Multiscale characterization of synthetic diamonds obtained by gas-jet deposition

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Abstract. Morphology, structure and surface composition of the synthetic polycrystalline diamond films grown by a gas-jet deposition have been studied with help of scanning electron microscopy, Raman scattering, X-ray photoelectron spectroscopy and near edge X-ray absorption fine structure spectroscopy. The diamond films were deposited from a high-speed jet of activated CH₄ + H₂ gaseous mixture on the Mo substrates heated to 900 °C with CH₄ flow rate of 8 sccm and 1000 °C with 12 sccm of CH₄. The high concentration of CH₄ in gas flow and the high substrate temperature resulted in an increase in the size and improvement of quality of the diamond crystals. A presence of sp² hybridized, hydrogenated and oxygenated carbon atoms on the surface of diamond films was revealed.

1. Introduction
Polycrystalline diamond films have specific properties for various applications, including advanced electronic devices. The diamond is the hardest known material, which also possesses an optical transparency in a wide range of the frequencies and good thermal conductivity [1, 2]. Hot-filament (HF) chemical vapor deposition (CVD) and microwave plasma enhanced CVD (MWCVD) techniques are widely used to produce diamond thin films [3, 4]. Nevertheless new techniques, approaches and setups for the synthesis of diamond films are still being actively developed. Recently, it was demonstrated a possibility to grow the diamond films by a variety of catalytic HF CVD procedures with the use of gas activation by an extended surface [5]. The distinguishing features of this approach are high-speed gas flows, allowing fast delivery of gas molecules to the substrate, and heterogeneous processes of dissociation of molecular hydrogen by multiple collisions with the extended surfaces of the activator. It is believed that a high concentration of atomic hydrogen in a gas flow is the main condition of the successful growth of diamond structures from the gas phase [6]. Moreover, for a stable growth of diamond crystals, a high ratio of hydrogen to hydrocarbon radicals is necessary [7]. The proposed method of the diamond deposition exactly allows achieving a high degree of hydrogen dissociation [8].
By using the gas-jet deposition, the diamond coatings can be formed on various types of the substrate. Previously it was shown, that in contrast to easy-etching silicon, application of molybdenum as a substrate improves quality of diamond film surfaces [9]. Moreover, molybdenum provides a high nucleation density (about $10^5$ cm$^{-2}$) which is very important for the continuous and smooth film growing [10]. The temperature of the substrate during the diamond deposition is another important parameter, which influences the concentration of carbon and atomic connectivity in the film [11]. Both growth and etching of diamond occur simultaneously and depend on the synthesis conditions, such as temperature, pressure and gas phase composition. A formed diamond crystal may interact with the atoms and molecules of the gas phase. These interactions depend on the chemical state of surface carbon atoms, the crystallographic orientation, defectiveness and size of the diamond crystal, and etc. Therefore, the structure and composition of the synthetic diamond surface carry the information about its formation process.

This paper reports on the effect of methane concentration in a hydrogen flow and the temperature of a molybdenum substrate on morphology, structure and surface composition of the synthetic polycrystalline diamond films, obtained by the gas-jet deposition. Morphology of the films was investigated by scanning electron microscopy (SEM). The chemical bonding in the films was clarified by Raman scattering, surface sensitive X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy.

2. Experimental section

Deposition of diamond coatings was carried out by chemical vapor deposition using a special reactor. The reactor and main parameters of the synthesis are described elsewhere [12]. A two-channel feed system was used to divide the hydrogen and methane mixed with hydrogen flow in order to reduce the degree of carbonization. Hydrogen (flow rate of 1500 sccm) and methane (flow rate of 8 or 12 sccm) were fed through the central channel, and a pure molecular hydrogen (1500 sccm) flowed separately through the outer channel. For heating the cylinder activator, where decomposition of mixed gas flow was occurred, a tungsten spiral with a diameter of 1 mm was used. The activator temperature was estimated to be 2100 $^\circ$C. The pressure in the deposition chamber was 20 Torr. The substrate was fixed at a distance of 10 mm from the reactor nozzle plane. The activated gas flow was deposited on the surface of a polished molybdenum substrate oriented by the (200) facets. The Mo substrates were heated to a temperature of 900 or 1000 $^\circ$C during a diamond film growth for 3 h. Two samples of diamond films grown on the substrate at 900 $^\circ$C at a CH$_4$ flow rate of 8 sccm (film 1) and at 1000 $^\circ$C at the rate of 12 sccm (film 2) were taken for investigation.

Morphologies of the samples were characterized by SEM on a JEOL JSM 6700F microscope. Raman spectra were measured with a LabRAM HR Evolution (Horiba) spectrometer using the He-Ne laser (514 nm). XPS and NEXAFS experiments were performed at the Berliner Elektronenspeicherring für Synchrotronstrahlung (BESSY II), using radiation from the Russian-German beamline. The XPS spectra were measured at a photon beam energies of 400 and 830 eV. The Gaussian-Lorentzian function was used to describe the components in the XPS C 1s spectra. NEXAFS spectra near the C K-edge were acquired in total electron yield (TEY) and Auger electron yield (AEY) modes.

3. Result and Discussion

Figure 1 shows SEM images of the surface of diamond films deposited using a methane flow rate of 8 and 12 sccm on Mo substrates heated to 900 and 1000 $^\circ$C, respectively. The Mo substrate surfaces are uniformly covered by diamond films. The polycrystalline structure of the samples are clearly seen. The large diamond particles with an average size of 3 μm were found on the surface of film 1 grown at 900 $^\circ$C. The surface morphology of this film is consisted of well-faceted (100) diamond grains. Micron-scale diamond crystals with an average size of 30 μm and the shape of rhombic dodecahedra have been seen on the surface of film 2 grown at 1000 $^\circ$C and at a higher concentration of CH$_4$. The higher magnified SEM images of both samples show the presence of small particles with a size of 10-100 nm, which are located in the crevices between well-formed diamond planes (figures 1a3, b3). We
suggest that these small particles are primary diamond crystals, grown on the surfaces of the substrate and diamond crystallites as a result of incessant re-nucleation process. The bigger particles were formed by repeated nucleation and association of small particles.

The nucleation density and size of diamond particles in the film 2 are higher than those for film 1 due to relative high concentration of carbon species in the activated gas flow.

Raman spectroscopy was carried out to evaluate the phase purity of diamond films. The spectra showed a narrow intense diamond peak at 1332 cm\(^{-1}\), a broad peak at 1550 cm\(^{-1}\) related to graphite-like carbon, and a weak broad peak between 2500 and 3000 cm\(^{-1}\) from C-H bonds [13] (figure 2). The sloping backgrounds from photoluminescence were observed in the spectra of both samples. The spectra of both films are similar in shape and intensity of the diamond and graphite-like peaks, confirming that the samples have a similar crystal structure.

The XPS and NEXAFS spectra of the diamond films were measured in order to reveal the atomic structure of diamond films and quantity of non-diamond phase on their surface. Overall XPS spectra of the samples showed signals of carbon as a dominant element and oxygen (8 at%) Negligible signals from molybdenum (0.01 at%) confirm that diamond films almost entirely cover the surface of the substrates. The XPS C 1s spectra were excited by photons with an energy of 830 and 400 eV (figure 3). The inelastic mean free path (IMFP) for emitted electrons from C 1s level in graphite and diamond is about 0.4 for 400 eV and 1.0 nm for 830 eV [14]. The spectra were fitted by four components. The parameters for the curve fitting are collected in table 1. The peak located at 284.5 eV corresponds to sp\(^2\)-hybridized carbon atoms. The peak at 285.0 eV can be assigned to sp\(^3\)-hybridized carbon atoms both from diamond and hydrogenated carbon species. The peaks located at 286.0 and 288.5 eV arise from carbon bonded with one and two oxygen atoms. The graphite-like carbon, hydrogenated and oxygenated carbon species existing on the surface of diamond particles have been previously detected in CVD diamond films and detonation nanodiamonds [15, 16]. According to the fitting of the spectra measured at 830 eV, the sp\(^3\)/sp\(^2\) carbon ratio for the film 1 is higher than that for the film 2. This peak does not arise only from diamond carbon, but hydrogenated carbon atoms also contribute to the formation of this peak. Analysis of the XPS C 1s spectra measured at 400 eV (figure 3b) revealed a decrease in the intensity of sp\(^2\) carbon peak, while the peak at 285.0 eV greatly increased. Since in this case the probing depth is no more than 0.4 nm, this peak is formed rather by
hydrogenated carbon located on the surface of diamond particles, than diamond core. Thus, the concentration of hydrogenated carbon on the surface of diamonds is higher in the film 1, where the amount of hydrogen radical in the gas flow was higher.

![Raman spectra of diamond film 1 grown using CH₄ flow rate of 8 sccm at 900 °C (a) and film 2 formed using CH₄ flow rate of 12 sccm at 1000 °C (b).](image1)

**Figure 2.** Raman spectra of diamond film 1 grown using CH₄ flow rate of 8 sccm at 900 °C (a) and film 2 formed using CH₄ flow rate of 12 sccm at 1000 °C (b).

![XPS C 1s spectra of diamond film 1 grown using CH₄ flow rate of 8 sccm at 900 °C at T\textsubscript{Mo} - 900 °C (a) and film 2 formed using CH₄ flow rate of 12 sccm at 1000 °C at T\textsubscript{Mo} - 1000 °C (b).](image2)

**Figure 3.** XPS C 1s spectra of diamond film 1 grown using CH₄ flow rate of 8 sccm at 900 °C (top) and film 2 formed using CH₄ flow rate of 12 sccm at 1000 °C (down). The spectra were measured at 830 eV (a) and 400 eV (b).
Table 1. Fitting parameters (energy and area of components) for XPS C 1s spectra of diamond films.

| Energy, eV | 284.5 | 285.0 | 286.0 | 288.5 |
|-----------|-------|-------|-------|-------|
| Assignment | Graphite $sp^2$ carbon | Diamond $sp^2$, hydrogenated carbon | Single oxygenated carbon | Double oxygenated carbon |
| Related area, at% | | | | |
| Excitation energy | | | | |
| 830 eV (IMFP – 1.0 nm) | | | | |
| $T_{Mo}$ – 900 °C CH$_4$ – 8 sccm film 1 | 39 | 41 | 17 | 3 |
| $T_{Mo}$ – 1000 °C CH$_4$ – 12 sccm film 2 | 48 | 35 | 14 | 3 |
| Excitation energy | | | | |
| 400 eV (IMFP – 0.4 nm) | | | | |
| $T_{Mo}$ – 900 °C CH$_4$ – 8 sccm film 1 | 11 | 65 | 21 | 3 |
| $T_{Mo}$ – 1000 °C CH$_4$ – 12 sccm film 2 | 31 | 50 | 16 | 3 |

The NEXAFS C K-edge spectra of the diamond films were registered using the TEY and AEY modes, that give additional information about the chemical bonding of carbon in volume and at the surface of diamond films (figure 4). The mean probing depth of the NEXAFS method in the case when electron current measured in the TEY mode was estimated to be no more than 7 nm [17]. AEY technique has a much lower probing depth, typically less than 1 nm due to the small IMFP of Auger electrons. The NEXAFS CK-spectra of the diamond films demonstrate peaks at 289.4 eV assigned to the $1s\rightarrow\sigma^*$ transitions within the $sp^3$–hybridized carbon and a dip at 302.5 eV corresponding to a second absolute gap in the diamond band structure. The spectra also show the low intensive features at 285.4 and 291.7 eV corresponding to electron transition from $1s$ to $\pi^*$ and $\sigma^*$ states within the $sp^2$–

Figure 4. NEXAFS C K-edge spectra of diamond films grown on the substrates heated at 900 and 1000 °C at methane flows of rate 8 and 12 sccm. The spectra were measured in TEY (a) and AEY modes (b).
hybridized carbon atoms, and two features at 286 and 287 eV from hydrogenated and oxygenated carbon atoms.

The presence of pronounced features, characteristic for the diamond, indicates good crystallinity of the diamond films. The spectra in TEY mode of the film 2 have more intense and sharp $\sigma^*$ sp$^3$ peak and more noticeable second gap dip, than those for the film 1. It means that diamond crystals have a better atomic order in the film 2. It should be noted that these features, especially a dip at 302.5 eV, are not very clearly observed in the NEXAFS C K-spectra measured in AEY mode. The sp$^2$-hybridized carbon, as well as hydrogenated and oxygenated carbon atoms are mainly present on the surface of diamond films. The film 2 is characterized by the lower concentration of sp$^3$ carbon and hydrogen-containing groups located on their surface. The higher concentration of hydrogenated and oxygenated carbon was detected on the surface of the sample 1, when concentration of methane in the gas mixture and temperature of Mo substrate were lower.

4. Conclusion

Two samples deposited on Mo substrates heated at 900 °C using methane flow rate of 8 sccm in the mixture with hydrogen and 1000 °C at methane flow rate of 12 sccm were investigated by a combination of characterization tools. Analysis of SEM revealed that synthetic polycrystalline diamond films have polycrystalline structure and are different in shape and size of the diamonds crystals. It was found that deposition from the gas mixture with higher concentration of methane on the substrate heated to 1000 °C results in an increase of the size of diamonds to 30 μm and improvement of their quality. XPS and NEXAFS studies discovered the presence of sp$^2$ hybridized carbon and hydrogenated and oxygenated carbon on the surface of diamonds. The film deposited at a methane flow rate of 12 sccm at 1000 °C was found to have the less amount of surface contaminations.

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References

[1] Ashfold M N R, May P W, Rego C A and Everitt N M 1994 Chem. Soc. Rev. 23 21
[2] Williams O A 2011 Diam. Rel. Mat. 20 621
[3] Zhou S, Zhihao Z, Ning X and Xiaofeng Z 1994 Mat. Sci. Eng. B 25 47
[4] Jiang X, Klages C P 1992 Appl. Phys. Lett. 61, 1629
[5] Rebrow A K, Andreev M N, Bieiadovskii T T and Kubrak K V 2017 Surf. Coat. Tech. 325 210
[6] Gicquel A, Silva F, Rond C, Derkaoui N, Brinza O, Achard J, Lombardi G, Tallaire A, Michau A, Wartel M, and Hassouni K 2014 Compr. Hard Mat. 3 217
[7] Mankelevich Yu A and May P W 2008 Diam. Rel. Mat. 17 1021
[8] Plotnikov M Yu, Shkarupa and E V 2016 Vacuum 129 31
[9] Francois N, Kim S H, Park Y S, Lee J-W, Hahn I T and Yun W S 1997 Diam. Rel. Mat. 61 959
[10] Liu H and Dandy D S 1995 Diamond Chemical Vapor Deposition Nucleation and Early Growth Stages, Noyes Publications, New Jersey, U.S.A.
[11] Fedoseeva Yu V, Pozdnyakov G A, Okotrub A V, Kanygin M A, Nastaushev Yu V, Vilkov O Y and Bulusheva L G 2016 Appl. Surf. Sci. 385 464
[12] Rebrow A. 2017 Diam. Rel. Mat. 72 20
[13] Kawarada H 1996 Surf. Sci. Rep. 26 205
[14] Tanuma S, Powell C J and Penn D R 2004 Surf. Interface Anal. 36 1
[15] Wilson J I B, Walton J S and Beamson G. 2001 J. Electron Spec. Rel. Phen. 121 183
[16] Fedoseeva Yu V, Bulusheva L G, Okotrub A V, Kanygin M A, Gorodetskii D V, Asanov I P, Vyalikh D V, Puzyr A P and Bondar V S 2015 Sci. Rep. 5 9379
[17] Hähner G 2006 Chem. Soc. Rev. 35 1244