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Heteroepitaxial Growth of Diamond Films Synthesized by Microwave Plasma Enhanced Chemical Vapor Deposition

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The highly oriented diamond particles were deposited on the mirror-polished (100) silicon substrates in the bell-jar type microwave plasma deposition system using a three-step process consisting if carburization, bias-enhanced nucleation and growth. By adjusting the geometry of the substrate and substrate holder, very dense disc-shaped plasma was formed over the substrate when the bias voltage was below -200 V. Almsot perfectly oriented diamond films were obtained only in this dense disc-shaped plasma. From the results of the optical emission spectra of the dense disc-shaped plasma, it was found that the concentrations of atomic hydrogen and hydrocarbon radicals were increased with negative bias voltage. It was also found that the highly oriented diamonds were deposited in the region, where the intensity ratios of carbonaceous species to atomic hydrogen are saturated.

Key words : Diamond, Heteroepitaxy, Bias-enhanced nucleation, Dense plasma

I. Introduction

The final goal of the diamond synthesis for the application of microelectronics would be the deposition of perfectly oriented heteroepitaxial films. Since Yugo et al[1] were able to greatly increase the nucleation density by the bias-enhanced nucleation (BEN) method, many researchers used this method to grow heteroepitaxial diamonds on the Si substrate in spite of the large lattice mismatch and the considerable surface energy difference between the two materials.[2-8] Unfortunately, there were some azimuthal rotation and tilt of grains in the reported heteroepitaxial diamond films.

The orientation of the film could be improved by understanding the mechanism of heteroepitaxial nucleation behavior during the BEN proposed by several researchers.[1,2,6,9-13] Most of them were based upon a subplantation mechanism whereby higher energy carbon-containing ions would be implanted beneath the surface, increasing the local carbon concentrations and leading to the formation of stable sp^3 clusters capable of nucleating diamond. However, this model can not fully explain how the stable sp^3 clusters are formed with orientation relationship between them and silicon substrate. And most of the proposed nucleation models of the BEN were based on surface and bulk analytical data.

There are several radical species in the diamiond nucleation and growth environment contributing to the deposition of diamond.[14] Because they contribute to the formation of diamond, it is important to investigate changes in local plasma chemistry created by the biasing environment to gain a better understanding of the heteroepitaxial nucleation process. Only a few researchers have been interested in the plasma chemistry during the BEN process. Stoner et al[15] proposed that the nucleation density of diamond was increased when the strong plasma glow was formed near the substrate surface. Chen et al[16] observed that various orientation relationships between diamond and Si substrates depended on the location where the plasma was applied. Shigesato et al[17] suggested that the plasma states, such as the concentration of atomic hydrogen and electron temperature, changed negative bias voltage might have an effect on the nucleation density of diamond. The effects of plasma states on the heteroepitaxial nucleation of diamond during BEN treatment, however, is not fully understood. In this work, we report the nearly perfectly oriented heteroepitaxial diamond film which was deposited using the BEN process in the locally dense plasma obtained by adjusting the geometry of the substrate and the substrate holder. The locally dense plasma was analyzed by the optical emission spectroscopy (OES) and the mechanism of the highly oriented nucleation of diamond by the BEN process is discussed.

II. Experimental

Deposition was carried out in a bell-jar type microwave-plasma CVD system equipped with an ASTeX 1.5 KW magnetron plasma source [18] The substrate was a mirror polished p-type (100) silicon wafer. In order to increase the plasma density near the substrate surface, the substrate was immersed inside the plasma ball during the whole deposition process using a graphite block which was inserted between the substrate holder and

Teble 1. Preparation Conditions of the Specimens

Process	Plasma etching	Carburi -zation	Bias	Growth
CH_4/H_2(%)	0	2	2~3	0.8~2.0
Gas pressure (Pa)	2000	200	1330 ~2650	3330
Substrate Temperature (°C)	~800	~800	~800	~850
Bias voltage (V)			-100 ~-250	
Microwave power (W)	700	700	700	800
Time (min)	10	30~60	10	1~18(hr)

the substrate. The substrate holder was connected to the d.c. power and the counterelectrode was grounded.

To remove the oxide layer of the surface, the substrate was immersed in the pure hydrogen plasma for 10 min before deposition. The highly oriented diamond film was prepared by employing carburization. bias-treatment and growth processes.[3,4,6-8] The detailed parameters are shown in Table 1. The surface morphology and orientation of the deposited diamond were analyzed by scanning electron microscpy (SEN). To characterize the orientation relationship of the deposited films, an X-ray diffractometer (RIGAKU, D/MAX-RC) attached with a thinfilm measurement system was used. During the BEN process, the OES was used to examine the effect of negative bias on the chemical species in the plasma by varying the applied voltage from -100 to -250 V. The plasma emission was transmitted throught the half inch diameter view into the monochrometer (LUXYRON 1015DS) via a bundle of optical fibers, which was focused on the dense disc-shaped plasma. The carbon content in the substrate was measured by Auger electron spectroscopy (AES). Auger spectra were acquired at a voltage of 5KeV and the AES depth profiling was conducted using Ar ions (2KeV, 25mA).

III. Results and Discussions

1. Highly oriented diamond

The highly oriented diamonds were nucleated by biasenhanced nucleation performed under the deposition conditions such as 2-3% methane concentration in hydroegen, 2000 Pa of total pressure, the negative bias voltage between -200 V to -250 V and the substrate temperature of 1073 K. Under these deposition conditions, the local plasma density near the substrate was enhanced by inserting the substrate in the plasma ball using the graphite block. When the negative bias was applied to the substrate holder below -200 V, very thin disc-shaped dense plasma was observed over the substrate. The schematic diagrams of the plasma, substrate, graphite block and substrate holder are shown in Fig. 1.

This dense plasma was not obtained simply by increasing microwave power, but by introducing a graphite block with a substrate whose size is almost the same as the block. The plasma was concentrated over the substrate with a thickness of several millimeters, especially around the four corners of the substrate where almost perfectly oriented diamonds were locally nucleated.

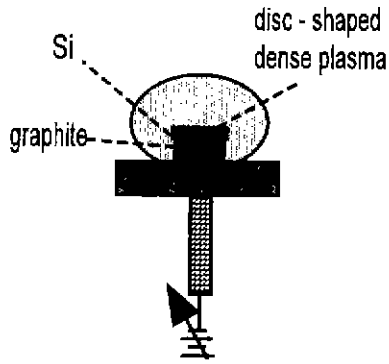

Fig. 1. The schematic diagram of the substrate geometry and the shape of the dense plasma as the negative bias is applied to the substrate holder below -200 V.

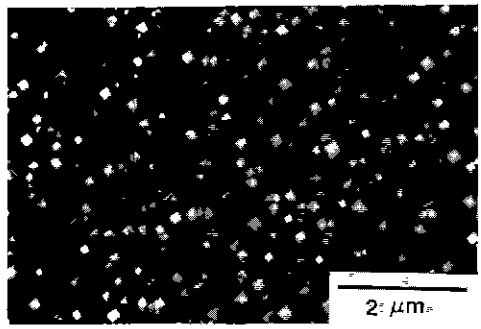

Fig. 2. The SEM micrographs of the perfectly oriented diamond film grown for 5 hours used 0.8% of methane after BEN step performed at 2000 Pa of total pressure and -250 V during 10 min.

The SEM surface images of diamond grown for 5 hours after the carburization and the BEN steps using 2% CH_4 in H_2 are shown in Fig. 2. All the crystallites in the SEM images are squares with the size of a submicron. It can be seen that the edges of the crystallites are aligned almost perfectly parallel to each other. The SEM surface image of the film grown for 18 hours is shown in Fig. 3. The surface of the film is composed of rectangular shaped grains which are formed parallel to each other. Figure 4 is the {111} diamond x-ray pole figure of the film as shown in Fig. 3. The film was clearly shown four-fold symmetry as expected for an epitaxial film.

2. The analysis of disc-shaped dense plasma

The bright thin dense disc-shaped plasma observed over the substrate may facilitate the formation of the oriented nuclei. To verify the roles of the dense plasma on the alignment of the diamond particles, we analyzed the plasma states by OES. Figure 5(a) shows the em-

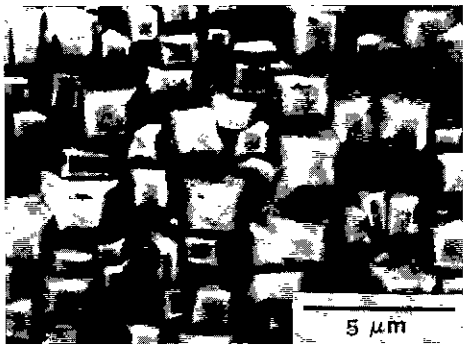

Fig. 3. The SEM image of the film grown for 18 hours used 2% of methane after BEN step conducted under the deposition conditions such as 2% of methane concentration in hydrogen, 2650 Pa of total pressure and -200V of negative bias voltage.

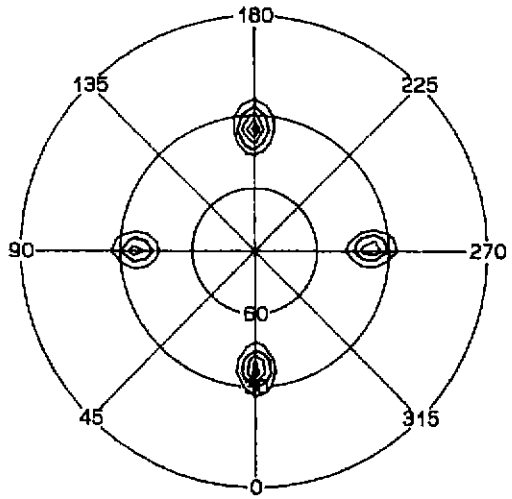

Fig. 4. Intensity profile of [111] x-ray pole figure of diamond film.

ission intensities of H_α(656.3 nm) and H_β(486.1 nm) peaks as a function of negative bias voltage at the pressure of 2000 Pa with 2% CH_4. The intensities of both peaks increase with the negative bias voltage. Both intensities were normalized to the value obtained without bias voltage. The dense disc-shaped plasma, as shown in Fig. 1, and the oriented diamond crystallites are obtained in the shaded region. The intensity ratio of H_β to H_α could be used to estimate the relative electron temperature in the plasma.[17-19] It increases as the bias voltage increases negatively and saturates below -200 V as shown in Fig. 5(b). This reflects the increase of the electron temperature with a negatively increasing bias voltage, due to an acceleration of electrons in the sheath region. That is, the kinetic energy of electrons in the sheath region is increased by negative bias. These electrons easily decompose molecular hydrogen to atomic hydrogen and excite these atomic hydrogen to reactive states. It is believed that the concentration and reactivity of atomic hydrogen in dense plasma are increased by negative bias and the formation of the oriented diamond crystallites is related

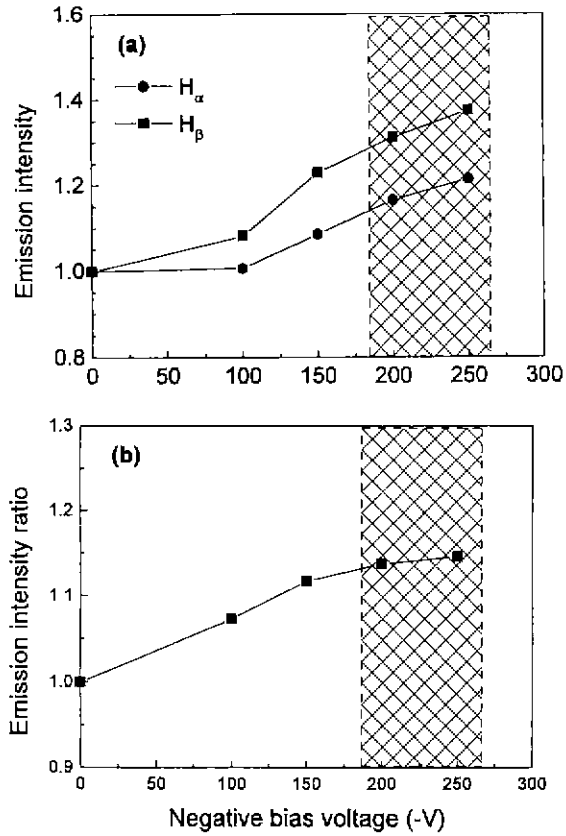

Fig. 5. (a) Emission intensities of H_α and H_β (All the intensities were normalized to the value when bias voltage was not applied) and (b) emission intensity ratio of H_β to H_α from 2% CH_4 plasma as a function of negative bias voltage at 2000 Pa. The disc-shaped dense plasma and the oriented diamond particles were obtained in the shaded region.

to the increase of them.

The emission intensities of CH(431.4 nm) and C_2(473.7 nm) peaks are increased. As to the deposition of the diamond, the diffusion layer is formed between the solid and vapor phase because diamond synthesis is performed at relatively low pressures.[20] The concentration of carbonaceous compounds on the substrate surface is very low because the feed gas is diluted with hydrogen. When a negative voltage is applied to the substrate, the diffusion layer is disturbed by positive ions arriving at the substrate surface from the gas phase. Because the positively charged ions decrease the thickness of the diffusion layer above the deposition surface, the diamond and non-diamond components(sp^2 carbon) are more rapidly deposited on the substrate during bias. Additionally, the non-diamond components co-deposited with diamond react readily with the atomic hydrogen, which is formed by accelerated electrons, near the sheath region and are gasified as hydrocarbons during BEN step. Therefore, the concentration of activated hydrocarbon radicals, which are precursors of diamond nucleation and growth, is increased in the diffusion layer as shown in Fig. 6. From the above results, it is found that plenty

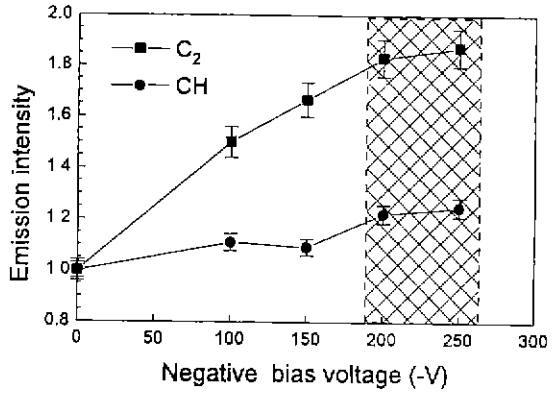

Fig. 6. Emission intensities of CH and C_2 from 2% CH_4 plasma as a function of negative bias voltage at 2000 Pa. All the intensities were normalized to the value when bias voltage was not applied.

of atomic hydrogen and carbonaceous species are formed in dense plasma by the negative bias applied to the substrate.

Figure 7 shows the AES depth profiles of the C-KLL peak and the Si-LMM peak. The peak intensity profile of C-KLL peak of the sample, which was obtained after the carburization process, drastically decreases and that of Si-LMM peak rapidly increases as shown in Fig. 7(a). It reveals that the very thin carbide and/or carbon layer was formed during the carburization process. The peak-to-peak intensity profile of C-KLL peak of the sample obtained after the carburization and bias treatment is divided into three parts, as shown in Fig, 7(b). In first part, the intensity of C-KLL peak rapidly decreases until two minutes sputter time. From two to ten minutes sputter time, in second part, the intensity of C-KLL peak is nearly constant. Finally, after 10 min. sputter time, the carbon intensity slowly decreases. From the AES results we believe that the top surface of the bias treated substrate was covered with carbons, whether those were diamond, graphite or amorphous carbon. The pleat region of the intensity profile of C-KLL peak shows that the carbide was formed during the bias treatment. The slow decrease of the carbon intensity during the sputtering shows the presence of the carbon diffusion region in the Si substrate. It is suggested that the bias treatment enhances the carburization of the substrate due to increasing the carbon concentration in the substrate by impinging action of the carbonaceous ions. In order to from a carbide layer, a little time is required in BEN process and this is the reason why delay time is for nucleation of diamond.

During the BEN process, a positive ion flux is decreased as the methane cotent in source gas increases, as shown in Fig. 8. This is the evidence that the hydrogen ions as well as carbonaceous ions are also bombarding the substrate surface. Lannon et al[21] reported that silicon atoms could be preferentially removed from the surface and near-surface layers of the silicon carbide deposited on silicon

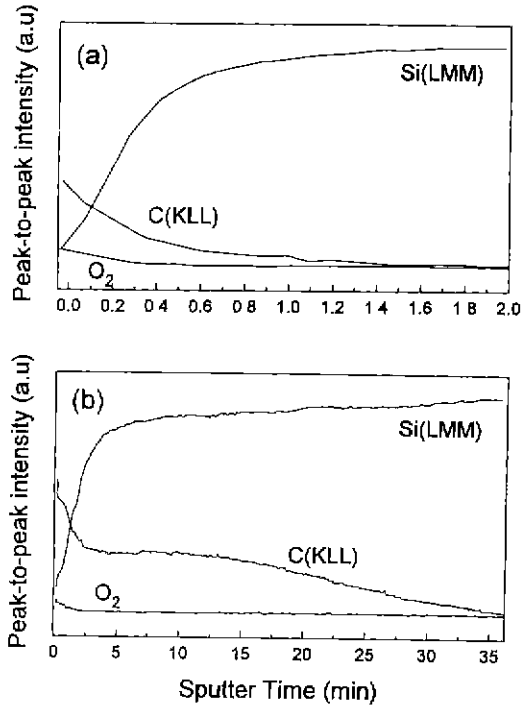

Fig. 7. AES depth profiles of the C-KLL peak and the Si-LMM peak of the sample (a) after the carburization process and (b) after the carburization and bias treatment.

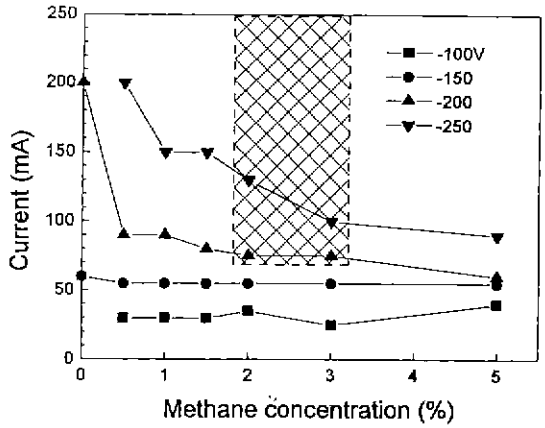

Fig. 8. The biasing currents as a function of methane content in the source gas at 2000 Pa.

substrate when the hydrogen ions bombarded the silicon carbide using ion gun. The resulting carbon-rich layers were concerted to a mixture of sp^2 and sp^3 carbon and the relative amount of sp^2 and sp^3 species formed were strongly depended upon the ion energy. They believed that the carbon atoms constructing silicon sites to form sp^3-bond C-C species because there is no carbon source except the carbon atoms in the network.

In the case of BEN process, however, large amounts of carbonaceous ions and radicals arrived at the substrate surface and subsurface. In order to sustain the lattice structure of silicon carbide, some of the carbonaceous ions and the radicals must be filled in the vacant silicon

sites instead of the lattice carbon atoms immediately after the silicon atoms are etched. The lattice carbon atoms need some activation energy to move into the vacant site because they must cut the bond between them and silicon atoms. On the contrary, the carbonaceous ions and the radicals have some mobility to occupy the vacant sites because they arrive at the substrate with some energy due to applied negative bias. In this manner, the sp^3-bond carbon clusters can be formed with the orientation relationship between them and silicon carbide which was grown epitaxially on silicon substrate during the carburization and bias treatment.

Some of the vacant silicon sites are not filled for relatively long time by the incident carbonaceous species. These sites are filled by the carbon atoms, which acquire energy enough to overcome the activation energy barrier to move into vacant sites by thermal energy or momentum transfer from the incident ions etc., at the silicon carbide lattice and convert to sp^3-bond carbon clusters without orientation relationship with silicon carbide. When a number of silicon vacancies are formed, the remaining carbon network collapses to form sp^3-bond carbon clusters for reducing the free energy.

The oriented sp^3-bond, off-oriented sp^3-bond and sp^2-bond clusters are grown to nuclei or etched away under the dense plasma where the hydrocarbon radicals and the atomic hydrogens prepared by negative bias are abundant as shown in Fig. 5 and Fig. 6. As the oriented sp^3-bond carbon clusters have the ordered chmical bonds with the substrate, that is, a heteroepitaxial relationship, they strongly bind with the surface of the substrate. On the other hand, the off-oriented sp^3-bond carbon clusters are relatively weakly bound with the surface of substrate only by simple adsorption. The flux of carbonaceous species from the plasma to the substrate surface increases by negative bias and the carbon clusters are grown by addition of them to oriented diamond embryos, off-oriented diamond embryos and non-diamond components, such as graphite, amorphous carbon embryos respectively. The atomic hydrogen of which the concentration and reactivity are increased near the substrate surface by the negative bias and the hydrogen ions extensively etch the clusters and the embryos.

It is expected that the deposition and etching rates of the oriented diamond, the off-oriented diamond and the non-diamond component will be different from each other and can be controlled by the intensity of an applied negative bias. The deposition rate as well as the etching rate is very fast with respect to the deposition without bias since there are large quantities of carbonaceous species, accelerated ions and atomic hydrogen in the dense plasma. Figure 9 shows the emission intensity ratios of CH/H_α and C_2/H_α as a function of the negative bias voltage. Both emission intensity ratios are saturated below -200 V, and the highly oriented diamond particles are obtained in this region. An increasing intensity ratio

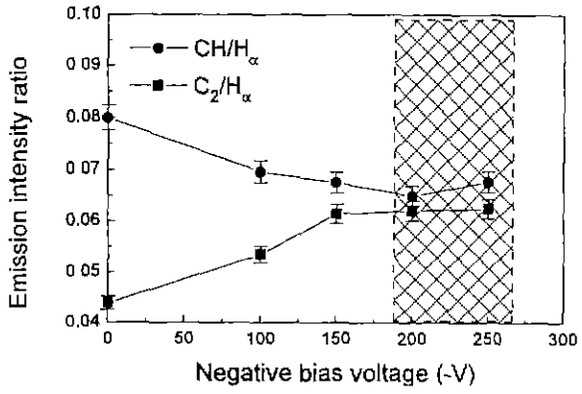

Fig. 9. *Emission intensity ratio of* CH/H_α *and* C_2/H_α *from 2%* CH_4 *plasma as a function of negative bias voltage at 2000 Pa.*

of C_2/H_α with a negatively increasing bias voltage is a disadvantage to the nucleation of oriented diamond because it enhances the deposition of non-diamond components.

But fortunately, many of the non-diamond components will be etched away by atomic hydrogen because their etching rate is about fifty times that of diamond.[14] When the negative bias is applied to the substrate, the intensity ratio of CH/H_α is smaller than that without bias. This means that the increasing amount of the etching rate is larger than that in the deposition rate of the diamond. The strongly-bonded embryos with substrates due to ordered chemical bonds are relatively difficult to etch away while the weakly-bonded embryos are easily etched by atomic hydrogen to become gasified or unstable embryos of diamond. Consequently, the fraction of oriented embryos in total embryos formed on the surface is increased by preferential etching of off-oriented embryos. The fraction is increased more as the intensity ratio of CH/H_α decreases. As a result, the orented embryos are grown by adding the diamond precursor to the stable nuclei. Finally, highly oriented diamond film is formed after a growth step, while a few off-oriented embryos, which are survived after the bias step, grow to form azimuthally misoriented grains.

IV. Summary

By adjusting the geometry of the substrate and substrate holder, very dense disc-shaped plasma was formed on the substrate when the bias voltage was below -200 V. Almost perfectly oriented diamond films were obtained only in this dense disc-shaped plasma. From the optical emission spectroscopy, it was found that the concentration of atomic hydrogen and hydrocarbon radicals increased in the disc-shaped plasma. It is suggested that the heteroepitaxial diamond can be obtained by the combination of the formation of silicon carbide, selective etching of silicon in silicon carbide network, filling the vacant silicon sites by carbonaceous ions and radicals. adding hydrocarbon radicals to the oriented sp^3-bond carbon clusters and

etching non-diamond component and off-oriented sp^3-bond carbon clusters during the BEN process.

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