Characterization of Helicon Plasma by H_2 Gas Discharge and Fabrication of Diamond Thin Films

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Helicon waves were excited by a Nagoya type III antenna in a magnetized plasma, and hydrogen and methane are fed through a Mass Flow Controller(MFC). We made a diagnosis of properites of helicon plasma by H_2 gaseous discharge, and fabricated the diamond thin film. The maximum measured electron density was 1×10^{10} cm^{-3}. Diamond films have been grown on (100) silicon substrate using the helicon plasma chemical vapor deposition. Diamond films were deposited at a pressure of 0.1 Torr, deposition time of 40~88 h, a substrate temperature of 700 ℃ and methane concentrations of 0.5~2.5 %. The growth characteristics were investigated by means of X-ray Photoelectron(XPS) and X-ray Diffraction(XRD). XRD and XPS analysis revealed that SiC was formed, and finally diamond particles were definitely deposited on it. With increasing deposition time, the thickness and crystallization of the daimond thin film increased. For this system the optimum condition of methane concentration was estimated to near to 1.5 %.

Key words : helicon plasma, double probe, diamond thin film, annealing

1. INTRODUCTION

Currently used in the thin film deposition and the etching process, the plasma causes little environment problems and has a very good efficiency. As the processing conditions of the high-tech devices have been improved, it is required to develop the low pressure and high efficiency plasma. Most of all, the helicon combined with the Electron Cyclotron Resonance(ECR) and the rf system attracts much attention[1]. The diagnosis about properties of helicon plasma need the double probe one to minimize the rf noise. The performance of helicon wave is much influenced by rf power, magnetic field, pressure and the design of rf antenna[2]. The helicon plasma has the following advantages :

*The high electron density can be accomplished even at the low value of the magnetic field;

*The pollution of the inside of the chamber can be minimized because antenna is mounted on the outside of it; and,

*The electron energy can be controlled at the low frequency[3].

The diagnosis about properties of helicon plasma for making diamond thin film is aimed at identifying the subordinate relationship of the density of plasma to the magnetic field, pressure and rf power. Diamond has the highest hardness and heat conductivity of substances on the earth. It also has superior thermal resistance, chemically-resistant property, high hole mobility, low permittivity and high permeability of light. Owing to these physical properties, diamond can be applied in various fields of industry. In terms of thermodynamics, diamond, an allotrope of carbon, can be more stabilized than carbon only under the high pressure. In 1954, Bundy and his fellows[4] first succeeded in synthesizing diamond under the high temperature and high pressure. But the synthesized diamond contains a lot of impurities due to its metal catalysts, such as Fe, Ni, Co, Mn, etc. In addition, it is difficult to control its size or properties. In the late 1950's, Eversole[5] in the U.S. made the first attempt to synthesize diamond by the method of vapor deposition under the low temperature and pressure. As the importance of the deposition technology has recently been emphasized in Korea, the Chemical Vapor Deposition(CVD) method, which is essential to protective film coating process to improve the life and performance of materials in the semiconductor industry, has actively been studied to maximize the area of film materials, shorten the synthesizing time and make the synthesizing variables optimum. The thin film technology is largely divided into the Phisical Vapor Deposition(PVD) and the CVD. The CVD method is mainly used in making diamond thin film. In 1970's, Spitsyn and his fellows[6] in the then Soviet Union announced the result of their research that atomic hydrogen removes graphite, activating the growth of diamond particles. Based upon this result, a Japanese Institute for Research in Inorganic Materials has turned out diamond thin film by means of the thermal filament CVD method[7] and the microwave CVD method[8]. The thermal filament CVD, the microwave CVD, the ECR PCVD, the rf PCVD and the dc PCVD methods are mainly used in order to synthesize diamond thin film. In this research, after making diagnosis of properties of helicon plasma by discharging hydrogen and methane in order to synthesize diamond thin film with high density plasma, we grew diamond on the silicon substrate and studied the influence of heat treatment temperature on the crystal structure and the property of thin film by means of XRD and XPS.

2. EXPERIMENT

Figure 1 shows the diagram of helicon plasma device produced by H_2 gaseous discharge. The source of high frequency is 13.56 MHz generator. The quartz tube (diameter: 74 mm) is used as reaction chamber, and the stainless steel (diameter: 384 mm) is used as a deposition chamber. The antenna is mounted between the reaction tube and the parallel magnetic field coil, and the section connected to rf power source is insulated with taplon tape. The tip of the probe made of tantalum(Ta) is connected to the probe lead wire with copper rod. The tip inserted into the substrate through a chamber is kept in a vacuum with a ceramic, and the other side with an epoxy. In order to find the I-V characteristic curve, the sweep voltage is applied to measure current value per 1 V by means of a source-meter(Keithley 2410).

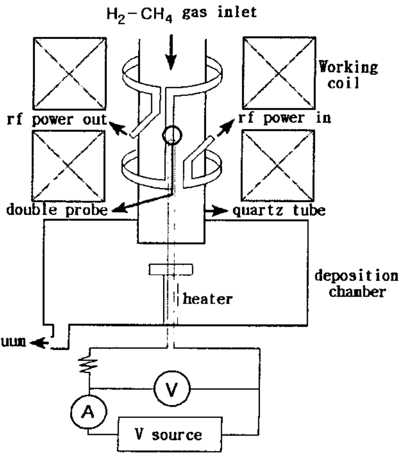


Fig. 1. Schematic diagram of appatus.

Table 1. Deposition condition of diamond thin films

rf power(W)	800
Total pressure(Torr)	0.1
Reaction time(h)	40 ~ 88
Magnetic field(G)	300
CH_4/H_2(%)	0.5 ~ 2.5
Substrate temprature(°C)	700

The interrelation of plasma is found from this wave as a function of pressure, rf power and magnetic field. The (100) p-type Si wafer is used as a substrate to fabricate diamond, and the 3 μm diamond suspension to increase the density of diamond nucleation. In order to remove an oxidized layer, the substrate is cleaned in HF for 20 minutes, and then in D.I. water with ultrasonic wave for 25 minutes before being dried with nitrogen. The plasma is created by flowing gaseous hydrogen in the substrate before deposition to etch the oxidized layer by flowing a sample in the chamber. CH_4/H_2 is changed to 0.5 ~ 2.5 %, and the temperature of the substrate is kept at 700 ℃ and rf power at 800 W. The surface and crystal of the diamond are observed with XRD and XPS. Table 1 shows the deposition conditions of diamond thin film in detail. The crystal of the thin film is determined according to the temperature of heat treatment after annealing the samples at 900 ℃ and 1100 ℃, respectively.

3. RESULTS AND DISCUSSION

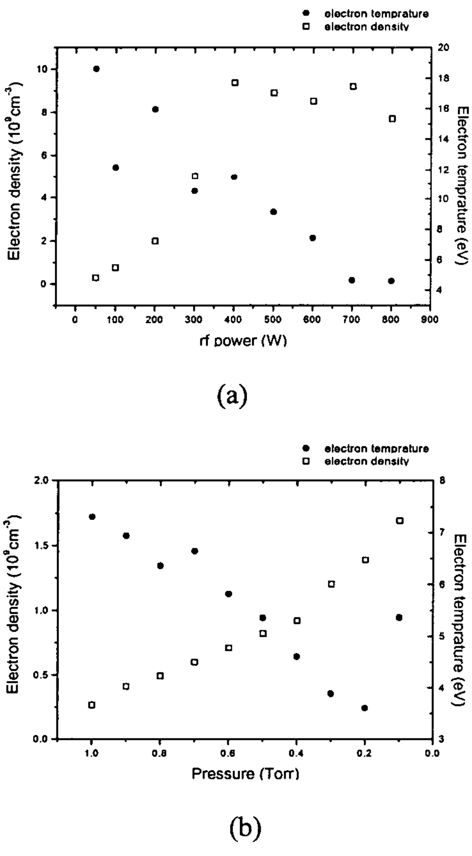
The electron density and electron temperature of helicon plasma is determined according to the discharge of gas mixture of hydrogen and methane by means of double probe[1]. The amount of methane of Ta probe is 0.55 mm and its cross sectional area is 3.96×10^{-5} m^2. In order to find the electron density from the I-V curve by increasing rated voltage by 1 V from -200 V to 200 V, the electron temperature T_e should be:

$$T_e = \frac{e}{k}\left(\frac{I_1 I_2}{I_1 + I_2}\right)\Big|_{I=0} \qquad (1)$$

where, $I_{1,2}$ are the saturation currents of the two probes and k is Boltzmann constant. If $I = I_1$ from the electron temperature and ion saturation current, the electron density should be:

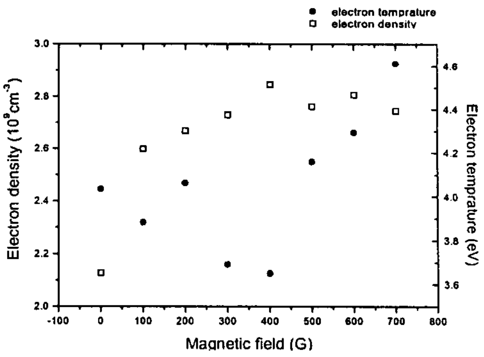
$$n = \frac{I}{0.91Ae}\sqrt{\frac{m_i}{kT_e}} \qquad (2)$$

where, m_i is ion mass and A is the cross sectional area of tip. Figure 2(a) shows the electron density and electron temperature determined by increasing rf power after mixing magnetic field and pressure at 300 G and 0.1 Torr, respectively. The rapid increase of plasma density is shown between 300 W and 400 W, which is caused by the resonance combination due to the increased movement energy according to the rise of rf power. This is called the "jump" phenomenon of helicon plasma. On the other hand, the value of electron temperature is rapidly decreased at 4~20 eV. Figure 2(b) shows electron density and electron temperature according to pressure. The rf power and magnetic field are fixed at 300 W and 300 G, respectively, and pressure is changed from 0.1 to 1 Torr. The electron density is linearly increased according to the decline of pressure, which is seemed to be caused by the declined ionization due to the collision of particles as the average free path of the particles is shortened in the reaction tube. The electron temperature is gradually decreased at 4~8 eV. Figure 2(c) shows the electron density and electron temperature according to the change of magnetic field with pressure and rf power fixed at 0.1 Torr and 300 W, respectively.



(a)

(b)



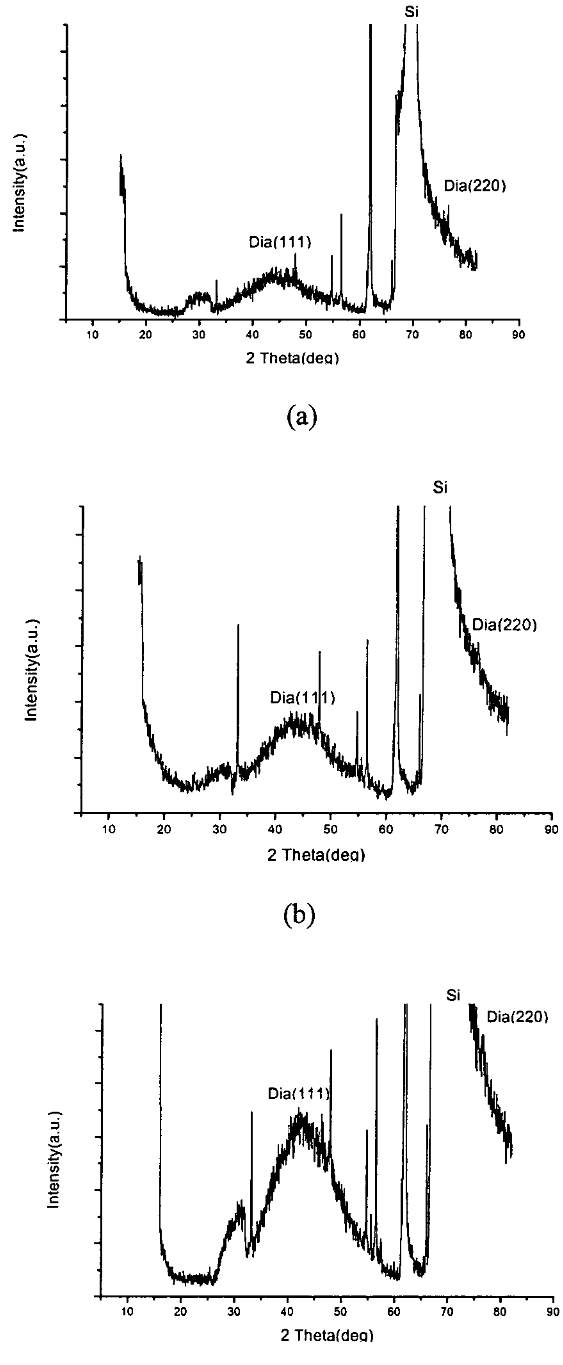
(c)

Fig. 2. Plasma density(□) and electron temperature(●) as a function (a) rf power (b) pressure (c) magnetic field.

As magnetic field is expanded, the density is rapidly increased before being kept stable. On the other hand, the electron density is determined at 3.5~4.5 eV.

The major variables in the course of making diamond thin film through the chemical vapor deposition method are deposition time, deposition temperature and the concentration ratio of hydrogen and methane. We studied properties of the thin film by analyzing XRD and XPS, changing the concentration ratio of methane for deposition time and gaseous hydrogen in order to fabricate diamond thin film through the helicon plasma chemical vapor deposition.

Figure 3(a) shows the analytic result of XRD for the concentration ratio of CH_4/H_2 =1.5 % deposited for 40, 64 and 88 hours with deposition time as a variable. The existence of diamond was able to be identified on the reason that XRD peak was located at the 43° of diamond section (111) and 77° of the fragile section (220). Figure 3(b) and (c) show the increase of the hardness of the section (111) according to the rise of deposition time. In the early stage of deposition, non-diamond materials are produced until the nucleations are actively created, but according to the increase of deposition time, the particle bond takes place on the continuous basis to create nuclei for the second time, stabilizing the thin film. Judging from the very large peak of silicon used as a substrate around 70° and the broad peak of (111) section at each of deposition time periods, the crystal property and thin film thickness seems not to be good. It is because sp^3 bonds do not actively take place with the carbon particles to form diamond having insufficient energy due to the low ionization rate.



(a)

(b)

(c)

Fig. 3. X-ray diffraction patterns of the diamond thin films on Si at the different deposition time.

Figure 4 shows the result of XPS according to deposition time. The Cls peak of homonuclear bond is shown around 285 eV. The hardness of Cls is gradually increased according to the increase of deposition time like the result of XRD.

Figure 5 shows the result of XRD according to the change of amount of methane. As the amount of methane is incresed, the crystal property is improved, but graphite tends to be deposited at the same time. For the amount of methane of 0.5 %, graphite is mainly grown. For the amount of methane of 1.5 % and 2.5 %, the hardness of sp^3 bond can be increased because the amount of hydrogen is relatively appropriate enough to dissociate methane molecules.

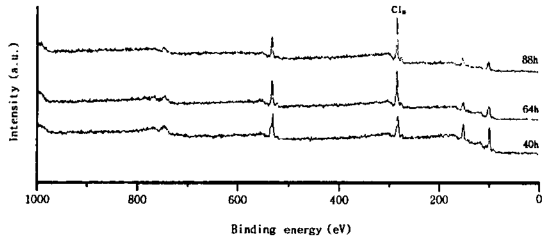
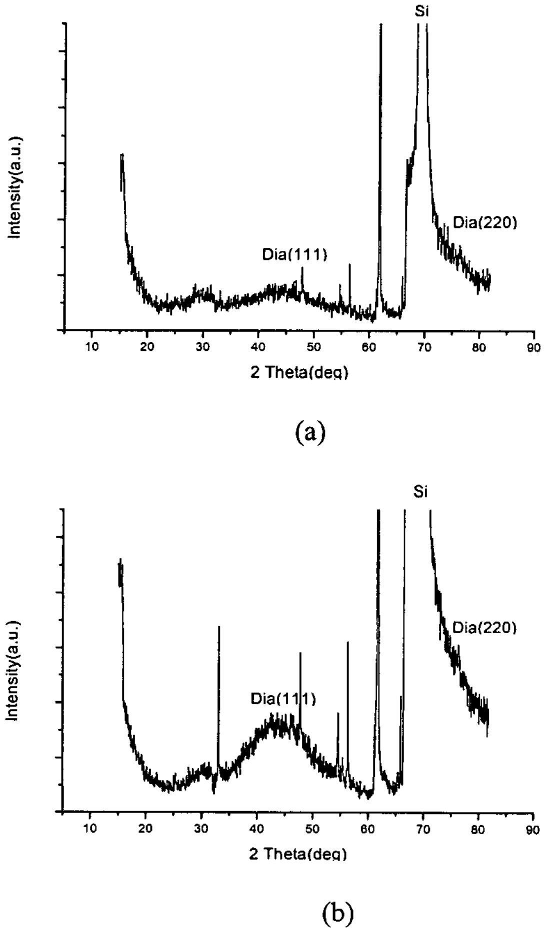
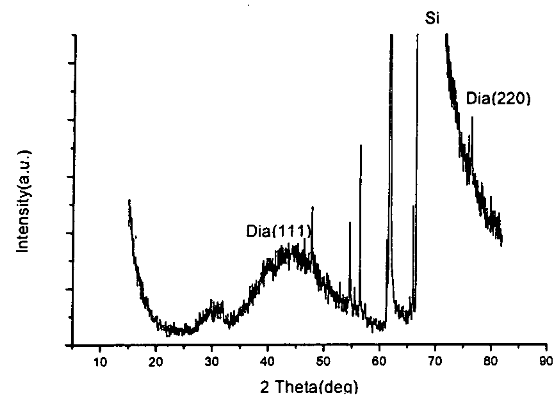


Fig. 4. Cls spectra from samples grown for various deposition time in a CH_4+H_2 plasma .



(a)

(b)



(c)

Fig. 5. X-ray diffraction patterns of the diamond thin films on Si at the different CH_4/H_2 : (a) 0.5%, (b) 1.5%, (c) 2.5%.

As indicated in Figure 6, however, the optimum condition of amount of methane in this system is found around 1.5 %. In order to find out the effect of heat treatment on the diamond thin film, Figure 3(c) is annealed in a high temperature furnace for 8 hours at 900 ℃ and 1100 ℃, respectively. Figure 7(a) and (b) show the XRD results of the sample annealed at 900 ℃ and 1100 ℃, respectively. Judging from Figure 3(a) and Figure 7(a)(b), the heat treatment at over 900 ℃ deteriorates the crystal property of the thin film. It is because diamond is carbonized while sp^3 bonds are broken down at a high temperature.

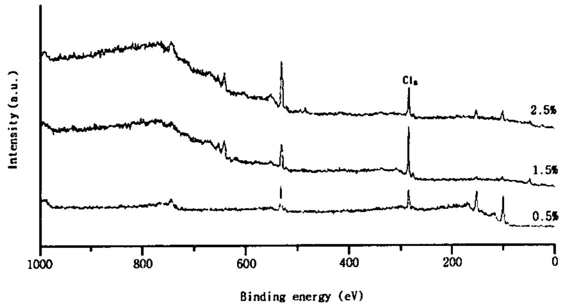
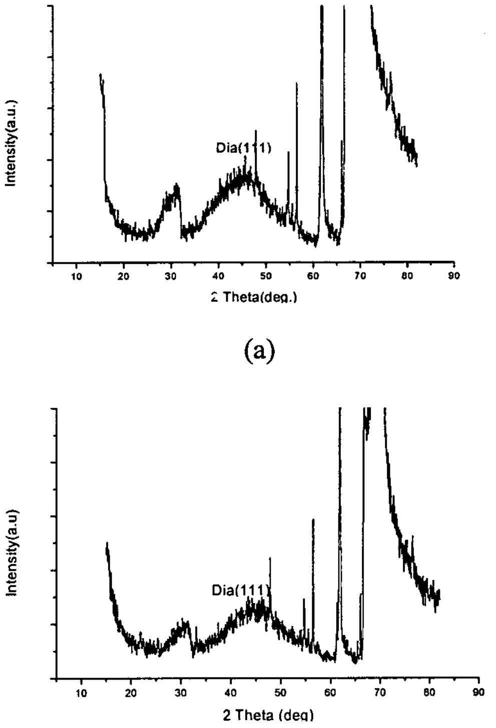


Fig. 6. Cls spectra of samples grown for various CH4/H2 in a CH4+H2 plasma at 700°C.

As indicated in Figure 6, however, the optimum condition of amount of methane in this system is found around 1.5 %. In order to find out the effect of heat treatment on the diamond thin film, Figure 3(c) is annealed in a high temperature furnace for 8 hours at 900 ℃ and 1100 ℃, respectively. Figure 7(a) and (b) show the XRD results of the sample annealed at 900 ℃ and 1100 ℃, respectively. Judging from Figure 3(a) and Figure 7(a)(b), the heat treatment at over 900 ℃ deteriorates the crystal property of the thin film. It is because diamond is carbonized while sp^3 bonds are broken down at a high temperature.



(a)

(b)

Fig. 7. XRD diffraction patterns of the diamond thin films annealed at (a) 900°C (b) 1100°C.

4. CONCLUSION

We made a diagnosis of the properties of helicon plasma by H_2 gaseous discharge, and fabricated the diamond thin film. The density of plasma is increased according to the increase of rf power and magnetic field, and the decrease of pressure. Especially, the "jump" phenomenon, the typical property of helicon plasma, is shown at 300 G and 400 G of rf power. The electron temperature for rf power has a tendency of a rapid decrease, but it falls gradually at 4~8 eV for the pressure and magnetic field. The diamond thin film has a long deposition time due to the insufficient density of plasma, and can be identified as a broad peak in a case of the XRD result. The increase of amount of methane causes the simultaneous deposition of graphite. In this system, the optimum condition of methane to fabricate good diamond thin film is around 1.5%. For the effect of the heat treatment of the thin film, the diamond is carbonized at over 900 ℃ to deteriorate its crystal property.

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