Effect of nitrogen on diamond growth using unconventional gas mixtures

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Abstract

The influence of nitrogen on the growth of diamond using unconventional gas mixtures of CH_4–CO_2 by microwave plasma chemical vapor deposition was investigated. A clear improvement in the surface morphology and quality of the diamond films indicates the beneficial effect of adding nitrogen to CH_4–CO_2 gas mixtures. However, most interestingly, for lower methane concentration, the addition of small amounts of nitrogen resulted in the formation of isolated diamond particles possessing a vacant "cage-like" structure with completed {100} facets. This result indicates that the continued addition of nitrogen gives rise to the deterioration of {111} facets and the retention of {100} facets. Analysis using Auger electron spectroscopy and secondary ion mass spectroscopy shows very low and uniform levels of nitrogen in the diamond films. Although the amount of atomic hydrogen in the ground state decreased and CN radicals increased with increasing amounts of added nitrogen, good-quality diamond films were deposited resulting from a larger amount of atomic oxygen and the decrease in the C_2 emissions in the gas phase under optimum conditions.

Keywords: Nitrogen; Diamond; Growth mechanism; Chemical vapour deposition

1. Introduction

The growth of diamond by low-pressure chemical vapor deposition (CVD) has attracted increasing interest in recent years, because of the outstanding mechanical, thermal, optical, electrical, and chemical properties of diamond [1,2]. The chemical vapor deposition of diamond has the potential to expand the applications of diamond, e.g. doping impurities for semiconducting devices. Nitrogen is the most important commonly occurring impurity in both natural and synthetic high-pressure, high-temperature (HPHT) diamond. It affects the growth of CVD diamond films and the physical properties of diamond [3]. Recently, the effect of nitrogen on the growth of CVD diamond films using CH_4–H_2 gas mixtures has been studied by several authors [3–6]. These effects include deterioration of the diamond film quality, namely the graphitic codeposits and non-diamond phase increased in the resultant films, at larger nitrogen concentrations in the reactant gases, and the formation of (100)-oriented diamond films when small amounts of nitrogen are added to the reactant gases.

In our previous report [7], we found that by substituting carbon dioxide for hydrogen in a CH_4–CO_2 gas mixture, diamond films could not only be synthesized but were also of good quality. Moreover, adding hydrogen to the CH_4–CO_2

gas mixtures had a negative effect on diamond growth, whereas adding oxygen had a beneficial effect [8]. In other words, the addition of hydrogen decreased the quality of diamond films created in a CH_4–CO_2 gas mixture, however, the quality of diamond films were improved due to the addition of oxygen.

In this article, we examine the effects of adding nitrogen to CH_4–CO_2 gas mixtures, not previously reported by other authors, on the growth of diamond films. The reactant gases of CH_4–CO_2–N_2 (i.e. a C/H/O/N gas system) used in the present experiment were different from those of CH_4–H_2–N_2 and CH_4–N_2 (i.e. a C/H/N gas system) used by others. Film characterization and plasma emission spectroscopy are used to investigate the relationship between film features and plasma species.

2. Experimental details

The experimental apparatus used was the same as that used in our earlier report [7]: a 1.3 kW (2.45 GHz) microwave generator with a vertical water-cooled cavity 62 mm in diameter set in the end of the waveguide. A quartz reactant tube 55 mm in diameter was placed inside the cavity. There was a quartz substrate holder (diameter 20 mm) inside the reactant tube, on which p-type Si (100) substrate was placed. The microwave power was set at 400 W and the reactant gas

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pressure was set at 3.3 kPa (25 Torr). The reaction duration was 2 h, and the flow rate of CO_2 was fixed at 30 sccm. The flow rate of the CH_4 was varied from 23 to 24 sccm and that of the nitrogen was varied from 0 to 20 sccm. An optical pyrometer was used to monitor the substrate temperature, which was maintained at about 820 °C. The p-type Si (100) substrate was scratched using diamond powder (approximately 4–6 μm) in order to enhance the nucleation density of the deposits. Scanning electron microscopy (SEM) was used to observe the morphology of the films. The quality of the films was then determined using Raman spectroscopy with a He–Ne laser (632.8 nm). The nitrogen concentrations in the films were investigated by Auger electron spectroscopy (AES) and secondary ion mass spectroscopy (SIMS).

Optical emission spectroscopy (OES) was used to examine the species in the plasma during the diamond deposition process. Species were identified in this study according to the methods used in Ref. [9]. Plasma emission actinometry (Ar, 4 sccm) [8,10,11] was used as an actinomer. The relative concentrations of atomic hydrogen in the ground state were noted using the ratio of H_α (656.3 nm) to the Ar line (750.4 nm). The system used for the OES experiments was a SOFIE instrument SD 20 system. The monochromator consisted of a Jobin–Yvon H 20 spectrometer equipped with a 1200 groove mm^{-1} grating (focal length, 20 cm; slit width, 0.125 mm) and a dispersion of 4 nm mm^{-1}. The resolution was 0.5

nm and the available spectral range was 200–800 nm. The spectrometer was connected by a silica optical fiber to a viewport of the deposition chamber equipped with a focusing lens (focal length, 100 mm). Optical emissions from the plasma center and near the deposition surface (1 mm above the substrates) were focused into an optical fiber and transferred to the monochromator.

3. Results and discussion

3.1. Effects of adding N_2 on diamond growth

Fig. 1 shows the influence of adding nitrogen on the surface morphology of diamond films deposited at CH_4 concentration of 80% (i.e. $CH_4/CO_2 = 24$ sccm/30 sccm) in a CH_4–CO_2 gas mixture. We found that the morphology of diamond films changed from cauliflower structures to well-defined facets. However, a discontinuous diamond film with well-faceted crystallites formed when more nitrogen was added. No carbon of any kind was deposited when the flow rate of added nitrogen reached 20 sccm. This implies that the effect of etching non-diamond and diamond components increased, and simply there was a dilution effect on reactant species in the plasma because of the larger addition of nitrogen. A clear improvement in the surface morphology of the diamond
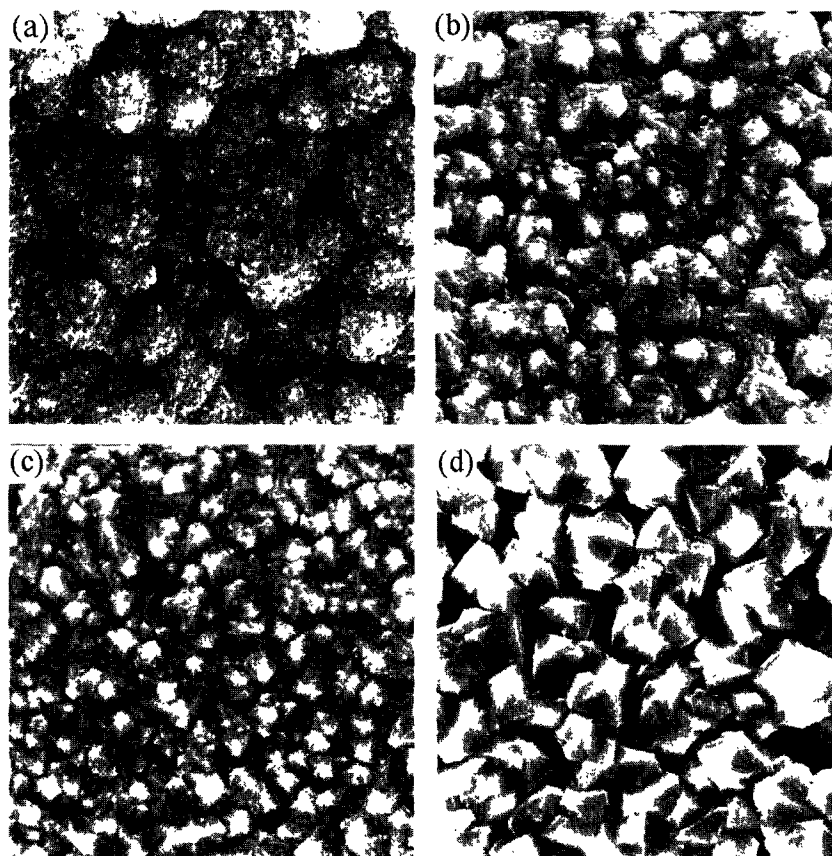

Fig. 1. Effects of adding nitrogen on the morphology of diamond films deposited in a CH_4–CO_2 gas mixture, $CH_4/CO_2 = 24$ sccm/30 sccm = 80% (fixed): flow rates of N_2 (sccm) are (a) 0, (b) 4, (c) 7, and (d) 13.
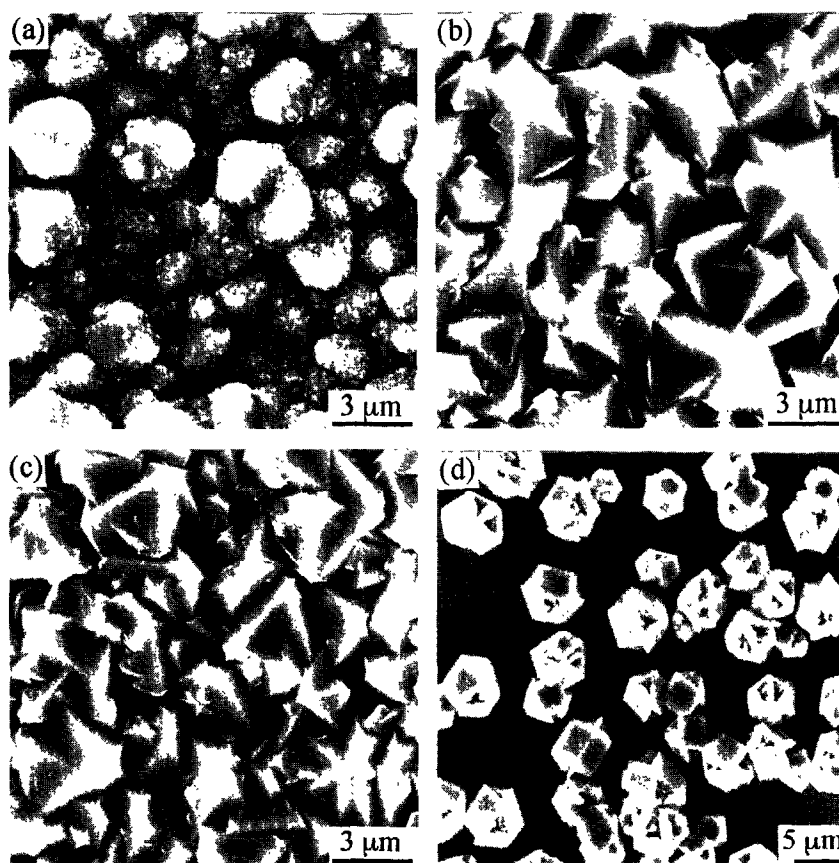
Fig. 2. Effects of adding nitrogen on the morphology of diamond films deposited in a CH_4–CO_2 gas mixture, $CH_4/CO_2 = 23$ sccm/30 sccm = 76.7% (fixed): flow rates of N_2 (sccm) are (a) 0, (b) 1.4, (c) 2.8, and (d) 4.

films, shown in Fig. 2(a)–2(c), also indicated the beneficial effects of adding nitrogen to the CH_4–CO_2 gas mixtures. Nevertheless, most interestingly, for lower methane concentrations (i.e. $CH_4/CO_2 = 23$ sccm/30 sccm = 76.7%) the

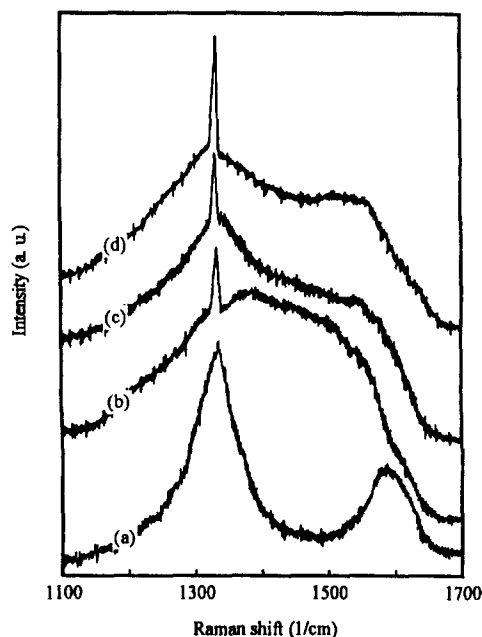Fig. 3. Effects of adding nitrogen on the Raman spectra of diamond films deposited in a CH_4–CO_2 gas mixture, $CH_4/CO_2 = 24$ sccm/30 sccm = 80% (fixed): flow rates of N_2 (sccm) are (a) 0, (b) 4, (c) 7, and (d) 13.

addition of nitrogen at a flow rate of 4 sccm resulted in the formation of isolated diamond particles possessing a vacant "cage-like" structure with completed {100} facets, as shown in Fig. 2(d). This result indicates that the continued addition of nitrogen gives rise to the deterioration of {111} facets and the retention of {100} facets. It has been demonstrated that the incorporation of nitrogen is determined by growth sector in single-crystal polyhedrons of CVD diamond [12], resulting in significantly larger nitrogen concentrations in {111} growth sectors as compared with {100} sectors. The considerable distortion along the (111) direction of the C–N bond [3], due to the incorporation of nitrogen, may also be responsible for the observed growth habit of diamond crystallites. Moreover, the formation of the observed crystal structures may be related to particular gas-phase reactions instigated by nitrogen in the plasma. However, it remains unclear how the addition of nitrogen to the gas mixtures with various CH_4/CO_2 ratios influences the crystal growth. The crystal morphology and surface morphology during growth are highly sensitive to growth conditions and reflect the growth mechanism. Therefore, more detailed studies are needed to clarify the mechanisms affected by the addition of nitrogen in the CH_4–CO_2 gas mixtures.

The effects of nitrogen addition on the Raman spectra of diamond films deposited in CH_4–CO_2 gas mixtures for CH_4 concentration of 80% are shown in Fig. 3. The Raman spectra present three main features: (i) a sharp peak at 1332 cm^{-1},
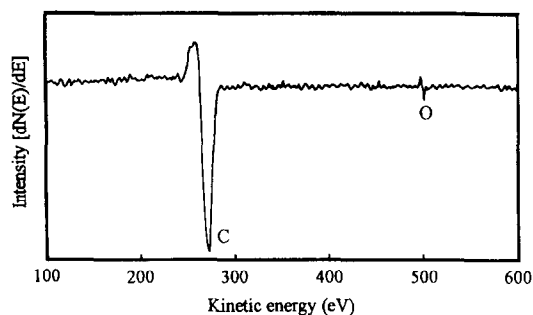
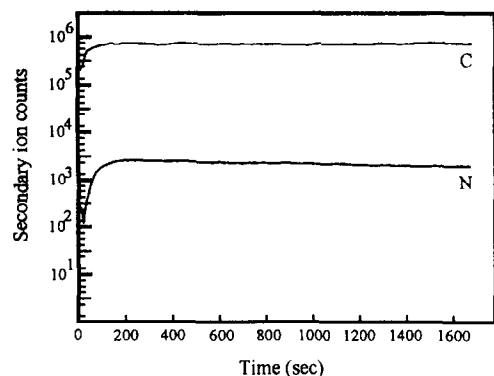Fig. 4. Auger spectrum of the film shown in Fig. 1(d).

Fig. 5. SIMS depth profile of nitrogen in the film shown in Fig. 1(d).

which is the characteristic line of crystalline diamond; (ii) a broad peak centered at about 1550 cm^{-1}, which is characteristic of diamond-like carbon; and (iii) peak at approximately 1580 cm^{-1} which is characteristic of polycrystalline graphite or amorphous carbon with graphitic bonding [13]. In Fig. 3 the Raman spectra exhibit an increase in the sp^3/sp^2 ratio, a decrease in the FWHM (full width at half maximum) value of diamond peaks at about 1332 cm^{-1}, and a lower luminescence background. This means that the quality of the diamond film increased as the amount of added nitrogen increased.

No nitrogen was detected in the Auger spectrum of Fig. 4 except for a small oxygen contamination, although the sensitivity for nitrogen detection by AES is about 0.5%. This means that the investigated diamond film was found to be below the detection limit of AES, 0.5% (8.5×10^{20} cm^{-3}), which suggest very low nitrogen-doping efficiency. SIMS analysis, which is much more sensitive than AES, was conducted to identify the nitrogen content in the films. The SIMS depth profile (Fig. 5) of the film indicated that the nitrogen concentration was uniform in the diamond film bulk. Unfortunately, accurate quantification of SIMS data is not possible without standards. Since such standards were not available for our experiment, accurate amounts of the nitrogen concentration in the films are not yet known. We found the amount of nitrogen incorporated into the diamond films to be very low, consistent with a model of film growth involving simultaneous deposition and etching processes [3].

3.2. Relationship between film features and plasma species

The results of the film characterization discussed in Section 1 showed that the diamond films were of good quality but

contained a small amount of amorphous hydrogenated carbon, which is attributable to the increased amounts of added nitrogen.

Species identified in this study include CO (the third positive and 5B bands system and the ångstrom system), OH (3064 Å system, 308.9 nm), N$_2$ (the first positive system and the second positive system), NH (3360 Å system, 336 nm), NO (β system, 421.5 and 420 nm, degraded to longer wavelengths and double-headed), CN (the violet system), CH (431.4 nm), C$_2$ (Swan band, 516.5 and 563.5 nm), O2$^+$ (the first negative system), atomic oxygen (777.2 nm), and atomic hydrogen (Balmer series: H$_\alpha$, 656.3 nm; H$_\beta$, 486.1 nm) [9].

The effect of adding nitrogen on the relative intensity of the H$_\alpha$ (656.3 nm) to Ar (750.4 nm) is shown in Fig. 6. This intensity ratio is proportional to the concentration of atomic hydrogen in the ground state. We found that the amount of atomic hydrogen in the ground state decreased relative to the increase of nitrogen. This may result from the fact that atomic hydrogen was depleted by the addition of nitrogen, since the nitrogen formed N–H bonds in the gas phase (see Fig. 7). It is generally believed that atomic hydrogen plays a significant role both in the gas phase and on the growing diamond surface. Moreover, an excess atomic hydrogen atmosphere is suitable for the growth of highly purified diamond films with good quality. Diamond film of good quality was formed under optimum conditions without an excess atomic hydrogen atmosphere, so we may assume that other species, such as atomic nitrogen [5] and oxygen-containing species (OH, O, and O$_2$), could influence the chemical reactions occurring in the gas phase and on the surface.
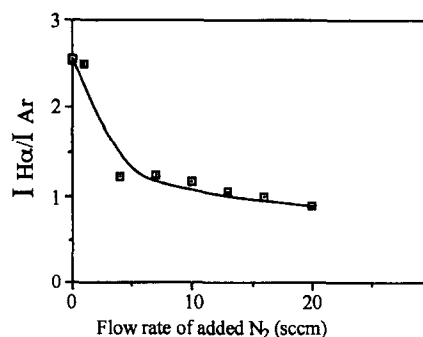

Fig. 6. The relative concentration of atomic hydrogen as a function of nitrogen flow rate.
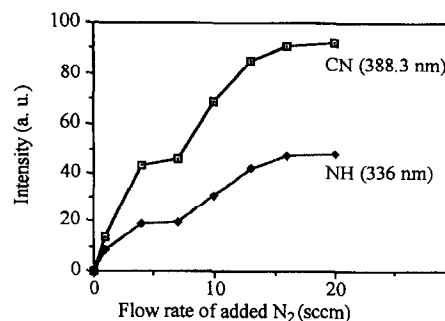

Fig. 7. Emission intensities of the observed lines as a function of added N$_2$.

Fig. 7 shows the emission intensities of the observed lines as a function of the added nitrogen. We here discuss the larger change in the emission intensity of species in the plasma qualitatively. NH and CN radicals tended to be increased by adding nitrogen to the reactant gases. This is attributable to the reactions of nitrogen with methane and carbon atoms in the gas phase, which probably formed HCN (not detected in our emission spectra), C_2N_2 and CN radicals. Alternatively, atomic nitrogen may remove carbon atoms from the growing surface and thus produce CN radicals. Badzian et al. [5] proposed that abstraction of hydrogen from the surface could occur via formation of NH_3 and HCN, resulting from the presence of atomic nitrogen and CN radicals, which allowed diamond to grow from the CH_4–N_2 gas mixtures. However, the crystal structure of the grown diamond was distorted, namely, the sequence of the tetrahedral layers was mixed (cubic and hexagonal) and the stacking suffered from turbostatic disorder. It is necessary to clarify the reaction behaviors of HCN and CN radicals occurring in our case. Once CN was formed in the gas phase, this molecule was extraordinarily stable, having one of the highest bond dissociation energies $(D_o = 180$ kcal $mol^{-1})$. The dimerization energy, however, was very large $(2CN(g) = C_2N_2(g)$ $\Delta H = -134$ kcal $mol^{-1})$ and would finally favor the formation of the C_2N_2 species [14]. HCN and C_2N_2, which were triple-bonded compounds, were not known to be diamond precursors. Because the covalent carbon-nitrogen triple bond was extremely stable, the remaining nitrogen was expected in the film and resulted in a higher fraction of non-diamond phase, which was also demonstrated in other reports [15,16].

It is important to note that the reactant gases of CH_4–CO_2–N_2 (i.e. a C/H/O/N gas system) used in the present experiment were different from those of CH_4–H_2–N_2 and CH_4–N_2 (i.e. a C/H/N gas system) used by others. Carbon dioxide in the reactant gases was considered to be decomposed into CO and atomic oxygen. This would affect the gas phase reactions and surface processes. Fig. 8 shows that the amount of atomic oxygen increased with increasing nitrogen. The possible reasons are discussed as follows. The reaction leading to the formation of NO was generally endothermic ($1/2N_2 + 1/2O_2 \rightarrow NO \, \Delta H_{298} = 21.6$ kcal mol^{-1}), and therefore is favored at high temperature. As NO was formed in the gas phase, a reaction with active nitrogen species resulted in a
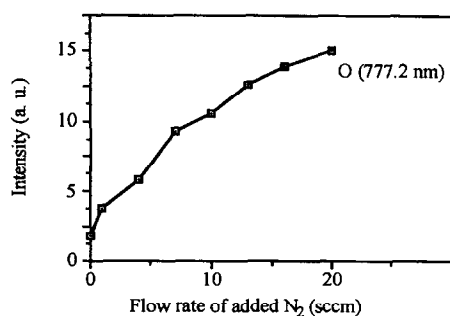
significant density of nitrogen atoms being present in the gas phase to engage in the titration reaction (a high-rate reaction) $N + NO \rightarrow N_2 + O$ [17]. This may give rise to the increase in the amount of oxygen atoms in the plasma. Therefore, we suggest that atomic nitrogen plays a dominant role in the C/H/O/N plasmas chemical vapor deposition processes because the amount of oxygen atoms increased via the titration reaction of nitrogen atoms. This would have a significant influence on diamond synthesis in a CH_4–CO_2–N_2 gas mixture.

Oxygen had several effects other than the increase of atomic hydrogen concentration (not found in our experiment), such as acetylene reduction in the gas phase, etching of polyacetylene and graphitic carbon deposits on the growing surface [18]. According to the combustion process described in Ref. [19], oxygen had the effect of converting cyanogen (C_2N_2) into CO and N_2. Therefore, oxygen may reduce the concentration of gaseous C_2N_2, which was suggested to be responsible for the deposition of paracyanogen component [14]. A variety of etchants (OH, atomic oxygen and O_2) seem to remove hydrogen cyanide (HCN) and cyanogen on the growing surface, except for the effect of etching amorphous and graphitic carbon. This contributes to reproducing diamond-growing sites and then promoting the deposition of diamond growth precursor.

The emission intensities of the observed lines are shown in Fig. 9 as a function of the added nitrogen. We found that the CH emission and C_2 radicals tended to be suppressed by the addition of nitrogen. On the basis of our results, we infer that more intensely excited C_2 emissions result in amorphous carbon and/or graphite that is deposited in a C/H/O/N system. This conclusion was evidenced by the Raman spectra (Fig. 3). The net growth rates are a result of the competition between the deposition and etching reactions. In the present experiment, there was simply a dilution effect on reactant species in the plasma and the effect of etching amorphous and graphitic carbon because of the addition of nitrogen. However, the more important influence is that the plasma species interact with each other and with the matrix gas through various chemical reactions and are directly involved in the deposition process. The lower growth rates (total, i.e. diamond + non-diamond components), resulting from the addition of nitrogen, were probably due to etching of carbon from the surface and depletion of the growth precursors of
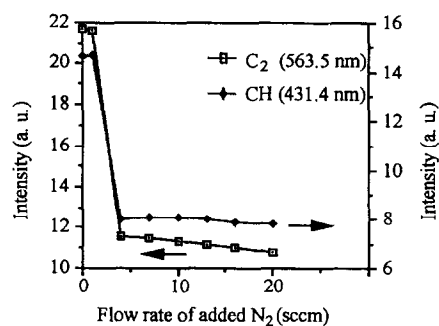

Fig. 8. Variation of the emission intensity of the atomic oxygen with the flow rate of added nitrogen.

Fig. 9. Emission intensities of the observed lines as a function of added N_2.

diamond and non-diamond components such as CH and C_2, respectively, in the gas phase. Furthermore, no deposition was observed in the CH_4–CO_2–N_2 system when a larger amount of nitrogen was added. This may be due to the high concentrations of etchants in the plasma removing diamond, amorphous deposits, and paracyanogen components faster than their growth rates.

We are currently preparing to analyze the stable species in the reactor using a differentially pumped quadrupole mass spectrometer, and thereby hope to obtain a more complete understanding of diamond growth mechanisms when nitrogen is added to the gas mixtures.

4. Conclusion

The effects of added nitrogen on the diamond growth using a CH_4–CO_2 gas mixture were examined. We found that the morphology of diamond films changed from cauliflower structures to well-defined facets due to the nitrogen addition. However, a discontinuous diamond film with well-faceted crystallites was formed resulting from the further addition of nitrogen. No carbon of any kind was deposited when the flow rate of nitrogen reached 20 sccm. Simply there was a dilution effect on reactant species in the plasma and the effect of etching amorphous and graphitic carbon because of the addition of nitrogen. However, the more important influence is that the plasma species interact with each other and with the matrix gas through various chemical reactions and are directly involved in the deposition process. The nitrogen incorporated into the diamond films was found to be very low, consistent with a model of film growth involving simultaneous deposition and etching processes [3]. Although the amount of atomic hydrogen in the ground state decreased and CN radicals increased with increasing amount of added nitrogen, a larger amount of atomic oxygen and the decrease in the C_2 emissions in the gas phase resulted in the deposition of good-quality diamond films under optimum conditions.

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