

A laser plasmotron for chamberless deposition of diamond films

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Abstract. The laser-plasma method is developed for diamond synthesis in air without using vacuum or reaction chambers. The design of a laser plasmotron based on a 3-kW cw CO₂ laser for synthesis of diamond films on substrates of size 3–4 times larger than the transverse size of the plasma jet is presented. Various regimes of plasmotron operation while moving the substrate relative to the laser plasma are considered. Possible directions in further investigations in the field of laser plasma synthesis of diamond on large areas are discussed.

Keywords: laser plasmotron, stationary optical discharge, polycrystalline diamond films.

1. Introduction

One of the most rapidly growing trends in modern science and technology is the development of highly productive techniques for synthesis of promising materials. These materials undoubtedly include synthetic diamond with a unique combination of physical and chemical properties. Synthetic diamond is widely used in industry and science due to its ultrahigh hardness, low coefficients of thermal expansion and friction, high thermal conductivity (five times higher than for copper and silver at room temperature), transparency in a wide spectral range of electromagnetic radiation (from X-rays to infrared radiation, with the exception of the ultraviolet spectral region), high mobility of carriers, wide forbidden gap, high electric breakdown threshold, high resistance to long exposures to nuclear radiation and high-energy particle flux, chemical inertness, biological compatibility with living tissues in organisms, etc.

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In nearly half a century following the synthesis of diamonds at high temperatures and high pressures, various techniques have been developed for production of this material in the form of powder or polycrystalline films, as well as single crystals, free-standing plates and layers.

Chemical deposition from the gaseous phase is one of the most promising methods of manufacturing diamond in the form of polycrystalline films. This technique involves heating of a gaseous hydrocarbon (e.g., methane-hydrogen) mixture to temperatures at which particles (radicals, ions, clusters) suitable for growth are formed and then participate in chemical reactions at the substrate surface, resulting in the formation of diamond films.

Well-studied and successfully used methods of chemical vapour deposition (CVD) of diamond employing an electric arc plasmotron, microwave and radio-frequency discharge, etc. [1], have been supplemented recently by a new technique for synthesis of materials from laser plasma with the help of a laser plasmotron [2–5]. This technique uses laser radiation as the energy source for sustaining a continuous optical discharge (laser plasma) in a jet of gaseous reagents flowing from the plasmotron nozzle on the substrate.

The main feature distinguishing the laser plasmotron technique from other CVD methods is that it does not require a vacuum or reaction chamber because the optical discharge plasma can be sustained by continuous laser radiation under atmospheric (or higher) pressure. This opens up a new perspective for a significant extension of the range of objects on which a diamond film can be deposited to increase their strength or to protect them from corrosion because it becomes possible to move components of virtually any size and quite complex shape relative to the plasma jet. Another advantage of the laser CVD method is a high plasma temperature (15–20) × 10³ K, which, in conjunction with a high gas pressure, i.e., a high density of active molecules, raises hopes of attaining record-high growth rates of diamond films (up to 10³ μm h⁻¹ [6]). The maximum rate of diamond deposition achieved so far with a laser plasmotron is ~ 120 μm h⁻¹ [5], which is comparable with the highest growth rates obtained in nonlaser CVD techniques.

The present work aims at the development of the laser-plasma technique for diamond synthesis. We study the basic possibility of high-speed deposition of diamond films on large areas and consider various regimes of laser plasmotron operation in open atmosphere with displacement (scanning) of the substrate relative to the laser plasma.

2. Experimental setup

All experiments were carried out at atmospheric pressure on a laser plasmotron whose scheme is shown in Fig. 1. The plasmotron consists of three main parts: the focusing system, the nozzle block, and the substrate holder. The radiation from a 3-kW cw CO₂ laser is focused by a K(Na)Cl lens ($F \sim 120$ mm) into a water-cooled nozzle through which the active-gas mixture flows. Optical breakdown plasma in which the heating and ionisation of the gas take place is produced in the waist of the laser radiation caustic. The plasma jet formed in this way falls on the surface being treated. A part of laser radiation ($\sim 40\%$) is not absorbed by the plasma and falls on the substrate, thus participating in its heating. The laser used in this work was a rapid-gas-flow electric-discharge cw CO₂ laser with a closed gas-dynamic contour. The radiation was extracted with the help of an unstable resonator, so that the shape of the output beam was annular. A major portion of the output power in the cross section of the beam passing through the laser plasma was concentrated in two crescent-shaped semi-rings.

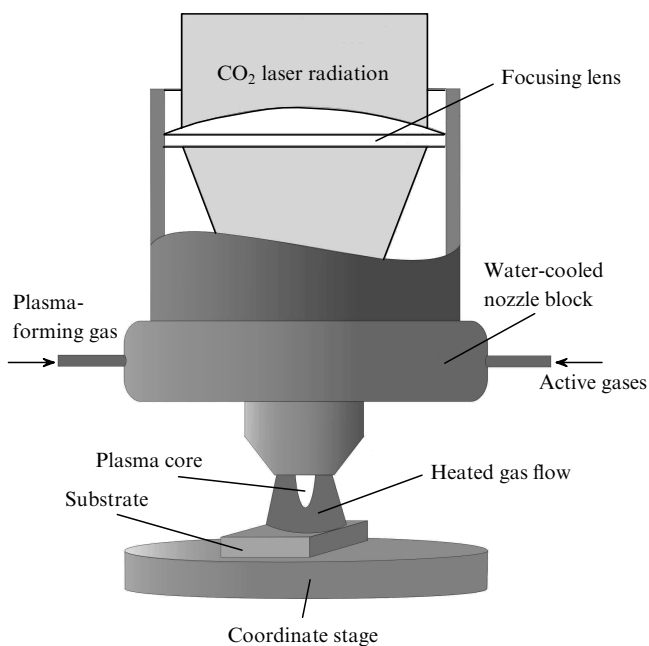


Figure 1. Scheme of the atmospheric-pressure laser plasmotron.

The construction of the nozzle block allows a supply of active gases alone or together with plasma-forming Ar into the plasma core region, above or below the laser radiation focus. The outlet nozzle of the plasmotron is detachable, and the focusing system allows a displacement of the laser radiation focus along the optical axis of the plasmotron above or below the minimum cross section of the nozzle, thus enabling an efficient control of the plasma jet and the maintenance threshold of the laser plasma.

Unlike the laser plasma reactor design presented in the pioneering work [1], where the exhaust gases displace the surrounding air through small slits between the walls of the substrate holder and the reaction chamber, the plasma jet flows freely from the plasmotron nozzle to the substrate in the design proposed here. Such an approach is more

advantageous from the technological point of view because it allows a free displacement of the substrate relative to the laser plasma and makes it possible to synthesise diamond films on large areas. It should be noted, however, that this raises problems associated with the protection of the diamond film deposition area from the surrounding air or, to be more precise, nitrogen whose atomic concentration $\sim 0.1\%$ completely suppresses the growth of the diamond phase of carbon. To prevent convective admixing of air, special attachments (not shown in the figure) were used to protect substrate by coaxial blowing of argon and by providing an effective shielding of the growing film from the surrounding atmosphere.

Laser plasma was initiated by briefly introducing a tungsten wire in the caustic region of the laser beam. Tungsten and molybdenum plate substrates were fastened to a water-cooled substrate holder that could be moved along three coordinate axes. The temperature was controlled by chromel–alumel thermocouples welded to the edge of the substrate at two or three different points. The obtained samples were analysed by Raman spectroscopy and by optical, interference and atomic force microscopy techniques.

3. Experimental results

3.1 Open-air deposition of diamond films

Before studying the synthesis of diamond films in the substrate scanning regime, we performed parametric experiments on diamond deposition in the stationary regime (the substrate remained immobile during the experiment). We studied different operating regimes of the plasmotron by varying the substrate temperature, distance between the surface being treated and the plasmotron nozzle, gas flow rates and the exposure time. The Ar – H₂ – CH₄ mixture, which was employed successfully in the laser plasma technology [2–5], was used in all the experiments. Figure 2 shows the photograph of a typical sample (tungsten plate of size $22 \times 35 \times 3$ mm) after treatment with a laser plasmotron. To create nucleation centres, the substrate was seeded

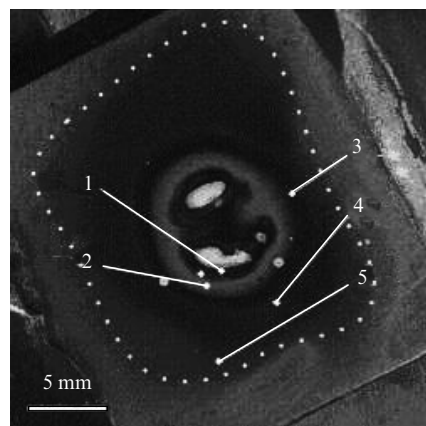


Figure 2. Photograph of a typical sample processed on a laser plasmotron in a stationary regime. The dots indicate the diamond film boundary, and the digits correspond to the points at which the Raman spectroscopic analysis of the film was performed (the spectra are shown in Fig. 3).

mechanically before deposition (the size of diamond particles used for sowing did not exceed $1\ \mu\text{m}$). The gas mixture composition was $\text{CH}_4 : \text{H}_2 = 0.03$ and $\text{H}_2 : \text{Ar} = 0.07$ and the flow rate was $\sim 9\ \text{L min}^{-1}$ for a minimum nozzle cross section of $7\ \text{mm}$. The temperature at the edge of the substrate was $T \approx 940^\circ\text{C}$. The distance between the substrate surface and the plasma core (laser beam focus) was about $13\ \text{mm}$ and the synthesis time was $\sim 25\ \text{min}$.

One can see from the photograph that the film formed on an area element of about $4\ \text{cm}^2$ has an annular structure. Two crescent-shaped spots (highest temperature zone) corresponding to two maxima in the radiation power distribution in the laser spot on the substrate can be seen in the centre. Figure 3 shows the Raman spectra of the deposited film at different points indicated in Fig. 2 (spectra from the central superheated region to the peripheral zone of the continuous diamond ring are shown from bottom to top). Depending on the temperature at the surface, different phase modifications of carbon are produced, from graphite at the centre with a characteristic peak in the spectrum at $1580\ \text{cm}^{-1}$ (point 1) to diamond, determined from the peak at frequency $1335\ \text{cm}^{-1}$ (points 4, 5). Glass-carbon with a diamond phase admixture was detected at point 3.

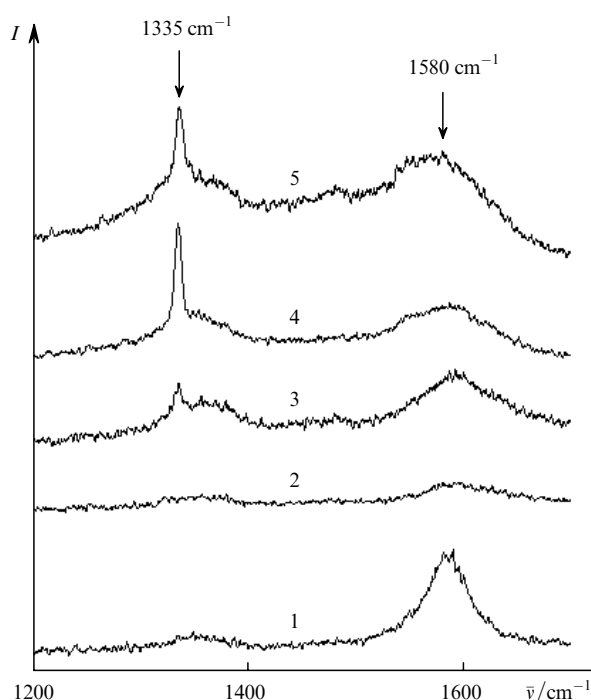


Figure 3. Raman spectra of a diamond film obtained in the stationary plasmotron operation regime at various points on the film surface (see Fig. 2).

The surface morphology was studied by optical microscopy and atomic-force microscopy using a Carl Zeiss UltraObjective atomic force microscope (AFM). Figure 4 shows the image of a continuous polycrystalline diamond film obtained with the help of the AFM (point 4 in Fig. 2). Well-faceted crystallites of size $1\text{--}3\ \mu\text{m}$ form a relief typical of polycrystalline films. The average roughness of the film was $R_a \approx 150\ \text{nm}$. Knowing the size of the crystallites, we can obtain a lower estimate of the growth rate for the continuous film ($2\text{--}6\ \mu\text{m h}^{-1}$).

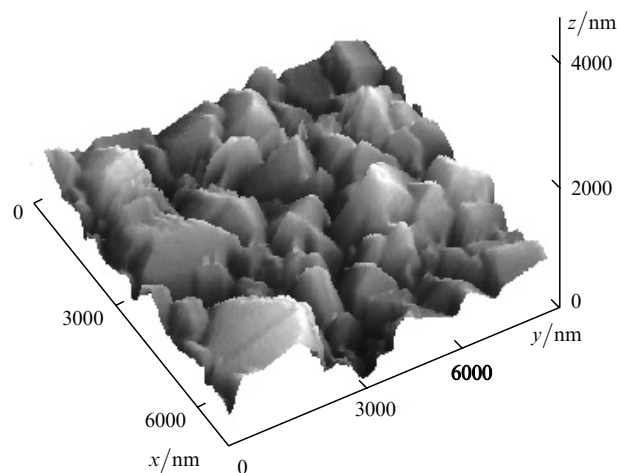


Figure 4. AFM image (frame size $7 \times 7\ \mu\text{m}$) of a continuous polycrystalline diamond film (point 4 in Fig. 2). The size of faceted diamond crystallites was $1\text{--}3\ \mu\text{m}$, and the average roughness of the film was $R_a = 149\ \text{nm}$.

Laser radiation passing through an optical discharge causes a temperature field inhomogeneity at the substrate and the central region is found to be strongly overheated. Consequently, the shape of the deposited diamond film is annular, which is not desirable from the technological point of view. Apparently, there are two ways of solving this problem. The first way involves a modernisation of the focusing system in such a way that a beam with uniform distribution of intensity in the cross section falls on the output focusing lens (and hence on the substrate) [5]. It is also necessary to use short-focus optics for focusing the laser beam. This reduces the intensity of the laser beam (incident on the substrate after passing through the plasma) due to an increase in the area of the laser spot. However, such an approach entails technical complications associated with a rapid failure of the focusing lens since in this case it is placed quite close to the optical discharge. The second way is the possibility of displacing the sample relative to the plasma jet. On the one hand, this prevents local overheating of the surface being treated for large scanning rates and levels the temperature field, which is a necessary condition for obtaining a homogeneous continuous film. On the other hand, scanning of the substrate opens in principle the possibility of depositing a diamond film on large components.

3.2 Deposition of diamond films during scanning of the substrate relative to the plasma jet

In experiments on deposition of diamond films during scanning of the sample relative to the plasma jet, we used tungsten substrates of size $22 \times 35 \times 3\ \text{mm}$ and a $\text{Ar-H}_2\text{-CH}_4$ gas mixture with component ratios $\text{H}_2 : \text{Ar} = 0.07$ and $\text{CH}_4 : \text{H}_2 = 0.03$ and a flow rate of $7\text{--}9\ \text{L min}^{-1}$. The distance between the lower exit section of the nozzle and the substrate varied between 15 and $3\ \text{mm}$, while the surface being treated (along the displacement axis) was inclined at an angle $5^\circ\text{--}10^\circ$ relative to the horizontal, thus eliminating the effect of radiation reflected from the substrate at the output window of the laser. The time operation of the plasmotron was $5\text{--}35\ \text{min}$.

Scanning was performed by horizontal displacement of the substrate holder at several ($2\text{--}5$) fixed positions, or

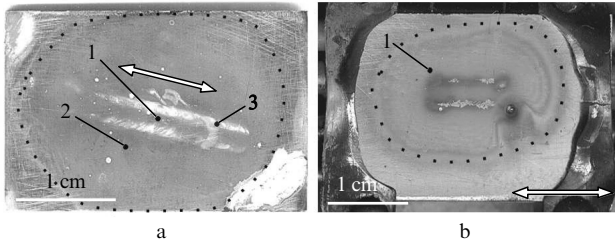


Figure 5. Photographs showing the characteristic regions of plasma plume action on the substrate surface during sample displacement (scanning) relative to the plasma jet. (a) Deposition was performed for 25 min in a continuous scanning regime at an average rate of 40 mm s^{-1} ; (b) deposition was performed for 30 min in discrete substrate displacement with a 30-s exposure in each of the three positions. The dots indicate the boundary of the region over which deposition was performed.

continuously, along a 6–17-mm long line. Depending on the experimental conditions, the time for which the sample was held in a given position varied between 1–3 s and 12 min.

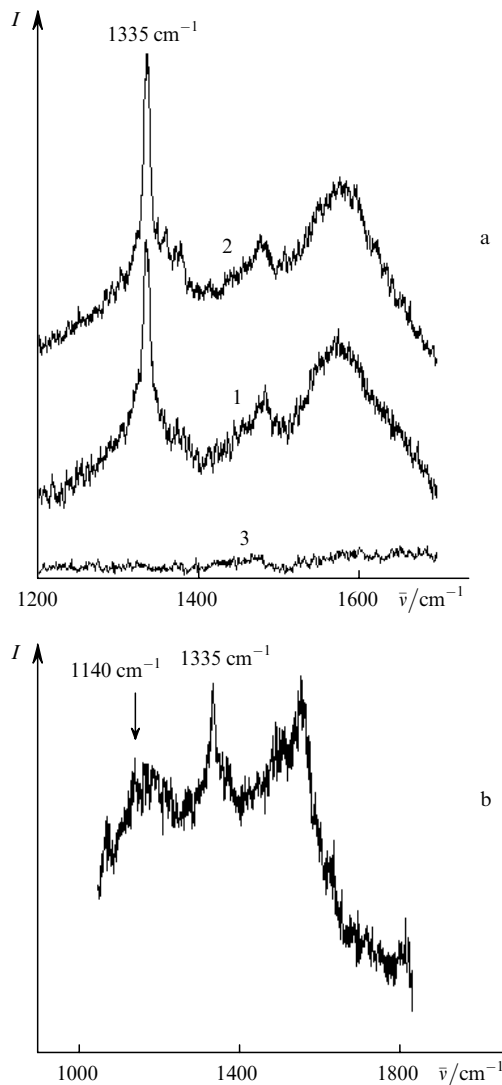


Figure 6. Raman spectra of (a) diamond and (b) nanocrystalline diamond films shown in Figs 5a and b, respectively.

Figure 5 shows the photographs of characteristic zones of plasma plume action on the substrate surface during displacement (scanning) of the sample relative to the plasma jet (the arrows show the direction of scanning, the dots mark the boundary of the diamond film), while Fig. 6 shows the corresponding Raman spectra at the points indicated in Fig. 5.

The sample shown in Fig. 5a was produced by deposition for 25 min during continuous scanning at an average rate of 40 mm s^{-1} . The area of the diamond film was $\sim 7.5 \text{ cm}^2$, which is about four times the size of the diamond ring ($\sim 2 \text{ cm}^2$) formed in the stationary mode. Two parallel strips along the scanning direction are the tracks of the laser beam with two maxima of the intensity distribution (see Fig. 2).

The Raman spectrum presented in Fig. 6a reveals the presence of a polycrystalline diamond film (Raman band at 1335 cm^{-1}). It is interesting to note that a diamond film is formed even between the strips of strongly overheated regions (point 1 in Fig. 5a). Thus, fairly homogeneous coatings can be expected for a uniform intensity distribution.

It was mentioned above that diamond films obtained by the CVD technique possess the unique properties of natural diamond. However, such films have a polycrystalline structure and a quite rough surface, which, as a rule, necessitates their processing (polishing) after deposition. The film roughness can be reduced by controlling the orientation of crystallites (by aligning the (100) plane parallel to the film surface [7]), or by reducing the grain size [8]. Smooth and well-faceted diamond films with a crystallite size from a few nanometres to dozens of nanometres transmit infrared radiation [9, 10] and also have a high hardness [11] and low coefficients of friction and abrasion [12, 13].

Figure 5b shows a photograph of a nanocrystalline diamond film obtained under conditions when the deposition performed successively in three different positions of the substrate with an exposure time of $\sim 30 \text{ s}$ in each regime. Figure 7 shows the surface relief of this film obtained with an AFM. The presence of nanodiamond (with a grain size of the order of a few nm and a few tens nm) can be judged [14]

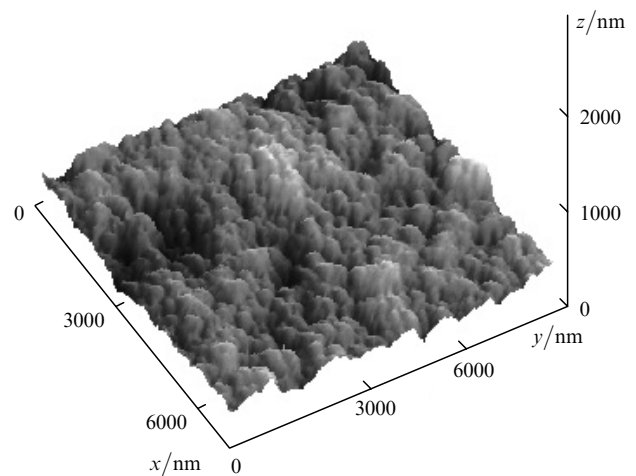


Figure 7. AFM image (frame size $7 \times 7 \mu\text{m}$) of a nanocrystalline diamond film. The size of diamond crystallites is $\sim 200 \text{ nm}$, and the average roughness of the film is $R_a = 50 \text{ nm}$.

from Raman band at 1140 cm^{-1} (Fig. 6b). The 1335-cm^{-1} Raman band corresponds to microcrystalline diamond (with a typical grain size of about 200 nm according to the AFM measurements), and its blue shift relative to the 1332.5-cm^{-1} Raman band for an unstressed single crystal is caused by compressive stresses (about 1.5 GPa) in the film due to the difference in the coefficients of thermal expansion of the film and the substrate. Raman bands at 1580 and 1350 cm^{-1} point to the presence of disordered graphite. Thus, the film has a complex composite structure in which the nano-diamond and graphite phases are localised, apparently, at the boundaries of larger diamond grains.

Irrespective of the scanning conditions, nonuniformity in the growth of the diamond film is observed in a direction perpendicular to the displacement axis. At the same time, the action of plasma on the substrate is quite uniform along the displacement axis.

4. Conclusions

The new chamberless laser-plasma technology of diamond synthesis seems to be quite promising, especially in applications where no stringent constraints are imposed on the optical quality of the material, and deposition is required on large articles or complex-shaped components. The laser plasmotron working at atmospheric pressure presented in this work was used in preliminary experiments on diamond film deposition on a substrate moving relative to the plasma jet in Ar – H₂ – CH₄ mixtures.

Further technological improvements must be directed primarily towards prevention of the strong effect of laser radiation passing through the plasma on the film being grown, in particular, due to two-coordinate scanning.

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References

1. Dischler D., Wild C. *Low-Pressure Synthetic Diamond: Manufacturing and Applications* (Heidelberg: Springer, 1998).
2. Konov V.I., Uglov S.A. *Kvantovaya Elektron.*, **25**, 291 (1998) [*Quantum Electron.*, **23**, 281 (1998)].
3. Konov V.I., Prokhorov A.M., Uglov S.A., Bolshakov A.P., Leoniev I.A., Dausinger F., Hugel H., Angstenberger B., Sepold G., Metev S. *Appl. Phys. A*, **66**, 575 (1998).
4. Bolshakov A.P., Konov V.I., Prokhorov A.M., Uglov S.A., Dausinger F. *Diamond Relat. Mater.*, **10**, 1559 (2001).
5. Metev S., Brecht H., Schwarz J., Sepold G. *Diamond Relat. Mater.*, **11**, 472 (2002).
6. Bachmann P.K., Leers D., Lydtin H. *Diamond Relat. Mater.*, **1**, 1 (1991).
7. Wild C., Koidl P., Muller-Sebert W., Walcher H., Kohl R., Herres R., Locher R., Smalemski R., Brenn R. *Diamond Relat. Mater.*, **2**, 158 (1993).
8. Ong T.P., Chang R.P.H. *Appl. Phys. Lett.*, **55**, 2063 (1989).
9. Konov V.I., Obratsova E.D., Pimenov S.M., Ralchenko V.G., Smolin A.A., Khomich A.V., Polyakov V.I., Rukovichnikov A.I., Perov P.I., Loubnin E.N. *Proc. SPIE Int. Soc. Opt. Eng.*, **2428**, 612 (1994).
10. Erz R., Dotter W., Jung K., Eharhard H. *Diamond Relat. Mater.*, **2**, 449 (1993).
11. Konov V.I., Smolin A.A., Ralchenko V.G., Pimenov S.M., Obratsova E.D., Loubnin E.N., Metev S.M., Sepold G. *Diamond Relat. Mater.*, **4**, 1073 (1995).
12. Wu R.L.C., Rai A.K., Garscadden A., Kee P., Desai H.D., Miyoshi K. *J. Appl. Phys.*, **72**, 110 (1992).
13. Bachmann P.K., Lade H., Leers D., Wiechert D.U., Theunissen G.S.A. *Diamond Relat. Mater.*, **3**, 799 (1994).
14. Nistor L.C., Van Landuyt J., Ralchenko V.G., Obratsova E.D., Smolin A.A. *Diamond Relat. Mater.*, **6**, 159 (1997).