Journal of the Korean Electrochemical Society
Vol. 3, No. 4, 2000, 200-203

Crystalline Growth Properties of Diamond Thin Film Prepared by MPCVD

Soo-Gil Park†, Gyu-Sik Kim, Yasuaki Einaga* and Akira Fujishima*

Dept. of Industrial Chemical Engineering, Chungbuk National University
**Dept. of Applied Chemistry, School of Engineering, The University of Tokyo, Japan.*
(Received April 7, 2000 : Accepted October 20, 2000)

Abstract : Boron doped conducting diamond thin films were grown on Si substrate by microwave plasma chemical vapor deposition from a gaseous feed of hydrogen, acetone/methanol and solid boron. The doping level of boron was ca. 10^2 ppm (B/C). The Si substrate was tilted ca. 10° to make Si substrate, which have different height and temperature. Experimental results showed that different crystalline of diamond thin films were made by different temperature of Si substrate. There appeared 3~4 steps of different crystalline morphology of diamond. To characterize the boron-doped diamond thin film, Raman spectroscopy was used for identification of crystallinity. To survey surface morphology, microscope was used. Grain size was changed gradually by different temperature due to different height. The Raman spectrum of film exhibited a sharp peak at 1334 cm^{-1}, which is characteristic of crystalline diamond. The lower position of diamond film position, the more non-diamond component peak appeared near 1550 cm^{-1}.

초 록 : Microwave plasma chemical vapor deposition을 이용하여 붕소가 도핑된 전도성 다이아몬드 박막을 제조하였다. 탄소원으로는 아세톤과 메탄올을 사용하였으며, 붕소원으로는 B_2O_3를 사용하고, 운반가스로는 수소를 사용하였다. 이때 붕소의 도핑농도는 약 10^2 ppm(B/C)이였다. Si 기질 각 부분의 온도와 플라즈마에서의 거리를 다르게 하기 위해서 Si 기질을 배치함에 있어 약 10°를 기울여 다이아몬드 박막을 성장시켰다. 실험결과 모두 동일한 조건 이였으나 같은 Si 기질 위에 높이에 따른 온도구배가 형성되었으며, 그에 따라 다이아몬드의 결정 또한 각기 달랐다. 다이아몬드 박막에 나타난 결정형태의 분포는 약 3~4부분으로 나뉘어 있었다. 제조된 다이아몬드 박막의 특성을 확인하기 위해 Raman spectrum을 이용해 다이아몬드의 결정성을 확인하였고, 표면의 형태를 관찰하기 위해 현미경을 사용하였다. 입자의 크기는 각기 다른 Si 기질의 높이에 의한 온도구배로 인하여, 기질의 높이에 따라 서서히 달라졌다. 다이아몬드 박막의 Raman spectrum 측정결과 1334 cm^{-1}에서 강한 peak가 발견되었으며, 이것은 결정성 다이아몬드의 일반적인 특성 이였다. Si 기질 중 낮은 곳에 위치한 부분의 Raman spectrum은 비다이아몬드의 peak인 1550 cm^{-1} 부근에서 넓게 peak가 상승된 것이 관찰되었다.

Key words : Microwave plasma CVD, Boron-doped diamond thin film, Raman spectroscopy, Grain size, Si substrate.

1. Introduction

Diamond thin film has been recognized as a promising material in electrochemistry because of its superior properties such as excellent hardness, physical and chemical stability, high resistivity and so on.[1,2] Diamond shows p-type semiconducting behavior with existence of boron. By using microwave plasma CVD method, boron can be introduced into the diamond matrix and these boron-doped diamond films have unique electrochemical properties. For example, the boron-doped diamond film has wider potential window range (ca. 2.5~3.0V), low resistivity (~$10^{-3}\Omega$cm), low background current and good reversibility for outer-sphere type one-electron redox couples such as $Fe(CN)_6^{3-/4-}$ and $IrCl_6^{2-/3-}$.[3-5]

So far, some groups have been reported about diamond crystallinity on <100> and <110> directions or single crystalline by temperature effect.[6-8] And some group including, Wild et. al. have reported the effect of substrate temperature and methane percentage on texture and morphology of diamond.[8,11,12] However, these reports were far from surface morphology and grain size.[9-11] There are so many factors in preparation of diamond thin film by microwave plasma CVD, such as substrate temperature, microwave power, chamber pressure, gas flow rate, deposition time, component of carbon source, etc.[12-18] According to condition, grain size and crystallinity are determined. In many experimental experiences, we thought that temperature of substrate is the most important factor, which determines the size of diamond grain. In this work, we have tried to realize temperature gradient by inclining a Si substrate and examine the size of diamond grain. By inclining, not only temperature of substrate by position but also distance between substrate and plasma core was changed.

2. Experimental

The boron-doped diamond thin films were grown on n-Si (100) substrate, which had been polished by 0.5 μm diamond powder (Type Micron + SND, De Beers). Microwave plasma chemical vapor deposition (CVD) method was adopted by

†E-mail: sgpark@cbucc.chungbuk.ac.kr

using commercial microwave plasma reactor(ASTeX Corp., Woburn, MA, USA). A 9:1 (v/v) mixture of acetone (Guaranteed, Koso Chemical Co., Ltd.) and methanol(Guaranteed, Nacalai Tesque) (volume ratio) was used as the carbon source. B_2O_3 (Extra pure, Wako Chemical Co., Ltd) was used as the boron source. We dissolved B_2O_3 in this mixture solution so that the B/C weight ratio was ca. 10^2 ppm. In order to make temperature gradient of substrate, it was inclined to ca. 10° (Fig. 1). The temperature profile of substrate, measured by optical pyrometer, was 750~980°C. 99.99% H_2 gas was used as the carrier gas, which carries carbon source into chamber. The H_2 flow rate was controlled at 532 sccm(standard cubic centimeters per minute) and the carbon source flow rate was 10 sccm with a mass flow controller. The total pressure was fixed 100 Torr. Diamond film deposition was carried out using a microwave power of 4000W. Deposition time was controlled each 1, 3, 5 hr. Scheme is the detailed flow diagram for synthesize of diamond film. Raman spectroscopy was carried out using an Ar^+ laser (wave length = 514.5 mm) in a Renishaw Raman imaging microscope system (Renishaw System 2000). Surface morphology was observed by laser microscope (KEYENCE Co., Ltd., Model no. VF-7510), which magnified 255 times.

3. Results and discussion

The thickness and grain size of diamond film was gradually changed by substrate position. Fig. 3 is laser microscope images of the diamond film, which deposited for 1 hr. In (a), the lowest part of the substrate, we could not find diamond grain because diamond grain just started to grow. The temperature of substrate, measured by optical pyrometer, was about 750°C, which has the lowest temperature among (a)~(d). We thought that the beginning of growth of diamond grain, not inclined substrate, has same surface morphology. On the other hand, if the growth condition, especially substrate temperature, is not suitable, the grain size of diamond cannot grow further. Substrate part (d), which has the highest temperature, has small diamond grain but we could find obvious diamond grain, which was size ca. 1~2 μm.

Fig. 4 is the Raman spectra of 1hr deposited diamond film. All of Raman spectra have a sharp peak at 1334 cm^{-1}, which is the characteristic of crystalline diamond.[19,20] As position of substrate changed from (d) to (a), a broad peak centered

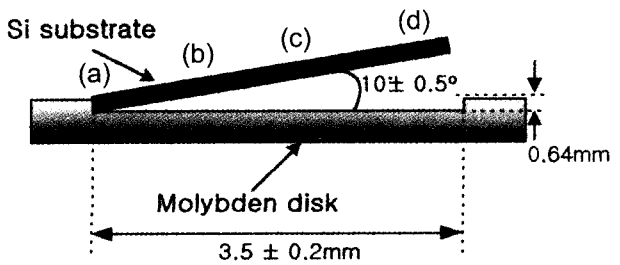

Fig. 1. Schematic Specimen setting for inclined substrate.

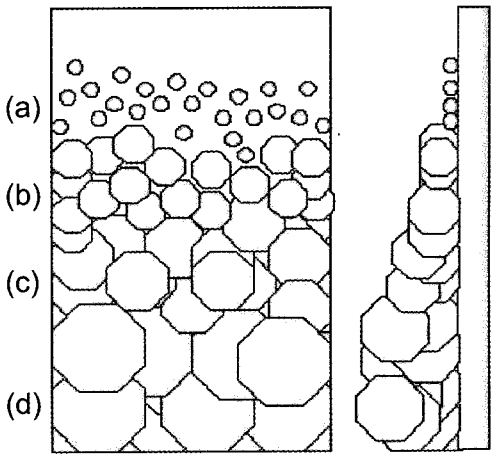

Fig. 2. Schematic diagram of diamond film which deposited on inclined substrate.

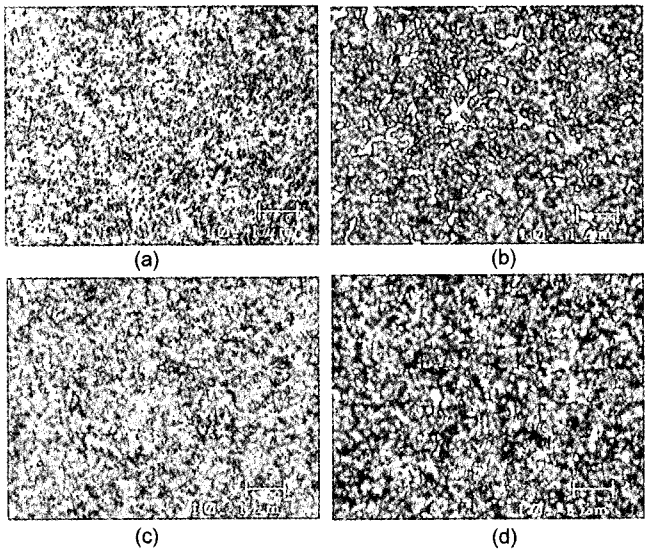

Fig. 3. Microscope images of diamond film, which deposited for 1 hr on Si wafer.(Magnified 2500 times); (a) : 750°C, (b) : 820°C, (c) : 860°C, (d) : 980°C.

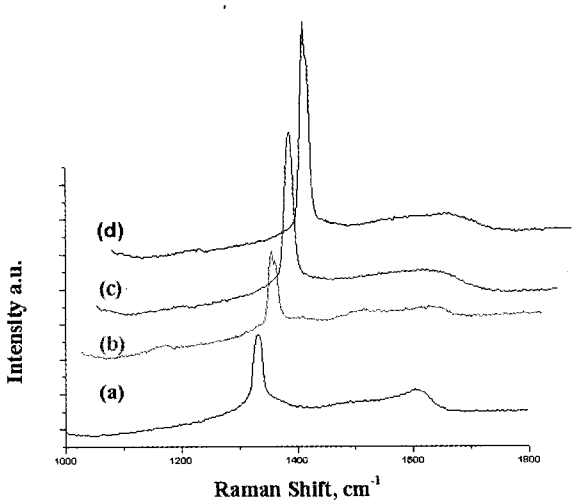

Fig. 4. Raman spectra of boron-doped diamond film(1hr); (a) : 750°C, (b) : 820°C, (c) : 860°C, (d) : 980°C.

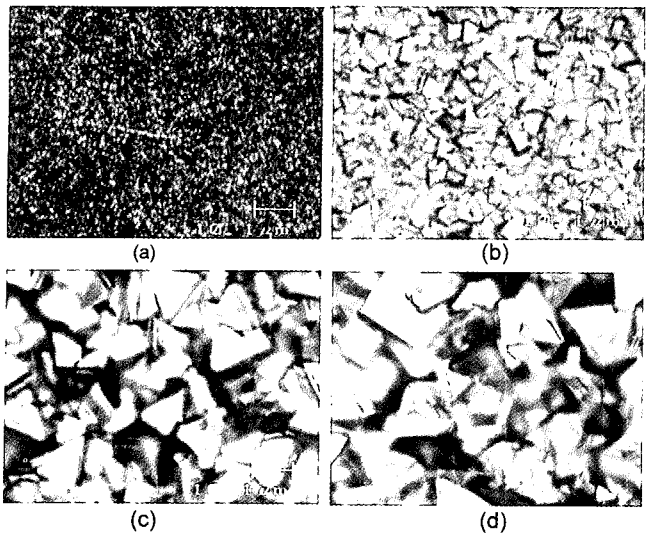

Fig. 5. Microscope images of diamond film, which deposited for 3 hrs on Si wafer.(Magnified 2500 times); (a) : 750°C, (b) : 820°C, (c) : 860°C, (d) : 980°C.

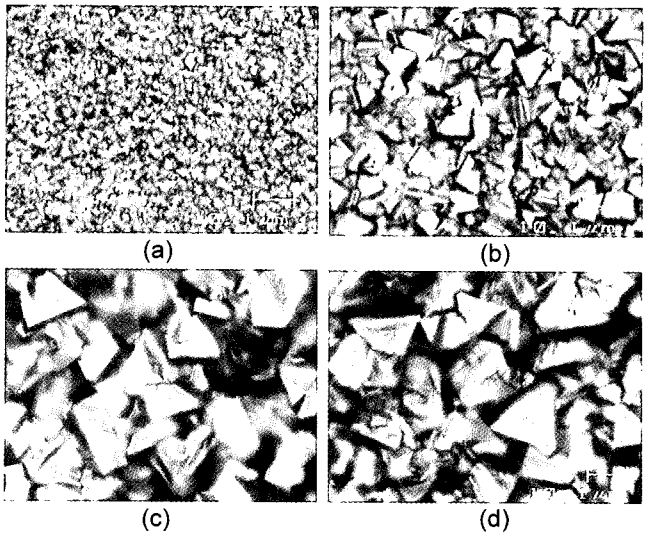

Fig. 7. Microscope images of diamond film, which deposited for 5 hrs on Si wafer. (Magnified 2500 times); (a) : 750°C, (b) : 820°C, (c) : 860°C, (d) : 980°C.

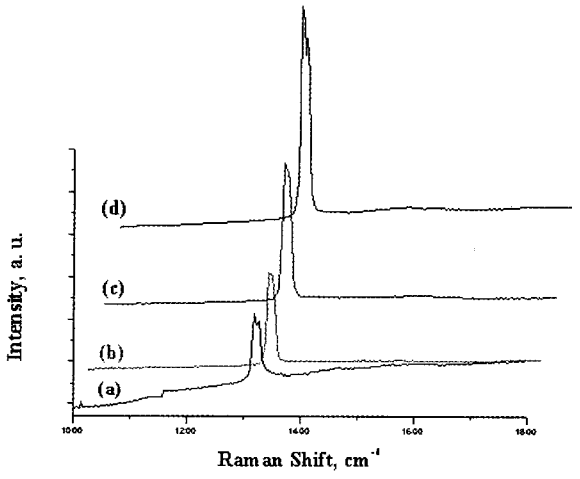

Fig. 6. Raman spectra of boron-doped diamond filmon Si wafer. (3 hrs); (a) : 750°C, (b) : 820°C, (c) : 860°C, (d) : 980°C.

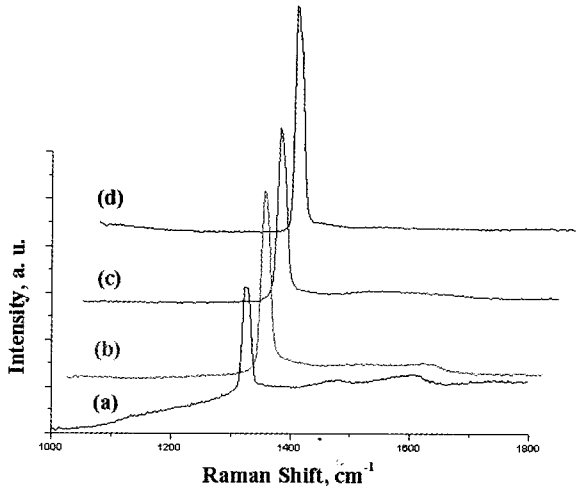

Fig. 8. Raman spectra of boron-doped diamond film(5 hrs); (a) : 750°C, (b) : 820°C, (c) : 860°C, (d) : 980°C.

at 1550 cm^{-1}, corresponding to non-diamond component (sp^2 carbon), could be observed.[20,21] These phenomena were caused by inadequateness of preparing condition. i. e., short deposition time, low substrate temperature.

Fig. 5 is microscope images of the diamond film, which deposited for 3 hrs. Except for (a), diamond grain size became more big than that of Fig. 3. The grain size of (d), which has the biggest diamond grain, was ca. 13 μm.

In Raman spectra of diamond grown for 3 hrs (Fig. 6), a sharp peak at 1334 cm^{-1}, which is the characteristic of crystalline diamond same as shown Fig. 4. However, a broad peak centered at 1550 cm^{-1}, corresponding to non-diamond component (sp^2 carbon), was decreased than Raman peak of 1hr deposited. These phenomena indicates that time is needed to grow diamond grain. However, time is not a main factor for making big diamond grain.

We can confirm this fact with Fig. 7, which has grown 5 hrs. Grain size of site (a), about 2 μm, shows somewhat bigger than that of Fig. 3 (grown 1 hr) or Fig. 5 (grown for 3 hrs). However grain size of other sites, i. e. (b), (c), (d), had almost same size that of Fig. 5. It indicates that time is not a main factor for being a big grain size of diamond but temperature is the main factor to bring up big size of diamond grain.

In Fig. 8, Raman spectra of diamond film, which deposited for 5 hrs, from (b) to (a), a broad peak centered at 1550 cm^{-1}, corresponding to non-diamond component (sp^2 carbon), was hardly seen but in site (a), sp^2 carbon peak (non-diamond) was seen and it was similar to that of 1 hr or 3 hrs. Therefore, we can guess that inadequate pre-paration conditions, i. e. low temperature, make not only sp^2 carbon in diamond film but also small grain size of diamond during preparation. Other preparation conditions, plasma power, chamber pressure, gas flow rate, are also important factors for synthesizing good diamond film.

Fig. 9 is the relationship between temperature and grain

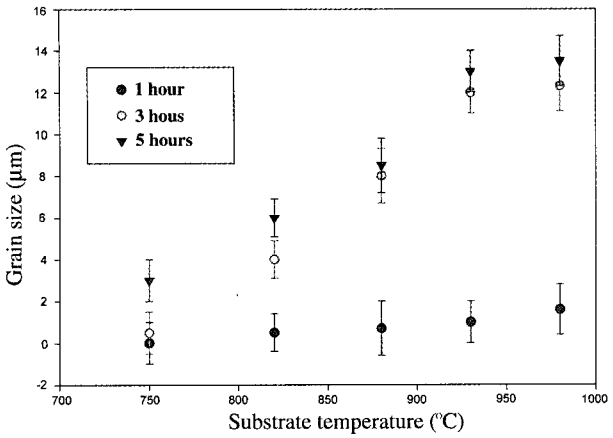

Fig. 9 Relationship between temperature and grain size.

size. The grain size is the function of temperature. Diamond grain size increased by growth time whereas, time is not a main factor for being a big diamond grain. Time mainly effect on determining film thickness.

To confirm these results, which referred above, now we are trying to make higher substrate temperature for not only getting big size of diamond grain but also eliminating sp^2 carbon. So far, the experiment was successful and size of diamond grain was ca. 40~60 μm.

4. Conclusion

In this work, we had tried to examine the relationship between substrate temperature and grain size of diamond. To make temperature gradient on Si substrate and examine the growth mechanism of diamond grain, substrate was 10° tilted. The substrate temperature profile was observed from 750°C to 980°C. By temperature, related to position, size of diamond grain was gradually changed and the biggest grain size was seen at the highest temperature. Raman results show that non-diamond peak appeared at low temperature site and was decreased by moving to high temperature site. By examining results, we could understand the process of diamond grain growth.

References

1. W. B. Wilson, *Phys. Rev.*, **127**, 1549 (1962).
2. H. B. Martin, A. Argoitia, A. Anderson, U. Landau and J. C. Angus, *J. Electrochem. Soc.*, **143**, 3382 (1996).
3. S. jolly, M. Koppang, T. Jackson, and G. M. Swain, *Anal. Chem.*, **69**, 4099 (1997).
4. J. Xu, and G. M. Swain *Anal Chem.*, **70**, 1502 (1998).
5. M. Yanagisawa, L. Jiang, D. A. Tryk, K. Hashimoto, A. Fujishima, *Diamond and Related Materials*, **8**, 2059 (1999).
6. K. Hirabayashi, Y. Hirose, *Diamond Relat. mater.*, **5**, 48 (1996).
7. J. W. Lindsay, J. M. Larson, S. L. Grishick, *Diamond Relat. Mater.* **6**, 481 (1997).
8. C. Wild, P. Koidl, W. Muller-Serbot, H. Walcher, R. Kohl, N. Herres, R. Locher, R. Samlenski, R. Brenn, *Diamon. Relat. Mater.* **2**, 158 (1993).
9. W. A. Yayarbrough, R. Messier, Science, **247**, 688 (1990).
10. K. Piekarczyk, W. A. Yayarbrough, *J. Cryst. Growth.* **108**, 583 (1991).
11. C. Wild, R. Kohl, N. Herres, W. Muller-Serbot, P. Koidl, *Diamon. Relat. Mater.* **3**, 373 (1994).
12. C. Wild, N. Herres, P. Koidl, *J. Appl. Phys*, **69**, 9973 (1990).
13. Y. V. Plescov, A. Sakharova, L. Bouilov and B. Spytsyn, *J. Electroanal. Chem.*, **228**, 19 (1997).
14. K. Hayashi, S. Yamanaka, H. Okushi, K. Kajimura, *Diamond Relat. mater.*, **5**, 1002 (1996).
15. A. Sakhariva, L. Nyikos, Y. Pleskiv, *Electrochemical Acta*, **37**, 973 (1992).
16. S. Morooka. T. Fukuji, K. Semoto, T. Tsubota, T. Saito, K. Kusakabe, H. Maeda, Y. Hayashi, T. Asano, *Diamond Relat. Mater.*, **8**, 42 (1992).
17. F. Silva, A. Gicquel, A. Tardieu, P. Cledat, Th. Chauveau, *Diamond Relat. Mater.*, **5**, 338 (1996).
18. N. Lee, A. Badzian, *Diamond Relat. Mater.*, **6**, 130 (1997).
19. D. S. Knight and W. B. White, *J. Mater. Res.*, **4**, 385 (1989).
20. L. Boonma, T. Tano, D. A. Tryk, K. Hashimoto, and A. Fujishima, *J. Electrochem. Soc.*, **144**, 6 (1997).
21. R. DeClements, B. L. Hirche, M. C. Granger, J. Xu, and G. M. Swain, *This Journal*, **143**, L150 (1996).