

## Effects of N<sub>2</sub> addition on nanocrystalline diamond films by HFCVD in Ar/CH<sub>4</sub> gas mixture

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### ABSTRACT

Nanocrystalline diamond (NCD) films were grown on silicon substrates by hot filament chemical vapor deposition in Ar/N<sub>2</sub>/CH<sub>4</sub> gas mixtures. The effects of seeding process prior to deposition, the total gas pressure, and concentration of nitrogen on the grain size, morphology and bonding nature in HFCVD technique were investigated. The results indicated that a low total gas pressure is favorable for nanosized diamond crystallites. Films micrograph obtained from scanning electron microscopy showed diamond nanograins elongated with the addition of nitrogen in the plasma. Crystal structure investigations were carried out by X-ray diffraction measurements for deposited films. An increase in the size of crystallite is also observed from XRD measurements in NCD film when nitrogen was added in plasma. From Raman spectra, it was observed that the relative intensity of G peak increases indicating more graphite content after nitrogen added in the plasma. The effects of the nitrogen incorporation in nanocrystalline films in HFCVD are discussed.

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## 1. Introduction

Nanocrystalline diamond films are a promising class of nanomaterials with tunable properties. An especially appealing field of application for NCD is nitrogen doped semiconducting films. By depositing diamond films from argon rich plasma it is possible to produce nanocrystalline diamond (NCD) films with grain sizes between approximately 5 and 100 nm [1] depending on the deposition parameters. Ar promotes an increase of C<sub>2</sub> radical amount close to the substrate surface which determines the growth morphology [2,3]. According to Zhang et al. [4], Ar could inhibit the diamond growing faces after nucleation, allowing the formation of new growth centers and raising the film renucleation rate. In 1999, Zhang et al. reported that diamond nuclei was reduced in size due to addition of Ar into the CH<sub>4</sub>/H<sub>2</sub> plasma gas in a hot filament chemical vapor deposition process and density also increases at higher nitrogen concentration [5]. Lin et al. also discussed the Ar-CH<sub>4</sub>-H<sub>2</sub> system for polycrystalline to nanocrystalline diamond film growth [6] and recently Azevedo et al. [7] discussed graphitization effect on NCD in HFCVD. These films are usually insulating, but n-doping is easily possible by admixture of nitrogen to the process gas [8,9]. It has also been found that the addition of nitrogen

has a profound impact on the field emission [10], and electrochemical behavior [11]. N<sub>2</sub> is proved to be effective in making nanodiamond films conductive and it modify the diamond nanograins structure like nanowires when its concentration is increased above a particular value [12,13]. NCD growth using N<sub>2</sub> in the Ar/CH<sub>4</sub> plasma has discussed by many researchers [14–21] in MPCVD system. But there is need to observe the morphology, structure and bonding nature of NCD in HFCVD system with nitrogen incorporation in Ar/CH<sub>4</sub> plasma in HFCVD.

The focus of the research discussed in this paper is to investigate the morphological structural changes in NCD films grown with and without adding nitrogen in the plasma in HFCVD system with the goal of gaining an insight into the growth mechanism in HFCVD technique. The changes in the morphology of the films and bonding nature with N<sub>2</sub> are interpreted as an increase in sp<sup>2</sup> bonding in the films.

## 2. Experimental details

A conventional HFCVD system used curved tungsten wire as a filament for diamond growth. Prior to deposition the substrates used were Si(1 0 0) wafer supersonically scratched with diamond powder. The substrate temperature was stabilized at 750 °C by adjusting the distance between the filament and the substrate to ~7 mm. The Ar-N<sub>2</sub>-CH<sub>4</sub> ratios were controlled by precision mass

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flow controllers. The concentrations of methane (2%) was kept constant, whereas the Ar flow rate was reduced when the concentration of  $N_2$  in the mixture increased to 1% and 20% to hold the total gas flow rate constant. The as grown films were examined by scanning electron microscope (SEM, LEO 1530VP), Micro-Raman spectroscopy (Dilor LabRam-1B) and X-ray diffraction spectroscopy (Cu  $K\alpha$ ,  $\lambda = 0.1541$  nm, D/max-2200 X-ray Diffractometer) at room temperature. The Raman spectra were obtained using an  $Ar^+$  laser with a wavelength of 514.5 nm. The spot size was approximately 1  $\mu m$ .

### 3. Results and discussion

#### 3.1. Effect of seeding process before deposition

The seeding process plays an important role in enhancing the initial nucleation density, as illustrated in Fig. 1 with the comparison of surface morphologies of diamond films deposited after using different seeding processes. The apparently discontinuous

film in Fig. 1a indicates that the NCD film prepared using the short time (30 min) seeding with nano diamond powder ultrasonication, with ethanol as solvent, is continuous, but exhibits a rough surface that is due to the agglomeration of diamond nano powders prior to growth and is undesirable since it limits the achievement of smooth NCD films. The dense and smooth film morphology in Fig. 1b clearly showed that ultrasonication for long time (5 h) is effective for the NCD film deposition.

#### 3.2. Effects of total pressure

NCD films were deposited by maintaining the substrate temperature at 750 °C under gas pressures from 5 to 30 Torr using 2%  $CH_4$  in Ar. Fig. 2 shows the SEM morphologies of NCD films deposited at various pressures. When setting the total pressure to 30 Torr, the NCD film surface was rough, with the average grain size greater than 500 nm, shown in Fig. 2c. By decreasing the total pressure to 15 Torr, the average grain size reduced to nearly 50 nm, shown in Fig. 2b. As the total pressures were decreased to 5 Torr, the aver-

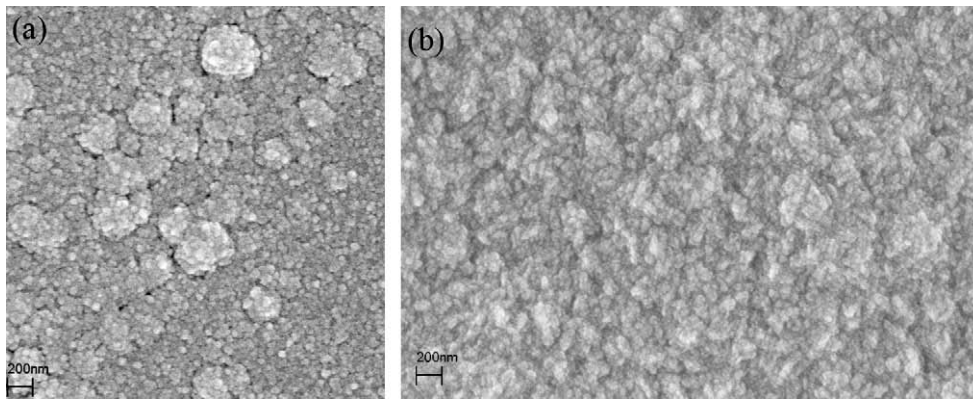


Fig. 1. SEM images showing the effect of (a) short time seeding process, and (b) long time seeding process on the microstructure development of UNCD films seeding with nano diamond powder via ultrasonication. The growth conditions for all the films are 4 h deposition, 49 SCCM Ar/1 SCCM  $CH_4$  and 750 °C.

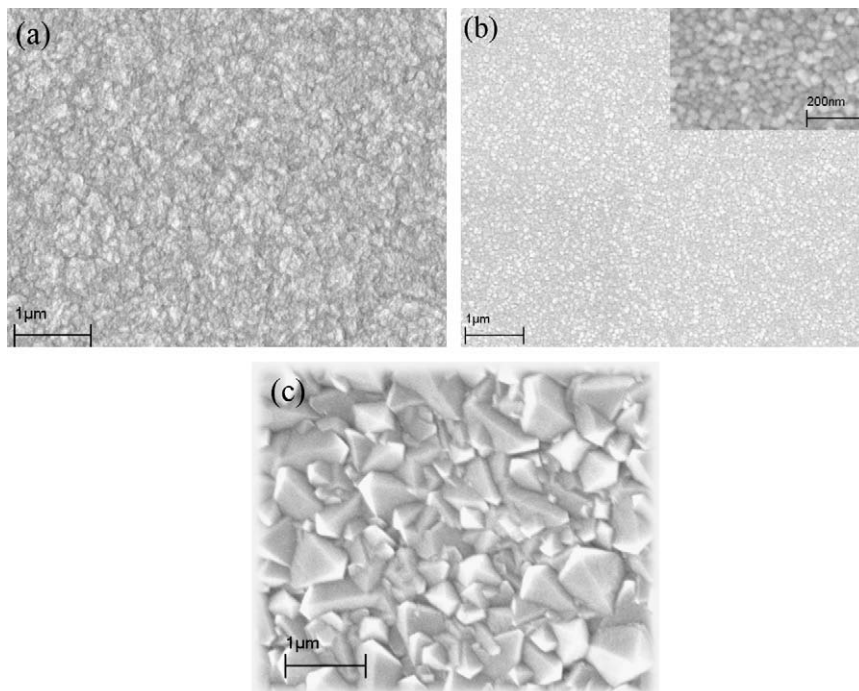


Fig. 2. SEM morphologies of the NCD films deposited under various total pressures: (a) 5 Torr, (b) 15 Torr, and (c) 30 Torr.

age grain size was found to decrease from around 50 nm to few nanometers and the film surface became smooth, shown in Fig. 2a. Similar trend was observed by You et al. [22] after using a mixture of hydrogen and methane in HFCVD system. The effects of total pressure on the growth behavior can be attributed by the following factors.

When a mixture of argon and methane comes near the hot filament, its temperature and consequently its composition will change. The nature and the amount of various species formed depend on such factors as the temperature of the hot filament, the system pressure, the composition and the flow rate of the incoming gas, and the extent of various chemical reactions on and near the

filament surface. In a HFCVD chamber, the Ar atoms can also achieve energy from the heater and electrons, which are emitted by hot W filament. The presence of argon can influence the formation and excitation of plasma species through energy and charge transfer processes, as well as affect the density and energy distribution of free electrons in the discharge. In Ar rich plasma, the discharge resulted in an increase in the  $C_2$  species. Lin et al. [6] shows the existence of  $C_2$  dimer in Ar rich plasma in HFCVD system.  $C_2$  species are supposed to be responsible to raise the secondary nucleation rate of diamond in Ar rich plasma and resulted in reducing the size of the grains. The secondary nucleation rate is enhanced under the low deposition pressure because of more  $C_2$

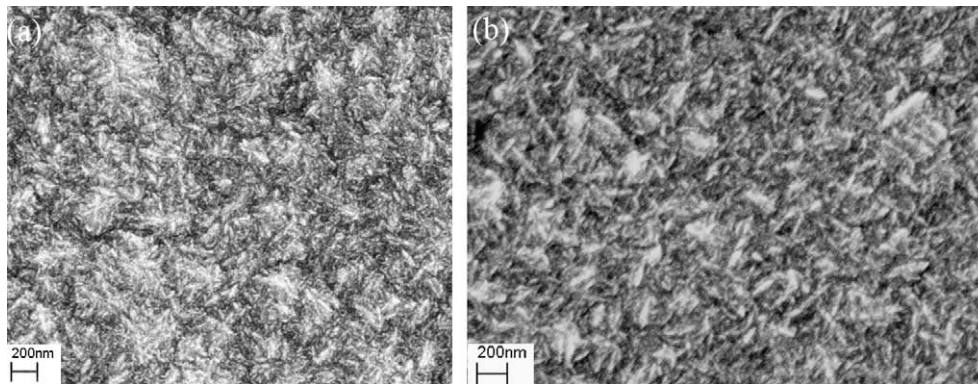


Fig. 3. SEM images of NCD films deposited for (a) 1%  $N_2$  (b) 20%  $N_2$ .

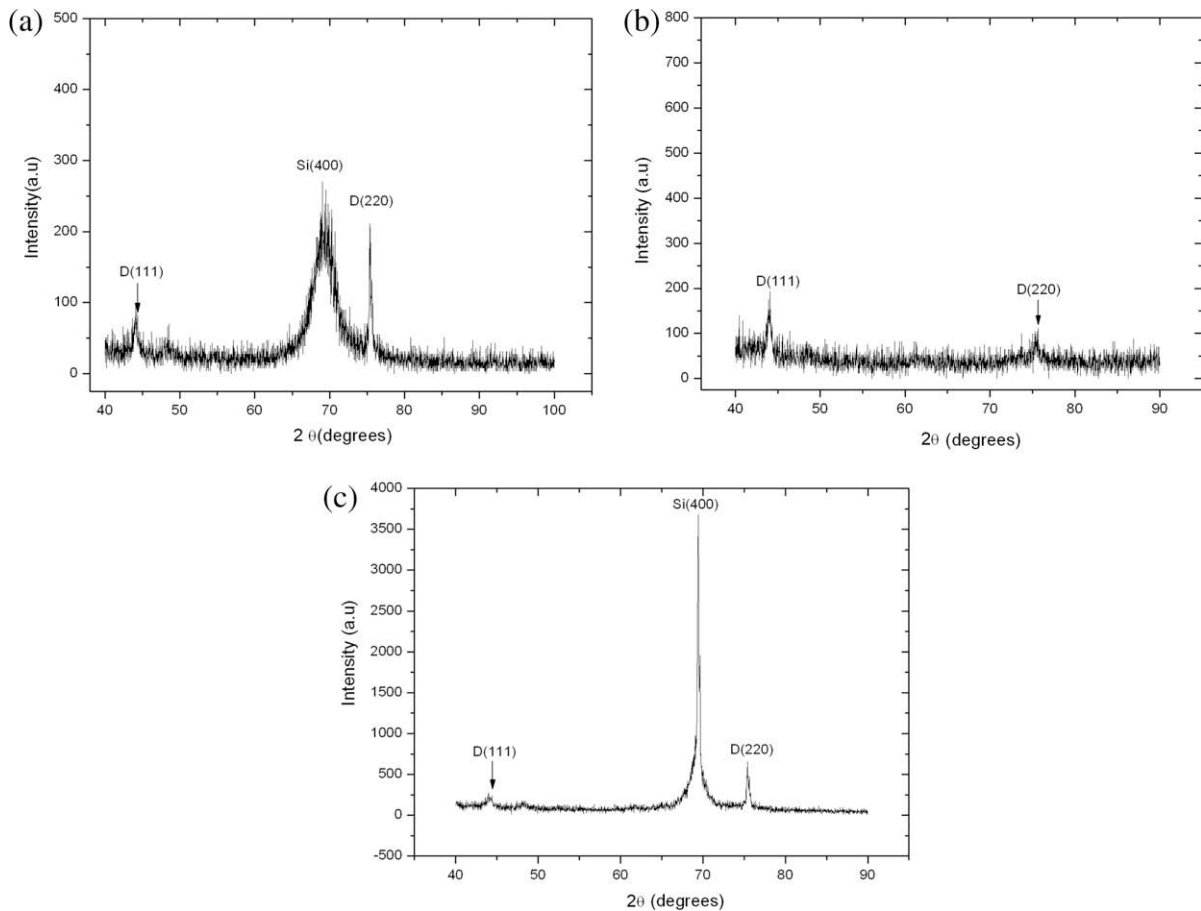


Fig. 4. XRD images NCD films for (a) 0% (b) 1% and (c) 20%  $N_2$ .

hydrocarbon radicals (larger than any other species in Ar rich plasma). The hydrocarbon radicals with higher kinetic energy due to larger mean free path can reach the substrate surface. An increased mean free path gave rise to an increased concentration of nucleating species at the substrate surface. The collision probability of the active species is smaller and thus they suffer less loss of energy during their transport to the substrate. From the point of view of kinetics, the driving power for nucleation is increased. The increment of interfacial energy required for forming new nuclei at low pressure is lower than that at high pressure, that is, the nucleation at lower operation pressure can be enhanced [23]. The concentration of hydrogen atoms (from decomposition of  $\text{CH}_4$ ) was reduced with descending pressure from 30 to 5 Torr at a filament temperature of 2100 °C in the presence of plasma [24,25]. Large hydrogen fractions affect the gas phase chemistry, influencing  $\text{C}_2$  destruction rates. The low hydrogen atom concentration reduced the etching of  $\text{sp}^2$  carbon phase, promoting the secondary nucleation and reducing the diamond crystallite size. Thus, the NCD films with a smaller average grain size and higher surface smoothness can be synthesized at a lower pressure. Under low deposition pressure, the quality of the film is not good due to dominantly adsorption of  $\text{sp}^2$  bonding carbon on the substrate surface because of a high concentration of hydrocarbon radicals resulting and weakly etching effect on nondiamond carbon phases due to reducing hydrogen atoms.

### 3.3. Effects of nitrogen concentration

The effects of nitrogen on the growth of NCD films were studied for 1% and 20% at a substrate temperature of 750 °C and a total pressure of 5 Torr. Films morphology was analyzed 0%, 1% and

20% nitrogen concentration (Fig. 3b–c). In NCD film grown without nitrogen only the diamond nano grains are observed (Fig. 1b). The high renucleation rate provided by the presence of  $\text{C}_2$  dimer in the plasma [26,27] limited the grain size within the range of few nanometers. Before a diamond crystal could grow larger, a new growth center is formed and the growth of the former crystal is inhibited. Thus the nano-crystalline diamond crystals are achieved. One of the downsides of a high re-nucleation rate is that it must result in an increased  $\text{sp}^2$  content of the film and this is apparent in the Raman spectra of Fig. 5. For 1%  $\text{N}_2$  there is not enough difference in the morphology apparently (Fig. 3a). The structural and bonding nature showing some differences as depicted in (Fig. 4b and 5b).

The morphology of the NCD film surface undergoes changes when 20% of nitrogen is added in the gas mixture (Fig. 3b): elongated nanostructures appear along with diamond nanograins, whereas a granular structure is typical for the film grown without nitrogen. It might be because of the formation of CN molecular species stimulated when more concentration of nitrogen was introduced into the plasma. It is also shown in the Raman spectra (Fig. 5b–c) of the nitrogen doped samples. CN molecular species reduced the renucleation rate by consuming  $\text{C}_2$  dimers [27,28]. This creates favorable conditions for an increase of the grain size and the formation of elongated diamond nanostructures.

The increase in grain size was observed by many researchers [12,13,27] as the nitrogen content increased from 0% to 20% in microwave plasma CVD. In our results, the length of diamond nanocrystallites is not as long as reported by using MPCVD system. It might be because of less energetic species in HFCVD as compared to energetic species produced in high power plasma field.

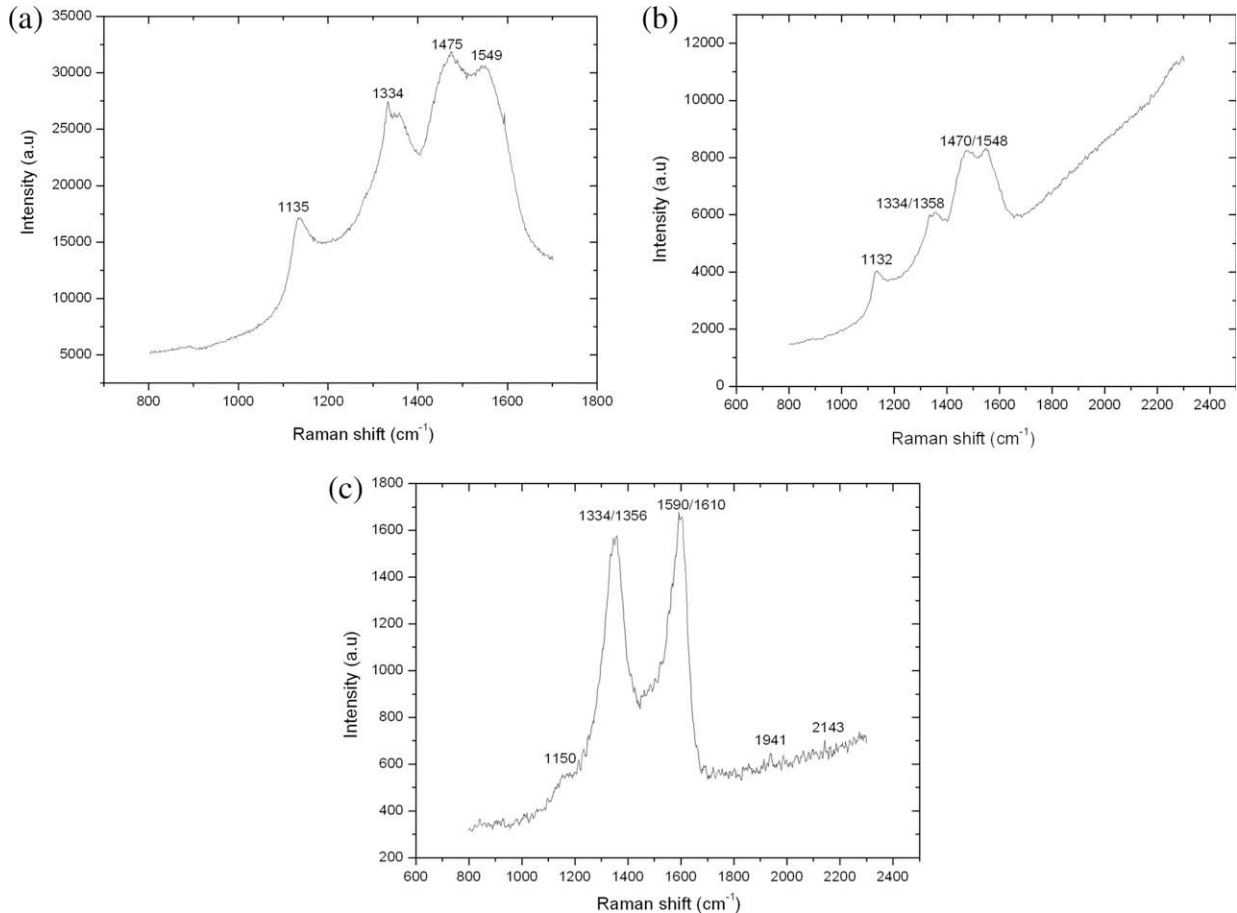


Fig. 5. Raman spectra of NCD films for (a) 0% (b) 1% and (c) 20%  $\text{N}_2$ .



XRD patterns of films are shown in Fig. 4a–c. The XRD spectra of the NCD films deposited from 0, 1 to 20 vol.% of N<sub>2</sub> are dominated by the diffraction peaks at 43.9° and 75.3° corresponding to the (1 1 1) and (2 2 0) diamond that confirmed the presence of crystalline diamond. It was observed in the XRD pattern (Fig. 4c) that the peaks became narrow indicating an increase in size after adding nitrogen 20% in the plasma. This behavior is in accordance with SEM images (Fig. 3b). This tendency is agreement with the argument that nitrogen reduces renucleation rate and size increases. It is also important to note that line broadening of XRD peaks, may be strongly affected by the crystal defect density [29,30]. So, it might also be considered as a result of the increased defect density induced by the increased nitrogen concentration. The intensity of (2 2 0) peak is higher than the intensity of (1 1 1) peak in 0% and for 20% nitrogen samples except for sample with 1% nitrogen. For CVD diamond, it is well established that the growth rate of the (1 1 0) planes is higher than those compared to the (1 1 1) and (1 0 0) planes [31]. For NCD, which seems to show an absence of well faceted crystals, it is rational to assume that the nanometric (1 1 0) growth sectors develop faster than the others, which could bring about structures elongated along the (1 1 0) axis. No crystalline graphite was observed in the XRD patterns.

Fig. 5 shows Raman spectra of three samples recorded at the excitation wavelength of 514.5 nm in a wide range of 1000–2400 cm<sup>-1</sup>. Raman measurements (Fig. 5a–c) are in good agreement with morphologic changes presented by SEM analyses. The resulting Raman signal intensity decrease for higher level N<sub>2</sub> doping, it might be because of the optical absorption of the films in the visible range gradually increased with nitrogen content. Raman spectra of film grown with 0% N<sub>2</sub> is shown in Fig. 5a. The diamond peak is at 1334 cm<sup>-1</sup>. A broad peak at 1357 cm<sup>-1</sup> (D) represents non-diamond phases and a G peak centered at 1549 cm<sup>-1</sup> correspond to graphite. It is suggested that this is due to the bond stretching of all pairs of sp<sup>2</sup> atoms in both rings and chains [32]. The two shoulders at 1135 and at 1475 cm<sup>-1</sup> that are much lower for spectra obtained with 1% and 20% N<sub>2</sub> (Fig. 5b–c). This pair of peaks is the transpolyacetylene (TPA) segments at the grain boundaries of NCD surface [33]. The main changes for these bands with N<sub>2</sub> content are: (i) increasing of the G peak intensity, and (ii) the shift in position of G band to higher wave numbers, from 1549 (0% N<sub>2</sub>) to 1590 cm<sup>-1</sup> (20% N<sub>2</sub>) indicating an increase in sp<sup>2</sup> phase after nitrogen addition in the films. Shifting of shoulder from 1135 to 1150 cm<sup>-1</sup> is observed. Frequency region of sp<sup>2</sup> and sp<sup>1</sup> hybridized CC(CN) [34] stretching modes in chain-like structures is from 1900 to 2400 cm<sup>-1</sup> (see Fig. 5c). Considering that PA was observed in our films, it is reasonable to ascribe the line at 1941 cm<sup>-1</sup> to the stretching vibrational modes of acetylene (–C≡C–) and allene (>C=C=C<) groups [35]. Other two lines are assumed to originate from vibrations of acetylene and allene derivatives, in which nitrogen substitutes carbon and/or is connected to the groups. Thus the line at 2143 cm<sup>-1</sup> is assigned to C=N vibrational modes of carbodiimides and paracyanogen-like chains (–N=C=N–, –N=C=C=N–) [35,36].

In order to investigate in more detail, additional microscopic studies are needed for a better understanding of the specific roles of nitrogen in NCD films in HFCVD.

#### 4. Conclusions

The changes in the morphology, crystalline structure and bonding nature of NCD films as a function of nitrogen concentration in HFCVD are studied. XRD characterizations presented diffraction peaks of crystalline diamond. The increased crystalline size of diamond nanograins was also observed by the narrowing XRD peaks

as the nitrogen concentration increases. The characteristic D and G Raman bands were presented in all the films. The increase intensity of G peaks indicated that graphite phase increased with the addition of nitrogen in the samples. The reduction in C<sub>2</sub> species due to the formation of CN species might be responsible for the increase in crystallite size.

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