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CVD synthesis of multi-layered polycrystalline diamond films with reduced roughness using time-limited injections of N₂ gas

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Abstract

Multi-layered polycrystalline diamond (PCD) films were synthesized using microwave plasma-assisted chemical vapor deposition (CVD) with periodical addition (injections) of N₂ gas to the standard CH₄-H₂ gas mixture. The aim of such approach was to reduce the roughness of the films while preserving the overall high quality and phase purity of the PCD material. The thicknesses of the films were in the range from 5 to 51 microns, while the number of layers was from 1 to 15. The introduction of even smallest amount of nitrogen leads to a significant (more than 2-fold) increase in the growth rate of PCD films. Optimized injection regimes allowed the reduction of the relative roughness (S_q /thickness) of the PCD films by more than 3 times in comparison with standard microcrystalline diamond film grown under similar conditions without N₂ addition. The proposed method of periodic injection of N₂ during growth restricted the formation of continuous NCD layers, which improved the overall sp³/sp² ratio in comparison with standard multi-layered MCD/NCD materials. The obtained multi-layered PCD materials with reduced roughness may be used for the formation of protective and hard covers, optical coatings, electrochemical and thermal management applications.

Keywords: polycrystalline diamond; CVD synthesis; microwave plasma; multi-layered films; roughness.

1. Introduction

The chemical vapor deposition (CVD) technique allows the engineering of various single- and poly-crystalline diamond materials [1] with a control over their crystalline quality [2–4], chemical purity [5–7], as well as the design of new composite [8–11] and multi-layered structures [12–14]. Such a variety of CVD-grown diamond materials is in high demand for gem industry [15], optics/photonics [16–18], electronics [19,20], tribology [21], biomedicine [22], etc. For all these applications, the control over structure and characteristics of the synthesized material is extremely important.

Yet, the structure of CVD-grown high-quality polycrystalline diamond (PCD) films is somewhat rather typical for different growth conditions and even for different CVD sub-types, as the synthesis in all cases follows the van der Drift competitive growth model [23]. The general trend for such growth process is that the average lateral size of crystallites increases with the thickness of the PCD film [24], which results in a proportional increase in the roughness of the film surface [25,26]. Thus, for the CVD-grown PCD films, a rough surface with large well-faceted randomly-oriented crystallites is to be expected [27]. The high roughness of as-grown PCD films is usually seen as a drawback for applications in optics, electronics and cutting tools, while mechanical polishing of PCD material is extremely difficult due to diamond being the hardest of all known materials [28–30]. Thus, the synthesis of polycrystalline diamond films with reduced roughness is an interesting and yet important objective.

One of the ways CVD allows to obtain diamond materials with desired properties is the ability to choose proper growth conditions with the option of altering them during the CVD process. The latter is widely used for the formation of multi-layered diamond films, which consist of alternating layers of microcrystalline and nanocrystalline diamond (MCD and NCD, accordingly) [31,32]. Such films may serve as hard covers to enhance the performance of various cutting tools [33–37].

The formation of MCD and NCD multilayers in one CVD process is achieved by drastically changing the methane concentration in the standard $\text{CH}_4\text{-H}_2$ reaction gas mixture during the deposition [4,38,39]. However, the drawback of such an approach is the relatively small gas flow rates in comparison with the chamber volume. Although, increased gas flows may be used to compensate such a problem [40,41], it would increase the total gas consumption per sample. In addition, such gradual changes in CH_4 concentration have a complex effect on the structure of the PCD film [4]. An alternative technique is to switch the CVD

process between “MCD” and “NCD” growth regimes is through the addition of nitrogen gas (N_2) to the standard CH_4 - H_2 reaction gas mixture [31,42–46]. However, in such cases, the overall crystalline quality of diamond deteriorates due to the reduction of the average grain size and the increase in the portion of sp^2 graphitic phase, which is present in the grain boundaries. Furthermore, the formation of continuous NCD layers limits the use of such multi-layered MCD/NCD films in optics and for heat-spreader applications due to a low thermal conductivity [47] and high optical absorption [48] of NCD material.

In this work, we propose a new approach to the formation of multi-layered PCD films using microwave plasma-assisted CVD with periodical time-limited addition (injections) of N_2 gas to the standard CH_4 - H_2 gas mixture. The purpose of N_2 gas addition is to stimulate secondary nucleation on already formed micrometer-sized faceted diamond grains, which limits their further growth (see Fig. 1). The introduction of nitrogen is expected to increase the sp^2 content in the PCD films, but, in contrast to uninterrupted N_2 feed, limited periodic N_2 injections allow to prevent the formation of the continuous nanocrystalline diamond (NCD) layers, making it possible to grow high-quality microcrystalline diamond layers between N_2 injections. Furthermore, this approach will reduce the roughness of the obtained films while preserving the overall high quality and phase purity of the PCD material.

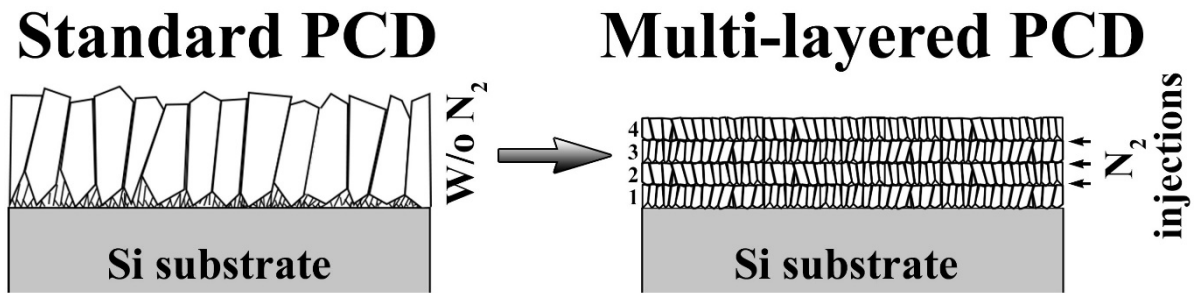


Fig. 1. Scheme for the cross-section of the standard CVD-grown PCD film and the multi-layered diamond film grown with N_2 injections.

2. Experimental

Single-crystal (100) silicon wafers with dimensions of $10 \times 10 \times 0.35$ mm³ were used as the initial substrates. To stimulate the growth of diamond, these substrates were seeded with diamond nanoparticles (5 nm) by immersing the substrate in an aqueous colloid containing the seeds. The details of the seed solution preparation can be found in Hees et al. [49]. Microwave plasma CVD synthesis of diamond was performed in an ARDIS-100 reactor (2.45 GHz, Optosystems Ltd., Russia) [4]. Growth conditions for all samples were: total gas

flow 500 sccm, chamber pressure 75 Torr, microwave power 4.5 kW, substrate temperature 850 ± 15 °C.).

In the normal regime, the gas feed was $H_2/CH_4 = 480/20$ sccm [4], while during nitrogen injections it was changed to $H_2/CH_4/N_2 = 480/20/20$ sccm [43,44] without changing any other parameters. A slight increase in substrate temperature (~ 25 °C) was observed during the injection phase of growth. The total deposition time was varied between 3 to 15 hours for different experiments.

The internal volume of the reactor is 10 liters (or 10000 cm^3), meaning that with a pressure of 75 Torr and gas flow of 500 sccm, it takes ~ 2 min to supply the amount of gas which is enough to fully renew the gas mixture in the chamber. This time can be viewed as the “relaxation” time for the gas concentration to reach new equilibrium state of newly set proportion of the gases in the chamber. The optical emission spectroscopy (OES, OceanOptics 4000 instrument) was used for the precise determination of such relaxation time by the dynamic of change of integrated intensity of CN band (violet band system, $\Delta v = -1$) near 421 nm [50,51]. This particular band was chosen due to absence of interfering peaks of standard H_2 - CH_4 plasma (see Fig 2a). A full cycle of injection and removal of N_2 was investigated. The experimental data were fitted with single exponents to calculate relaxation times for both of these processes, which were found to be near 95 s (Fig. 2b). We also note the interesting fact that N_2 decreases the intensity of the CH- and C_2 - related bands at (i) 431 nm and (ii) 474/516 nm, respectively, which might be explained by the consumption of carbon atoms needed for the formation of CN radicals in plasma.

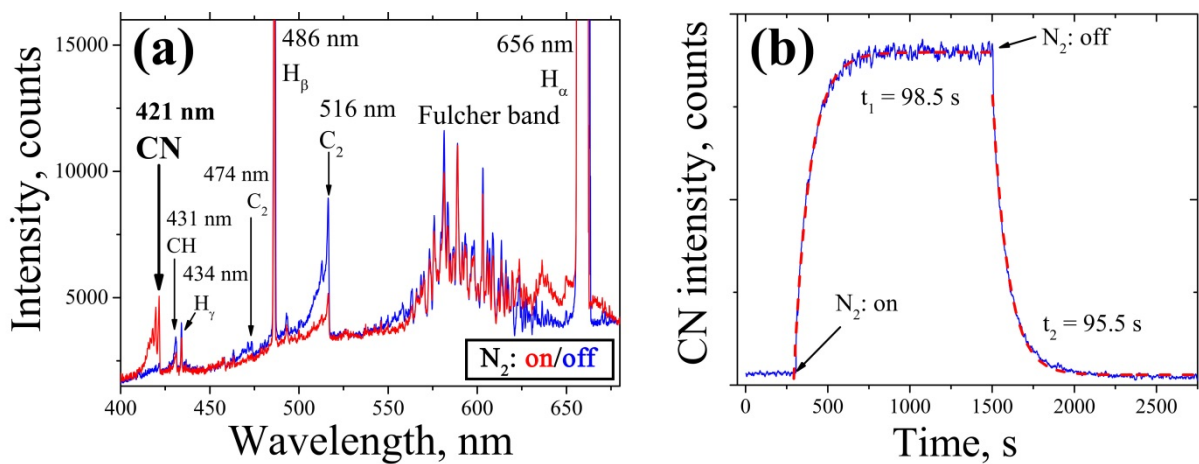


Fig. 2. The OES spectra of the H_2 - CH_4 plasma in regimes with- and without N_2 addition (a), and the dynamic of the change of nitrogen-related CN set of peaks near 421 nm (b).

The surface and cross-sectional morphology of the synthesized films were examined with scanning electron microscope (SEM), Tescan MIRA3. The “root mean square height of the surface” values (S_q as in *ISO 25178*) for the films were measured over the area of $140 \times 140 \mu\text{m}^2$ using an optical profilometer ZYGO NewView 5000 with a $\times 100$ objective lens with lateral resolution of $0.45 \mu\text{m}$ and vertical resolution of 3 nm .

The phase composition of the films were analyzed at room temperature with micro-Raman spectroscopy using LABRAMHR-800 spectrometer equipped with a diode-pumped solid-state laser ($\lambda_{\text{exc}} = 473 \text{ nm}$). The spectrometer operated in a confocal mode, while the laser beam was focused in a spot of $\leq 1 \mu\text{m}$ in diameter on the sample surface.

3. Results

3.1. Effect of N_2 injection times in four-layered PCD films

The initial experiments were performed using a wide range of possible nitrogen injection regimes with a total of 4 injections (thus, 4 layers) serving as an indicator of the structure of multi-layered PCD film. On the other hand, the different periods of the “normal growth” regime ($H_2/CH_4 = 480/20 \text{ sccm}$) between injections were also tested. Hereinafter one “normal growth” period (t_{norm}) was always followed by one “nitrogen injection” period (t_{N_2}) and is called one “cycle” ($t_{\text{cycle}} \equiv t_{\text{norm}} + t_{N_2}$). The performed preliminary experiments showed following tendencies: (i) in cases of $t_{\text{cycle}} < 30 \text{ min}$, the PCD film tends to be either NCD or MCD, with little evidence of the layered structure, (ii) even short-term periodic injections with $t_{N_2} < 1 \text{ min}$ led to the decrease in the film roughness, (iii) the regime with $t_{\text{cycle}} = 60 \text{ min}$ and $t_{N_2} = 5 \text{ min}$ lead to the formation of the desired multi-layered structure of the film. Considering the fact that such t_{N_2} are comparable with gas relaxation times of t_0 (Fig. 2b), we conclude that actual nitrogen concentration never reaches the saturation, which is determined by the gas feed. Thus, hereinafter, we use the term “injections” for such short-term gas addition regimes.

SEM images of the surface and cross-section of such PCD film grown with $t_{\text{cycle}} = 60 \text{ min}$ and $t_{N_2} = 5 \text{ min}$ are shown in Fig. 3. On the surface, well-faceted diamond crystallites with the size of $\sim 2 \mu\text{m}$ were observed (Fig. 3a). The cross-section images revealed a 4-layered structure in the film (Fig. 3b). Interfaces between neighboring layers (Fig. 3c) were clearly distinguishable and included smaller diamond crystallites with the sizes of $20\text{-}50 \text{ nm}$. The thickness of such NCD interlayer was $\sim 250 \text{ nm}$ (Fig. 3d). The further investigation of the CVD

synthesis and injections regimes was performed in an attempt to obtain multi-layered PCD films without the formation of the continuous NCD layer.

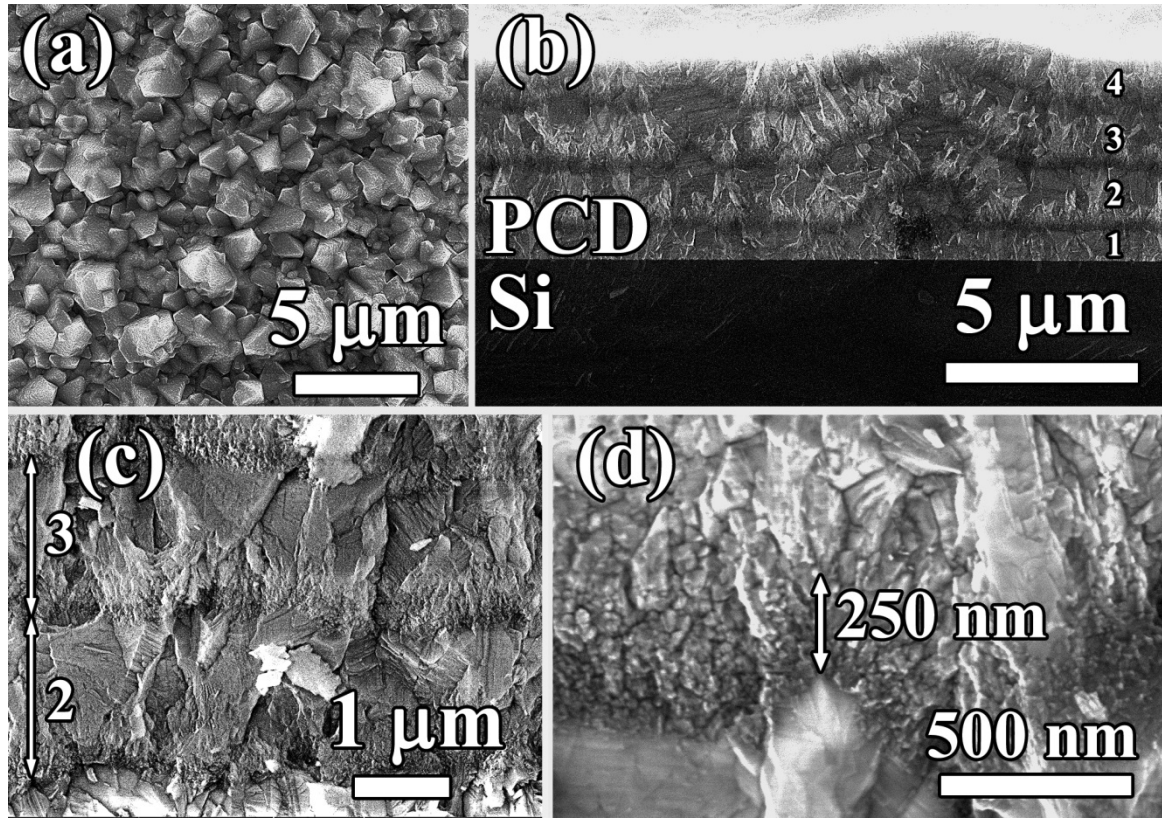


Fig. 3. SEM images of the 4-layered PCD film grown with $t_{\text{cycle}} = 60$ min and $t_{\text{N}_2} = 5$ min: (a) film surface, (b) cross-section, (c) close-up view of the interface between layers, (d) close-up of the interface between two layers. Note in (b) that the layered structure follows the macro-defects of the film as the whole.

As the presence of high amount of the NCD phase was unwanted, similar regimes with $t_{\text{cycle}} = 60$ min and t_{N_2} from 1 to 7 minutes were investigated in more details.

3.2. Synthesis and study of fifteen-layered PCD films

One reference PCD film was synthesized using the "normal" regime with $t_{\text{norm}} = 15$ h without any nitrogen additions at any stage of CVD growth. This sample served as a standard for comparison with the subsequently grown multi-layered samples. Next, a series of 4 samples were synthesized with the only variable parameter of $t_{\text{N}_2} = 1, 3, 5$ and 7 min. The total deposition time for each sample was also 15 hours. Thus, each of these multi-layered samples was synthesized in 15 growth cycles.

A series of SEM images of surfaces and cross-sections of all films are shown in Fig. 4. The images show a clear decrease in the average crystallite size of the

diamond film even with smallest addition of nitrogen. The cross-sections of all films synthesized in the regime with periodic nitrogen injections show a multi-layer structure. A significant increase in the overall thickness of the films (from 21 μm up to 51 μm , or by a total factor of 2.4) was observed.

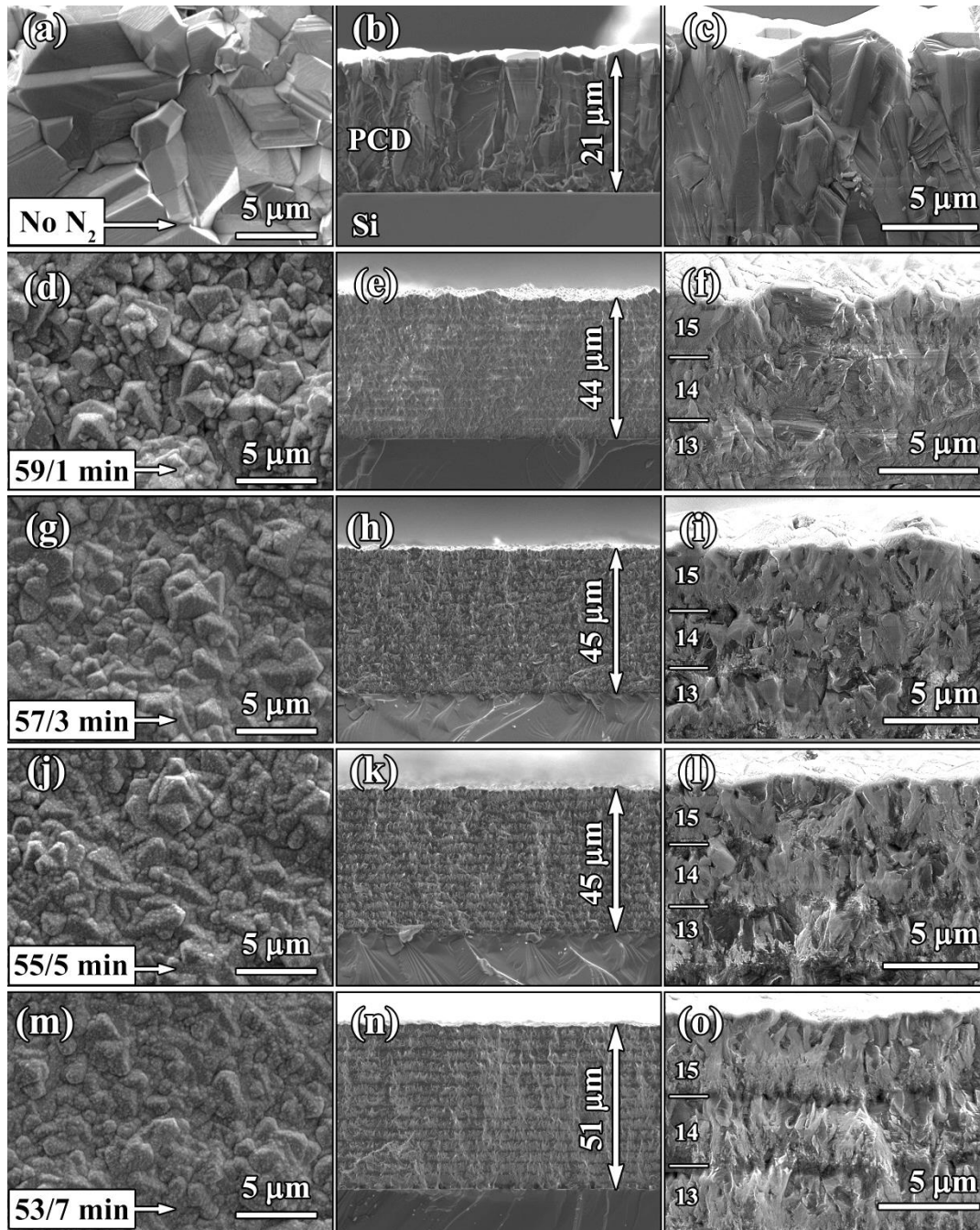


Fig. 4. SEM images of the surfaces (a, d, g, j, m) and cross-sections (b, e, h, k, n) and close-ups of the cross-sections near the surface (c, f, i, l, o) of the multi-layered PCD films, synthesized in microwave plasma CVD in similar growth conditions with different N_2 injection times (t_{N_2}). The growth regimes for each row of images are indicated in the bottom-left corner of the first picture in a row.

The trend for the gradual formation of the continuous NCD layers with increasing t_{N_2} may be observed in the close-up images of the cross-sections of the films near their surfaces (Fig. 4, right column of images). For the regime with $t_{N_2} = 1$ min, no sign of a separate NCD phase is seen. However, the further increase in the t_{N_2} leads to the formation of separate NCD islands, resulting in the formation of the continuous NCD layer at $t_{N_2} = 7$ min (see Fig. 4o).

3.3. Surface roughness

The surface roughness of the films was studied by optical profilometry (Fig. 5a). The profiles (see Fig. 5a, inset) were used to determine the S_q values for each sample. In order to exclude the factor of different film thicknesses (h), the ratio of roughness of the sample to its total thickness (S_q/h) was also taken as an additional parameter under study. For the single-layer (no N_2 injection) sample the roughness was $S_q = 645$ nm, while corresponding value of $S_q/h = 0.311 \pm 0.005$, which is close to the values of S_q/h for typical CVD-grown microcrystalline diamond films in other experimental works, for example in [25,26]. A rapid decrease in the relative roughness was registered even for short-termed addition of nitrogen. However, further increase of t_{N_2} leads to an increase in surface roughness. The cross-section of the PCD film grown with $t_{N_2} = 7$ min is shown in Fig. 5b. Detailed analysis of the film structure showed that the reason for such increase is not in the formation of faceted diamond crystallites, but rather in the formation of large ($>10 \mu m$) ball-shaped cluster defects (Fig. 5b and 5c), which are frequently observed in CVD-grown NCD films [52,53]. In spite of locally smooth surface, the formation of such clusters affects the overall roughness of the film. Still, the cross-section of such a cluster reveals its layered structure (Fig. 5c).

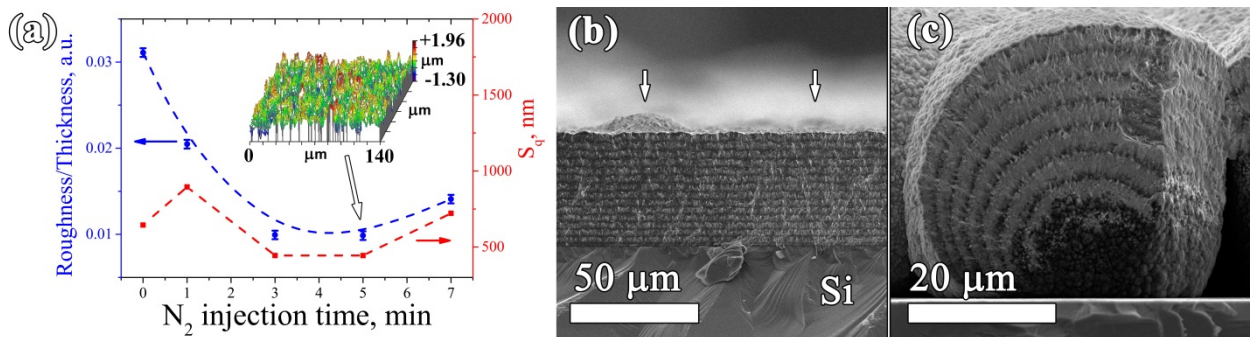


Fig. 5. Dependence of the relative and absolute roughness S_q of synthesized PCD films on t_{N_2} . The "0" value corresponds to a "normal" CVD regime without nitrogen additions (inset – optical profilometry image of the sample grown with $t_{N_2} = 5$ min); Cross-section SEM images of the film grown with $t_{N_2} = 7$ min: (b) cross-section of the film (tops of cluster defects on the background shown with arrows), (c) cross-section of the large cluster defect.

3.4. Raman spectra of multi-layered PCD films

The phase composition of the obtained films was studied by Raman spectroscopy (Fig. 6). The main feature of the spectra is a characteristic peak of diamond at 1333.3 cm^{-1} . The additional features observed only for multi-layered samples are the D- and G- peaks of the graphitic sp² phase (1350 cm^{-1} and 1580 cm^{-1} , accordingly) and the wide band at 1480 cm^{-1} is trans-polyacetylene (t-PA), present on the grain boundaries. It was found that the fraction of sp² carbon in multi-layered samples significantly increases with the transition from “normal” CVD synthesis to injection regimes even with the smallest amount of nitrogen. For each multi-layered sample, all peaks were approximated with Gaussians, and the area under each peak was separately calculated. Based on this data, the sp³ phase (area under diamond peak) to sp² phase (combined area under graphite and t-PA peaks) ratio dependence on the amount of injected nitrogen was calculated (Fig. 6b) which shows a near-linear decrease in the sp³/sp² ratio with the t_{N_2} .

The phase composition of the layers was studied in more detail using Raman mapping on the cross-section in the central $5 \times 5\text{ }\mu\text{m}^2$ area (30x30 pixels) of the multi-layered film grown with $t_{\text{N}_2} = 3\text{ min}$ (see Fig. 4h). For every pixel, a full Raman spectrum was taken. After such procedures were performed for the whole area of the study, an averaged spectrum was compiled to be used as a reference for the evaluation of each individual spectrum for each pixel: green color corresponding to excessive sp³ phase with increased diamond peak (integrated intensity for $1325\text{-}1345\text{ cm}^{-1}$), while red pixels indicate an increased sp² band ($1450\text{-}1645\text{ cm}^{-1}$).

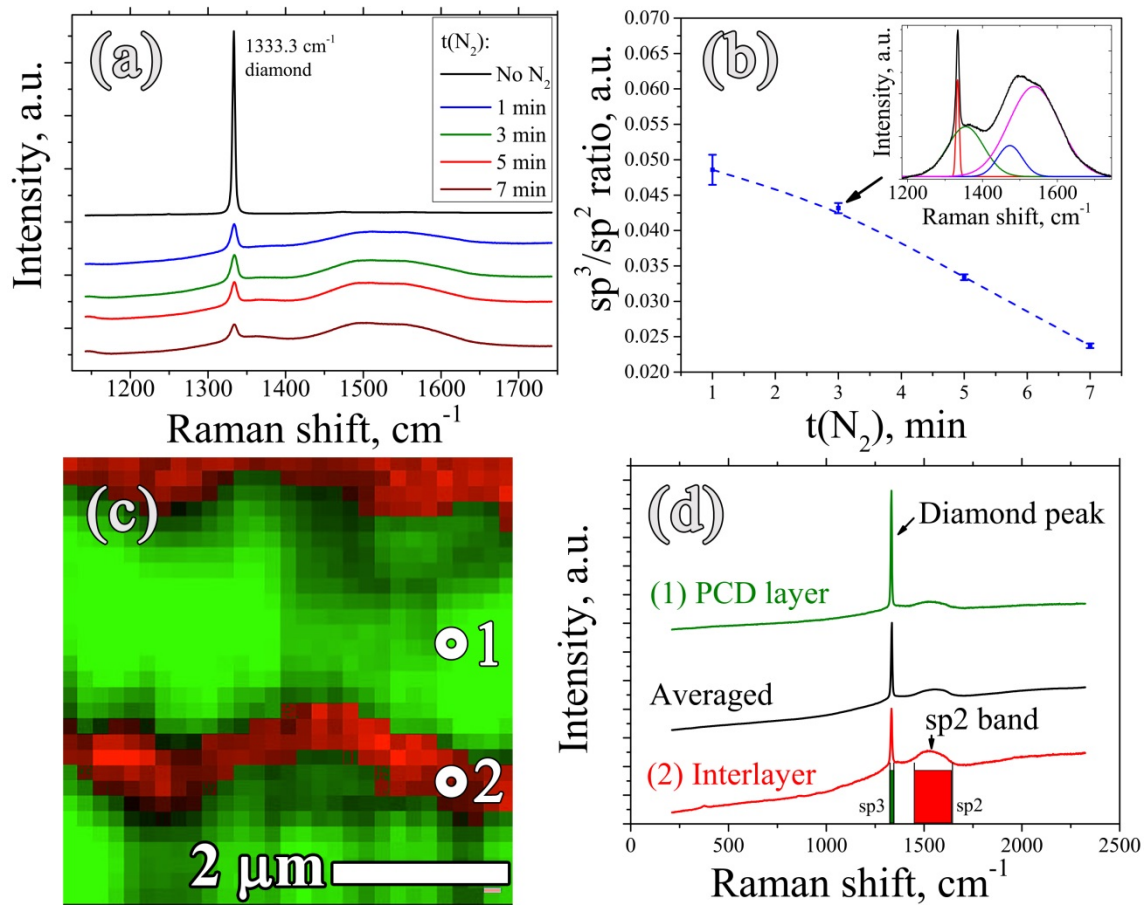


Fig. 6. Raman spectra of the diamond films grown with different regimes of nitrogen injections as measured on the top of the film (a); integrated sp^3/sp^2 ratio as function of N_2 injection time for the multi-layered films, based on the Raman spectra. Inset: the spectrum decomposition for sp^3 and sp^2 components (b); Raman mapping of the cross-section of the multi-layered PCD film grown with $t_{\text{N}_2} = 3 \text{ min}$. Green zone (high sp^3/sp^2 ratio) and red zone (lower sp^3/sp^2 ratio) correspond to deposition without and with N_2 injection (c); Raman spectra taken in PCD layer and interlayer parts (see locations #1 and #2 in Fig. 6c) of the sample cross-section (d). In (a) and (d) spectra were shifted along the y-axis for better visibility. In (c), the spectra from the main layer and interlayer are compared with an averaged spectrum for the whole measurement area ($5 \times 5 \mu\text{m}^2$) on cross-section.

4. Discussion

Based on the experimental data, we can summarize that the nitrogen injections stimulates secondary nucleation which directly influences the multi-layered structure of the PCD films. The most prominent effect of such growth regimes is the prevention of the formation of large faceted crystallites, which in turn reduces the overall relative roughness of the film. On the other hand, such multi-layered structure inevitably leads to higher fraction of grain boundary regions, which is confirmed by the decrease of the sp^3/sp^2 ratio. That effect may influence optical properties and thermal conductivity of diamond which needs to be studied in detail.

The observed increase of the PCD film thickness even for smallest N_2 addition suggests that injection regimes of CVD growth tend to increase the average deposition rate of such films. This is in good agreement with previous works in the literature [40,54–57], where increase in the deposition rate of CVD diamond was seen when much smaller amounts of nitrogen were added to the standard CH_4-H_2 gas mixtures.

The shortest injection time of 1 min was less than the gas exchange time $t_0 \approx 2$ min in the reactor, therefore the further reduction of t_{N_2} is expected to lead to a low effective N_2 content in gas mixture, which would result in a better diamond quality, but to lower growth rate and higher surface roughness. A similar effect (no benefit) is expected for longer of t_{N_2} with lower N_2 flow rate. That's why we optimized the injection time to a few minutes. Thus, short-term injections with $t_{N_2} = 1-3$ min were found to be optimal for the reduction of relative roughness with the minimization of the formation of sp^2/NCD phases, while regimes with $t_{N_2} > 5$ min were found to have tendencies towards the formation of cauliflower-like structures.

5. Conclusions

Multi-layered polycrystalline diamond films with a thickness from 5 to 51 microns have been synthesized using microwave plasma chemical vapor deposition in regimes with an optional use of periodical short-termed injection of nitrogen to the reaction (CH_4-H_2) gas mixture. The introduction of even small amount of N_2 (1-3 min injection time per every 60 min growth time) leads to a significant (more than 2-fold) increase in the growth rate of the diamond films, couple to reducing the surface roughness of the films by more than 3 times under optimized injection parameters. This periodic injection of N_2 restricted the formation of continuous NCD layers, thus improving the overall sp^3/sp^2 ratio in comparison with standard multi-layered MCD/NCD materials.

A combination of high thermal conductivity (as expected because of absence of the NCD component) with smooth growth surface of the diamond coatings could be beneficial for superhard tool applications. Using N₂ addition in gas mixture for the stimulation of secondary nucleation we recently [44] produced microcrystalline diamond coatings with NCD top diamond films [35,58], as well as layered MCD/NCD films, on WC-Co cutting inserts, and obtained reduced roughness and good adhesion. After further application-oriented studies, the obtained multi-layered PCD materials have the potential to be used to fabricate protective and hard covers, optical coatings, and thermal management applications.

Prime novelty statement

The multi-layered PCD films were synthesized in a microwave plasma CVD in regimes with short-term periodic N₂ injections in CH₄-H₂ process gas; the average growth rate is doubled owing to the pulsed nitrogen injection, while the surface roughness is reduced by more than 3 times in comparison with a standard (no N₂ injection) microcrystalline film.

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