Microstructural and electrical studies of nitrogen doped diamond thin films grown by microwave plasma CVD

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Abstract

We present a study of the microstructural and electrical properties of nitrogen doped diamond (NDD) thin films deposited on Si(111) by microwave plasma enhanced chemical vapor deposition (MWCVD). The conductivity of NDD thin film increases with increasing bias. In contrast, we also found the conductivity decreased with the increasing growth temperature and the increasing thickness of the diamond film after longer deposition. According to the microstructural analysis of NDD thin films by means of SEM, we found that the thicker the diamond thin film is, the bigger the grain size of the diamond grows, and the fewer interfaces the grain boundary of the NDD has, yield to a larger resistance. We propose that the nitrogen in the NDD was not doped into diamond crystallines but was located in the interlayer of the grain boundaries of the NDD.

Keywords: Microwave CVD; Nitrogen doped diamond; Conductivity; Microstructure

1. Introduction

The outstanding physical, chemical, electrical, and optical properties of diamond films hold great promise for a wide range of applications; for example, diamond has a negative electron affinity, which promotes the use of diamond as solid-state electron emitters in vacuum microelectronic devices for flat panel display applications [1]. The impurity atoms and defects in the diamond films control the emission current and the threshold electric field [2]. Several mechanisms have been suggested to explain the excellent field emission characteristics of diamond films, such as negative electron affinity, graphitic carbon formation, impurity incorporation and surface morphologies [3].

N-type conductivity in CVD diamond thin films remains one of the most challenging topics in the field of diamond research. CVD diamond thin films differ from single-crystal diamonds in that they are polycrystalline in nature with many grain boundaries and defects [4]. Nitrogen is expected to behave as a donor and has been observed, particularly at low concentrations, that nitrogen atoms occupy the diamond lattice sites producing substitutionally N-doped semiconducting diamond films [5]. However, for higher concentrations, N may incorporate in cluster form, which may also change the bonding and morphological structure of the films. Its atoms acts as donors in diamond, and their electronic energy level is at about 1.7 eV below the conduction band [6].

In particular, nitrogen incorporation either in small aggregates or diluted in substitutional sites of the diamond lattice has a direct effect on the growth phenomenon and on the electric resistivity of diamond. Nitrogen incorporation also results in significant stress due to the distortion of the diamond lattice [7]. The species of nitrogen atoms has an enormous influence on the structural and morphological properties of CVD diamond [8].

The synthesis of nano-crystalline diamond thin films in argon and methane plasma will provide new knowledge...
about the understanding of the CVD diamond thin films deposition mechanism [9]. Argon can be more easily ionized than hydrogen, with the same input microwave power and the same pressure. Han et al. proposed that the addition of argon to CH₄ feed gas could improve the crystalline and quality of the diamond deposits [10]. Using argon and hydrogen, a catalytic effect appears through the additional reactions in the present argon plasma or through the promotion of a super saturation of hydrogen atoms and ions, leading to an increase of plasma electron density.

2. Experimental details

Nano-diamond films were deposited with a home made microwave plasma CVD system operating at 2.45 GHz. Fig. 1 represents the MWCVD system, where microwaves entered the reaction chamber through a quartz entrance window and ignited the plasma above the Si substrate and the substrate was heated by a Mo resistant heater. The substrate temperature was measured with a thermal couple, which was fixed through a hole in the graphite holder contacting the substrate, as shown in Fig. 1.

N-type silicon (single-crystal (111)orientation, 0.2–0.01 Ω cm⁻¹) was used as the substrate in this work. A Si wafer was cut to a size of 16 × 16 mm² and its surface was scratched using silicon carbide powder for enhancement of nucleation. A clean process was performed after the sample was loaded into a reaction chamber: H₂ pressure was 30 Torr, microwave power was 600 W and the sample was heated up to 800 °C for 30 min. The deposition experiment consisted of two steps: (1) nucleation—a DC bias of −320 V was applied to enhance the nucleation; and (2) growth—the deposition parameters, including pressure, temperature,
microwave power, DC bias, time duration of growth and the ratio of gas mixtures, were varied.

The nucleation was continued for 20 min using the source gases of H₂ and CH₄ with flow rates of gas mixtures H₂/CH₄ = 170:10 sccm. The optimal working pressure was found to fix at 30 Torr and the microwave power to fix at 600 W. A DC bias of ~320 V was applied to assist the nucleation while the substrate was grounded during the nucleation process. The deposition process followed with the introduction the source gases Ar, H₂, CH₄ and N₂. The experimental parameters were optimized and we report here the results of variations of bias from 0 to 250 V, growth temperature from 700 to 900 C and growth time from 30 to 120 min for different film thicknesses.

The surface morphology of diamond thin films was analyzed using a scanning electron microscope (JEOL JSM-6330TF). The thin film growth rates were obtained by measuring the thickness of the deposited films from the cross-sectional micrograph of the samples. X-ray diffraction measurements were applied with a SIMENS D-5000 diffractometer. The structure of diamond, graphite and various carbides in the samples was characterized. The

![SEM micrographs of the samples grown under different DC biases](image1)

**Fig. 2.** SEM micrographs of the samples grown under different DC biases, a) 0 V, b) 100 V, c) 150 V, d) 200 V, and e) $I-V$ responses of the nitrogen-doped diamond thin films deposited with different biases.
3. Results and discussion

We have studied the influence of DC bias on growing nitrogen doped diamond film. Fig. 2a to d show the SEM micrographs of the samples grown under DC bias of 0, 100, 200, and 250 V. Fig. 2a shows the morphology of the sample covered with diamond film very well for no bias. Fig. 2b presents the NDD film grown under +100 V bias, where we can still observe the scratched line of the substrate, thus showing that the rate of deposition of NDD had become slower. Fig. 2c and d show that the shape and size of diamond grains became bigger again: the thickness was measured as being bigger than the depositions with either no DC bias or with +100 V DC bias. In Fig. 2d, the diamond crystallites were bigger and formed a more smoothly covered deposit than in the former cases. It was found that the growth rate became faster with higher DC biases.

Fig. 2e shows the $I-V$ measurements of nitrogen-doped diamond thin films deposited with different DC biases. It reveals that as the DC bias increased, the resistance of the diamond thin films decreased. Through this electrical measurement, we found that nitrogen could not be doped into diamond unless a positive bias was applied during the deposition, without bias the resistance of diamond thin film presented larger than $10^9 \ \Omega \ \text{cm}^{-1}$. The conductivity of NDD thin film increased with increasing bias. This result indicates that the higher the DC bias applied, the more negative nitrogen ions were attracted into the substrate to participate in the deposition of diamond thin films, which also induced the higher conductivity of the NDD thin films.

Fig. 3 shows the Raman spectra of the diamond films grown in dependence of bias. Raman peaks around 1332 cm$^{-1}$, representing C–C sp$^3$ diamond bonds, and 1580 cm$^{-1}$, representing sp$^2$ bonds of amorphous carbon, were observed. For the bias of 100 V, the broad band at 1580 cm$^{-1}$ was much weaker than that for no bias, indicating that the NDD thin films tend to have more sp$^3$ structure and to have better diamond quality. These Raman results are consistent with the SEM analysis, which indicated that the sp$^3$ species are depressed. Due to the experimental stability with a DC bias of +200 V, this bias was chosen for the following experiments.

The effect of temperature on growing NDD films was also studied. Samples N05, N06, N07 and N08 were grown at temperatures of 700, 750, 850 and 900 °C, respectively. SEM analysis revealed increased grain size of the NDD. Moreover, the thickness of the NDD thin films revealed an increased deposition rate with increasing temperature. The $I-V$ response of NDD thin films deposited at different temperatures is shown in Fig. 4. As the temperature increased, the resistance of the diamond thin films also increased. This result will be discussed later.

We have studied the film thickness of NDD depending on growth times from 60 min to 150 min. Fig. 5a and b show the SEM micrographs of the cross-sections of the samples deposited for different times of 90 and 150 min, respectively. The film thickness for the sample in Fig. 5b became thicker after longer deposition, and the grain size of the diamond crystallites in NDD increased from about 300 nm for 90 min to 700 nm for 150 min. Similar results have been reported for nitrogen doped nanocrystalline diamond and a mechanism due to grain boundary conduction was proposed in Ref. [11].

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**Fig. 3.** Raman spectra of nitrogen-doped diamond thin films dependent on bias.
Fig. 4. $I-V$ behaviors of the corresponding diamond thin films deposited at different temperatures.

Fig. 5. SEM micrographs of the cross-sections of the samples a) N18, b) N20, for the growth times of 90 and 150 min, respectively. c) $I-V$ measurements of nitrogen-doped diamond thin films for different deposition times of 60, 90, 120 and 150 min.
The $I-V$ measurements of NDD thin films deposited for different growth times are shown in Fig. 5c, where the resistance of the diamond thin films increased dramatically when the growth time was longer. This result indicates that the doping of nitrogen is decreased in NDD with longer growth times. This inverse behavior is not normal and therefore needs to be explained. If we consider the results of Figs. 2 and 5 together, where the higher the growth temperature or the longer the growth time, the lower the conductivity of the NDD thin film crystals. We propose that the conductive current must flow through another path—the grain boundaries and the interfaces among the NDD crystallites. Since the crystallites grew and the grain boundaries became fewer and smaller, this would lead to a decrease of electrical conductivity. Accordingly, nitrogen would actually be doped into grain boundaries or at the interfaces of diamond crystallites with the sp$^2$ structure.

From the results above, it can be seen that with increased nitrogen the Raman intensity of the sp$^2$ component increases. The increased non-diamond carbon phase is a result of the deterioration of the crystal growth, which is also the most probable reason for multiple nucleation and overgrowth of the diamond to be induced, and which would finally lead to the deposition of amorphous.

4. Conclusions

We present a characterization of the microstructural and the electrical properties of diamond thin films deposited with nitrogen doping on Si by MPCVD. The dependence of the characteristics of nitrogen-doped diamond thin films on the applied DC bias, growth time, and growth temperature were studied.

The $I-V$ characteristics show that nitrogen could not be doped into diamond unless a positive bias was applied during the deposition. DC bias is an important factor for controlling the doping of diamond. The conductivity of nitrogen doped diamond thin films decreased with growth time. Analyzing the electrical properties and microstructure by means of SEM revealed that throughout the growth time, diamond crystallites grow and grain boundaries become fewer. From the correlations we confirm the proposal of Ref. [11] that nitrogen was actually not doped into the diamond crystallites but located in the grain boundaries and interfaces among diamond crystallites with the sp$^2$ structure.

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References