Optics

Difference in the structure and morphology of CVD diamond films grown on negatively charged and grounded substrate holders: Optical study

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Abstract. Microcrystalline diamond films were grown by plasma-enhanced chemical vapor deposition from a CH₄/H₂ gas mixture on Si single-crystalline substrates placed on negatively charged and grounded substrate holders. The obtained diamond films had the (100) predominant faceting of microcrystals. The film structure and morphology were analyzed by scanning electron microscopy, photoluminescence, Raman and FTIR spectroscopies. The main physical factor causing the difference in the structure of the diamond films grown on the grounded and charged substrate holders was found to be the flow of low-energy (up to 200 eV) Si⁺, N₂⁺, H, O ions in the latter holder. These ions predominantly embedded into the structure of the diamond films grown on the charged substrate holder leading to appearance of residual mechanical stress up to 2 GPa. Ion bombardment led to increase in the volume fraction of non-diamond carbon component in the film grain boundaries, decrease in sp^3 -bonded carbon fraction and reduction of the diamond microcrystals lateral size. Larger amount of grain boundaries in the diamond films grown on the charged substrate holder promoted diffusion of Si atoms from the substrate to the plasma and growing film surface, inducing formation of SiV centers in the diamond microcrystals even in the 150...200 µm thick films. The concentration of Si-related defects was much smaller in the films grown using the grounded substrate holder. These films had substantially smaller volume fraction of graphite-like carbon in the grain boundaries and were more homogeneous.

Keywords: diamond films, PECVD method, photoluminescence, Raman scattering, SiV center.

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1. Introduction

Mechanical stress (σ) in diamond microcrystals of polycrystalline diamond films grown on metal substrates by plasma-enhanced chemical vapor deposition (PECVD) can reach up to ~2.1 GPa. This stress is caused by two main factors [1, 2]. The first factor is the influence of the difference in the lattice parameters and thermal expansion coefficients of diamond and the substrate material. The second factor is related to the presence of certain amount of structural point defects such as substitutional impurity atoms, interstitials and vacancies as well as dislocations. The mechanical stress has a negative influence on the growth process of polycrystalline diamond films (DFs) with maximum thicknesses for electronic applications. When the film thickness reaches $180...200 \,\mu$ m, the stress in the film destroys the metal (molybdenum, stainless steel) substrate [3]. Partial stress decrease can be achieved by using single-crystalline Si wafers as the substrates. The thermal expansion coefficient and lattice constant of Si single crystals are closer to those of diamond

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Fig. 1. Schematic representation of the PECVD growth set-up: configuration with (a) negatively charged substrate holder and (b) with grounded substrate holder.

as compared to metals. Actually, $\alpha(C) = 1 \cdot 10^{-6} / C$ and $\alpha(Si) = 3 \cdot 10^{-6} / ^{\circ}C$, in contrast with widely used molybdenum, for which $\alpha(Mo) = 4.8 \cdot 10^{-6} / ^{\circ}C$. Alternative method to decrease the stress in the grown films includes the seeding procedure, which was described in our previous work [4]. Covering the substrate with diamond seeds leads to the increase in the volume fraction of nondiamond carbon component of the film. This component is a graphite-like mixture of sp^3 and sp^2 carbon bonds located on the film surface and in the grain boundaries. It plays the role of impurity getter during the PECVD growth [5]. Nevertheless, as-grown PECVD polycrystalline DFs have uncompensated mechanical stress $(\sigma \leq 1 \text{ GPa})$ and contain large amount of point defects related to nitrogen and silicon impurities. We believe that the mentioned defects are responsible for the uncompensated stress. The possible origin of such point defects is bombardment of the growing surface by low-energy ionized molecules CH_3^+ , H_x^+ (the energies ~10...50 eV) and uncontrolled impurity ions Si^{2+} and N^+ as well as by electron flux from the direct current discharge plasma [6]. Bombardment of the substrate with electrons, ions and ionized molecules has a positive effect at the beginning of the growth process [8]. The ions form crystallization centers, while electron irradiation stimulates synthesis of atomic hydrogen, which etches the nondiamond carbon component off the growing surface [9, 10]. With the increase of the DF thickness, ion bombardment starts to play a negative role. Namely, it induces lattice disordering and embedding of large amounts of uncontrolled impurity atoms, which increase mechanical stress [2, 10, 11]. At this stage, lateral growth of diamond grains stops and column-like growth predominates. This process is accompanied by formation of a large number

of grain boundaries (non-diamond component). At the same time, the DF homogeneity decreases.

To solve the problem of residual stress in DFs and their low homogeneity, we suggested to use a grounded substrate holder in the PECVD system. Use of such holder leads to a decrease in the DF growth rate [2, 10]. In this work, we compensated the unsubstantial growth rate by increasing the CH_4 fraction in the CH_4/H_2 mixture. We expect that the positive ion and ionized molecules flux will be minimized in the case of the grounded substrate holder due to leakage of negative charge carriers from it.

The aim of the present work is to analyze the differences in the structure and defect states of the polycrystalline DFs grown from the CH_4/H_2 mixture by PECVD using the negatively charged and grounded substrate holders. We also aim to compare the structure and defect states of our films with the respective properties of high quality diamond single crystals.

2. Experimental

The studied DFs were grown by PECVD in the glow discharge stabilized by magnetic field [4, 12]. The growth set-up is schematically presented in Fig. 1a. It has the following peculiarity of the CH_4/H_2 mixture activation. The discharge burns between the cathode and anode in the crossed *E/H* fields. As a result, the discharge rotates around the anode, which prevents its contraction and transformation into an arc discharge at the pressure above 100 Torr.

In this configuration, the substrate holder is isolated from the anode and is under the floating potential, which can reach a few hundred volts depending on the holder



Fig. 2. SEM images of the surface of the DFs grown by the PECVD technique on the biased (a) and grounded substrate holder (b).

size and deposition conditions. The floating potential is created by electron irradiation from the cathode [2, 10].

As a result, the substrate holder is negatively charged and attracts positively charged ions. However, presence of high floating potential (~200 eV) leads to bombardment of the condensation surface by accelerated ions and formation of structural defects in the crystalline lattice resulting in the appearance of residual compressive stress.

To improve the crystalline quality of the DFs and energy-efficiency of the deposition process, the experimental equipment was modernized as shown in Fig. 1b. In the new configuration, the substrate holder was grounded and played the role of anode. The shape of the cathode was also changed from the semispherical to cylindrical one. A permanent magnet with a copper support was mounted in the vacuum chamber. Permanent magnetic field enables the increase of electron density in the plasma, which raises the efficiency of the growth process of diamond films due to additional activation of the gas mixture by electron collisions.

The growth process on the negatively charged substrate holder was carried out from the CH₄/H₂ mixture with the methane fraction of 0.25% at the pressure in the growth chamber of 160 mmHg. The growth rate was 2 μ m/h and the temperature *T* = 1150 °C. The average film thickness was ~35 μ m.

Growth on the grounded substrate holder was carried out from the CH_4/H_2 mixture with the methane fraction of 0.75%. The pressure in the reactor chamber was 100 mmHg, the growth rate was 2.5 µm/h and the temperature T = 980 °C. The substrates were mechanically polished Si single-crystalline plates in both cases.

The morphology of the studied DFs was investigated using a Tescan Mira 3 LMU SEM microscope. Fourier transform infrared (FTIR) analysis was performed using a Bruker Vertex 70V spectrometer. Raman (RS) and photoluminescence (PL) measurements were carried out at room temperature using a Horiba spectrometer.

3. Results and discussion

3.1. SEM characterization

Fig. 2 shows the SEM images of the surface of the studied DFs obtained at similar magnifications. One can see from this figure that the microcrystals on the both DF types have the same (100) predominant faceting. It is clearer for the DFs grown using the negatively charged substrate holder under ion bombardment. The average lateral size of the diamond microcrystals on the samples grown using the charged substrate holder is equal to $2 \mu m$, while it is equal to $6 \mu m$ on the samples grown on the grounded substrate holder. The morphology of the DF in Fig. 2b is more homogeneous as compared to the DF in Fig. 2a, which has column-like crystals with the larger volume fraction of grain boundaries. Hence, absence of ion bombardment leads to formation of more homogeneous DFs with larger microcrystals and indistinct grain boundaries.

3.2. Raman measurements

Fig. 3a shows the RS spectra of the studied DFs normalized to the intensity of the diamond vibrational band at 1332.5 cm⁻¹ (ω_{diam}) corresponding to the F_{2g} symmetry, with decomposition into elementary contours. The RS spectra of both DF types also contain the vibrational bands t-PA₁ and t-PA₂ at 1165 and 1511 cm⁻¹, respectively. These bands are attributed to the presence of trans-polyacetylene (CH_x) molecules on the DFs surface and in the grain boundaries [13]. The band ta-C at 1278 cm⁻¹ is caused by the vibrations in the tetrahedral amorphous carbon structure, namely the sp^3 carbon bonds in the grain boundaries [14]. The well-known bands D and G at 1395 and 1616 cm⁻¹ are caused by the graphite amorphous and crystalline carbon phases, respectively [15–17]. The integral intensity of the RS bands attributed to the non-diamond carbon phases (t-PA_{1.2}, ta-C, D and G) is substantially larger in the DFs



Fig. 3. Room temperature RS spectra of the DFs grown on the negatively charged (1) and grounded (2) substrate holders (a). Shift of the position of the band at ω_{diam} in the spectra of the DFs grown on the negatively charged substrate holder (b).

grown on the negatively charged substrate holder. The mentioned difference in the RS spectra is caused by the larger amount of the non-diamond carbon phase in the grain boundaries of the DFs grown under the ion bombardment. For quantitative analysis of the structural quality of DFs, the authors of [18] introduced the dimensionless quantity called q-factor. This factor can be calculated using the following semi-empirical equation:

$$q = \frac{75I_{\omega diam}}{75I_{\omega diam} + I_D + I_G + I_{t-PA1} + I_{t-PA2} + I_{ta-C}} \cdot 100\%$$

where I_{ootiam} is the area under the band at ω_{diam} , and $I_D + I_G + I_{t-PA1} + I_{t-PA2} + I_{ta-C}$ is the total area under the bands D, G, t-PA₁, t-PA₂ and ta-C, respectively. The coefficient 75 is used to compensate the light scattering cross-sections of the sp^2 and sp^3 carbon phases. The *q*-factor for the DFs grown on the negatively charged substrate holder is equal to 87%, which is somewhat smaller than that for the DFs grown on the grounded substrate holder (96%).

The position of the band at ω_{diam} in the spectra of the DFs grown using the negatively charged substrate holder is shifted by $\Delta \omega = 2.7 \text{ cm}^{-1}$ compared to the spectra of the non-stressed bulk diamond single crystal [19]. Using the shift of the band at ω_{diam} , the value of the residual stress in the diamond microcrystals can be evaluated by $\sigma = A_D \cdot \Delta \omega$, where $\Delta \omega$ is the shift of the frequency position of the band at ω_{diam} in the RS spectrum of the stressed crystals compared to that of the non-stressed crystal. The proportionality coefficient A_D can be calculated as $A_D = \frac{2\omega_0}{p(S_{11} + S_{12}) + q(S_{11} + 3S_{12})}$, where S_{11} , S_{12} are the elastic constants, and p and q are the phonon deformation potentials, respectively. The values of the mentioned constants for diamond are the following: $S_{11} = 1.01 \text{ TPa}^{-1}$, $S_{12} = -0.14 \text{ TPa}^{-1}$, $p = -2.82\omega_0^2$, $q = -1.78\omega_0^2$ [19]. In our case, the calculated value of the residual comprehensive stress in the diamond microcrystals of the DFs grown using the negatively charged substrate holder is $\sigma \approx 1.2$ GPa.

The full width at half maximum (FWHM) of the band at ω_{diam} in the spectra of the DFs grown using the grounded substrate holder ($\approx 4 \text{ cm}^{-1}$) is substantially smaller than for the DFs grown using the negatively charged substrate holder ($\approx 7 \text{ cm}^{-1}$). Both FWHMs exceed the respective value for the high quality diamond single crystal ($\approx 2.1 \text{ cm}^{-1}$) [18, 19]. The substantially smaller FWHM of the band at ω_{diam} in the spectrum of the DFs grown using the grounded substrate holder is caused by the increase in the lifetime of Raman phonons due to the lower concentration of structural defects, which takes place in the case of the absence of lowenergy ion bombardment.

Consequently, the films grown using the negatively charged substrate holder are stressed and have larger fraction of the non-diamond component on the surface and in the grain boundaries. The peak position of the band at ω_{diam} in the RS spectra of the DFs grown using the grounded substrate holder (without ion bombardment) is similar to that for the non-stressed bulk diamond single crystals [20].

As was mentioned above, the DFs contain a nondiamond component in the grain boundaries. This component is a mixture of sp^3 and sp^2 hybridized carbon bonds. Therefore, it is expediently to know how the lowenergy ion bombardment affects the sp^2/sp^3 carbon phase composition [21]. For calculation of the sp^3 carbon bonds fraction in the grain boundaries, two following approaches can be used. The first one is that the sp^3 bonds fraction can be evaluated from the simple ratio of the intensity of the ta-C RS band to the intensities of the RS bands attributed to the sp^2 -bonded carbon, because tetrahedral amorphous carbon contains sp^3 -bonded atoms:

$$sp^{3} cont = \frac{75I_{ta-C}}{75I_{ta-C} + I_{G} + I_{D} + I_{R1} + I_{R2}} \cdot 100\%,$$

where I_{ta-C} is the area under the ta-C band, and $I_G + I_D + I_{R1} + I_{R2}$ is the total area under the t-PA₁, t-PA₂, D and G bands, respectively. As was mentioned above, the coefficient 75 is used to compensate the difference in the light scattering cross-sections of the sp^2 and sp^3 carbon phases [18].

On the other hand, the positions of the G vibrational bands are sensitive to the sp^2/sp^3 carbon phase composition. In this case, the sp^3 carbon fraction can be evaluated by the relation first proposed by the authors of [22]:

$$sp^{3} cont = (0.24 - 48.0(\omega_{G} - 0.1580)) \cdot 100\%$$
,

where ω_G is the frequency position of the *G* band expressed in $[\text{cm}^{-1} \times 10^{-4}]$.

The values of the fraction of sp^3 carbon bonds calculated using the two approaches are approximately equal and make ~20% for the DFs grown using the negatively charged substrate holder and ~30% for the DFs grown using the grounded substrate holder. This means that the fraction of tetrahedral amorphous carbon (non-diamond sp^3 carbon phase) in the grain boundaries of the DFs grown without low-energy ion bombardment is larger. Tetrahedral amorphous carbon connects the sp^2 clusters, which constitute approximately 80% and 70%, respectively, of the total amount of the non-diamond carbon phase in the grain boundaries. The intensities of the D and G vibrational bands enable evaluation of the average lateral size of graphite-like clusters using the following equation [15, 16]: $\frac{I_D}{I_G} = \frac{C(\lambda_{ex})}{L_a}$, where I_D and

 I_G are the areas under the D and G vibrational bands, respectively, C is the constant, which depends on the excitation wavelength, $C(\lambda_{ex} = 488 \text{ nm}) = 44 \text{ Å}$, and L_a is the average lateral size of the graphite-like clusters on the surface and in the grain boundaries of the DFs, respectively. The calculations show that the DFs grown on the charged substrate holder are characterized by the graphite clusters ~ 40 Å in size, while use of the grounded substrate holder leads to a decrease in the cluster lateral size to 30...33 Å.

Thereby, absence of low-energy ion bombardment in the PECVD process leads to formation of non-stressed DFs with lower fraction of non-diamond component in the grain boundaries. This component consists of graphite clusters ($L_a \approx 30...33$ Å) surrounded by the larger (30% as opposed to 20% in the DFs grown using the negatively charged substrate holder) volume fraction of tetrahedral carbon bonds. We have performed PL investigations to compare the defect-impurity states in both DF types.

3.3. PL analysis

In the case of the grounded substrate holder, absence of ion bombardment in the PECVD process led to substantial change in the DF structure and morphology. Therefore, excluding ion bombardment from the growth process should affect the DFs radiative properties. Fig. 4a shows the PL spectra of both DF types. One can see from this figure that NV and SiV optical centers dominate in the PL spectra of both film types. An NV center is a defect consisting of a carbon vacancy (V) and a neighboring nitrogen atom in substitutional position (N_s) [23–27]. There are two types of NV centers. The first type is neutral (NV⁰) centers that cause the zerophonon luminescence (ZPL) band at 2.15 eV. This ZPL is followed by three phonon replicas I_1 , I_2 , I_3 separated from each other by ~42 meV with FWHM increasing with the number of replica. Another ensemble of emission lines with ZPL at ~1.945 eV is caused by negatively charged NV⁻ centers. In this case, the phonon energy is equal to 65 meV (see the green set of contours in Fig. 4). A SiV center is the defect, which consists of a carbon vacancy and a neighboring Si atom [26, 27]. ZPL of the radiative recombination with participation of SiV centers is centered at ~1.68 eV [26, 27]. The NV^0 , $NV^$ and SiV bands are formed as a result of intracenter luminescence. Presence of nitrogen-related impurities in the DFs is caused by vacuum imperfection in the reactor chamber [2, 10]. One can see that the integral PL intensity for the DFs grown using the negatively charged substrate holder is substantially larger due to the larger concentrations of SiV and NV optical centers in the diamond microcrystals and larger volume fraction of the non-diamond carbon component in the grain boundaries. Wide PL background W with the peak position at ~2.0 eV is attributed to radiative transitions between the energetic subbands created in the diamond energy gap due to dispersion of the angle and length of C-C bonds in the non-diamond component of the DFs [28-30]. The energy peak position at ~ 2.0 eV correlates well with the average lateral size of graphite clusters evaluated using the RS data and Tauc gap ($\approx 1.95 \text{ eV}$) obtained by the semi-empirical equation proposed in [22]: $E_{p}(\text{Tauc}) = 0.92 + 28410(\omega_{G} - 0.1580)^{2}$. In the latter equation, the Tauc gap is expressed in [eV] and ω_G is the frequency position of the G band expressed in $[cm^{-1} \times 10^{-4}]$.

The smaller intensity of the W band in the spectrum of the DFs grown using the grounded substrate holder can be caused by the larger concentration of nonradiative recombination centers produced by carbon dangling bonds [31]. Actually, decrease in the size of the graphite-like clusters should increase the carbon dangling bonds concentration [31].

Hence, ion bombardment leads to the effective embedding of nitrogen and silicon atoms into the diamond microcrystals. In this case, Si atoms get into the glow discharge plasma during the ion bombardment of the Si substrate [32, 33]. Thermal diffusion from the substrate should also occur. When DF becomes continuous



Fig. 4. PL spectra of the studied DFs grown using the negatively charged (1) and grounded (2) substrate holders (a). Schematic representation of the growth processes with the negatively charged substrate holder (b) and with the grounded substrate holder (c).

(reaches the height h = 100...200 nm), the substrate can no longer be a source of SiV centers [32, 33]. Presence of the SiV centers in the upper layers of the thick DFs (the height $h = 30...100 \ \mu m$) evidences another source of Si atoms. We believe that at a high substrate temperature (~1000 °C) and presence of a voluminous system of the grain boundaries, which takes place in the DFs grown under the ion bombardment, Si atoms can diffuse on the surface of a growing film via the grain boundaries [33]. During the interaction of the non-diamond DF component with the plasma, Si atoms reach the plasma, form ions and incorporate as SiV centers into the diamond microcrystals. Therefore, the substantially larger SiV band intensity in the spectra of the DFs grown using the negatively charged substrate is caused by the open grain boundaries and their larger volume fraction. Figs. 4b, 4c schematically show the diffusion processes for both reactor configurations. As follows from the SEM images, the DFs grown on the negatively charged substrate holder has columnar grains with open boundaries. Grounding the substrate holder leads to the formation of continuous DFs with closed boundaries, which makes impossible Si atoms from the substrate to get into the plasma.

3.3. FTIR measurements

Fig. 5 presents Fourier-transform infrared spectra (FTIR) of the studied DFs as well as the HPHT diamond single crystal grown under the thermo-baric impact in the

toroid-like high pressure chamber at the pressure of 5 GPa and the temperature of 1500 °C using the Ni-B-Ti-C catalyst [34]. This diamond single crystal was used as a benchmark sample to compare the structural properties. The spectra show a wide range of vibrations corresponding to boron-related defects (700...950 cm⁻¹), nitrogen-related defects (950...1450 cm⁻¹), diamond lattice absorption in the two-phonon region $(1500...2700 \text{ cm}^{-1})$ and C-H stretching vibrations $(2700...3700 \text{ cm}^{-1})$ [35, 36]. To simplify the analysis of the wide range spectra, we divided them into three regions: 700...1500, 1500...2700 and 2700...4000 cm⁻¹. Fig. 6 presents the FTIR spectra of the studied samples in the frequency range associated with absorption due to the vibrations of the defects that contain boron and nitrogen atoms. The boron atoms induce the adsorption band at ~ 856 cm⁻¹. One can see the non-zero absorption near 856 cm^{-1} in all samples, which indicates presence of boron-related impurities in the DFs and diamond single crystal.

Presence of boron impurities in the structure of the HPHT diamond can be explained by the peculiarities of the growth process with boron-containing catalyst [34]. Presence of boron impurity in the diamond microcrystals of the studied DFs is caused by the diffusion of the boron atoms from the Si single crystalline substrate, which was previously doped with B atoms ($N_{\rm B} \le 10^{16}$ cm⁻³). In the spectral region of 1000...1400 cm⁻¹, the absorption bands corresponding to nitrogen-containing defects such



Fig. 5. Room-temperature absorption spectra of the high quality bulk diamond single crystal and the studied DFs grown using the negatively charged (1) and grounded (2) substrate holders.



Fig. 6. Room-temperature absorption spectra of the studied materials in the one-phonon region.

as C-centers (isolated single substitutional nitrogen atoms) and B- and A-centers (defect agglomerates, which include several nitrogen atoms surrounding a carbon vacancy V_C) dominate [20]. One can see that the intensities of the absorption bands attributed to isolated substitutional nitrogen atoms are larger in the spectra of the bulk single crystals. The latter can be explained by the peculiarities of the growth processes of the HPHT crystals and the PECVD films. The concentration of nitrogen atoms can be calculated using the following semi-empirical equation proposed in [37]: $C_{\rm N} = 160.49 \cdot 10^{18} \left(\frac{S_{\rm N}}{S_0}\right)^{0.9919}$, where $C_{\rm N}$ is the concentration of nitrogen atoms in [at./cm³], $S_{\rm N}$ is the total area of the absorption bands in the range of 950...1450 cm⁻¹ (N-related defects), and S_0 is the total area of the absorption bands in the range of 1500...2700 cm⁻¹ (diamond lattice absorption), respectively. The concentration of nitrogen atoms in the DFs grown using the grounded substrate holder is approximately equal to $5.1 \cdot 10^{19} \text{ cm}^{-3}$, which is substantially larger than in the HPHT diamond crystal $(2.3 \cdot 10^{19} \text{ cm}^{-3})$. Calculation of the concentration of nitrogen atoms embedded in the structure of the DFs grown using the negatively charged substrate holder is difficult due the absence of the absorption bands in the range of $1500...2700 \text{ cm}^{-1}$ in the corresponding spectra. The assumption about larger concentration of N atoms in the structure of the DFs grown using the grounded substrate holder has a good correlation with the domination of the absorption bands caused by the defects attributed to conglomerates of N atoms (A- and B-centers) in the DFs absorption spectra.

Fig. 7 presents the FTIR spectra of the studied samples in the spectral range of diamond lattice absorption. One can see from this figure that the main peaks of intrinsic two-phonon absorption of the studied DFs and HPHT diamond crystal are the following: 1971 cm⁻¹ (LO + TA), 2031 cm⁻¹ (TO + TA), 2165 cm⁻¹ (LO + LA) and 2441 cm^{-1} (TO + LO). The mentioned absorption bands, but with smaller intensities, are also present in the spectra of the DFs grown using the grounded substrate holder, see Fig. 7, curve 2. It is worth noting that there are no bands in the mentioned spectral region in the spectra of the DFs grown using the negatively charged substrate holder. The significantly decreased intrinsic absorption of diamond lattice in the studied DFs can be caused by the small lateral sizes of the diamond microcrystals (2...10 µm) and their disturbed and strained crystalline structure as compared to the bulk diamond crystal.



Fig. 7. Room-temperature absorption spectra of the studied materials in the two-phonon region of intrinsic absorption of diamond lattice.



Fig. 8. Room-temperature absorption spectra of the studied materials in the three-phonon region and the region of C–H absorption (a). Decomposition of the spectra in the range of C–H absorption (b).

Fig. 8a shows the absorption bands of the studied samples in the range of $2700...4000 \text{ cm}^{-1}$. The absorption in the mentioned range is dominated by the bands attributed to C-H bonds, which include C atoms of both sp^2 and sp^3 hybridization [38]. The broad $(\sim 200...250 \text{ cm}^{-1})$ and strong band at 3654 cm⁻¹ in the spectrum of the single crystal is attributed to the part of three-phonon absorption of diamond lattice [20]. The absorption bands at 2828 and 2920 cm⁻¹ are attributed to sp^3 CH₂, while the bands in the range of 2950...3400 cm⁻¹ are attributed to sp^2 CH₂ [38]. One can see non-zero absorption at 2828 and at 2920 cm⁻¹ in the spectrum of the bulk single crystal. This fact indicates non-substantial amount of hydrogen on the surface of the bulk crystal as a result of contamination. The increased absorption bands in the range of 2700...4000 cm⁻¹ in the DFs spectra indicate the presence of hydrogen impurity not only on the surface of the diamond microcrystals, but also in the grain boundaries. Non-zero absorption intensity at 3654 cm^{-1} in the spectrum of the DFs grown using the grounded substrate holder indicates better crystalline perfection of the diamond microcrystals as compared to the ones in the DFs grown using the charged substrate holder.

Using the intensities of the absorption bands attributed to sp^3 CH_x and sp^2 CH_x, the volume fraction of sp^3 bonds in the non-diamond component can be evaluated using the following equation [38]:

$$sp^{3} cont = \frac{I_{2828} + I_{2920}}{I_{2820} + I_{2920} + I_{2950} + I_{3220}} \cdot 100\%.$$

In the latter equation, $I_{2820} + I_{2920}$ is the sum of the areas under the Gaussian contours centered at 2828 and 2920 cm⁻¹ attributed to the absorption with participation of sp^3 CH₂ (Fig. 8b), and $I_{2950} + I_{3220}$ is the sum of the areas under the Gaussian contours centered at 2950 and 3220 cm⁻¹, respectively. We can summarize that the volume fraction of the sp^3 bonded carbon in the nondiamond component of the studied DFs is ~34% for the films grown using the charged substrate holder and ~18% for the films grown using the grounded substrate holder. The found values of the sp^3 bonded carbon fraction in the DFs have a good correlation with the values obtained from the Raman scattering data.

4. Conclusions

Using PL, Raman scattering and FTIR spectroscopy, it was found that the growth scheme with the grounded substrate holder enables the formation of non-stressed microcrystalline DFs with the smaller volume fraction of non-diamond carbon phase and two times larger diamond microcrystals as compared to the films grown using the negatively charged substrate holder. The decrease in the residual stress value and the non-diamond carbon phase fraction is caused by the absence of low-energy ion bombardment. It was shown that ion bombardment during the growth process with the negatively charged substrate holder affects the crystal lattice of the diamond microcrystals, effectively embedding SiV and NV defects from the glow discharge plasma. The increase in the lateral size of the diamond microcrystals can be explained by the decrease in the efficiency of secondary nucleation due to the low-energy ion bombardment. It was shown that embedding Si atoms into the structure of the diamond microcrystals depends on the diffusion efficiency from the Si substrate and the volume fraction of the grain boundaries, which play the role of diffusion channels. The amount of these channels is larger in the DFs grown using the negatively charged substrate holder, which causes the larger intensities of the PL bands corresponding to SiV intracenter electron transitions. The main feature that differentiates the crystalline structure of bulk diamond from that of the diamond microcrystals in the studied DFs manifests itself in the dominating embedding of N-related complexes, which include single substitutional N atoms, while embedding N-conglomerates near neighboring carbon vacancies is typical for DFs.

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Різниця в структурі та морфології CVD алмазних плівок, вирощених на від'ємно заряджених та заземлених підкладкотримачах: оптичні дослідження

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Анотація. Мікрокристалічні алмазні плівки були вирощені плазмохімічним методом на Si монокристалічних підкладках, розміщених на від'ємно зарядженому та заземленому підкладкотримачах із газової суміші СН₄/H₂. Отримані алмазні плівки складалися з мікрокристалів з переважною огранкою (100). Структуру і морфологію плівок досліджували за допомогою скануючої електронної мікроскопії, методами фотолюмінесценції, комбінаційного розсіювання світла та ІЧ-спектроскопії. Встановлено, що основним фізичним фактором, який зумовлює різницю в структурі алмазних плівок, осаджених на заземлений та від'ємно заряджений підкладкотримачі, є потік низькоенергетичних (до 200 еВ) іонів Si⁺, N₂⁺, H, О в останньому випадку. Ці іони переважно вбудовуються у структуру алмазних плівок, осаджених з використанням зарядженого підкладкотримача, та сприяють утворенню залишкового механічного напруження до 2 ГПа. Таке іонне бомбардування приводить до зростання об'ємної частки неалмазної вуглецевої компоненти плівок на границях зерен зі зменшенням частки sp³-зв'язаного вуглецю та латеральних розмірів алмазних мікрокристалів. Більша кількість границь алмазних зерен у плівках, осаджених з використанням зарядженого підкладкотримача, дає можливість атомам Si дифундувати з підкладки у плазму та на ростову поверхню. Такий процес приводить до формування SiV центрів у алмазних мікрокристалах навіть у плівках товщиною до 150...200 мкм. У плівках, осаджених з використанням заземленого підкладкотримача, концентрація кремнієвих дефектів сугтєво нижча, такі плівки мають суттєво меншу частку графітоподібного вуглецю на границях зерен та є більш однорідними.

Ключові слова: алмазні плівки, PECVD метод, фотолюмінесценція, комбінаційне розсіювання світла, IЧспектроскопія, SiV центр, NV центр.