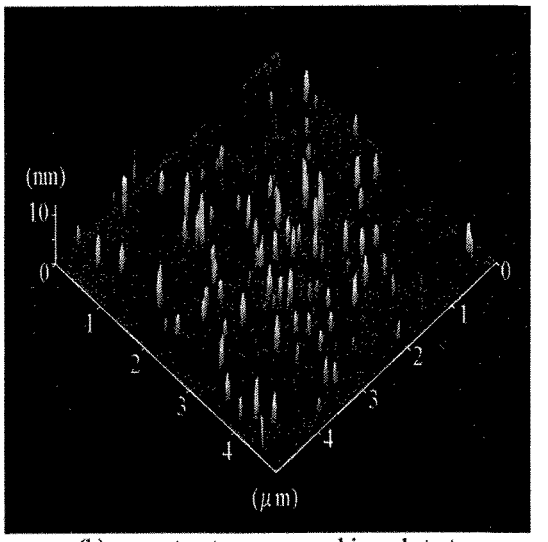
3. RESULTS AND DISCUSSION

3.1 Surface morphology

Figure 2(a) and (b) show AFM images of the surface of the films on Si(100) and on sapphire substrates. The laser fluence, repetition rate and deposition time are 6 J/cm^2, 5 Hz and 4 hours, respectively. The deposition temperature is 550 °C. As shown in Figure 2(a), the surface mainly consists of small and sharp particles of which size is in the range of 10 - 100 nm and some micrometer line structures. On the other hand, nano structures on sapphire substrate consist of only small particles. We found that such carbon nano particles could be grown under oxygen pressures ranging from 0.5 to 1.5 Torr. The nucleation densities of nano particles on Si and on sapphire substrates were 3×10^9/cm^2 and 6×10^8/cm^2, respectively. The nucleation density of nano particles on sapphire substrate was about 20 % of that on Si substrate. The oxygen pressure either below 0.04 Torr or above 0.2 Torr, we observed the growth of graphite films or the absence of film growth, respectively.



(a) nano structures on Si substrate



(b) nano structures on sapphire substrate.

Figure 2. Three-dimensional AFM image scanned in an area of 5×5 μm^2 of the carbon nano structures grown on Si(100) and sapphire substrates

3.2 Crystal structure

In order to investigate the crystal structure of these grains in our films, XRD measurements were performed in the 2θ range from 40° to 90°. Figure 3 shows X-ray diffraction patterns of the films shown in Figure 2. One peak from the prepared nano structures on Si substrate is observed at 44.1°. The FWHM of this peak and the corresponding interplanar spacing are 0.62° and 0.205 nm, respectively. This interplanar spacing value is close to the lattice constant of cubic diamond (111) plane (d = 0.206 nm). We could not find this diffraction peak from diamond (111) below 0.5 Torr. On the other hand, we could not see any diffraction peaks from carbon nano structures on sapphire substrate. One possible interpretation of no diffraction peak is that the nucleation density of nano particles on sapphire substrate is too small for XRD measurement.

The size of the grains can be estimated by using the Scherrer formula: $T=0.9\lambda/\Delta\cos\theta$, where λ is the X-ray wavelength (1.54 Å), Δ is the half-width value of the XRD spectrum, θ is the angle satisfying Bragg's law and T is the grain size [17]. The estimated grain size is about 15 nm for the nano structures on the Si substrates prepared under 100 mTorr oxygen pressure, 550 °C substrate temperature and 6 J/cm^2 laser energy fluence. This value corresponds to the height of particles in Figure 2.

X-ray diffraction from diamond (111) plane and the small size of estimated grains suggested the growth of nano crystalline diamond on Si(100) substrate.

Yoshimoto et al. have reported the microcrystalline diamond particles growth by using a PLD method in oxygen atmosphere to form crystals that are hetero-epitaxially aligned on an ultrasmooth single crystal sapphire substrate [16]. In our results, microcrystalline diamonds were not grown on an as-supplied the Si nor on the sapphire substrates, while nanocrystalline diamonds were grown on the Si substrates. Chen et al. have reported the nanocrystalline diamond growth on the sapphire substrate [17]. They set the substrates that were positioned parallel to the laser incident direction at a distance of 4 cm away from target. In our case, the angle of substrates with laser incident direction was not parallel but was 135°, and they faced on target with the distance of 3 cm. The mechanism of growing diamond particles is not clear. These results, however, indicate that the growth strongly depends on kind of substrates and experimental conditions. To our best knowledge, it has not been reported that the nanocrystalline diamond growth on Si substrate by PLD method in oxygen atmosphere, our results show the possibility of it.

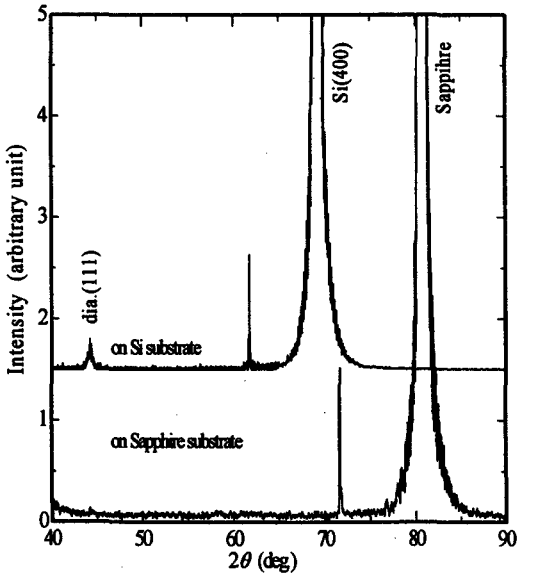


Fig. 3 X-ray diffraction patterns of deposited carbon nano structures on Si and sapphire substrates.

3.3 Raman spectroscopy

The Raman measurement is also carried out for the further characterization of deposited structure. We could not observe a first-order diamond Raman peak centered at 1332 cm^{-1}, while the broad band could be observed near 1150 cm^{-1}. The Raman intensity of diamond at 1332 cm^{-1} diminished rapidly with decreasing crystallite size. The band near 1150 cm^{-1} is shown to be related to the calculated phonon density of states of diamond and proves the presence of the nanocrystalline phase of diamond [19]. Some other groups reported that the Raman spectrum of nanocrystalline diamonds showed the broad peak at 1150 cm^{-1} without 1332 cm^{-1} peak [20].

This broad band at 1150 cm^{-1} indicates the presence of cubic nanocrystalline diamond on Si substrate, which is in agreement with the AFM and XRD measurement.

In our work, cubic nanocrystalline structure of diamond was grown on Si(100) substrate by PLD method.

4. CONCLUSIONS

We have studied the morphology and structure of carbon nano structures grown on Si(100) and sapphire substrates by PLD method. We found that carbon nano particles could be grown under oxygen pressures ranging from 0.5 to 1.5 Torr. The oxygen pressure either below 0.04 Torr or above 0.2 Torr, we observed the growth of graphite films or the absence of film growth, respectively. XRD measurement showed a diamond (111) peak from carbon nano particles on Si substrate. The estimated grain size of particles grown at the substrate temperature of 550 °C and in an oxygen pressure of 100 mTorr was 15 nm on the basis of a Scherrer formula. The nucleation densities of nano particles on Si and sapphire substrates were 3×10^9/cm^2 and 6×10^8/cm^2, respectively. The Raman spectrum showed an 1150 cm^{-1} broad peak, which is in agreement with that of the nanocrystalline diamond. These results indicated that the nanocrystalline diamond particles were grown on the Si substrate in an oxygen atmosphere using a PLD method.

Acknowledgement

The authors deeply thank Professor Yoshinori Nibu, Fukuoka University, for the Raman spectrum measurements. This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan, and by the 'Encouragement of Young Scientists' Program (No.13750280) of the Japan Society for the Promotion of Science.

References

[1] N. Jiang, S. Kujime, I. Ota, T. Inaoka, Y. Shintani, H. Makita, A. Hatta, A. Hiraki, J. Cryst. Growth 218 (2000) 265-271.

[2] A. A. Voevodin, M. S. Donley, Surf. Coat. Technol. 82 (1996) 199-213.

[3] M. J. Matthews, M. S. Dresselhaus, G. Dresselhaus, M. Endo, Y. Nishimura, T. Hiraoka, N. Tamaki, Appl. Phys. Lett. 69 (1996) 430-432.

[4] J. Hone, M. C. Llaguno, N. M. Nemes, A. T. Johnson, J. E. Fischer, D. A. Walters, M. J. Casavant, J. Schmidt, R. E. Smalley, Appl. Phys. Lett. 77 (2000) 666-668.

[5] T. Takida, K. Inoue, S.-G. Ri, H. Kimura, H. Kiyota, I. Saito, T. Kurosu. M. Iida, Jpn. J. Appl. Phys. 39 (2000) L56-L58.
[6] O. Yavas, T. Hashimoto, N. Suzuki, M. Takai, Y. Higuchi, M. Kobayashi, A. Hosono, S. Okuda, Jpn. J. Appl. Phys. 38 (1999) 7208-7212.
[7] K. Ebihara, F. Mitsugi, M. Yamazato, Y. Yamagata, Composites B 30 (1999) 685-689.
[8] A. Erdemir, G. R. Fenske, A. R. Krauss, D. M. Gruen, T. McCauley, R. T. Csencsits, Surf. Coat. Technol. 120-121 (1999) 565-572.
[9] P. Hollman, O. Wänstrand, S. Hogmark, Diamond Relat. Mater. 7 (1998) 1471-1477.
[10] V. Ralchenko, A. Karabuto, I. Vlasov, V. Frolov, V. Konov, S. Gordeev, S. Zhukov, A. Dementjev, Diamond Relat. Mater. 8 (1999) 1496-1501.
[11] X. L. Peng, Thin Solid Films 370 (200) 63-69
[12] S. Gupta, B. L. Weiss, B. R. Weiner, G. Morell, J. Appl. Phys. 89 (2001) 5671-5675.
[13] K. Chakrabarti, R. Chakrabarti, K. K. Chattopadhyay, S. Chaudhuri, A. K. Pal, Diamond Relat. Mater. 7 (1998) 845-852.
[14] D. M. Greun, X. Pan, A. R. Krauss, S. Liu, J. Luo, C. M. Fosteo, J. Vac. Sci. Technol. A 12 (1994) 1491.
[15] B. Felde, A. Mehner, J. Kohlscheen, R. Gläbe, F. Hoffmann, P. Mayr, Diamond Relat. Mater. 10 (2001) 515-518.
[16] M. Yoshimoto, K. Yoshida, H. Maruta, Y. Hishitani, H. Koinuma, S. Nishio, M. Kakihana, T. Tachibana, Nature 399 (1999) 340.
[17] Z. Y. Chen, J. P. Zhao, T. Yano, T. Ooie, M. Yoneda, J. Sakakibara, J. Cryst. Growth 226 (2001) 62-66.
[18] T. Sharda, T. Soga, T. Jimbo, M. Umeno, Diamond Relat. Mater. 9 (2000) 1331-1335.
[19] V. Paillard, P. Melinon, V. Dupuis, J. P. Perez, A. Perez, Phys. Rev. Lett. 71 (1993) 4170.
[20] T. Sharda, M. Umeno, T. Soga, T. Jimbo, Journal of Applied Physics. 89 (2001) 4874

(Received December 20, 2001; Accepted January 31, 2002)