Journal of Ceramic Processing Research. Vol. 4, No. 4, pp. 173~176 (2003)

J O U R N A L O F
Ceramic Processing Research

Cathodoluminescence characteristics of nitrogen-incorporated diamond films grown by microwave plasma CVD

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In this paper, we present experimental results regarding the growth of nitrogen-incorporated diamond films grown by employing a microwave plasma CVD method. For grown films, cathodoluminescence (CL) characteristics are examined in terms of growth conditions, such as gas mixture ($N_2/(CH_4+H_2)$) ratio and microwave power. From the CL characteristics the relative intensity of the so called band-A (related to a dislocation, I_A) centered at 430 nm to the nitrogen-related band (I_N), which is composed of two peaks centered at 578 nm (related to a nitrogen-vacancy complex) and at 637 nm (related to a vacancy trapped at a substitutional nitrogen site). The effect of oxygen, which is added during diamond growth, on the CL property is also investigated. In addition, the Raman spectra, XRD patterns, and field-emission SEM morphologies are analyzed for all the films grown.

Key words: diamond film, nitrogen incorporation, cathodoluminescence, band-A emission, nitrogen-related band.

Introduction

With a rapid development of chemical vapor deposition (CVD) technology, CVD-produced diamond films are considered to have potential for high temperature and high power electronic device applications [1]. Doping of diamond with either n-type or p-type elements may be one of the important procedures for implementing diamond-based electronic devices [2, 3]. It has been known for some time that p-type doped diamond films can easily be prepared mainly using boron (B) because the formation energy of boron substitutional acceptors is of negative value (-0.5 eV). In the case of n-type doping, however, successful results rarely have been reported in the literature although many efforts have been made using various elements, such as lithium (Li), phosphorus (P), and nitrogen (N) [3]. This may be why a large variety of systematic studies of n-type doping of diamond is still required.

In this paper, we present experimental results regarding the growth of nitrogen-incorporated diamond films by microwave plasma CVD and the analysis of their cathodoluminescence (CL) characteristics [4]. The effects of growth conditions, such as gas mixture ($N_2/(CH_4+H_2)$) ratio and microwave power as well as the addition of oxygen on the CL properties are investigated. In addition, the Raman spectra, scanning electron microscope (SEM) surface morphologies, and x-ray diffraction (XRD) patterns are presented for all the films grown.

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Experimental

Polycrystalline diamond films were deposited on Si (100) substrates using a 2.45 GHz microwave plasma CVD method. The microwave power was varied from 800 W to 950 W (corresponding substrate temperature; from 703±7°C to 725±3°C). The bias-assisted formation of diamond nuclei on Si was performed by applying a negative bias voltage of -200 V to the substrate. The background pressure prior to the film deposition was kept as low as 6.7×10^{-4} Pa to minimize the effect of residual elements which may remain inside the chamber. In preparing undoped diamond films the CH_4/H_2 ratio was fixed at 0.5%, while for nitrogen-incorporated films the $N_2/(CH_4+H_2)$ ratio was varied from 0% to 2.0 %. In addition, the oxygen-added films were grown at a fixed ratio of $O_2/(CH_4+H_2)$=0.5%.

For all the grown films, Raman spectroscopy (System 1000, Renishaw) was used to monitor the characteristic peaks which occurred at various wave numbers, such as 1332 cm^{-1} (representing the cubic-diamond), 1550 cm^{-1} (reflecting the graphite-related phase), 1140 cm^{-1} (related to the nano-sized diamond), and 1500 cm^{-1} (related to the amorphous carbon phase). The CL characteristics were measured using an Oxford Mono CL system interfaced to a field emission SEM (JSM-6330F, JEOL).

The CL emissions were collected by an ellipsoidal mirror and the CL spectra were obtained at 20 kV (accelerating voltage) and 12 µA (beam current). Crystal orientations and film morphologies of deposited films were also examined by analyzing the XRD (Cu-K_α radiation, θ-2θ scan, D/MAX 2000 +Ultima, Rigaku) spectra and field-emission SEM images, respectively.

Results and Discussion

The SEM surface morphologies for diamond films grown at the different $N_2/(CH_4+H_2)$ ratios are depicted in Fig. 1(a)~(d). It was found that increasing the $N_2/(CH_4+H_2)$ ratio made a little alteration in the surface morphology from the truncated-octahedral shape of larger grains (mainly for undoped film) to the pyramid-like shape of smaller grains (mostly for nitrogen-incorporated films). The film grown at a higher $N_2/(CH_4+H_2)$ ratio (2%) exhibited a cauliflower-like structure composed of small pyramidal grains. This may be explained by the previous report [5] that the incorporation of substitutional nitrogen atoms in diamond may play a significant role in the distortion of the diamond lattice since the bond length of C-N is longer by about 36% than that of C-C.

Figure 2(a) and (b) show the CL characteristics obtained from grown films, in terms of $N_2/(CH_4+H_2)$ ratio varying from 0% to 2%. With increasing the $N_2/(CH_4+H_2)$ ratio, the CL intensities were reduced, which was believed to be due to the decrease of grain size as already shown in Fig. 1. From the CL spectra, three distinguishable emission bands were observed; 1) the so-called band-A centered at about 430 nm (related to growth-induced dislocations), 2) nitrogen-related emission bands which are composed of two peaks centered at 578 nm (a nitrogen-vacancy complex) and 637 nm (a vacancy trapped at a substitutional nitrogen site), 3) a Si-defect related band centered at 738 nm [3-4, 6]. No nitrogen-related bands were observed for undoped films or the film grown at a very low $N_2/(CH_4+H_2)$ ratio (0.2%), while the nitrogen-related emission rather than the band-A emission became more conspicuous with further increase in the $N_2/(CH_4+H_2)$ ratio (0.5~2 %).

The relative intensity ratio of band-A to the nitrogen-related band (denoted by I_A/I_N) may reflect the incorporation of nitrogen into diamond films [3]. The I_A/I_N values were estimated from the CL spectra shown in Fig. 2(a) and (b) and are depicted in Fig. 3, along with the preferred orientations, represented by $I_{(220)}/I_{(111)}$ and $I_{(100)}/I_{(111)}$, which were analyzed from their XRD patterns. It was clearly established that the I_A/I_N value was significantly reduced when the $N_2/(CH_4+H_2)$ ratio exceeded 0.2%. In addition, it has been claimed [4, 7, 8] that the nitrogen-related band is often observed for (100)-oriented diamond with the band-A for (111)- and (220)-oriented diamond. However, this may not be the case in our study. The variations of $I_{(220)}/I_{(111)}$ and $I_{(100)}/I_{(111)}$ shown in Fig. 3 indicate that the preferred orientation of diamond films with relatively strong

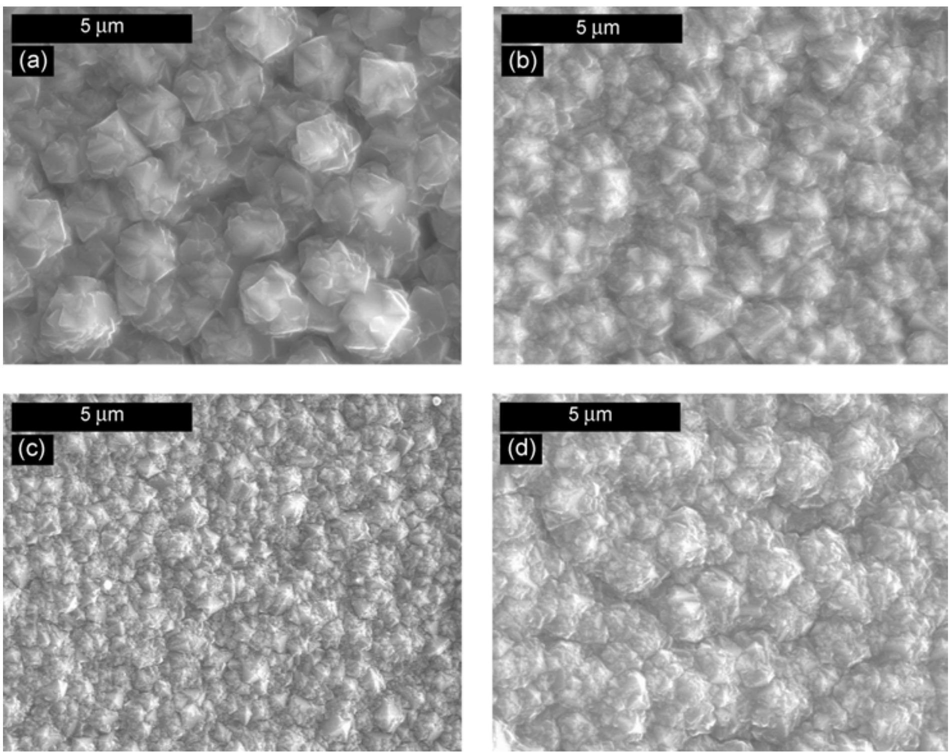

Fig. 1. The FE-SEM images of diamond films grown at 800 W; (a) $N_2/(CH_4+H_2)$=0%, (b) $N_2/(CH_4+H_2)$=0.5%, (c) $N_2/(CH_4+H_2)$= 1.5%, (d) $N_2/(CH_4+H_2)$=2.0%.

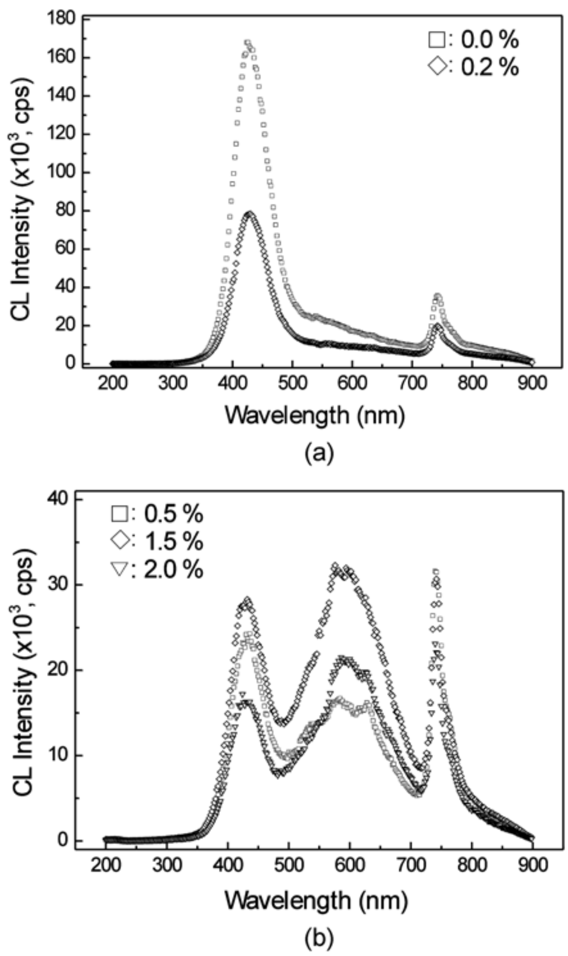

Fig. 2. The CL spectra of diamond films grown at 800 W, in terms of $N_2/(CH_4+H_2)$ ratio (0~2.0%).

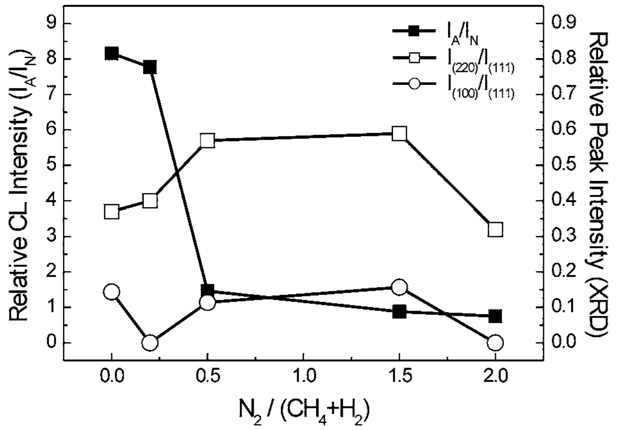

Fig. 3. Relationships between CL properties (I_A/I_N) and XRD orientations ($I_{(220)}/I_{(111)}$ and $I_{(100)}/I_{(111)}$) of diamond films grown at 800 W, in terms of $N_2/(CH_4+H_2)$ ratio (0~2.0%).

nitrogen-related band intensities (i.e., relatively small I_A/I_N values) may be represented mainly by the (111)-orientation, rather than the (100)-orientation.

The microwave power applied during deposition was changed from 800 W to 950 W for nitrogen-incorporated films grown at $N_2/(CH_4+H_2)$=1.5% and their CL spectra are compared in Fig. 4. It was found that all the films revealed very similar CL spectra, while the I_A/I_N value was slightly increased from 0.88 for 800 W to 0.92 for 950 W. Although the dependence of CL property on the applied power was almost inconspicuous on the whole, it was noted that for the film grown at a relatively higher power (950 W) the peak at 637 nm, rather than the peak at 578 nm, governed the nitrogen-related emission band.

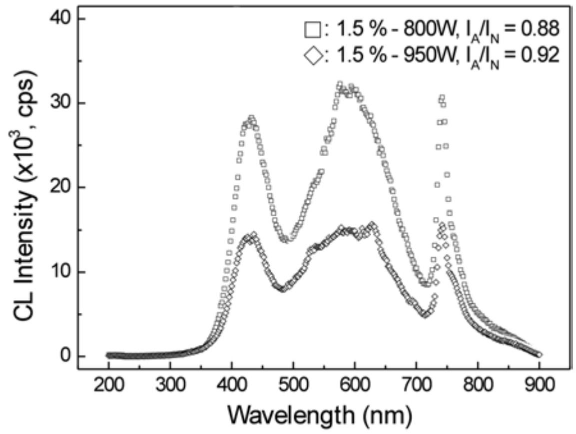

Fig. 4. The effect of microwave power (800 W and 950 W) on the CL spectra ($N_2/(CH_4+H_2)$=1.5%).

To examine the effect of oxygen on the CL property, the SEM surface morphologies and Raman spectra were measured for nitrogen-incorporated diamonds ($N_2/(CH_4+H_2)$=0.5%) grown without oxygen and with oxygen ($O_2/(CH_4+H_2)$=0.5%), and these are depicted in Fig. 5(a)~(d). The film grown without oxygen exhibited the typical morphology of a micro-crystalline film with a grain size of about 1 µm (see Fig. 5(a)). On the other hand, the oxygen-added diamond film, as shown in Fig. 5(b), showed a surface morphology composed of spherical

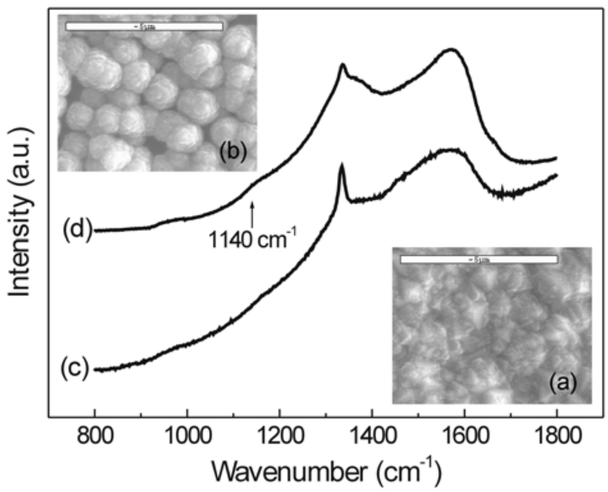

Fig. 5. The FE-SEM images ((a) and (b)) and Raman spectra ((c) and (d)) of nitrogen-incorporated diamond films grown at $N_2/(CH_4+H_2)$=0.5 % and 800 W; (a) and (c) without oxygen, (b) and (d) with oxygen ($O_2/(CH_4+H_2)$=0.5%).

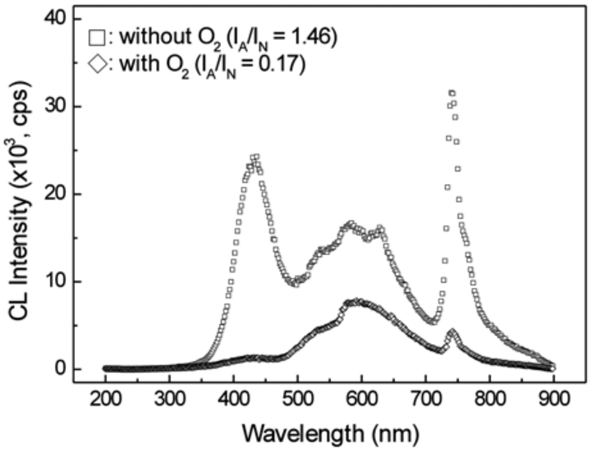

Fig. 6. The CL spectra of nitrogen-incorporated diamond films grown at $N_2/(CH_4+H_2)$=0.5% and 800 W (□ ; without oxygen, ◇ ; $O_2/(CH_4+H_2)$=0.5%).

diamond grains, which indicated the co-existence of nano-sized and micro-crystalline diamond grains. The weak peak observed at 1140 cm^{-1} in the corresponding Raman spectrum (Fig. 5(d)) may also reflect the existence of nano-sized diamond grains.

Figure 6 shows the corresponding CL spectra of the films shown in Fig. 5. By the addition of oxygen, the band-A intensity was significantly lessened, but the nitrogen-related band dominated the CL spectrum; the I_A/I_N value of the oxygen-added film was much lower (0.17) than that (1.46) of the film grown without oxygen. From the variation of the CL spectra shown in Fig. 6, it should also be noted that the nitrogen-incorporation into diamond may proceed more effectively when the oxygen is added during the film growth process, while the crystal quality of the film grown may be degraded a little by the addition of oxygen.

Conclusion

CL characteristics, surface morphologies, Raman spectra, and crystal orientations of nitrogen-incorporated diamond films grown using a microwave plasma CVD method were examined as a function of various growth conditions. It was found that the surface morphology of grown films was altered by changing the $N_2/(CH_4+H_2)$ ratio from a truncated-octahedral shape of larger grains (mainly for the undoped film) to a pyramid-like shape of smaller grains (mostly for nitrogen-incorporated films). The nitrogen-related emission, rather than the band-A emission, became conspicuous when the film was grown at higher $N_2/(CH_4+H_2)$ ratios (0.5~2%). It was also clearly established that the I_A/I_N value was significantly reduced as the $N_2/(CH_4+H_2)$ ratio exceeded 0.2%. From the observation of $I_{(220)}/I_{(111)}$ and $I_{(100)}/I_{(111)}$ in XRD patterns, the preferred orientation of diamond films with relatively small I_A/I_N values was found to be characterized mainly by the (111)-orientation, rather than the (100)-orientation. The oxygen-added diamond films showed a surface morphology composed of spherical diamond grains, which indicated the co-existence of nano-sized and micro-crystalline diamond grains and a lower I_A/I_N value, compared with the film grown without oxygen. In addition, it may be suggested that the nitrogen-incorporation process into diamond can be further activated further by adding the oxygen during film growth.

Acknowledgement

This work was carried out using the facilities of Center for Electronic Materials and Components (EM&C) at Hanyang Univeristy (Ansan Campus).

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