Synthesis of Diamond Thin Film by Helicon Plasma Chemical Vapor Deposition

June-Won Hyun and Yong-Jin Kim
School of Natural Science, Dankook University, 140-714, Korea

E-mail : jwhyun@dankook.ac.kr

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Diamond films have been achieved on Si (100) substrates using helicon plasma chemical vapor deposition(HPCVD). Gas mixtures with methane and hydrogen have been used. The growth characteristics were investigated by means of X-ray photoelectroton spectroscopy, Atomic force microscopy and X-ray diffraction. We obtained a plasma density as high as 10^{10} ~ 10^{11} cm^{-3} by helicon source. The smooth (100) faces of submicron diamond crystallites were found to exhibit pyramidal shaped architecture. The XPS spectrum for the nucleation layer indicates the presence of diamond at 285.4 eV, close to the reported value of 285.2 eV for diamond. XRD results demonstrates the existence of polycrystalline diamond as the diamond (111) and (220) peaks.

Key words : HPCVD, Diamond thin film, XPS, XRD, AFM.

1. INTRODUCTION

Diamond is expected to be a material for electronic and devices which operate under severe conditions, such as high temperature and strong irradiation environment. Diamond also has the highest thermal conductivity (20 W/cm · K) of any solid, about 5 times larger than the value for Cu[1]. Synthetic diamond is formed by two techniques, one using a high temperature, high pressure and the other using a gas at lower temperature and low pressure. In recent years, the diamond thin films have been fabricated by chemical vapor deposition(CVD) [2,3], sputter method[4], ion beam deposition[5,6], and etc. The synthesis of diamond films under metastable condition has been developed very active during the last decade due to its potential usefulness. The hydrocarbon and atomic hydrogen play an important role in film deposition of diamond from vapor phase in plasma such as CVD. Hydrogen is thought to function in the growth process in a number of ways, including maintenance of sp^3 hybridization of carbon atoms at the growth surface[7,8]. In most cases conventional type CVD methods so far used as a diamond deposition and there have been very few ways of using the rf helicon wave discharge for diamond deposition on a large scale area. An inductively coupled helicon wave plasma potentially attractive features in plasma applications because of the efficiency for high density plasma production compared with other conventional type plasma sources. Helicon waves, known as bounded whistlers, are attractive for plasma processing because they have high plasma density in low magnetic fields[9]. They have the properties of high density (10^{13} cm^{-3}), high efficiency, low magnetic field (100~300G), no internal electrodes, remote operation and control of electron energies[10,11]. Our helicon plasma CVD system consists of plasma generation tube, deposition chamber, pumping lines and gas lines for deposition system. A number of methods can be used to study diamond films, such as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, Atomic force microscopy (AFM), Scanning electron microscopy (SEM), etc. In this study, Diamond films have been achieved with helicon plasma CVD under the following conditions : 1 % CH_4 / H_2 as reactant gas, working pressure of 0.2 torr and silicon substrate at 750 ℃. XPS, AFM and XRD have been used to characterise diamond films produced by helicon plasma CVD method on a Si substrate.

2. EXPERIMENT

A schematic diagram of the experimental apparatus for the diamond growth is shown in Figure 1.. The upper quartz generation tube is 760 mm in length and 74 mm

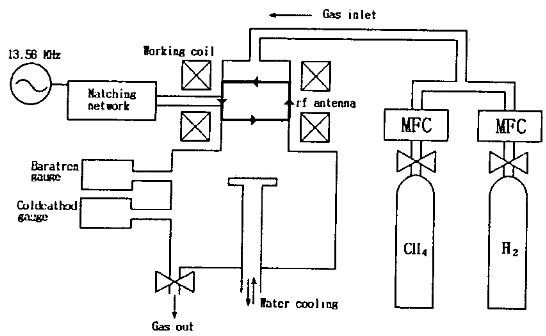

Fig. 1. Schemtic diagram of helicon plasma CVD.

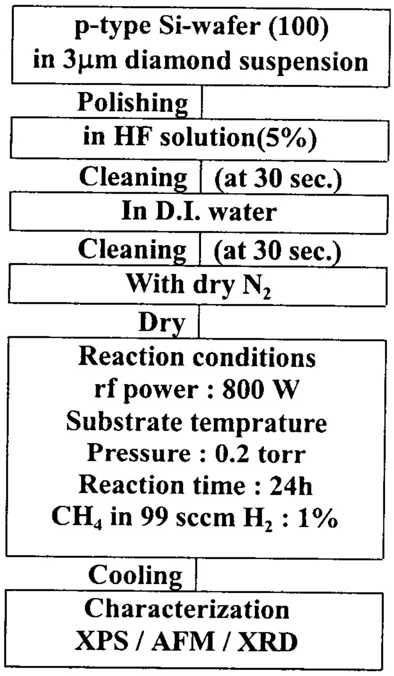

Fig. 2. Experimental procedure.

in diameter and the lower chamber composes of a stainless-steel, 384 mm in diameter and 200 mm in length. The pumping system consists of both conventional diffusion and rotary pump. Diamond was prepared by helicon plasma CVD using a 1 % CH_4 /H_2 mixture as a feed gas and the gas pressure was measured by a Baratron gauge and Cold cathod gauge. A helicon antenna of Nagoya III type of 130 mm in length is located around the upper quartz tube and couples rf power of 13.56 MHz. The input rf power to the helicon plasma source was 800 W and the substrate temperature was 750 ℃. High purity Si (100) wafer scratched with 3 μm diamond suspension were used as the substrate. The typical growth conditions are summarized in Figure 2.. The film morphology and the film thickness were measured by AFM. The film crystallinity and structure were analyzed by XRD and XPS. XPS data were taken using Mgk α radiation with pass energy of 23.5 eV.

3. RESULTS AND DISCUSSION

3.1. Effect of magnetic field on helicon plasma density

From the dispersion relation, in a fixed frequency, the density of helicon plasma, under the fixed wavelength, is proportioned to the magnetic field, and shows inversed proportion to the radius of reaction chamber. It is proved by the way of experiment, helicon antenna, rf power and the magnetic field influenced much to the density of plasma, and the change of the electron density influenced propagation shape of the helicon wave. In the case of the general equipment of CVD, simple investigative method is used by the way of the measurement in difference of the voltage between the chamber and plasma, on the other hand, the diagnostics of the characteristic of the helicon plasma should minimise the noise of rf power, and should consider the effect of the magnetic field, it is necessary to confirm the diagnostics of double probes. In the experiment, the tip of double probes is made of Ta, and minimise the width of the sheath of two tips. Figure 3. is the magnetic function and it shows the change of the density of plasma. As for the value of the magnetic field, above 300 G, with the rapid increase of the density of plasma, we noticed the colour of the electric discharge of plasma brightening notably. As for the reason, in magnetic field, having the critical value, the electrons accelerate largely, as for the frequent collision with neutral gas, the density of plasma is increased. From the results of the Figure 3., under the 300 G in critical magnetic field, a kind of electronic discharge named "low mode" is formed, and above 300 G, it is presumed that helicon mode is existing. From these facts, above the critical magnetic value, we know, the combination between the antenna of helicon plasma is made well.

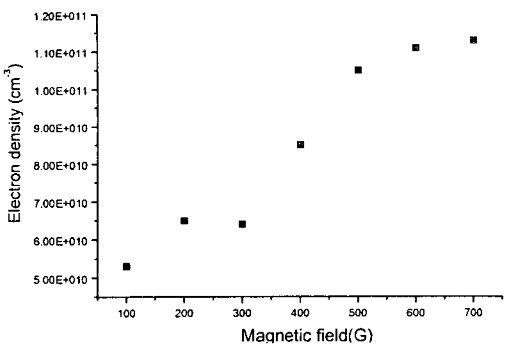

Fig. 3. Plasma density as a function of magnetic field.

3.2. Characterization of diamond films

XPS is the technique to study the early nuclear formation and its development and the electronic structural characteristics in microcrystalline diamond. Figure 4. shows the spectra of the diamond film of C1. C1 located almost nearer to 285.4 eV, and the binding energy of diamond is 285.2 eV (The binding energy of graphite is 284.2 eV). The chemical reaction in plasma ; mixed gas, is started from the hydrogen molecule dissociation, which occupy the almost part of the chemical compound, the successive chemical reaction in the state of gas is continued by the response of the hydrogen atom and the kinds o carbonated hydrogen which are found in voluantary electronic collision found in early stage by the free electrons. In early stage of the formation of the nucleus of diamond, with the saturation of the elements of carbon, especially, under the low pressure, with the reduce of the density of the active species in plasma, graphite, SiC ; which are low in free energy formed first, and with the sufficient supply of the energy, the binding power raised gradually. In the state of non-balanced in the time of making diamond, the graphite need to be etched by atomic hydrogen, because atomic hydrogen makes sp^3 bonds in the process of recombination made by defected sp^2[12]. The rate of ionzation of hydrogen gas not only take part a role of seperating carbon element from methane, but also take part an important role to pass the energy. The transmission of energy in the substrate is made by the recombination of these ionized hydrogen. Belton et al. reported, carbon responses to oxygenated solution and after, formed SiC, and the formation of nuclear of diamond is begun[13,14]. SiC peak was observed on 283.3 eV in Figure 4.. Comparing C-C bond peak, the film of C1 spectra show the non-symmetrical peculiarity in highly binding energy. These C1 spectra show the existence of the element of oxygen in thin film, thus, the sp^3 bond of the surface of the diamond eliminated by the element of the oxygen, in the range of 288.5 ~ 286 eV, there existed the oxygenated compound such as C-O-C, C=O. The quantitative analysed was O : C : Si = 21.01 : 51.88 : 21.11. Figure 5. (a), (b) show the images of AFM of diamond film obtained 24 and 36 hours separately. It was possible to investigate the typical form of cubic diamond crystal only classed as (100). As for the deposition time of 24 hours, the crystals sized 0.2μm

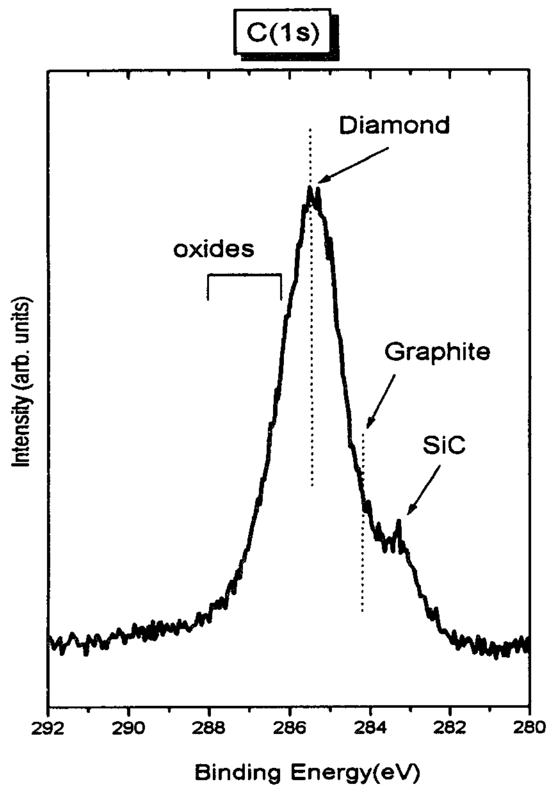

Fig. 4. XPS Cls core –level spectra of sample grown for 24 h in a CH_4+H_2 plasma.

arranged as pyramidal shape, but 36 hours case, the size of the particle increased a little such as 0.3 ~ 0.4 μm, we investigated the particle enlarged non equally.

The increase of time on thin film, we consider such of the two cases as follows:firstly, the case of the formation of good natured film, with the break out of sp^2 mixed structure, secondly, in the case of the low qualified caused by the reformation of the new nucleus except the nucleus already formed, the film of diamond obtained by the deposition time of 36 hours considered, correspond to the case of the latter. The thickness of the film was about 0.4 μm, and it was not improved largely in spite of the increase of time. It is considered, with the flowing

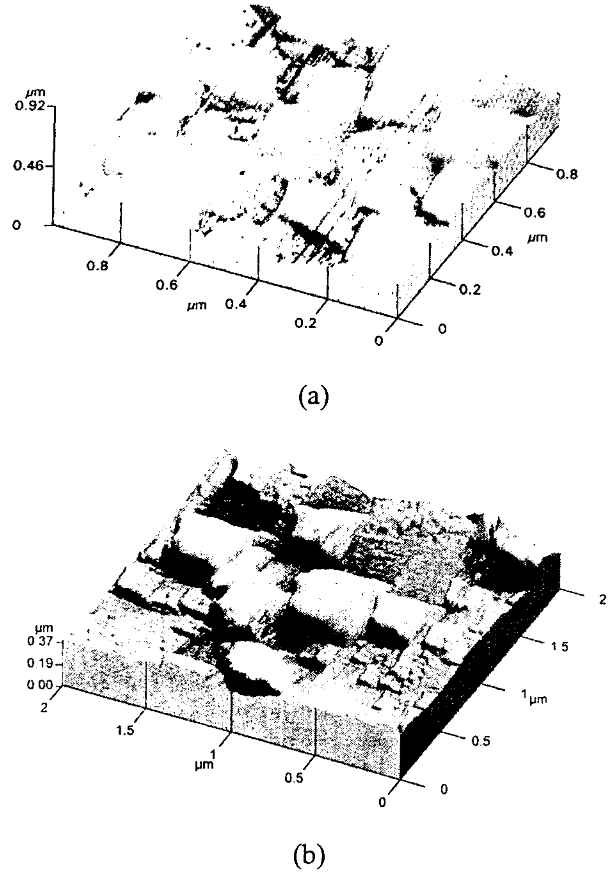

Fig. 5. AFM images of diamond thin films grown for differnet depositon times (a) 24h (b) 36h

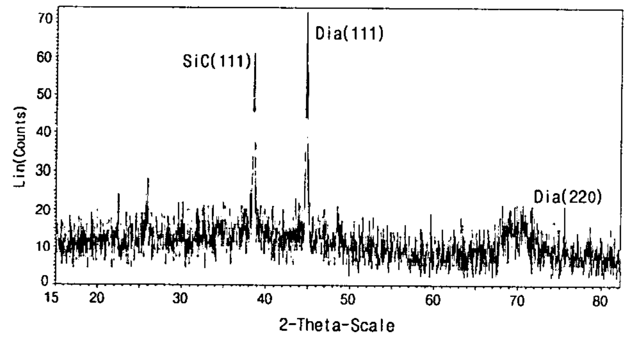

Fig. 6. X-ray diffraction pattern for the diamond film.

of plasma from the case of small radius respondent chamber to moving chamber, get out of the effect of the magnetic field, dispersed rapidly, the plasma potential reduced grately. Thus, permitting the secondary restraint magnetic field (supporting coil), preventing the disperse of plasma, it is considered creating plasma which have the even density. XRD used mainly to analyse the structure of the crystal of the film. Figure 6. is the XRD revolution pattern, from the peaks of the cute surface (111) and very faible surface (220), it was possible to confirm the existence of diamond. As like (111), from the position and the width of line, the diamonds were very minute in the size of crystal particle below micro in its size which were proved in AFM. And also, we confirmed the deposition of diamond only the case of helicon plasma.

4. CONCLUSION

Using the source of helicon plasma, we deposited the diamond film on the waper of Si p-type (100) in the mixture of methane and hydrogen gas. Through the analysis of XPS, AFM and XRD, and by the observing the formation of nuclear on diamond surface, we obtained conclusions as below.

(1) Above 300 G ; the value of critical magnetic field, the density of plasma increased rapidly, and the colour of discharge of electricity brightened notably. It is interpreted such as, having the critical value in magnetic field in the range of plasma, the electron accelerated grately, and with the more frequent collision of the neutral gas, the density of plasma increased. The density of plasma measured was $10^{10} \sim 10^{11}$ cm^{-3}.

(2) In analysis of XPS, binding energy was 285.4 eV nearly approached to diamond peak, and SiC peak was investigated in 283.3 eV. It is because, in early period in the formation of nuclear, with the phenomenon of the excess saturation of carbon atoms, SiC formed firstly, and with the sufficient supply of energy, by the reformation course of sp^2 ,sp^3 formation is made.

(3) After the result of the analysis of AFM, the surface of the crystal proved as the typical form of diamond (100) : cubic form, and the crystals sized 0.2 ~ 0.4 μm structured the pyramidal shape.

(4) In XRD, from the peaks of the cute surface (111) and the very faible surface (220), we were possible to confirm the existence of diamond.

From the results above, the quality of the film of diamond enlarged and attached was not fairly good, but it was possible to confirm the possibility of making of film of diamond by the way of helicon plasma.

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