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Chun-Hsi Su and Ching-Yu Chang

Institute of Manufacturing Technology, National Taipei University of Technology, Taipei 106, Taiwan, R.O.C.

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This study investigated chemical species in the plasma while synthesizing nitrogen-doped nanocrystalline diamond (NCD) films using microwave plasma jet chemical vapor deposition (MPJCVD) system. The investigation is done by using *in-situ* plasma optical emission spectroscopy (OES). The electrical resistivity of the nitrogen-doped NCD films increases by 6 orders of magnitude (up to $6.7 \times 10^{-4}\,\Omega\,\mathrm{cm}$) with increasing nitrogen content. This approach also helps us in further understanding of the plasma species during depositing NCD films and also the electronic structure of grown conductive diamond phase through analysis of as-doped nitrogen contents.

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1. Introduction

In synthesizing nanocrystalline diamond films in a chemical vapor deposition (CVD) system, n- or p-type transistor can be formed by the addition of nitrogen or boron atoms, respectively. However, the process control is relatively difficult in appropriate addition to achieve the excellent n-type transistor property. As for the effect of nitrogen addition on the growth rate of nanocrystalline diamond (NCD) films,[1] by adding a small amount of nitrogen during CVD process, the excitation state of species containing nitrogen, like NH_x or CNH_x, can increase the growth rate of diamond on a diamond surface, but nitrogen atoms enter the diamond structure inefficiently at the same time.

In additions, regarding the effect on the bonding structure of synthesized diamond films, when the gas phase nitrogen to carbon ratio (N/C) is larger than 10%, the growth rate of diamond films will be larger than a factor of 2 from those produced at $N/C = 0.1\%$. The Raman spectra of N-doped diamond films will also become sharper as a result of the addition of nitrogen.[2] Hence literatures proposed the theory of defect-induced stabilization of diamond.[3] Such theory points out that the vacancy caused by the addition of nitrogen will increase the diffusion rate of carbon species into the diamond surface, thus promoting the growth rate of diamond. Therefore, the addition of impurities (n- or p-type) can relatively promote the diffusion of carbon atoms onto the diamond films and achieve the purpose of stabilizing the diamond phase.

As a matter of fact, only a limited number of nitrogen atoms exist within diamond structure by substitution. In the work on nitrogen dopant in NCD films by Birrell,[4] it is discovered that the addition of an appropriate amount of nitrogen can increase the sp^2 bonding structure in NCD films, prevent clustering on diamond surface, promote the smoothness of diamond surface, and effectively raise the conductivity of electrons, thereby making the films possessing characteristics of n-type transistor property.

In order to obtain convincing analytical result, the optical emission spectroscopy (OES) is employed in this study to diagnose and characterize chemical species during the process of synthesizing NCD. The scanning electron microscopy (SEM), Ar laser (514.5 nm) Raman spectroscopy, Four-point probe, and X-ray photoelectron spectroscopy (XPS) are utilized to identify the NCD film's surface morphology, bonding structure, and resistivity with different N_2 concentrations.

2. Experimental Methods

The microwave plasma jet chemical vapor deposition (MPJCVD) system is used to grow NCD film on Si substrate (n-type). A microwave generator of up to 2 kW is powered on to generate microwave, which will propagate along an antenna with a conical slow-wave structure that serves to transmit microwave to the antenna tip. When the reactive gas ($CH_4 + H_2 + N_2$) is introduced, plasma will be sprayed and NCD films can be synthesized.

The technique of synthesizing diamond film is as follows: when the gases are introduced to the antenna tip and are disassociated by the microwave energy, they will be reacted to synthesize NCD film. Since the complex reaction process is to be studied, OES is employed to identify the content of the plasma gas in the period of diamond synthesis. The optical emission spectrum from the plasma will be filtered and transmitted to B&W Tek BTC112E charge-coupled device (CCD) spectrometer, where the wavelength from 300 to 800 nm with a resolution of 0.5 nm will be sorted out. Besides, the computer software BWSpect will be started to control the on-site OES system as shown in Fig. 1.

3. Results and Discussion

3.1 Chemical species analysis

N_2 gas is used to synthesize nitrogen doped NCD films, and a discussion will be presented on the effect of N_2, CN species on growing NCD films. In accordance with the above experimental conditions, the synthesis of nitrogen doped NCD films was carried out under the optimized process parameters, with changing $N_2/(CH_4 + H_2)$ concentrations from 0 to 12.5%. Also, OES is employed to diagnose plasma optical emission spectra. The emission spectra are derived under different concentrations of N_2, with the major optical emission spectrum signals between 300 and 800 nm, as shown in Fig. 2.

As can be known from the optical emission spectra, in the process of synthesizing nitrogen doped NCD films, $CH_4 + H_2 + N_2$ plasma will produce species like: H_α, H_β, C_2, N_2^+ (418.3 nm), CN (388.3 nm), and N_2 (356.0 nm) by ways of dissociation and activation. This study will mainly calculate

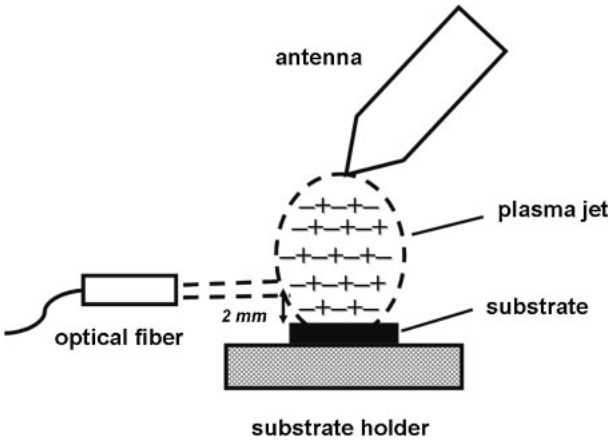

Fig. 1. Schematic representation of the installation of OES experiment.

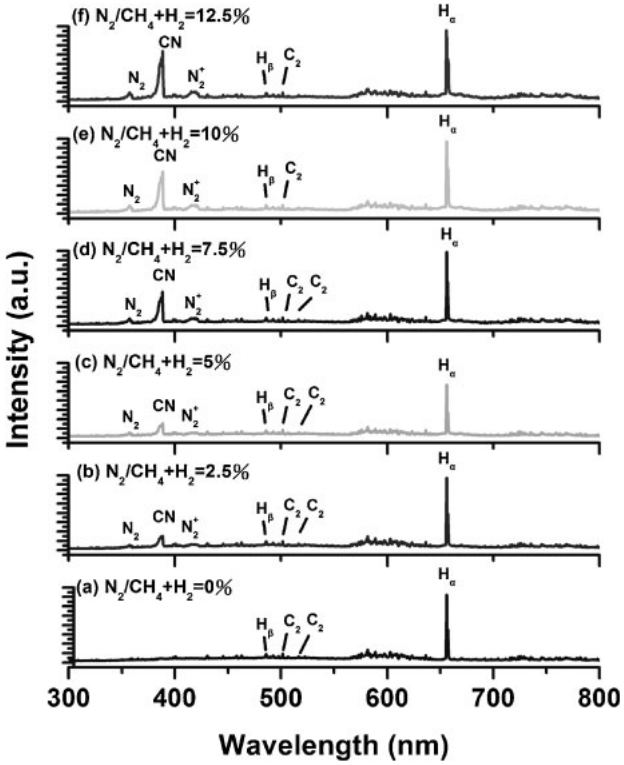

Fig. 2. The optical emission spectra for various nitrogen doped NCD films.

the relation among C_2, CN, N_2, and H_α emission intensities and changes in N_2 concentration. Among them, the ratios of C_2, CN, and N_2 emission intensities to H_α emission intensity will be used to measure the species concentrations excited by N_2, CN, and C_2. Therefore, the optical emission spectrum analysis was herein conducted with H_α as the standard count. The species C_2, CN, N_2, and H_α with stronger signals and relevance to NCD film synthesis were chosen for discussion and normalization. The results are shown in Fig. 3. As can be seen from the diagram of relative concentration ratios of various species, the C_2/H_α emission intensity ratio assumes a stable state when N_2 concentration changes. Therefore, it shows that concentrations of added nitrogen do not have a great effect on the concentration of C_2 species.

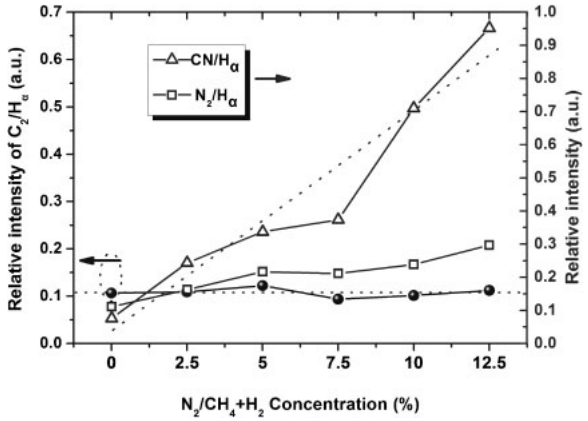

Fig. 3. The relationship between N_2 concentrations and plasma species.

In additions, as the N_2 concentration increases, the emission intensity ratios of N_2/H_α and CN/H_α take a linear upward trend, with the N_2/H_α ratio increased about 2.7 times from 0.111 to 0.296 and CN/H_α ratio increased about 12 times from 0.076 to 0.952. Thus, the CN/H_α ratio can be used as the major criterion to judge the changes of N_2 concentration. From the theory of plasma dissociation, it is known that threshold energy (E_{th}) should be offered for the ionization of species, and when the energy is sufficient, the probability of collision (collision cross section, σ) should also be considered. The value of σ_{max} will become higher and the ionization of species will become easier if the probabilities for collision are in a great number, therefore the plasma density will be raised and the electron concentration can be increased. As mentioned in Grill's research,[5] the E_{th} for nitrogen and hydrogen are 15.6 and 15.4 eV, respectively, while their σ_{max} are 1.23×10^{-16} and 1.6×10^{-17} cm^2, respectively. Therefore, the ionization of nitrogen will be easier. Hence when the content of nitrogen is higher, the electron concentration in plasma will be higher, when compared to hydrogen plasma. For the above reasons, it can be said that the N_2 and CN species in Fig. 3 will take a linear upward trend with increasing nitrogen content. The above results should be of great help to the technology of *in-situ* plasma diagnosis in the process of synthesizing NCD films in an MPJCVD system.

As can be known from the effect of concentrations of various species on the growth of nitrogen doped NCD films, the concentrations of N_2 and CN species are very important parameters for growing nitrogen doped NCD films. Generally, in the plasma environment with a high N_2 concentration, the increase in the nitrogen proportion will promote the ionization of reacting gas and the dissociation rate of other species, which increases the content of CN species and excitation state for species containing nitrogen as CN_x or CNH_x. The high concentration of CN species will affect the process of growing NCD films and synthesizing nitrogen doped NCD films.

3.2 Characterization of nitrogen-doped NCD films

Figure 4 shows the SEM surface morphology of NCD films synthesized in various N_2 concentrations. As is discovered, with increasing N_2 concentrations, more clusters occur to

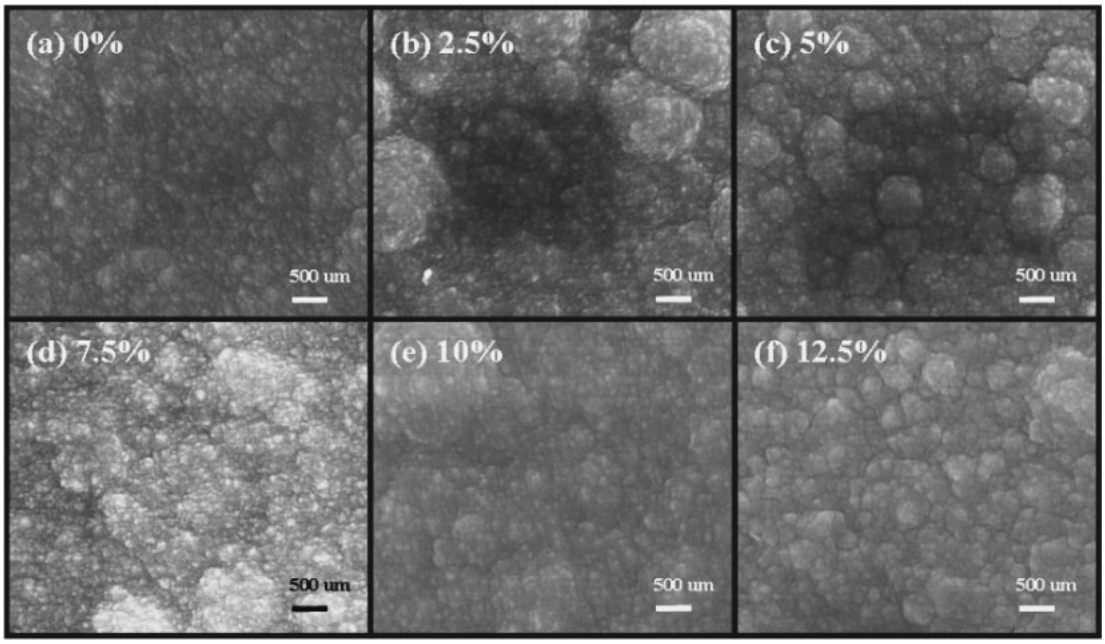

Fig. 4. SEM images for various nitrogen doped NCD films.

nitrogen doped NCD films, but the cluster size tends to be smaller. When the concentration reaches 12.5%, the cluster size reaches the minimum. The average cluster size is nearly 400 nm, which is still larger than the cluster size registered in non-doping NCD films (<100 nm), as shown in Fig. 4(f). Besides from Figs. 4(a)–4(f), it can be observed that with the increase in N_2 concentration, the grain size of NCD films will become larger and further deviate from 20 nm, at the same time when non-doping nitrogen reaches about 100 nm, but still belong to NCD films. In addition to the changes of grain and cluster sizes, it can also be discovered that the grains of nitrogen doped NCD films are non-uniform circles; rather, some grains are oval shaped. Thus it can be inferred that nitrogen will make the growth of NCD grains assume a particular direction.

Thus by integrating the analytical OES results, we can infer that the addition of nitrogen will promote the ionization of reacting gas and the dissociation rate of other species, and that the large amount of CN and N_2^+ species will result from the increased dissociation rate of CH_4 gas. Next, according to the research conducted by Cao *et al.*,[1] the excited species containing nitrogen, like CN_x or CNH_x, can increase the diffusion of carbon species on the surface of diamond films and form a particular growth direction.

Figure 5 shows the Raman spectra for NCD films grown with different N_2 concentrations. It can be seen that the bonding structure of film changes dramatically with the increase of nitrogen flow. In conditions with non-doping, Raman spectra possess the spectrum signals for typical NCD film's bonding structure. With the exception of D_f-peak diamond characteristic peaks (sp^3 bonding), whose intensity is on the wane, there should also exist the D- and G-peak signals belonging to sp^2 bonding and ν_1- and ν_3-peak belonging to trans-polyacetylene,[6] namely five obvious Raman characteristics peaks. However, with increasing N_2 concentration, three phenomena can be observed. The first is the noticeable weakening of ν_1- and ν_3-peak belonging to

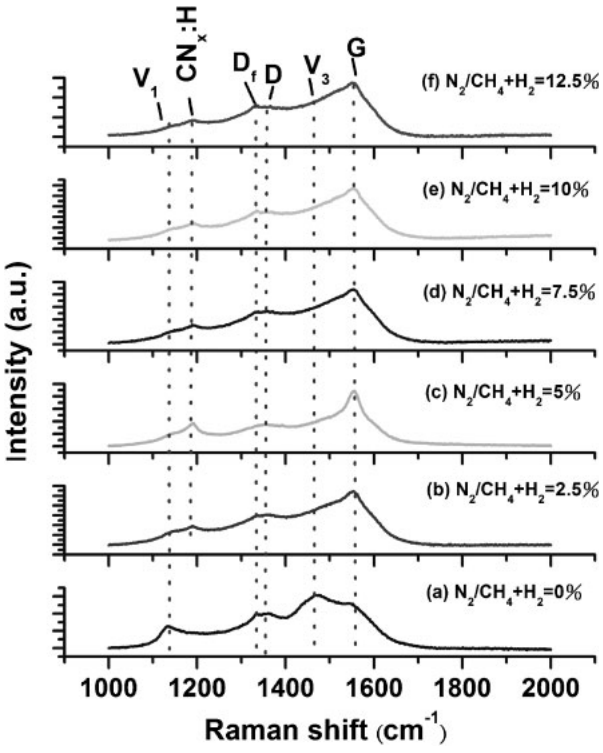

Fig. 5. Raman spectra for various nitrogen doped NCD films.

trans-polyacetylene. The second is the strengthening and sharpening of D_f-, D-, and G-peak, which conforms to the theory advanced in literatures that deficiency leads to the stability of diamond. And the third is the evident Raman spectrum occurring approximately at 1200 cm^{-1}, which can be further determined by OES analysis as CN_x:H bonding formed by tracing N atoms excited in a N_2 plasma environment. It is generally believed that the Raman spectra for sp^2 bonding and *trans*-polyacetylene stem from the grain boundary of NCD films, thus from the changes in Raman

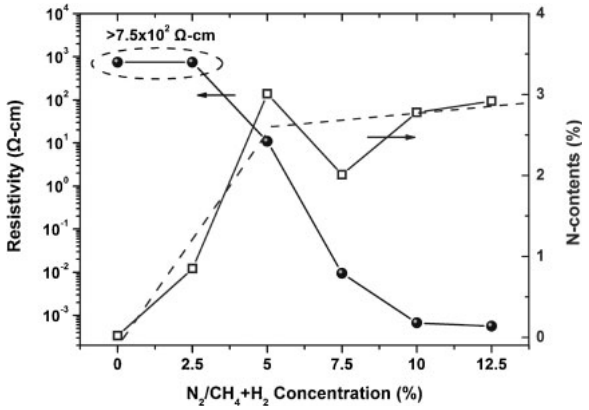

Fig. 6. The resistivity of N content as a function of various nitrogen doped NCD films.

spectra caused by the increased nitrogen flow. It can be inferred that nitrogen indeed affects the crystallization structure of the grain boundary of NCD films. This result is consistent with the inferences advanced in literatures.

3.3 Electric property of nitrogen-doped NCD films

In order to better understand the effect of nitrogen dopant on the electrical property of NCD films, a four-point probe is used to measure the resistivity of NCD films after doping nitrogen to determine the effect of nitrogen dopant on NCD films. Figure 6 shows the resistivity of NCD films synthesized in various N_2 concentrations and the N atom content relations measured by XPS. It is found that the resistivity of NCD films without doped nitrogen is nearly $>7.5 \times 10^2$ Ω cm (four-point probe measures the resistance range from 2 mΩ to 5 MΩ), while with the increased N_2 concentrations, the resistivity takes a downward trend. Especially when N_2 concentration stands at 5%, the resistivity falls quickly from $>7.5 \times 10^2$ to $1.09 \times 10\,\Omega$ cm. And when N_2 concentration is larger than 7.5%, the film resistivity will be stabilized at $6.70 \times 10^{-4}\,\Omega$ cm. As indicated in the measurement of NCD films resistivity, when N_2 concentration is lower than 5%, there will be little chance to form effective nitrogen doped NCD films, but when N_2 concentration is larger than 7.5%, N atoms will efficiently enter the grain boundary of NCD films and form nitrogen-doped NCD films. This result is consistent with the measured N atom content. By a comprehensive analysis combining the measurement of resistivity with Raman spectrum results, it can be deduced that the addition of N atoms into the grain boundary of NCD films has altered the grain boundary structure and formed the channels for the conduction of electrical current. Therefore, the addition of nitrogen will effectively promote the conductivity of NCD films. As can be discovered from the Raman spectra for N_2 concentrations larger than 7.5%, ν_1- and ν_3-peak belonging to *trans*-polyacetylene have weakened noticeably, while D_f-, D-, and G-peak become more distinct and sharper. It can be speculated that this more distinct and sharper characteristic peak probably has something to do with the increased grain size. Thus it is inferred that the nitrogen atoms are not really doped and enter the grains of NCD films, but only affect the structure of grain boundary. Therefore, such nitrogen doped NCD films has no n-type semiconductor property. However, this is indeed an effective way to promote the conductivity of NCD films.

4. Conclusions

The research achieves the synthesized nitrogen doped NCD films, and obtains the relations between the changes in N_2 concentrations and the concentration of each excited species. Through the integrated analysis of SEM, Raman spectra, resistivity, and N atom content in the films, it can be inferred that the doping of N atoms into the grain boundary of NCD film will change the structure of grain boundary and form the channel for the conduction of current. Therefore, the dopant of nitrogen will effectively promote the conductivity of NCD films to $6.70 \times 10^{-4}\,\Omega$ cm.

Acknowledgement

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