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Large Area Diamond Nucleation and Si (001) Using Magnetoactive Microwave Plasma Chemical Vapor Deposition

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Diamond was uniformly nucleated on large area Si(001) substrate (3 cm×4 cm) using the low pressure magnetoactive microwave plasma chemical vapor deposition. CH_4/He gas mixture was used as source gas in order to obtain high radical density in the nucleation enhancement step. CH_3 radical density was measured by means of infrared laser absorption spectroscopy. The effect of substrate bias voltage on diamond nucleation was examined. The results showed that a suitable positive bias voltage applied to the substrate with respect to the chamber could enhance diamond nucleation while a negative bias voltages leaded to deposition of only non-diamond phase carbon.

Key words : Diamond, Nucleation, Magnetoactive microwave plasma, Radical density, Substrate bias

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I. Introduction

The heteroepitaxial diamond thin film over large area is quite important in realizing diamond based electronic devices. Recently, it has been reported that the highly oriented diamond of high density is nucleated on Si[1] and β-SiC[2] by microwave plasma CVD(MWPCVD). In the MWPCVD, the diamond deposition processes are generally divided into two steps, that is, the bias enhanced nucleation (BEN) step[3] where the substrate is negatively biased with respect to the counter electrode and the growth step. It has been demonstrated that the bias enhanced nucleation treatment in MWPCVD is very useful for heteroepitaxial growth of diamond on silicon.[4-6] Now many efforts are devoted to improvement in the BEN. In this study, low pressure magnetoactive microwave plasma is used for uniform diamond nucleation over large area. In case of low pressure magnetoactive microwave plasma, the plasma volume is large owing to long mean free path and the plasma temperature and density are relatively uniform at electron cyclotron resonance point (ECR point).

The main difference between low pressure magnetoactive microwave plasma and conventional microwave plasma is operating pressure which governs the collision frequency of electrons, ions, or reactive species. CH_4/He gas mixture is used as source gas in place of the CH_4/H_2 gas mixture of MWPCVD in order to obtain high radical density in the nucleation enhancement step. Because the plasma density in pure He plasma is higher than that in pure H_2 plasma by one order,[7] the higher radical density is expected in CH_4/He plasma. CH_3 radical density is measured using infrared laser absorption spectroscopy (IRLAS). CH_3 radical is an important precursor for the diamond deposition.[8]

Also, it is expected that a positive substrate bias voltage is proper for the diamond nucleation in case of low pressure magnetoactive microwave plasma. During the bias pretreatment of microwave plasma, ions fall on the substrate from the plasma through many colisions in the sheath. The ion energy will be determined by the mean free path of the ion rather than the bias voltage. In case of the low pressure plasma, however, the ion energy can be controlled directly by the bias voltage because ions fall on the substrate without collision. In order to obtain ion energy as low as several eV which is required in the BEN treatment of MWPCVD under the pressure of several kPa, the substrate should be positively biased with respect to the grounded chamber wall.

II. Experimental

Magnetoactive microwave plasma CVD system used in the present study is schematically shown in Fig. 1. P-type Si (001) was used as the substrate. The substrate was loaded into the depostion chamber made of stainless steel after HF-H_2O treatment and de-ionized water rinse. The deposition chamber was evacuated to 10^{-4} Pa, before the substrate positioned at ECR point (875G) was annealed by the resistive heater beneath the substrate holder. Although the temperature of the heater was kept at 600°C, the resulting temperature of the Si substrate was about 350°C because of low thermal conductivity between the substrate and the heater. Microwave of 2.45 GHz was introduced into the cylindrical discharge cavity through the quartz window positioned at the peak of the

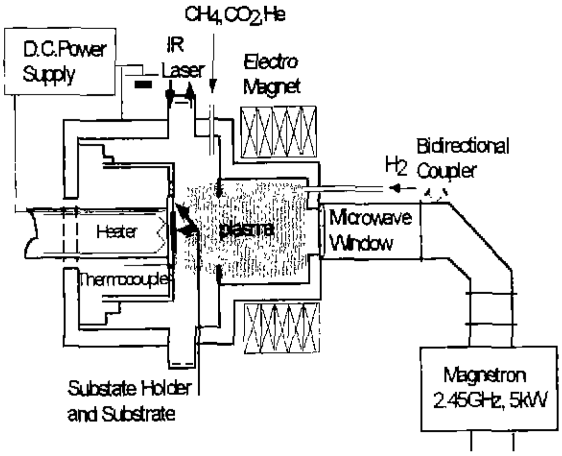

Fig. 1. The schematic diagram of magnetoactive microwave plasma CVD for diamond deposition. The IR Laser beams for measurement of the radical density passed 24 times through plasma by mirrors.

magnetic field after applying DC substrate bias voltage with respect to grounded chamber wall. The CH_4 plasma diluted with He was used for nucleation enhancement and as the gas mixture for diamond growth, $CH_4/CO_2/H_2$ gas mixture was used. The condition for diamond growth was not changed in this study. Diamond could be reproducibly grown on a scratched Si substrate in that condition.[9] Details of the experimental parameters in both two steps are given in Table 1. The chamber cleaning using pure O_2 plasma and pure H_2 plasma sometimes preceded the loading of the substrate.

The CH_3 radical density was measured in the nucleation enhancement step using IRLAS. The IRLAS measurement unit with a white-type multi-reflection cell was mounted on a vibration isolator separated from the plasma chamber. The unit was composed of an infrared diode laser emitting 14 μm range light which was cooled by liquid He, a monochromator for mode separation and detection units for reference and absorption signals. The laser beam passed 24 times through the plasma and the substrate was positioned at ECR point.

Table 1. Experimental Condition

Parameters	nucleation enhancement	growth*
gas composition [%]	CH_4/He [3/97]	$CH_4/CO_2/H_2$ [5/10/85]
flow rate [sccm]	100	100
pressure [Pa]	10	10
substrate temp. [°C]	550 [3 kW]**	580
microwave power [kW]	3	5
bias voltage [V]	-60~+60	+30
treatment time [min]	10	120

*The substrate temperature was measured with thermocouple. And the substrate temperature depends on the microwave power.

**The growth condition was not exchanged and constant in this study.

III. Results and Discussion

CH_4/He gas mixture was used in the nucleation enhancement step in order to obtain high radical density. CH_3 radical density was measured by IRLAS. The CH_3 radical is an important precursor for the diamond deposition. The CH_3 radical density in the CH_4/He plasma was compared with that in the CH_4/H_2 plasma which has generally been used during BEN of microwave plasma CVD as a function of gas concentration ratio. The results are given in Fig. 2. The CH_3 radical density in the CH_4/He plasma was about one and a half times as high as that in the CH_4/H_2 for the same CH_4 concentration, although the plasma density was higher in CH_4/He plasma by one order. However, the diamond nucleation density was significantly enhanced by using the CH_4/He plasma.

The nucleation density as high as about 10^9 cm^{-2} was obtained with the CH_4/He plasma at the bias voltage of +30 V and the microwave power of 3 kW as shown in Fig. 3, while it was very low even for the CH_4 concentration as high as 25%. The nucleation density was calculated after 2 hrs growth from SEM images.

On the other hand, the diamond nucleation density was considerably influenced by the chamber condition. Faceted diamond particles could not be observed when the depositon chamber was contaminated probably by the residual carbon-included species. On the contrary, the enhanced nucleation density could not be attained in new chamber condition which had been obtained by a repetitive cleaning process of pure O_2 and pure H_2 plasma. Therefore, this enhanced diamond nucleation in CH_4/He plasma seemed to be due to residual species. When the residual species were sputtered, it can influence the composition of CH_4/He plasma and, in turn, the diamond nucleation condition. Especially in case of CH_4/He plasma,

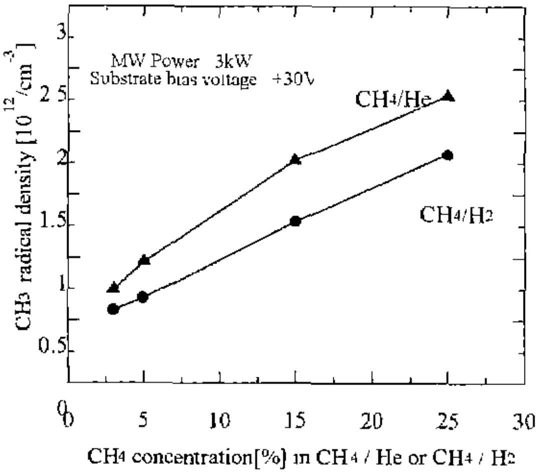

Fig. 2. The dependence of the CH_3 radical density on CH_4 concentration both in CH_4/He and CH_4/H_2 gas mixtures. CH_3 radical density is measured using IRLAS (Infrared Laser absorption spectroscopy). For neutral radical density measurement, substrate is positioned at ECR point, that is, 875 Gauss in 2.45 GHz microwave.

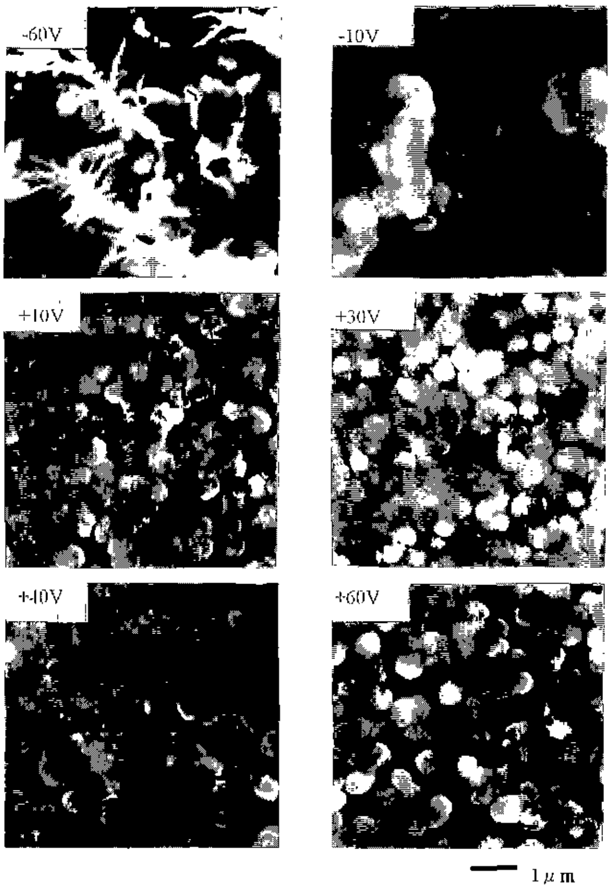

Fig. 3. The dependence of the diamond deposition on the substrate bias voltage in nucleation enhancement step. The substrate bias voltage is applied with respect to the grounded chamber wall.

this effect may become larger because of its high plasma density.

The dependence of diamond nucleation on the substrate bias voltage applied with respect to the grounded chamber wall was examined under the condition of 3% CH_4 concentration and microwave power of 3 kW. The results obtained are given in Fig 3 which shows SEM images of diamond particles grown for 2 hrs. From the SEM images, it was concluded that diamond was not nucleated at negative substrate bias voltage but only noncrystalline carbon was deposited. Especially at -60 V, the substrate seemed to get damaged. At the positive substrate bias voltage such as +10 V, +30 V, and +40 V, diamond particles were observed, and the nucleation density was the highest at 30 V. Therefore, substrate bias voltage should be positively applied with respect to the grounded chamber wall in order to prevent the substrate damage from the high ion energy.

Figure 4 and 5 show how plasma potential changes with bias voltage and how bias current change with bias voltage in 10 Pa magnetoactive microwave plasma, respectively. The result of Fig. 4 was obtained by the Langmuir single probe mesurement in 10 Pa, 5 kW and pure H_2 plasma. The dotted line indicates the substrate bias voltage. Both potentials were measured with respect to the grounded chamber wall. As shown in Fig. 4, it is found that the plasma potential decreased with decreasing the positive substrate bias voltage and then became constant from about -20 V. Also, a similar result is shown in Fig. 5, that is, bias current was already saturated from about -10 V.

Therefore, an additional negative substrate bias voltage increases only ion energy, because ions fall on substrate through a plasma sheath without collision in case of low pressure magnetoactive microwave plasma. At positive substrate bias voltage applied with respect to the grounded chamber wall, the substrate damage was able to prevented from high ion energy bombardment. However, the plasma sheath voltage between the plasma and

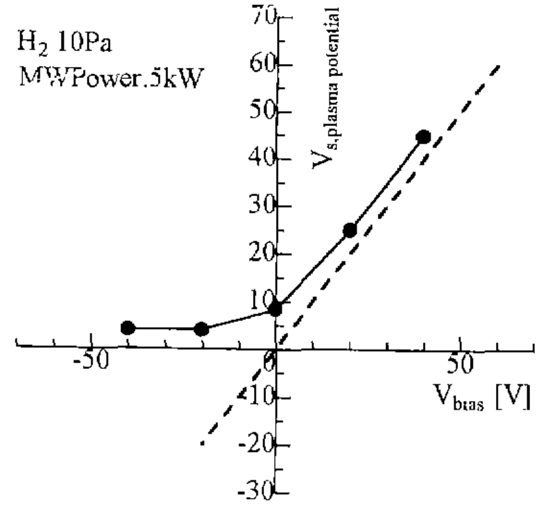

Fig. 4. The dependence of the plasma potential on the substrate bias voltage in 10 Pa H_2 magnetoactive microwave plasma. At negative substrate bias voltage the plasma potential is not changed, and at positive substrate bias voltage, the plasma potential is increased with bias voltage.

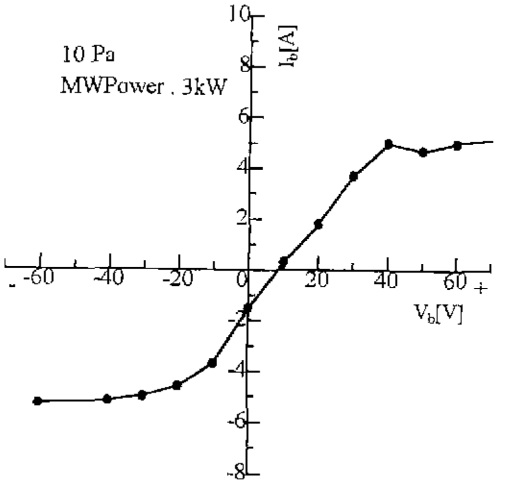

Fig. 5. The dependence of the bias current on the substrate bias voltage in 10 Pa, CH_4 (3%)/He plasma. The ion current becomes saturated at the substrate bias voltage of -10.

the chamber wall such as the cavity or the microwave will be increased with a positive substrate bias voltage applied with respect to the grounded chamber wall. When the chamber is contaminated by a residual carbon-included molecules, its sputtering by high energy ion bombardment can result in the change of the plasma composition, which, in trun, may influence the diamond nucleation density considerably.

IV. Conclusions

Diamond was uniformly nucleated on Si substrate over large area (3 cm×4 cm) using low pressure magnetoactive microwave plasma CVD and the diamond nucleation was enhanced to the density as high as 10^9 cm^{-2} by using CH_4/He in stead of CH_4/H_2, when the substrate was positively biased with respect to the grounded chamber wall. However, the result seems to be due to the plasma composition which is changed by the residual carbon-included molecules sputtered mainly from microwave window. Especially in case of low pressure CH_4/He plasma, the effect may become larger because of its high plasma density.

When a negative substrate bias voltage was applied, diamond could not be nucleated due to high energy ion bombardment on the substrate. The results of single probe measurement and I-V curve of Fig. 5 showed the plasma potential became constant and the ion current was saturated already at the substrate bias voltage of -10 V.

Acknowledgment

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