Gradual transitions in morphology of diamond films grown by using N₂ admixtures of CH₄+H₂ gas in a hot filament assisted chemical vapour deposition system

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Abstract

A study of the evolution of morphology of diamond films grown as a function of N₂ gas additions to the CH₄+H₂ precursor in an HF-CVD system is presented. With the increase of admixture of N₂ fraction, in contrast to earlier studies, the morphology was observed first to gradually change from {111}-faceted crystallites texture to that of an intermediate cubo-octahedral crystallite texture and then gradually but finally to transform completely into that of {100}-faceted crystallites. The threshold nitrogen concentration, [N₂]^{thr}, required to bring about the said transition in morphology was much larger than it was reported previously. Moreover, the morphology transition required a larger [N₂]^{thr} when a large fraction of methane was employed. Further additions of nitrogen, that just exceeded the [N₂]^{thr}, resulted in growth of films containing slightly bigger {100}-multi-layered grains or isolated planar {100}-platelets. For extremely large nitrogen additions, the growth of nanocrystalline or amorphous carbon films was observed. The N₂ additions more than 50 vol.% did not yield any deposition. Raman scattering and photoluminescence measurements were used respectively for characterizing the quality and nitrogen doping in the films. These results are attributed to the possible catalytic role of atomic nitrogen at the growing surface.

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1. Introduction

Much progress has been made in production of polycrystalline diamond films from a hydrocarbon gas (typically methane) diluted in an excess of hydrogen by using the low pressure chemical vapour deposition (CVD) techniques where the gas excitation is accomplished through the energy transferred by a microwave plasma or by an electrically energized hot tungsten filament [1]. Using these techniques, particularly over the past 10 years, a considerable success has been achieved in deposition of

diamond films having desired morphology, crystallite orientation and crystallite shape. These three parameters control the quality of surface texture required for typical device applications [2]. The diamond films composed of pyramidal or cubo-octahedral shaped crystallites grown respectively along <111> or <110> directions acquire a rough surface texture. These films promise good field induced electron emitters [3,4]. On the other hand, the films composed of square platelets or cube shaped crystallites grown along <100> direction acquire smooth surface texture [5]. These {100}-textured films are suitable for the fabrication of optical windows for transmission of X-ray and infrared radiations [6]. Moreover, a coplanar growth of {100}-platelets can lead to formation of heteroepitaxial diamond films, which are of immense importance for manufacture of active electronic devices

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that can operate in severe ambient conditions [7,8]. Recently the ultra-nanocrystalline diamond (UNCD) films having altogether different surface texture and micro-structure have been synthesized and shown to be useful for sensitive field emission devices [9,10]. These discoveries have attracted widespread research interest and prompted many groups to investigate the growth of selectively textured CVD-diamond films.

Some researchers reported the growth of textured diamond films from the standard gas precursor (SGP) viz. methane diluted in hydrogen [1 to 5 vol.% CH₄ in H₂], and identified the parameters viz., the methane fraction in hydrogen [11] and the substrate temperature [12,13], as the key parameters for the controlled growth of diamond films having desired textures. Recently, addition of small quantity of oxygen (<0.5 vol.%) to the SGP is shown to enhance the growth of diamond films with {111}-faceted texture [14–16]. Similarly, addition of small quantity of nitrogen (<0.1 vol.%) to the SGP has been demonstrated to produce dramatic changes in morphology, crystallite shape and growth rate [16–19]. The research emphasis in CVD diamond has since then focused on the nitrogen-assisted production of textured films.

Just a few years ago, Locher et al. [20] and Cao et al. [21] reported a morphology transition in CVD diamond films from {111}-crystallite texture to {100}-crystallite texture on addition of small fraction of N₂ (~0.05 vol.%) to the SGP while slightly larger fraction (>0.1 vol.%) of N₂ was observed to cause deleterious effects. The subsequent microwave plasma assisted CVD (MW-CVD) studies revealed a strong dependence of morphology, surface texture and growth rate on the carbon-to-nitrogen ratio in the gas phase [19,22–24]. Most of these investigations have used extremely dilute admixtures of pure N₂ with the SGP [23,24]. On the other hand, the HF-CVD investigations have mostly used ammonia (NH₃) for easy generation of large flux of reactive atomic nitrogen. Interestingly, in both the techniques, the growth of good diamond films has been observed only for low concentration of atomic nitrogen [25–28].

Owing to the low dissociation efficiency of N₂ at the prevailing filament temperatures employed, a considerable part of the N₂-fraction used in HF-CVD might behave as a spectator [29,30] and, therefore, a larger N₂-fraction may be required for HF-CVD to produce the same effects as observed for additions of small N₂-fractions in MW-CVD. However, the use of such large N₂-fractions in HF-CVD received only little attention, e.g., Barnauska et al. [31] who have used 20 vol.% of N₂ addition to the [C₂H₅OH+H₂] gas precursor and produced good quality {100}-textured diamond films. Surprisingly, however, XPS and AES measurements in most of the previous studies did not show any significant evidence for N-incorporation in the diamond films though it has been recently reported that the tetrahedrally coordinated nitrogen resides only on the crystallite surfaces while the crystallites themselves remain

pure UNCD [10]. The absence of N-incorporation in the N-assisted CVD-growth of diamond films was proposed to be due to the process of formation of HCN species. This process may assist in clean diamond growth by removing weakly bonded graphitic carbon from the substrate surface and even may act as a sink for carbon that would have otherwise contributed to diamond growth [32,33]. Alternately, nitrogen is also proposed to behave as a catalyst to convert atomic H into H₂, a reverse process that depletes the deposition zone of atomic H, which is otherwise essential for standard H-assisted CVD-diamond growth [30]. Thus, the nitrogen addition to the precursor gas appears to play a variety of roles but understanding of these roles appears to be still incomplete [30,31].

In this paper, we have presented a study of the evolution of morphology and corresponding textures of diamond films grown as a function of strong N₂ admixtures of the CH₄+H₂ precursor in an HF-CVD system, particularly, employing high filament temperature (T_F), moderate methane concentration ([CH₄]) and large fractions of N₂ gas.

2. Experimental

The HF-CVD system used here consists of a stainless steel (ss) chamber, about 12 in. in diameter and 10 in. in height, at the center of which an M-shaped filament, made out of tungsten wire (diameter ~0.5 mm) and well supported by thick (0.75 mm) tungsten hooks, was installed. This planar filament covered deposition area of about 1 in.². The opening of ss inlet tube introducing the gas mixture in the deposition zone was situated ~5 cm above the center of the filament and the {100}-Si substrates supported by an iron disc were placed about 10 mm below the center of the filament. A Pt/13%Rh–Pt thermocouple tip, partially inserted in a 1.5 mm diameter well drilled in the iron disc, was located just near the substrates so that the thermocouple tip and Si substrates could simultaneously face the hot filament from the same distance. The Si substrates cut from as-received 3-in. diameter optically polished Si wafers (p-type, B-doped, resistivity ~10 Ω cm, {100}-orientation, thickness ~300 μ m) were lightly scratched by using diamond powder (~0.5 μ m) and were ultrasonically degreased in high purity acetone, then treated with 48% HF acid, and subsequently washed with deionized water and dry methanol prior to loading in the deposition chamber. The chamber was evacuated to a base pressure of about 10^{–3} Torr prior to the start of deposition experiment. The chamber pressure for growth of the diamond films was measured by using a transducer coupled (MKS, USA, Type-270) pressure gauge and maintained constant at 25 Torr. The atmospheric leak rate of the chamber at gas pressure of 25 Torr was estimated to be less than 0.01 sccm. The filament temperature (T_F) was measured by using an optical pyrometer and adjusted to 2400±30 °C through out the

course of this work. The substrate temperature was maintained at 900 ± 20 °C. The gas flows were measured and controlled by using the electronic mass flow meters (Unit Instruments, USA).

The Leica Stereo Scan-440 Scanning Electron Microscope (SEM) was used to photograph the changes in surface morphology as a function of N_2 gas fraction added to the source gas. The Raman scattering (RS) and Photoluminescence (PL) measurements were carried out at room temperature in backscattering geometry by placing the samples in an evacuated sample holder and using the SPEX-1403 Ramalog double monochromator [27]. The 514.5nm radiation from an argon ion laser was used to excite the RS and PL. The RS-measurements were used to investigate the carbon microstructure of the films whereas the PL-measurements were used to trace the presence of nitrogen, if any, in the diamond crystallites.

For studying the effect of large concentration of nitrogen on the growth and properties of diamond films, all the deposition experiments were carried out by adding pure N_2 gas to the (CH_4+H_2) gas mixture and using freshly carbonized tungsten filament each time. The N_2 proportion was varied from 1 to 150 sccm while methane gas flow was varied from 1 to 10 sccm. The total gas flow was either 200 sccm or 300 sccm. This allowed $[N_2]/[CH_4]$ ratio variation from 0.1 to 15. These depositions experiments generated large number of samples. Our results presented here differ considerably from those previously reported in the literature.

3. Results

The results presented here are for two series of diamond films prepared from: (1) 6 sccm of CH_4 with total gas flow of 200 sccm, and (2) 10 sccm of CH_4 for total gas flow of 300 sccm where, in each case, the part of hydrogen concentration ($[H_2]$) replaced by nitrogen ($[N_2]$) is varied from 0.5 vol.% to 50 vol.% or more. The square parentheses, e.g., [G], show the flows of particular gas, where $G=H_2$, N_2 , or CH_4 .

3.1. Morphology

In the first series of diamond films i.e., for 6 sccm of CH_4 with total gas flow of 200 sccm, the H_2 was replaced by N_2 in various proportions in the source gas so that $[H_2]=194-[N_2]$, where $[N_2]$ added was varied as 0, 1, 3, 6, 12, 24, 36, ... sccm. The actual gas compositions used for growth of various films are shown in Table 1. This series of films did not show any serious deterioration of texture for $[N_2]<36$ sccm (~ 18 vol.%) which corresponds to ratio $[N_2]/[CH_4]<6$. This is a much larger gas phase accommodation of N_2 compared to the one reported in previous results where growth degradation was observed just for $[N_2]/[CH_4]>0.1$ [21]. Secondly, the growth rate was found to increase from 0.25 $\mu\text{m/h}$ to 0.45 $\mu\text{m/h}$ for increase of $[N_2]$ from 1 sccm to

Table 1

Deposition conditions for series-1 and series-2 films

Sr. no.	CH_4 (sccm)	H_2 (sccm)	N_2 (sccm)	N_2/CH_4	N_2/H_2	N_2 (%)	T_s (°C)
<i>Series-1</i>							
1	6	194	0	0	0.000	0	910
2	6	188	6	1	0.031	2	890
3	6	182	12	2	0.065	6	910
4	6	170	24	4	0.141	12	900
5	6	164	30	5	0.183	15	910
6	6	158	36	6	0.228	18	900
7	6	140	54	9	0.390	27	900
<i>Series-2</i>							
1	10	290	0	0.0	0.000	0.00	930
2	10	270	20	2.0	0.074	6.66	930
3	10	250	40	4.0	0.160	13.33	930
4	10	230	60	6.0	0.260	20.00	940
5	10	200	90	9.0	0.450	30.00	940
6	10	190	100	10.0	0.530	33.30	930
7	10	165	125	12.5	0.860	41.66	940

54 sccm and it decreased for 60 sccm $< [N_2] < 100$ sccm (i.e., 30 vol.% $< [N_2] < 50$ vol.%). For $[N_2] > 100$ sccm, almost no deposition was observed. The morphology, film texture and crystallinity were observed to change gradually on addition of N_2 :

- (1a) The surface morphology of the diamond films grown without addition of N_2 , i.e., $[N_2]/[CH_4]=0$, shown by the SEM micrograph presented in Fig. 1a, consists of crystallites having various shapes but no sharp edges. These films may be said to have a mixed crystallite morphology, which is characterized by different populations of triangular plates, cubo-octahedral crystallites, square platelets and cubic crystallites. The size of these crystallites varies from 0.5 μm to 0.8 μm while the film appears to be densely packed. These features indicate slight larger density of nucleation that is commonly related to larger gas phase content of CH_4 (~ 2 vol.% in H_2) than it is normally (~ 1 vol.% in H_2) used in synthesis of good quality diamond films.
- (1b) For the additions of $[N_2] < 10$ sccm, which corresponds to $0 < [N_2]/[CH_4] < 1.66$, the crystallite size increases from 1 μm to 2.2 μm while the film morphology shows improvement in growth of $\{111\}$ -faceted crystals in respect of the crystal size, triangular shape and sharpness of edges as clearly seen in SEM micrograph shown in Fig. 1b. The increase in $[N_2]$ is also seen to cause increase in population of $\{111\}$ -faceted twin crystals.
- (1c) For the next range of nitrogen addition, viz., 10 sccm $< [N_2] < 20$ sccm, which corresponds to $1.66 < [N_2]/[CH_4] < 3.33$, the cubo-octahedral crystals, bound by $\{111\}$ and $\{100\}$ facets with the growth direction $\langle 110 \rangle$ nearly coinciding with the normal to the substrate surface, start appearing among the other

Fig. 1. SEM photographs of the surface morphology of the diamond films grown from 6 sccm of CH_4 and different percent fractions of N_2 as: (a) 0%; (b) 2%; (c) 6%; (d) 12%; (e) 15%; (f) 18%; and (g) 27%.

$\{111\}$ -faceted triangular and cubic crystals as seen in SEM micrograph shown in Fig. 1c. It appears that the growth rate of $\{111\}$ facets reduces on increase in N_2 and growth rate of $\{100\}$ facets becomes competitive, which results in growth of cubo-octahedral crystals.

- (1d) For the next $[\text{N}_2]$ range, i.e., $20 \text{ sccm} < [\text{N}_2] < 30 \text{ sccm}$, which corresponds to $3.33 < [\text{N}_2]/[\text{CH}_4] < 5$, a clear and complete transition from $\{111\}$ -faceted twin crystal morphology to cubo-octahedral crystal morphology was observed. A typical SEM micrograph showing closely packed cubo-octahedral crystal morphology of the film grown from $[\text{N}_2]/[\text{CH}_4]=4$, i.e., $[\text{N}_2]$ corresponds to 12 vol.% of N_2 , is shown in Fig. 1d. The $\{100\}$ facets of some of these cubo-octahedral crystals appear larger in size compared to those of $\{111\}$ facets and hence slight tilting of the

growth direction $\langle 110 \rangle$ with respect to the normal to the substrate surface appears. This indicates that the growth rate of $\{100\}$ facets probably overtakes the growth rate of $\{111\}$ facets and results in larger $\{100\}$ facets.

- (1e) For further increase of $[\text{N}_2]$ addition, $30 \text{ sccm} < [\text{N}_2] < 40 \text{ sccm}$, which corresponds to $5 < [\text{N}_2]/[\text{CH}_4] < 6.66$, a clear transition to $\{100\}$ -faceted cubic crystal morphology with the growth direction $\langle 110 \rangle$ now more tilted with respect to the normal to the substrate surface has been observed. A typical SEM micrograph of this cubic crystal morphology of the film grown with $[\text{N}_2]/[\text{CH}_4]=6$, i.e., $[\text{N}_2]=18 \text{ vol.}\%$, is shown in Fig. 1e.
- (1f) For next higher additions of nitrogen, i.e., the range $40 \text{ sccm} < [\text{N}_2] < 50 \text{ sccm}$, which corresponds to $6.66 < [\text{N}_2]/[\text{CH}_4] < 8.33$, the cubic crystallites appear

to have formed of {100}-layers as seen in Fig. 1f. Similar results on growth of {100}-layers has been reported recently by Ayres et al. [24] in their studies on MW-CVD of diamond films grown by using nitrogen addition to SGP.

- (1g) For larger concentrations of nitrogen, i.e., the range 50 sccm < [N₂] < 60 sccm, which corresponds to 8.33 < [N₂]/[CH₄] < 10, a featureless particles morphology (Fig. 1g) was observed and it appears to be similar to the nanocrystalline film growth observed by others in different studies [34].

In the second series of diamond films, the replacement of H₂ by N₂ was further investigated for [CH₄]-10 sccm, total flow of 300 sccm and the reduced flow of [H₂]-290-[N₂], where [N₂] added was varied as 10, 20, 30, ..., 100, ..., sccm which allowed [N₂]/[H₂] ratio variation from 1 to 10 or more. These series-2 films also displayed sequence of results similar to those observed for series-1 films. The growth rate was found to increase from 0.25 µm/h to 0.65 µm/h for increase of [N₂] admixture from 0 to 70 sccm, i.e., [N₂]/[CH₄] < 7, and it was larger than those of series-1 films prepared from comparable gas compositions. However, for increase of [N₂] > 70 sccm the growth rate decreased gradually until [N₂] reached 100 sccm (or [N₂]-33 vol.%). Moreover, this series of films also did not show any serious deterioration of texture for [N₂] < 60 sccm, i.e., [N₂]/[CH₄] < 6, which corresponds to [N₂]-20 vol.%. The surface morphology, film texture and crystallinity were observed to change gradually on addition of N₂ as described below:

- (2a) For no addition of N₂, i.e., [N₂]/[CH₄]=0, the diamond films grown from gas flow containing 10 sccm of CH₄ and 290 sccm of H₂, which corresponds to 3.33 vol.% of CH₄ in H₂, acquired mixed crystallite morphology as shown by SEM micrograph in Fig. 2a. The crystallites are seen to have less sharp edges while average crystallite size is ~0.8 µm.
- (2b) For the nitrogen additions in the range, viz., 0 < [N₂] < 30 sccm, i.e., 0 < [N₂]/[CH₄] < 3, the SEM micrograph (Fig. 2b) of surface morphology shows increase in population of {111}-faceted twin crystals as well as cubo-octahedral crystals. The edges, particularly of triangular crystallites, show improved sharpness while the average crystallite size appears to have increased to ~1.8 µm.
- (2c) For the range of addition of nitrogen, viz., 30 < [N₂] < 50 sccm, i.e., 3 < [N₂]/[CH₄] < 5 the surface morphology was observed to change gradually to cubo-octahedral crystallite morphology as shown by SEM micrograph in Fig. 2c. The population of cubo-octahedral crystallites is much larger than those of other forms. These crystallites appear to have smooth faces with sharpened edges and corners. The average crystallite size shows increase to ~2 µm.

- (2d) For more additions of nitrogen, 50 sccm < [N₂] < 70 sccm, i.e., 5 < [N₂]/[CH₄] < 7, films show a clear transition to cubic crystallite morphology (Fig. 2d) with the growth direction <100> for majority of crystallites almost normal to the substrate surface. Some of these crystallites appear to have form of stacked {100}-layer or flaky structure. It is interesting to note that these crystallites are cuboids and not square platelets as some other investigators have observed in their studies focused on the effect of nitrogen admixtures on the growth of diamond films [17].
- (2e) For higher additions of nitrogen, 70 sccm < [N₂] < 90 sccm, i.e., 7 < [N₂]/[CH₄] < 9, films show cuboid crystal morphology having mainly flaky structure and non-uniform size, e.g., crystals with size as big as 4 µm, shown in Fig. 2e, appear to be interspersed amidst the others of average size 1.5 µm. Some crystals show step growth or secondary growth. The morphology appears to be made up of etched crystals.
- (2f) For larger additions of nitrogen, 90 < [N₂] < 100 sccm i.e., 9 < [N₂]/[CH₄] < 10, the film texture completely changed to isolated {100}-crystal plates grown on the top of hips of flaky or nanocrystalline carbon phase (Fig. 2f), and the morphology looks more or less as co-planar {100}-crystallite growth. The growth direction <100> appears to be almost normal to the substrate surface.
- (2g) For the nitrogen addition in the range, 100 < [N₂] < 130 sccm i.e., 10 < [N₂]/[CH₄] < 13, irregular shaped grains constituted the morphology as seen in the SEM micrograph of the film surface shown in Fig. 2g. The grains appear to have fine nanocrystalline structure. However, no depositions were observed when [N₂] addition was increased beyond 150 sccm, i.e., [N₂]/[CH₄] > 15 or [N₂] > 50 vol.% in the source gas.

Thus our SEM results show that the diamond film morphology does not change directly from {111}-faceted or mixed crystallites morphology to that of {100}-crystallites but it gradually evolves through a well-defined sequence of intermediate texture transitions. These intermediate transitions involve mainly cubo-octahedral crystallites, which change in shape and size as a function of gas phase nitrogen content. In the presence of nitrogen, the {100} facets of these cubo-octahedral crystallites grow in size at the expense of the {111} facets and thus the cubo-octahedral crystals systematically get transformed into the {100}-crystallites. It is a two-step transition in contrast to the single step transition reported in previous studies. Moreover, there exists a threshold value of nitrogen admixture, [N₂]^{thr}, required to bring about the morphology transition from mixed or {111}-faceted morphology to that of {100}-faceted crystallites. The magnitude of [N₂]^{thr}

Fig. 2. SEM photographs of the surface morphology of the diamond films grown from 10 sccm of CH_4 and different percent fractions of N_2 as: (a) 0%; (b) 6.66%; (c) 13.33%; (d) 20%; (e) 30%; (f) 33.3%; and (g) 41.66%.

depends on the concentration of CH_4 in the source gas, e.g., the said transition has occurred at $[\text{N}_2] \sim 30$ sccm for $[\text{CH}_4] \sim 6$ sccm and at $[\text{N}_2] \sim 60$ sccm for $[\text{CH}_4] \sim 10$ sccm. These values of $[\text{N}_2]^{\text{thr}}$ are significantly larger than reported earlier. For larger fractions of nitrogen that just exceeded the $[\text{N}_2]^{\text{thr}}$, a morphology consisting of large crystallites or big $\{100\}$ -multi-layered grains or isolated planar $\{100\}$ -platelets interspersed among microcrystalline material is also observed for both concentrations of CH_4 . Again a multi-layered $\{100\}$ -crystal growth and etched $\{100\}$ -crystal morphology at $[\text{N}_2] > [\text{N}_2]^{\text{thr}}$ are also observed for both CH_4 concentrations. For extremely large additions of nitrogen, $[\text{N}_2] > 30$ vol.%, the films grow as nanocrystalline or amorphous carbon films. For N_2 concentrations greater than 50 vol.% almost no deposition occurred. These results thus differ significantly from previously published reports.

3.2. Raman measurements

The Raman spectra of the series-1 diamond films, i.e., films grown using 6 sccm of CH_4 and various concentrations of nitrogen in the source gas, were excited by exposing the films to 514.5 nm Ar-laser line and are presented in Fig. 3. The strong band at 1332 cm^{-1} , characteristic of the first order Raman scattering due to the optical vibrations of sp^3 -bonded carbon atoms in diamond crystal structure, is present in all spectra [35]. With addition of N_2 to the source gas, following variations in Raman spectra were observed: (a) the optical vibration band at 1332 cm^{-1} appears to shift towards lower wave number (red shift) side i.e., to $\sim 1325 \text{ cm}^{-1}$ for $[\text{N}_2] > 6$ vol.%. (b) The bandwidth of the optical band increases from $\sim 5 \text{ cm}^{-1}$ to $\sim 10 \text{ cm}^{-1}$. (c) The intensity of the 1332 cm^{-1} -band slowly decreases relative to that of other bands in the

Fig. 3. Raman spectra of the diamond films grown from 6 sccm of CH_4 and different percent fractions of N_2 as: (a) 0%; (b) 2%; (c) 6%; (d) 12%; (e) 15%; (f) 18%; and (g) 27%.

spectra. The lowest bandwidth and highest intensity of the 1332 cm^{-1} band, in general, implies minimum strains and defects in the diamond crystallites despite their dense packing in the film (Fig. 1d) [36]. (d) The Raman scattering in the frequency range $1500\text{--}1600\text{ cm}^{-1}$ for the films prepared from the $[\text{N}_2] < 6\text{ vol.}\%$ is seen to be comparatively weak, and it increases with increase of $[\text{N}_2] > 6\text{ vol.}\%$ (Fig. 3). This region of vibration frequency is generally correlated to the vibrations of the sp^2 -bonded graphitic carbon in crystalline or amorphous phase [37]. This Raman band, well known as G-band, is known to shift to lower frequency ($\sim 1500\text{--}1550$) and broaden proportionately on either reduction of graphite crystallite size or its conversion into amorphous carbon [38]. Moreover, the scattering cross section for sp^2 -bonded C–C species is almost ~ 50 times larger compared to that of sp^3 -bonded C–C species in the film [39]. The intensity of this band thus would diminish further by a factor of ~ 50 when its strength is normalized with respect to that of the optical vibration band at 1332 cm^{-1} . The Raman spectra in Fig. 3, thus, indicate the presence of small proportion of amorphous or fine grains of sp^2 -bonded carbon species for films prepared by addition of $[\text{N}_2] < 12\text{ vol.}\%$. The intensity of G-band is also seen to increase with the increasing proportion of $[\text{N}_2]$, particularly, in films prepared from the addition of $[\text{N}_2] > 12\text{ vol.}\%$. Alternately, this normalization indicates that the population of the graphitic sp^2 -bonded species compared to that of sp^3 -bonded diamond species still might be low.

The Raman spectra of the series-2 diamond films, i.e., films grown using 10 sccm of CH_4 and various concen-

trations of nitrogen in the source gas, are shown in Fig. 4. These spectra show nitrogen concentration dependent strong to weak signatures of diamond band at $\sim 1332\text{ cm}^{-1}$ for all samples, which ensures the presence of diamond crystals in the films. The G-band is also seen to have its weak signature in these spectra at $\sim 1550\text{ cm}^{-1}$, which indicates the presence of small traces of amorphous carbon in these films. The strength of diamond band compared to that of G-band, however, is seen to increase with increase in admixture of $[\text{N}_2]$ in the range $0 < [\text{N}_2] < 13\text{ vol.}\%$, whereas it decreases steadily for $13 < [\text{N}_2] < 40\text{ vol.}\%$ in the SGP. Alternatively, the G-band strength is seen to increase with respect to that of diamond band for the nitrogen admixture range, $13 < [\text{N}_2] < 40\text{ vol.}\%$. However, the large scattering cross section of the G-band reduces the proportion of graphitic carbon with respect to that of sp^3 -bonded carbon.

Raman spectra of Fig. 4 also show signatures of vibrational bands at $\sim 1140\text{ cm}^{-1}$ and 1480 cm^{-1} for $[\text{N}_2] > 30\text{ vol.}\%$. These bands are believed to have one of the two possible origins. First, the band at 1480 cm^{-1} may be due the vibrational modes of the nanocrystalline diamond particles or amorphous sp^3 -bonded carbon present in the films [9,10,40,41]. Secondly, it has been recently pointed out that the band at 1140 cm^{-1} is also likely to originate from the *trans*-polyacetylene (*trans*- CH_x) species in the nanocrystalline diamond film [34]. However, the stability of the *trans*- CH_x species at the substrate tempe-

Fig. 4. Raman spectra of the diamond films grown from 10 sccm of CH_4 and different percent fractions of N_2 as: (a) 0%; (b) 6.66%; (c) 13.33%; (d) 20%; (e) 30%; (f) 33.3%; and (g) 41.66%.

Fig. 5. The PL spectra of the diamond films grown from 6 sccm of CH_4 and different percent fractions of N_2 as: (a) 0%; (b) 2%; (c) 6%; (d) 12%; (e) 15%; (f) 18%; and (g) 27%.

ratures ($\sim 930^\circ\text{C}$) employed by us needs to be investigated separately.

Thus our Raman measurements show that the quality of diamond films, in respect of incorporation of sp^2 -bonded carbon, remains more or less unchanged for smaller admixtures of nitrogen but it degrades for larger admixtures of $[\text{N}_2]$ irrespective of the methane fraction used.

3.3. Photoluminescence

The photoluminescence spectra of the series-1 samples are presented in Fig. 5 as a function of nitrogen concentration in the SGP. These spectra were excited by using the 514.5 nm (photon energy ~ 2.41 eV) radiation from an argon ion-laser and recorded in the form of shift from the excitation radiation frequency ($\sim 19,432\text{ cm}^{-1}$) using the same spectrometer that was used for the Raman scattering measurements. The emission bands seen in the photon energy range 2.3 eV to 2.2 eV are the intrinsic vibrational Raman bands corresponding to vibration frequency range 1000 to 2000 cm^{-1} discussed above. The prominent broad band positioned in the energy range ~ 1.8 eV to 1.6 eV of the PL spectra (curves shown by labels 'a', 'b' and 'c' in Fig. 5) of diamond films prepared by adding nitrogen, $0 < [\text{N}_2] < 6$ vol.%, is attributed to the GR1 emission from multiple vacancy cluster related intrinsic defects in the diamond crystals [42]. For the films deposited from larger admixtures of $[\text{N}_2]$, $6\text{ vol.}\% < [\text{N}_2] < 20\text{ vol.}\%$, the broad GR1 band, however, disappears and, instead, a sharp and strong emission band appears at photon energy of about 1.68 eV in the PL spectra (curves shown by labels 'd', 'e' and 'f' in Fig. 5). Moreover, the strength of this latter band is seen to

decrease with increasing $[\text{N}_2]$ addition while its position red shifts from 1.68 eV to 1.66 eV. Some researchers have attributed this sharp band at 1.68 eV to an emission from transitions of the defect center formed by Si-impurity and a related vacancy complex in diamond crystals [43,44]. In our previous studies [27], the strength of the 1.68 eV band was observed to pass through a maximum for very dilute range ($0 < [\text{N}_2] < 2\text{ vol.}\%$) nitrogen admixtures of SGP and the origin of the band was correlated to defects formed by mono-vacancies in the diamond crystals [45]. In the present work, this band is seen to disappear completely (curve shown by label 'g' in Fig. 5) for strong admixtures of $[\text{N}_2] > 27\text{ vol.}\%$, i.e., when the material becomes nano-crystalline or amorphous. Though the nitrogen appears to have strong contribution to this band, its role in forming these defects is not yet clear.

Other nitrogen related PL bands in the energy range of 2.2 eV to 2.0 eV have shown their comparatively weak signatures for the large concentrations of nitrogen (Fig. 5) and these bands may be attributed to transitions in the centers consisting of single substitutional nitrogen atoms with one or more related vacancies in the diamond crystals though clear evidence for this attribution is still not available [46].

Fig. 6. The PL spectra of the diamond films grown from 10 sccm of CH_4 and different percent fractions of N_2 as: (a) 0%; (b) 6.66%; (c) 13.33%; (d) 20%; (e) 30%; (f) 33.3%; and (g) 41.66%.

The PL spectra of the series-2 samples prepared from 10 sccm of CH_4 are presented in Fig. 6. These spectra are similar to those of series-1 samples. The band at about 1.68 eV is again seen to show up for samples prepared from nitrogen admixture (curves shown by labels ‘b’, ‘c’, ‘d’, ‘e’ and ‘f’ in Fig. 6) while the sample prepared without addition of nitrogen shows the broad GR1 emission band (curve shown by labels ‘a’ in Fig. 6). The nitrogen concentration dependence of the strength of the 1.68 eV band is again observed similar to that of samples of series-1. Moreover, the band strength is also seen to decrease with $[\text{N}_2]$ while it disappears for the nanocrystalline or amorphous sample prepared from nitrogen admixture of 41 vol.%. (curve shown by label ‘g’ in Fig. 6). There is weak PL emission in the energy range 2.15–2.05 eV for large concentration of nitrogen that has already been attributed to the single substitutional nitrogen atoms-vacancy centers.

The PL spectra labeled as ‘f’ in Fig. 5 and as ‘d’ and ‘e’ in Fig. 6 show an additional band at ~ 1.885 eV. The origin of this band is not yet known.

Thus our photoluminescence measurements show that nitrogen might influence the microstructure of these diamond films in respect of the vacancy distribution. The independence of strength of PL bands in the range 2.2 eV to 2.0 eV may be attributed either to a poor incorporation of nitrogen at substitutional sites or to the increase of stress in the films.

4. Discussion

These results may be discussed briefly in terms of possible growth dependence on deposition parameters and involvement of nitrogen in gas phase and solid-surface reactions.

First of all, we see that there is no serious degradation of diamond growth for additions of nitrogen as large as 30 vol.%, which differs from the earlier studies where degradation was observed for nitrogen additions as small as 0.1 vol.% [25]. Moreover, there is significant improvement of growth rate and film quality for moderate additions of N_2 . For the filament temperature $T_F \sim 2400$ °C and large N_2 concentration in the $\text{CH}_4/\text{N}_2/\text{H}_2$ gas mixture, we expect two possibilities to occur: (a) the proportion of reactive atomic nitrogen produced by the hot filament might be beneficially low, some of which might have formed CN species and (b) the atomic H concentration might have reduced in proportion to the admixed nitrogen gas leaving the overall dilution of CH_4 almost unchanged. The increase of H_2 replacement by N_2 enhances the $[\text{CH}_4]/[\text{H}_2]$ ratio. However, this may not increase the growth rate as the volume distribution and/or partial pressures of the gas phase growth species, such as CH_3 , C_2H_2 , CH_2 , etc., and the rates of reactions producing these growth species might only decrease. Moreover, the gas phase formation of HCN species, compared to other

carbon/nitrogen precursors, may get largely suppressed, which otherwise would have reduced the carbon supersaturation in the gas phase by removing the useful carbon species to HCN-sink as reported previously [28]. The number of CN species in the gas phase might have enhanced because we have used large $[\text{N}_2]/[\text{H}_2]$ ratios in the input gas mixture thereby improving the $[\text{CN}]/[\text{CH}_3]$ ratio [29]. These CN-radicals while condensing on the growing surface can take the role of atomic H in stabilizing the diamond growth by abstraction of H from sp^3 -bonded hydrogenated carbon species, viz. $\text{C}_D\text{-H}$, leaving the dangling bond at the diamond surface atom (C_D), which can provide an active site to absorb new CN or C-H species [32]. These processes may contribute to the increase of growth rate for moderate additions of N_2 to the CH_4+H_2 gas mixture [26]. For larger admixtures of N_2 , the growth rate declines due to the reduction in the dissociation rate of CH_4 in the absence of sufficient concentration of atomic H in the gas phase. The absence of deposition for N_2 additions more than 50 vol.% can then easily follow from the same mechanism.

The growth process involving condensation of C-N species may also lead to N passivation of diamond surfaces by forming $\text{C}_D\text{-N}$ bonds. X-ray photoelectron spectroscopy measurements on most of our films showed that the nitrogen concentration was less than the detection limits of our spectrometer. Only the nanocrystalline films prepared by using N_2 concentration as large as 40 vol.% have revealed a very weak signature of N_{1s} band at binding energy ~ 400 eV compared to that of C_{1s} band at 285 eV. The deconvoluted C_{1s} and N_{1s} XPS spectra excited by Al $\text{K}\alpha$ radiation are shown in Fig. 7. The C_{1s} at 285 eV band is slightly asymmetric on the higher energy side and is likely to involve overlap from a weak broad band at ~ 286 eV due to C-N bonding. The corresponding N_{1s} band also shows asymmetry and involves at least two peaks near 399.25 eV and 400.74 eV. Some other XPS studies have recently shown that the N in nanocrystalline diamond films stays in bonded conditions only at the grain surface [10]. This implies that the possibility of abundance of such N-terminated surfaces may become significant with increase of $[\text{N}_2]/[\text{H}_2]$ while the abundance of H-terminated surfaces may reduce proportionately. Such N-terminated surfaces may not grow easily further along $\langle 111 \rangle$ direction as N is proposed to involve in forming stable trigonal bonds with surface carbon atoms and leads to distortion of C-N bonds along the $(-1-1-1)$ direction [47]. The removal of N from these sites would involve surface reactions with atomic H and CH species. Such processes are energetically less favourable and hence can decelerate the growth velocity on $\{111\}$ facets. The decline in growth rate for $[\text{N}_2] > 30$ vol.% may also be accounted additionally by these processes.

The N passivation is probably also responsible for the growth of $\{100\}$ facets at the expense of $\{111\}$ facets. It is known that the fastest growth direction determines diamond

Fig. 7. The C_{1s} (a) and N_{1s} (b) XPS spectra of the film prepared by using 40% of gas phase nitrogen concentration.

film texture [48]. If v_{100} and v_{111} denote the respective relative growth velocities on the {100} and {111} facets, then the growth parameter defined by $\alpha = (\sqrt{3})(v_{100}/v_{111})$ is shown to control the film structure and morphology. In case of precursor gas mixture of CH₄+H₂, which does not contain nitrogen, the parameter α is also shown to depend on the deposition temperature and methane concentration [5]. The growth of octahedron crystal form with {111} facets corresponds to $\alpha < 2$ whereas the growth of cubic crystal form with {100} facets requires $\alpha > 2.5$ [48,49]. This suggests that the N passivation of surface C_D atoms may decelerate growth rate on {111} facets and can thus encourage growth of twins or {100} facets as observed in our results. Alternately Yu et al. [16] have suggested that nitrogen activates C_D–H sites and increases the C_D–H site energies and thus decreases α , which in turn makes {100} facets energetically preferential for growth. This implies that the N may be involved in catalytic subsurface reactions during the diamond growth.

The diamond films deposited on non-diamond substrates from an H₂+CH₄ gas mixture generally have polycrystalline structure with some crystallites having preferential orientation. Under normal conditions of deposition, the {100} facets show predominance at low T_s (<725 °C), while the

{111} facets become predominant at high T_s (>725 °C) [11]. This has been supported by T_s dependence of free energy changes at the substrate surface [49]. In the present work, we have employed high T_s >900 °C and hence the {111}-faceted morphology was expected to be predominant. This is true for our gas compositions where the nitrogen was either not added or it was very low in concentration. However, in spite of keeping the same T_s and [CH₄], we have observed mixed or {100}-faceted crystallite morphology for films prepared from gas composition containing nitrogen greater than 10 vol.%. These results suggest that the nitrogen may have some special role in influencing the surface morphology.

In the HF-CVD, many investigations have revealed that the use of pure H₂+CH₄ gas mixture leads to the production of dominant deposition species, viz., CH₃ and C₂H₂ and that the ratio ([C₂H₂]/[CH₃]) determines the morphology of the diamond films [14]. When the ratio exceeds a certain value, diamond crystallites with {100} facets make their appearance. Thus, nitrogen in the gas phase may be proposed to enhance the ratio ([C₂H₂]/[CH₃]) by involving in gas phase reactions such as, e.g., CH₃+N→HCN+H₂ and, therefore, may favour the growth of {100} facets. In our work, the ratio ([C₂H₂]/[CH₃]) may also be influenced by the value of [CH₄] since it can change the value of [CH₃]. Consequently, higher atomic N concentration shall be required to produce the transition of {100}-morphology when larger values of [CH₄] were employed.

Among several reaction pathways describing deposition of diamond initiated by different gaseous species, including CH₃ and several C₂H_x species, the H-abstraction – C₂H₂-addition mechanism appears to dominate [50]. Kaukonen et al. [51] have studied the role of N as a catalyst in surface reactions and have suggested a zipper mechanism for the growth of {100}-layers via migration of the extra electron from subsurface N_D atom to its neighbouring H–C–C–H dimer species whereby already thermally excited C–C bond can get opened. This open site has been shown to be ideal for absorption of a CH₂ species. As soon as a CH₂ is adsorbed to this open dimer, the excess electron becomes free to mediate a similar reaction at the adjacent site where subsequently another CH₂ is absorbed. Each of these adsorbed adjacent two CH₂ adspecies may eject one of their H atoms to form an H₂ molecule and bond together to form an isolated dimer localized in the upper layer with its orientation perpendicular to the original dimers in the lower layers. Abstraction of an H₂ molecule from the two CH₂ adspecies completes the CH₂ adhesion at this bridging site and the excess free electron keeps migrating to next neighbour dimers, which eventually can translate the dimer species into formation of {100}-layers. Thus the transfer of electron from N_D atom may catalyze the growth of whole {100}-layer. Our observations of layered growth of cubic crystal are probably indication of presence of such growth processes when nitrogen added was excessively large.

5. Summary

The influence of N₂ addition on various features of hot-filament chemical vapour deposition (HF-CVD) of diamond layers is studied. A morphological transition from {111}-faceted crystals to {100}-faceted crystal was observed with increase of nitrogen concentration but the threshold nitrogen concentration required for the said transition was found to increase with increase of CH₄ gas concentration. Moreover, a well-defined sequence of intermediate morphology transitions with increase of nitrogen concentration was observed. A pre-transition morphology of large crystallites interspersed among microcrystalline material was also observed. Raman spectra showed that no serious degradation of the growth process takes place even after addition of 20 vol.% of nitrogen and nanocrystalline diamond growth occurs for [N₂]-35 vol.%. XPS and photoluminescence measurements show only very weak signatures due to nitrogen incorporation in the films. A preliminary analysis of these results suggests that nitrogen might have behaved as a catalyst in the growth of diamond films.

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