

Research Article

Comprehensive Evaluation of the Properties of Nanocrystalline Diamond Coatings Grown Using CVD with E/H Field Glow Discharge Stabilization

Iu. Nasieka,¹ V. Strelchuk,¹ Yu. Stubrov,¹ M. Boyko,¹ S. Dudnik,²
K. Koshevoy,² and V. Strel'nitskij²

¹V.Ye. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine, 45 Pr. Nauki, Kyiv 03028, Ukraine

²National Science Center "Kharkov Institute of Physics and Technology", Akademicheskaya Street, Kharkov 61108, Ukraine

Correspondence should be addressed to Iu. Nasieka; yunaseka@gmail.com

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The nanocrystalline diamond films (coatings) were prepared using the plasma enhanced chemical vapor deposition (PECVD) technique. In this method, direct current (DC) glow discharge in the crossed E/H fields was used to activate the gas phase. The diamond coatings were deposited from the working gas mixture CH₄/H₂ with addition of nitrogen in various concentrations. It was ascertained that addition of N₂ to the working gas mixture leads to reduction in the sizes of diamond grains as well as to the substantial decrease in the resistivity of the studied films. The electrophysical data are in good agreement with the changes induced by varying the N₂ content in the Raman scattering spectra. The increase in the N₂ concentration causes significant lowering of the crystalline diamond related peak and increase in the intensity of the peaks related to the sp²-bonded carbon. These changes in the spectra indicate significant disordering of the structure of prepared films and its uniformity in the nanodiamond film volume. With the great possibility, it is associated with a decrease in the sizes of diamond crystalline grains and tendency of NCD film to amorphization.

1. Introduction

Previously, it was ascertained that reducing the crystallite sizes in polycrystalline diamond films causes the substantial decrease in growth of the surface roughness and induces changes of electrical, morphological, and structural and emission properties inherent to these films [1–5]. Up to date, nanocrystalline diamond (NCD) films are regarded as a new material with a high application potential in electronic and optical devices as well as medicine. In Ukraine, the works for the synthesis of NCD films are carried out in National Science Center "Kharkov Institute of Physics and Technology"; here, the deposition method and corresponding setup for diamond films deposition based on the direct-current glow discharge in the crossed E/H fields (chemical vapor deposition) were developed [6, 7]. Morphological and structural investigation of these diamond materials are

performed in V.Ye. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine, Laboratory of Optical Submicron Spectroscopy.

One of the ways to achieve the grain refinement down to nanosizes in the diamond films prepared by chemical vapor deposition (CVD) is partial or full hydrogen substitution in the CH₄/H₂ precursor gas mixture with nitrogen. Thus, the deposition process is followed by intense secondary nucleation hindering the growth of the large diamond crystallites and holding their nanosizes even at a significant film thickness (micrometers) [8–11].

Microscopy of the cross-section in the above films indicates that under a high N₂ content the columnar growth of diamond crystallites is hindered, and the grain size minimization to nanosizes in all directions occurs. It is important to note that transition from large size crystalline structure to microcrystalline and nanostructure, which is seen from

[12–14], can be stimulated not only by changing the content of gas-precursor phase but also by bombing the surface of growing coating with ions from the gas discharge under supplying the accelerating potential to the substrate holder.

This work is aimed at detailed studies of the morphological, structural, and electrical properties of NCD films (coatings) after hydrogen substitution in the CH_4/H_2 precursor gas mixture with nitrogen during the growth process.

2. Experimental Part

2.1. Nanocrystalline Diamond Films Growth. In National Science Center “Kharkov Institute of Physics and Technology,” the method and setup for polycrystalline diamond film deposition where activation of the gas phase is realized through the DC glow discharge in crossed E/H fields are developed and successfully used [6, 7]. The presence of crossed magnetic field in this scheme of gas discharge leads to stabilization of the normal glow discharge in a wide range of discharge currents at the current density higher than 1 A/cm^2 . Herewith, the power density used for activation of the working gas reaches 1000 W/cm^3 , which corresponds to energetic characteristics typical for the high-efficient industrial equipment for synthesis of diamond coatings. Contrary to the classic scheme of glow discharge used for activation of the gas phase (where substrate holder is one of the electrodes (anode) for discharge), in the construction of developed equipment the substrate holder is electrically isolated from the anode as well as from cathode. Nevertheless, at the discharge excitation, as presented in [7], the substrate acquires the negative (floating) potential relatively to earthed anode and reaction chamber walls. The value of the potential can reach 40% from the voltage between anode and cathode and depends on discharge conditions. It results in additional bombardment of the substrate surface by plasma ions. To provide formation of nanostructured diamond coatings in the glow discharge N_2 was added to CH_4/H_2 working gas mixture (CH_4 part was 0.5%). All experiments were performed at the glow discharge current 4.5 A, total pressure in the chamber $8 \cdot 10^3 \text{ Pa}$, and the total gas flux $300 \text{ cm}^3/\text{min}$. These parameters were constant for all diamond coatings studied in the present work. The deposition time was chosen taking into account the stipulation of the preparation of the continuous coatings without open pores.

2.2. Resistivity Measurements. In our case, conducting doped Si plates serve as substrates, which allows applying the simple two-electrode scheme for measurements. It is noteworthy that, providing the mentioned measuring scheme, it is very important to implement full contact of measuring electrode over the whole area of its touching to the surface of the film. When providing the latter, the probe electrode that contacts with the coating surface was moistened with gel electrolyte based on liquid soap. Avoiding the polarization effect at the current conduction through liquid electrolyte film on the results of resistivity measurements, the scheme with alternating current power supply was used. The measurement

of Si substrate electrical resistance before deposition of coatings at different frequencies indicates that the polarization effect when the current passes through the electrolyte film has a substantial influence on results of measurements only at the frequencies lower than 10–15 kHz. Therefore, further measurements of electrical resistance inherent to the studied samples with a diamond coating were carried out at the frequency 20 kHz. The electrical resistance of substrate and electrode was equal to $30 \pm 0.5 \text{ Ohm}$ and taken into account when determining the electrical resistance of diamond films. The resistivity ρ of diamond films was obtained using the equation $\rho = R_{\text{diam}} \cdot (S/h)$, where h is the diamond film thickness and S is the measuring electrode contact area. It is worth noting the following fact. The diamond film thickness was determined by the weight change per area unit during the experiment. Herewith, the film density was taken equal to the diamond one 3.5 g/cm^3 .

2.3. Optical Characterization. The structural quality of NCD films was characterized using micro-Raman scattering (μ -RS) spectroscopy. The μ -RS spectra were measured at $T = 300 \text{ K}$ using the triple Raman spectrometer HORIBA Jobin-Yvon T64000 equipped with a confocal microscope UV-Visible-NIR Olympus BX4 for micro-Raman sampling. As an excitation tool for μ -RS, the 3.82 eV (325 nm) line from He-Cd laser was used. In this configuration, the laser spot was focused using the X100 objective to a diameter less than $1 \mu\text{m}$. Morphology of the studied NCD films was investigated using the atomic-force microscope NT-206 and scanning electron microscope JSM-7001F.

3. Results and Discussion

Figure 1 presents SEM images of the surface of diamond films with the thickness 8–10 μm prepared at various N_2 concentrations. One can see that the films deposited from CH_4/H_2 mixture with 6% of N_2 consist of relatively large grains with clear faceting. Increase of N_2 incorporation up to 25% leads to a substantial decrease in the diamond grain sizes and to disappearance of clear faceting. As it follows from Figure 1, the microstructure of studied samples has accreted globule-like view with the sizes less than $1 \mu\text{m}$, where their surface is coated with nanoscale globule-like formations. The sizes of globule-like formations and microroughness of the surface decrease when the N_2 concentration in the gas mixture increases. Thus, for the coatings prepared at 6% of N_2 , the microroughness of the surface $R_a = 72.2 \text{ nm}$, while for the coatings prepared at 25% of N_2 , $R_a = 32 \text{ nm}$, that is, more than 2 times lower. Simultaneously, the sizes of globule-like formations are within the range 20–40 nm (Figure 2). According to the results of X-ray diffractometry, the diamond coatings deposited from the CH_4/H_2 mixture are characterized by a block structure with the size of coherent scattering region close to 70 nm and unit cell parameter $a_0 = 0.3567 \text{ nm}$, which is typical for natural diamond. Addition of 25% of N_2 to the gas mixture leads not only to decrease in the sizes of coherent scattering region up to 25 nm but also to decrease in the unit cell sizes of diamond to 0.3563 nm.

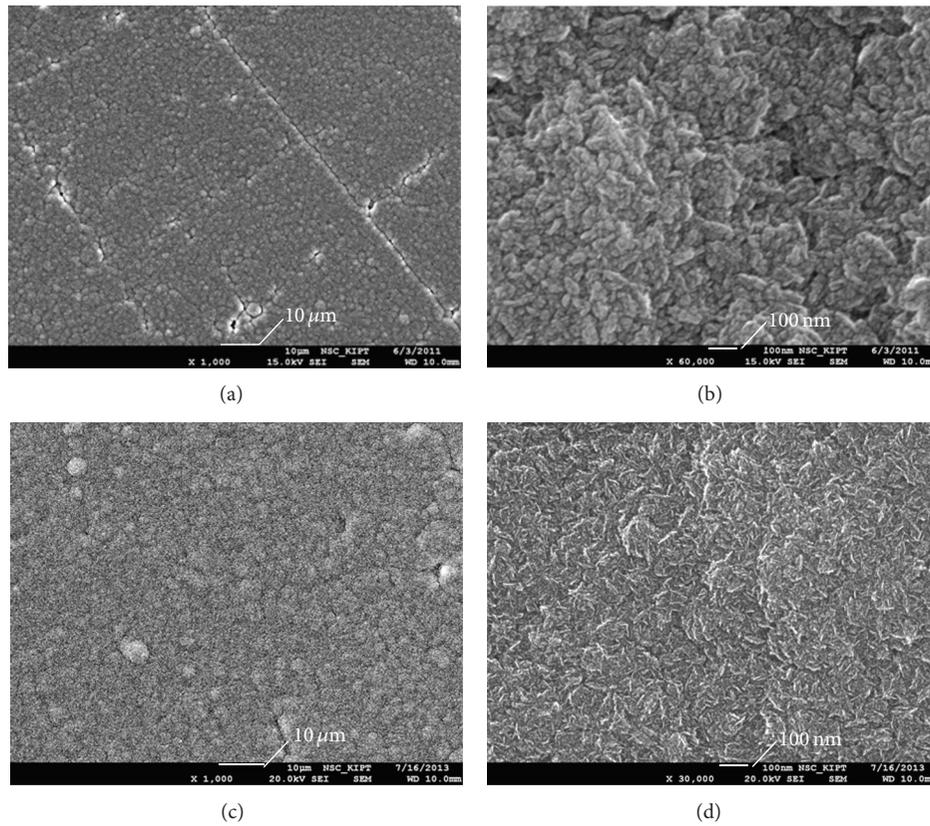


FIGURE 1: SEM images of the surface of diamond films: (a), (b) obtained for the films grown with 6% of N_2 in working gas mixture; (c), (d) 25% of N_2 .

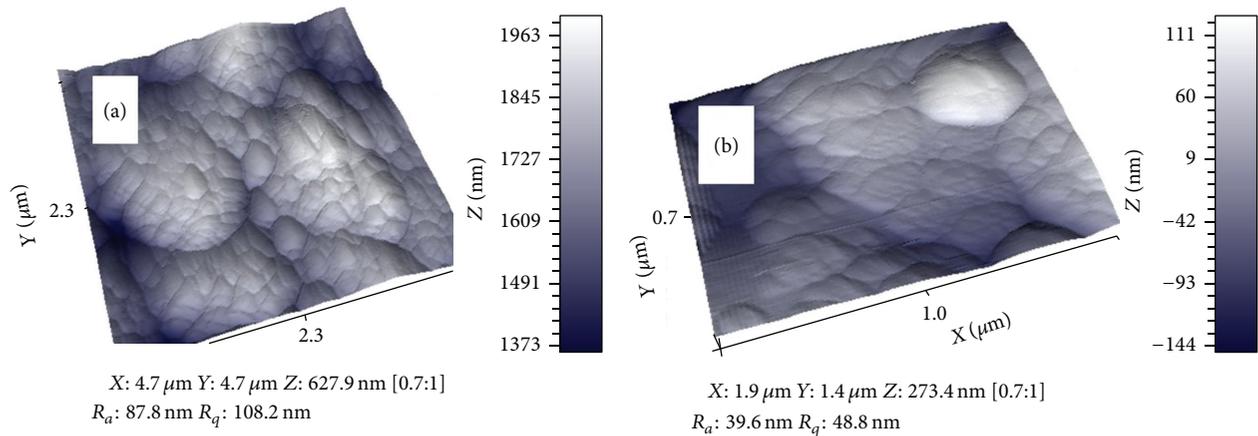


FIGURE 2: AFM images of the surface of diamond films: (a) obtained for the films grown with 6% of N_2 in working gas mixture; (c) 25% of N_2 .

The decrease in the crystal lattice parameters in comparison with the tabulated values typical for bulk crystals is a distinctive feature of nanostructured materials.

Figure 3 shows Raman scattering spectra of NCD films grown with 12% of N_2 content in gas-precursor mixture. Also, Figure 3 presents decomposition of typical spectra by

elementary Lorentz and Gaussian contours. The correctness of this decomposition was proved by the curve of the sum of decomposed contours (dotted line). One can see a good agreement between the experimental and dotted lines. It is important to note that we decomposed all the obtained spectra, and further discussion operates with different spectral

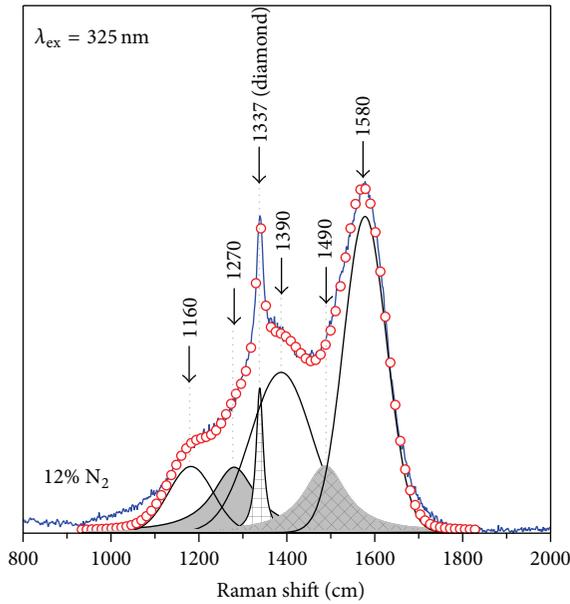


FIGURE 3: Room-temperature Raman scattering spectra registered for diamond films prepared in the plasma of glow discharge with 12% of N_2 in working gas mixture. Also, decomposition on elementary contours was presented. The dotted curve is the sum of decomposed contours.

parameters based on the mentioned decomposition. Further, we did not display all the decomposed contours with the aim to prevent complications in the figures. From the specific features and decompositions in the spectra, the following phases can be identified:

- crystalline diamond at 1337 cm^{-1} ;
- sp^2 -bonded carbon (disordered graphite) with D and G peaks at 1390 cm^{-1} and 1580 cm^{-1} ; D line is induced by “breathing” vibrational mode of sp^2 atoms vibrations in the rings; G line is caused by crystalline graphite, sp^2 phase;
- trans-polyacetylene (t-PA) with two peaks at 1160 cm^{-1} (C-H in-plane bending mode) and 1490 cm^{-1} (CC stretch) [14–16];
- line at $1180\text{--}1270\text{ cm}^{-1}$ is induced by sp^3 diamond bonding in tetrahedral amorphous carbon (ta-C) [16–18]; it is typical for nanocrystalline diamond.

Figure 4 displays evolution of Raman scattering spectra inherent to the studied NCD films for various N_2 concentrations. One can see that the increase in the N_2 concentration causes the decrease in the intensity of crystalline diamond related peak as well as lines associated with trans-polyacetylene and increase in the intensity of peaks related to sp^2 -bonded carbon. The shift of the positions of D and G lines towards high frequency (from 1578 to 1594 cm^{-1}) with increase in the N_2 concentration was registered indicating an increase in sp^2 bond angle order for trivalent carbon atoms in graphitic components. The ratio of intensities of the D and G peaks increases (from 0.5 to 0.58) with the N_2

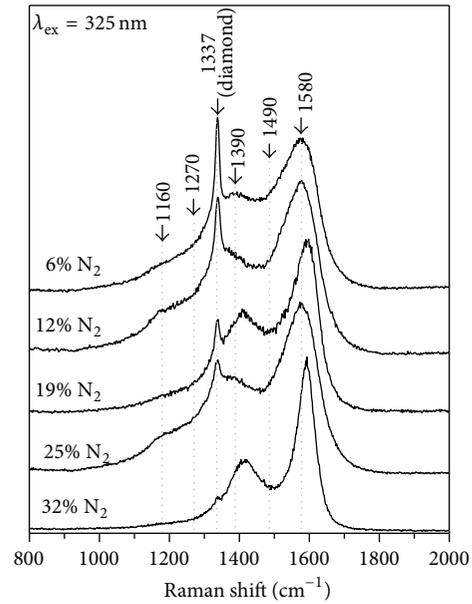


FIGURE 4: The series of room-temperature Raman spectra of PECVD NCD films deposited from gas-precursor mixtures with various N_2 content. The excitation wavelength is 325 nm.

concentration in operation gas mixture indicating a decrease in the average in-plane size graphitic components. These changes can be explained by the increase of disorder level due to the decrease in sizes of crystalline diamond grains and increase in the number of regions with sp^2 -bonded carbon. Also, transformation of the well-defined peak at 1160 cm^{-1} to a very weak shoulder suggests an improvement of sp^2 -bonded carbon in the grain boundaries of NCD films. The relative sp^3 content in grain boundaries of NCD films with various N_2 concentrations can be determined using the following equation [18–24]:

$$sp^3 \text{ content} = 0.24 - 48.9(\omega_G - 0.1580). \quad (1)$$

Using (1), one can determine that the increase in the N_2 concentration from 6 up to 30% leads to changes in the relative sp^3 content in diamond crystalline grain boundaries from 0.25 down to 0.15.

It is important to note that the data of Raman scattering investigation good correlates with SEM and AFM studies. For the comprehensive evaluation of the influence of the presence of N_2 in operation gas mixture on the physical properties of NCD coatings the electrophysical study was performed. It is known from [22–24] that availability of N_2 in the reacting gas mixture substantially influences electroconductivity of nanostructured diamond coatings. Our investigations of the dependence of diamond film electrical resistance on the N_2 concentration in the gas phase were performed with the samples prepared at various CH_4 concentrations (1%, 1.5%, and 2%). The H_2 content in the gas phase depends on the total number of other components. In this work, the H_2 concentration was varied from 0 up to 33%. The obtained dependences are presented in Figure 5. The most significant

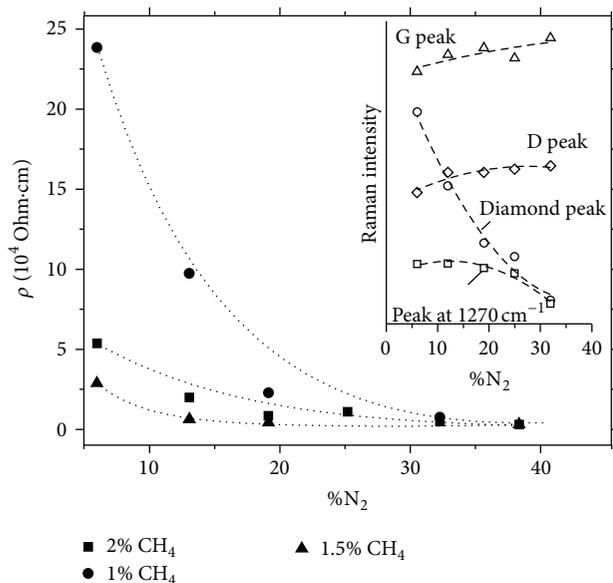


FIGURE 5: The dependence of resistivity of diamond film on the N_2 concentration in the gas phase at various CH_4 concentrations. With the aim to display the correlation between morphological and structural investigation data and electrophysical data, the dependence of corresponding Raman modes intensity on the N_2 concentration is presented in the insertion.

decrease in the resistivity of N-doped diamond films occurs when the N_2 concentration in the gas phase increases to approximately 15–20%. Upon reaching the N_2 concentration 25–30% and higher, the diamond film resistivity changes insignificantly approaching the value $1.7 \times 10^3 \text{ Ohm} \times \text{cm}$ without any dependence on the CH_4 concentration. For comparison, the diamond coating at the Ar concentration 60%, H_2 38%, and CH_4 2% was prepared without addition of N_2 in the gas phase. The resistivity of the above film amounted to $7 \times 10^6 \text{ Ohm} \times \text{cm}$. The dependence of corresponding Raman modes intensity on the N_2 concentration is presented in the insertion to Figure 5. One can see that the behavior of electrical resistance with the increase in N_2 concentration good correlates with the behavior of the intensities of sp^3 -bonded carbon related vibrational peaks. The latter can be explained by the increase in the density of the diamond crystalline grain boundaries of the amorphous nature with a higher sp^2 content. The regions with the sp^2 content have smaller resistivity and can shunt the detector volume.

4. Conclusions

The investigations of the influence of the N_2 content in gas-precursor mixture on the morphological, structural, and electrophysical parameters of diamond coatings synthesized from CH_4/H_2 mixture in the plasma of DC glow discharge stabilized by crossed E/H fields have been carried out. It has been ascertained that transition from coarse-crystalline diamond coatings to the small-crystalline and nanocrystalline

ones occurs at N_2 concentration $\sim 20\%$. The data of morphological and structural investigations have good correlation with results of electrophysical measurements as well as AFM and SEM measurements forming the comprehensive idea relatively to the nature of the processes that occurs under feeding N_2 into the reacting gas mixture. Evolution of Raman scattering spectra in the studied NCD films with increasing the N_2 concentration up to 32% displays the decrease in the intensity of crystalline diamond related peak and increase in the intensity of the peaks related to sp^2 -bonded carbon. These changes in the spectra indicate significant disordering of the structure of prepared films and its uniformity in the nanodiamond film volume. With a great possibility, it is associated with decreasing the sizes of diamond crystalline grains and tendency of NCD film to amorphization.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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