Preparation and Crystalline Growth Properties of Diamond Thin Film by Microwave Plasma CVD

MWPCVD법에 의한 다이아몬드 박막의 제조 및 결정성장 특성

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Abstract

The growth properties of diamond grain were examined by Raman spectroscopy and microscope images. Diamond thin films were prepared on single crystal Si wafers by microwave plasma chemical vapor deposition. Preparation conditions, substrate temperature, boron concentration and deposition time were controlled differently. Prepared diamond thin films have different surface morphology and grain size respectively. Diamond grain size was gradually changed by substrate temperature. The biggest diamond grain size was observed in the substrate, which has highest temperature. The diamond grain size by boron concentration was slightly changed but morphology of diamond grain became amorphous according to increasing of boron concentration. Time was also needed to be a big diamond grain. However, time was not a main factor for being a big diamond grain. Raman spectra of diamond film, which was deposited at high substrate temperature, showed sharp peaks at 1334cm^{-1} and these were characteristics of crystalline diamond. A broad peak centered at 1550cm^{-1} , corresponding to non-diamond component (sp^2 carbon), could be observed in the substrate, which has low temperature.

Key Wards(중요용어) : Diamond thin film, Microwave plasma CVD, Raman Spectra, Si wafer, Boron-doping

1. Introduction

Diamond thin film is very expected material because of its superior properties such as excellent hardness, physical and chemical stability, high resistivity and so on. Diamond shows p-type semiconducting behavior with existence of boron. Using microwave plasma CVD method, boron can be doped and these boron-doped diamond film has unique electrochemical properties. For example boron-doped diamond film has wider potential window range (ca. 2.5~3.0V), low resistivity (~$10^{-3}\Omega$cm), low background current. Diamond film isused in many fields, i. e. High temperature durable electronic device (transistor, SAW device, laser diode, heat sinks, microwave substrate etc.).

So far, some groups have reported about diamond crystallinity on <100>and <110> directions or single crystalline by temperature effect. And some group including, Wild et al. have reported the effect of substrate temperature and methane percentage on texture and morphology of diamond. But these reports were far from surface morphology and grain size. 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. According to condition, which is referred above, grain size and crystallinity are determined. We thought that temperature of

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substrate is the most important factor, which determines the size of diamond grain. So, in this work, we have tried to change temperature of Si substrate and examine the size of diamond grain.

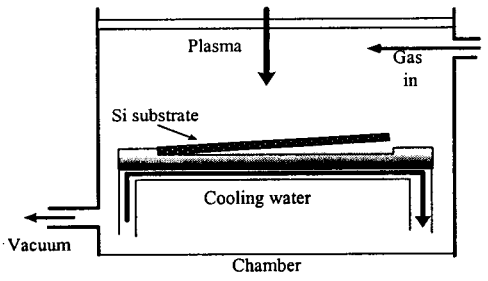
2. experimental

The boron-doped diamond thin films were grown on n-Si(100) substrate, which had been polished by 0.5m diamond powder (Type Micron+SND, De Beers). Microwave plasma chemical vapor deposition (CVD) method was adopted by 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. $10\sim10^4$ppm.

In order to make temperature gradient of substrate, it was inclined about 10° (Fig. 1)and substrate was accumulated. The temperature profile of substrate, measured by optical pyrometer, was 750~1080℃. 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, 10, 18hr.

Fig.1 Schematic substrate setting diagram

Raman spectroscopy was carried out using an Ar^+ laser (wave length = 514.5mm) 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 magnification was 2500.



3. Results and discussion

3-1. Boron concentration and crystallinity.

Fig. 2 is the microscope images of boron-doped diamond film, which deposited for 10hrs. Diamond grain size of Fig. 2a was ca.7~9㎛. The change of grain size by boron concentration was hardly observed but morphology of diamond grain became amorphous according as increasing of boron concentration.

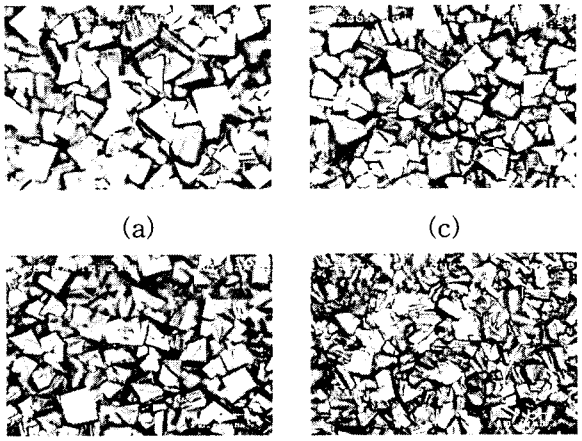


Fig.2 Microscopeimages of diamond film, which deposited for 10 hrs

Fig. 3 is the measurement results of resistivity of diamond film, which boron concentration was controlled from 10ppm to 10^4ppm. According to increase of boron concentration, the resistivity of diamond film decreased. When 10ppm of boron concentration, resistivity was 15.154Ωcm and at 10^4ppm, resistivity was 0.00316Ωcm. By boron-doping, the diamond thin film is changed to p-type semiconductor by formation of electron hole caused by boron.

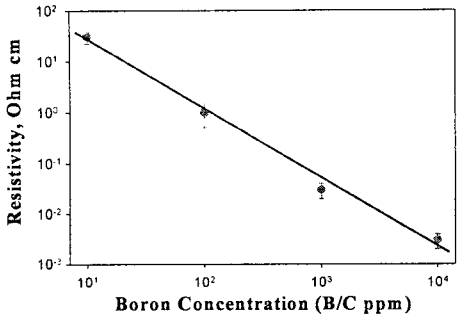
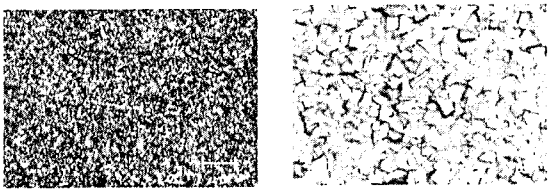


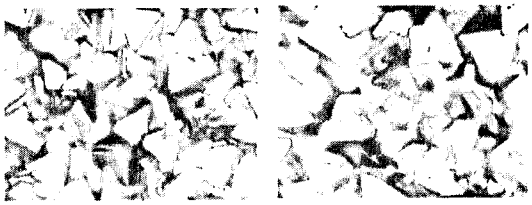
Fig. 3 Relationship between boron concentration and resistivity(grown for 10 hrs)

3-2. Temperature and grain size.

the Fig. 4 is a microscope image of diamond film, which deposited for 3hrs. Except for (a), diamond grain shows big size. The grain size of (d), which has the biggest diamond grain, was ca. 13m. Fig. 5 is a Raman spectra of diamond which grown 3hrs. There was a sharp peak at 1334cm ^{1}, which is the characteristic of crystalline diamond. A broad peak centered at 1550cm ^{1} , corresponding to non-diamond component (sp^2 carbon), was observed in (a), which temperature was 750℃. Theses phenomena indicates that time is needed to grow diamond grain. But, time is not a main factor for making big diamond grain. As increase substrate temperature, the Rama peak at 1334 ^{1}cm was gradually increased and broad peak centered at 1550cm ^{1} , corresponding to non-diamond component (sp^2 carbon), was decreased. These phenomenon indicate that main factor for enlarges grain size was not growth time but substrate temperature. Fig. 6 is the graph of Relationships between grain size and growth time(a), growth time and film thickness(b).



(a) (b)



(c) (d)

Fig. 4 Microscope images of diamond film, which deposited for 5hrs at different substrate temperature; (a)750℃, (b) 820℃, (c)860℃, (d)930℃

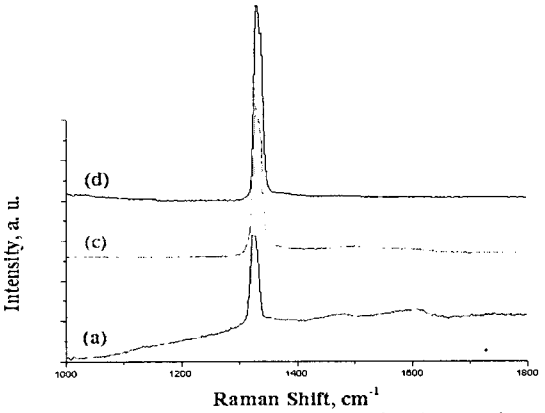


Fig. 5 Raman spectra of boron-doped diamond film(3hr)

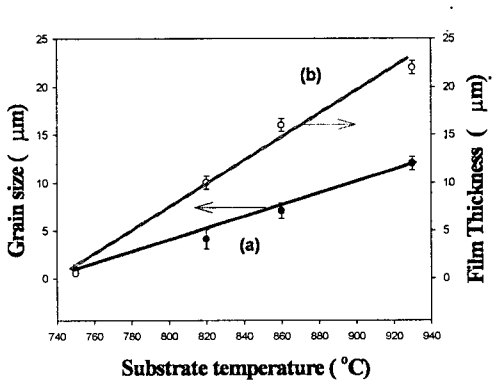
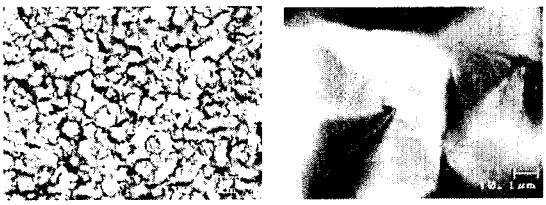


Fig. 6 Relationships between grain size and growth time(a), growth time and film thickness(b)

3-3. Growth properties at accumulated Si substrate

Fig. 7 is a microscope image of diamond film deposited for 18 hours on Si substrate, which was laid from one layer to three layers. Grain size of Fig. 7a and Fig. 7b is quite different. The substrate temperature of Fig. 7a was ca. 1080℃ and diamond grain size was ca. 50~60㎛. One can doubt that the reason of big diamond grain is the long deposition time. However, the diamond grain size of Fig. 7a shows normal one. The substrate temperature of Fig. 7a was ca. 750℃. Crystalline diamond was confirmed by Raman spectroscopy. A sharp 1334cm-1 peak was observed both Fig. 8a and Fig. 8b. By these fact, we could confirm that important factor for big diamond grain was substrate temperature.



(a) (b)

Fig. 7 Microscope images of diamond film, which deposited for 18hrs at different substrate temperature; (a)750℃, (b) 1080℃

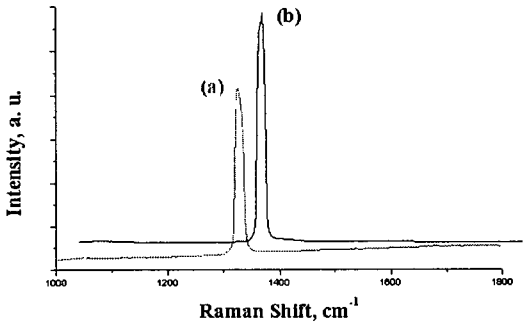


Fig. 8 Raman spectra of diamond film(18 hrs)

4. Conclusion

In this work, we have tried to examine the relationship between substrate temperature and grain size of diamond. Experimentation was carried out in two ways. First, we controlled boron concentration for the purpose of examining the relationship between grain size and boron concentration. Secondly, we inclined Si substrate in order to make temperature gradient of substrate. Thirdly, In order to make higher substrate temperature, Si substrates were laid from one layer to three layers. The size of diamond grain was gradually changed by substrate temperature. The higher substrate temperature, the bigger grain size appeared. Raman results show that non-diamond peak appeared at low temperature site and it decreased by moving to high temperature site. By these results, we could understand the process of diamond grain growth and confirmed that the main factor for being a big diamond grain was substrate temperature.

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