

OPTICAL PROPERTIES OF DIAMOND-LIKE CARBON AND NANOCRYSTALLINE DIAMOND FILMS

B. Mednikarov*, G. Spasov, Tz. Babeva, J. Pirov, M. Sahatchieva, C. Popov^a,
W.Kulisch^a

Central Laboratory of Photoprocesses, Bulgarian Academy of Sciences,
Acad. G. Bonchev St. Bl. 109, 1113 Sofia, Bulgaria

^aUniversity of Kassel, Institute of Microstructure Technologies and Analytics (IMA),
Heinrich-Plett-Str. 40, 34132 Kassel, Germany

Thin diamond-like carbon (DLC) coatings deposited by DC or RF magnetron sputtering of a graphite target in argon/methane ambients, and nanocrystalline diamond/amorphous carbon (NCD/a-C) films prepared by microwave plasma chemical vapour deposition (MWCVD) from methane/nitrogen mixtures were investigated with respect to their basic and optical properties. The influence of the process parameters on the growth rate, morphology, topography and chemical bonding structure of the films was studied and correlated with the results concerning the transmittance, reflectance, refractive index and extinction coefficient of the layers.

(Received April 25, 2005; accepted May 26, 2005)

Keywords: Diamond-like carbon, Nanocrystalline diamond, Optical properties

1. Introduction

In the last decades hard amorphous carbon coatings have attracted great research interest as protective optical or tribological coatings because of their smooth surface, chemical inertness, high hardness and wear resistance, and low friction coefficient [1,2]. Known also as “diamond-like carbon” (DLC), these materials consist of a mixture of sp^3 - and sp^2 -bonded carbon atoms and can be prepared by a variety of physical or chemical vapour deposition techniques, e.g. sputtering, RF plasma enhanced CVD, cathodic-arc, ion beam, laser ablation, etc. Their properties can vary over a considerable range depending on the sp^3/sp^2 ratio and the content of hydrogen in the films from soft polymer-like carbon to hard coatings with predominantly tetrahedrally coordinated (“diamond”) carbon atoms. However, applications of the latter are restricted due to adhesion problems and significant compressive stresses which limit the film thickness.

Recently, it has been shown that nanocrystalline diamond (NCD) films can overcome this problem as they can be deposited by CVD techniques, i.e. without ion impact on the growing films [3]. The nanocrystalline nature of such coatings leads to very smooth surfaces, as in the case of DLC, but they inherit the main properties of diamond [4]. In most cases, the diamond nanocrystallites are embedded in an amorphous carbon matrix (a-C), which can influence the properties of these composite films.

In the present work DLC and NCD/a-C films were investigated with respect to their basic (growth rate, morphology, topography, chemical bonding structure) and optical (transmittance, reflectance, refractive index, extinction coefficient) properties, and some conclusions on the influence of the process peculiarities on the film properties were drawn.

* Corresponding author: bormed@clf.bas.bg

2. Experimental

The DLC films were deposited by DC or RF magnetron sputtering. Pure (5N) isostatically pressed graphite with a bulk density of 2.17 g/cm^3 was used as a target. The power applied to it was $1.6 - 2.0 \text{ W/cm}^2$ for both, DC or RF sputtering. The process was carried out in Ar (DC), Ar/CH₄ (RF) or CH₄ (RF) atmospheres with a working pressure of 4×10^{-3} mbar. The films were deposited onto glass and silicon substrates, chemically cleaned before charged in the deposition reactor, and placed on a rotating holder 45 mm from the target. The rotation improved the homogeneity and morphology of the layers, which was applied for all deposition runs. The substrates were kept at room temperature.

Nanocrystalline diamond/amorphous carbon (NCD/a-C) composite films were prepared by MWCVD from 17% CH₄/N₂ mixtures in a deposition set-up described in detail elsewhere [5,6]. All deposition experiments were performed at a substrate temperature of 770°C , working pressure of 26 mbar and MW plasma input power of 800 W. The duration of the deposition processes was 420 min. The films were grown onto monocrystalline silicon wafers, etched in NH₄F/HF and then pretreated ultrasonically in a suspension of diamond powder (grain size up to 500 nm) in n-pentane in order to promote diamond nucleation.

The film thickness, from which the growth rates for each process was calculated, was determined by a profilometer (*Talystep*) and by cross-section scanning electron microscopy (SEM). Atomic force microscopy (AFM, *NanoScope II*) provided information on the topography of the films. The chemical bonding structure of the DLC and NCD/a-C films was investigated by Auger electron spectroscopy (AES, *Las3000*, *Riber*) and Raman spectroscopy (*Ramanscope 1000*, *Renishaw*) with an Ar⁺ laser at 514.5 nm. The AES analyses were performed without sputter cleaning of the samples in order to prevent their amorphisation and/or graphitisation.

The total transmittance T_{tot} and the absolute specular reflectances $R_{f,tot}$, $R_{b,tot}$ and R_m of the samples were measured by a high precision spectrophotometer (*Cary 5E*) at normal light incidence in the spectral range of 400 - 1200 nm with an accuracy of 0.1% and 0.5%, respectively. The subscripts "f" and "b" denote reflectance measurements from the front (film) and back (substrate) side of the samples on glass substrates. R_m is the reflectance of the films deposited onto Si substrate. The transmittance T and the reflectance R_f of the films utilized in the calculation of the optical constants and thickness were evaluated from T_{tot} , $R_{f,tot}$ and $R_{b,tot}$ after applying a correction [7]. The model used for T and R_f after this correction is applicable for uniform layers on a semi-infinite substrate. The refractive index n , extinction coefficient k , and the thickness d of the films were determined simultaneously by a previously developed three-step algorithm [8]. It includes the application of the algebraic inversion method (TR_fR_m) [9], followed by double (TR_f) and (TR_m) [10] and single $T(k=0)$ [11] methods, and finally a selection of the most accurate solutions of all applied methods. The (TR_fR_m) method is based on three spectrophotometric measurements (T , R_f and R_m) for the simultaneous determination of n , k and d at each wavelength. The most accurate solution for d is used as a parameter in the double and single methods. The combination of these methods makes the evaluation of n and k with high accuracy possible: $\Delta n/n$ and $\Delta k/k$ are about 1-2% and 4-5%, respectively. The calculated thicknesses are in a good agreement with those obtained by profilometry or cross-section SEM.

3. Results and discussion

The thicknesses of the DLC films were in the range of 40 – 580 nm, whereas that of the NCD/a-C films varied between 700 nm and 4 μm . For example, the growth rate of DLC films in pure Ar atmosphere is on the order of 12 nm/min, while it increases by an order of magnitude in Ar/CH₄ (for the same other process parameters), reaching 150 nm/min. This result shows that methane plays an active role in the deposition process either via enhanced sputtering or by co-deposition of carbon species originating from CH₄ molecules. In the case of MWCVD, the growth rate was 9.5 nm/min.

The morphology of the films prepared by both techniques was studied by scanning electron microscopy, which showed smooth and uniform surfaces. These results were supported by AFM observations; typical AFM images of DLC and NCD/a-C films are shown in Fig. 1.

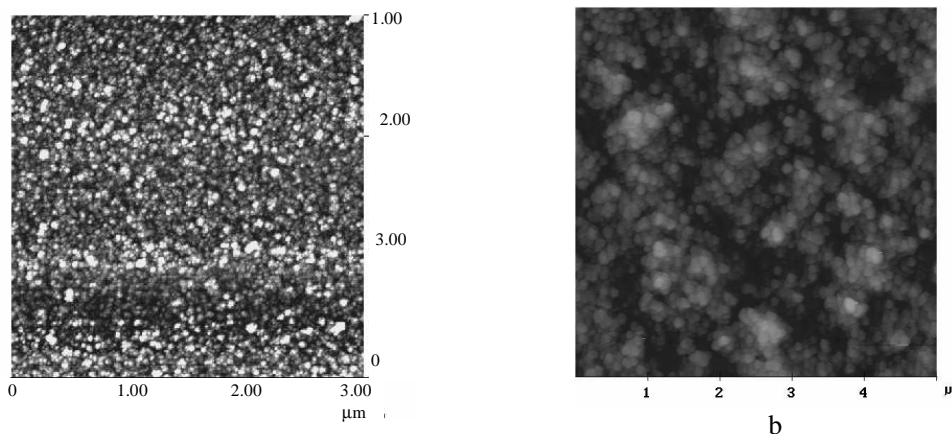


Fig. 1. Typical AFM images of (a) DLC films (Z scale 10 nm) and (b) NCD/a-C films (Z scale 50 nm).

The NCD/a-C films possessed a rms roughness of 12 nm and grain heights up to 43 nm; the DLC films were even smoother with rms roughnesses below 10 nm.

The bonding structure of the DLC and NCD/a-C films was investigated by AES; their derivative Auger C_{KLL} spectra are shown in Fig. 2 together with the spectra of graphite and polycrystalline diamond (PCD) films as references measured under the same conditions. The binding energy width D between the most positive maximum and the most negative minimum was determined for all samples; the results are compared with data taken from literature in Table 1.

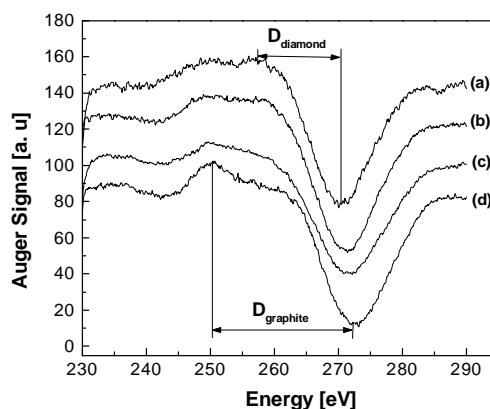


Fig. 2. Auger spectra of (a) PCD, (b) NCD/a-C, (c) DLC and (d) graphite films. The values of D width are given in Table 1.

Taking into account the two extreme cases – diamond (100% sp^3 -bonded carbon atoms) and graphite (100% sp^2 -bonded carbon atoms) – a linear interpolation between the D values can be used to determine the ratio of sp^3/sp^2 -hybridized atoms in any carbon film [12-14]. For the PCD films D was 13.0 eV, the same value was found for natural diamond [12]. It should be mentioned that D values of diamond cited in literature vary between 13.0 and 14.5 eV depending on the type and facets of the examined material. In the case of graphite, we found a value of 22.6 eV, which is within the range reported in literature (up to 22.8 eV for highly oriented pyrolytic graphite HOPG). The difference of D for diamond and graphite was 9.6 eV in our measurements.

Table 1. D widths and percentage of sp^2 -bonded atoms in different carbon materials

Carbon material	D width, eV	sp^2 -carbon atoms, %	Reference
Natural diamond	13.0	0	[12]
Natural diamond	13.2-14.5	0	[13]
Natural diamond	14.2-14.3	0	[14]
PCD films	13.0	0	this work
NCD/a-C	13.9	10	this work
a-C (cathodic arc)	16.3	32	[13]
a-C (dual ion sputt.)	18.8-20.0	55-69	[14]
a-C (magn. sputt.)	19.5	66	[13]
DLC	19.3	66	this work
Graphite	22.5	100	[14]
Graphite	22.6	100	this work
HOPG	22.8	100	[13]

The D values for the DLC and NCD/a-C films under investigation fall between these two extremes; from the linear relation between D and the fraction of sp^2 carbon atoms, the bonding structure was determined. For DLC films prepared with 100% CH_4 D is 19.3 eV, corresponding to 66% sp^2 -carbon atoms, while the NCD/a-C films ($D = 13.9$ eV) are composed predominantly of sp^3 -bonded atoms (10% sp^2 -atoms). The latter is in a good agreement with the XPS results, which revealed sp^2 -contents about 10% [15].

The Raman spectra of the films prepared with both techniques were fitted using Gaussian peaks with variable parameters for peak width (FWHM), position and area. In order to obtain a good fit, different numbers of peaks were used for the DLC and NCD/a-C films, respectively, which reflects their different nature. All spectra of the DLC films had a very similar structure and showed a rather flat background indicating low (if any) concentrations of hydrogen [16]. They were fitted with two Gaussians at 1418 and 1562 cm^{-1} , which can be attributed to the D and G bands of graphite, respectively (Fig. 3 (a)); their I_D/I_G ratios were on the order of 2.96. This ratio and the positions of the D and G bands indicate the presence of an amorphous DLC phase only in the films [17].

Attempts to deconvolute the spectra of the NCD/a-C films with two or three Gaussians did not give a sufficiently good fit; for this reason the spectra were fitted with four peaks (Fig. 3 (b)). In general the differences concerning the position, the width and the areas of the four peaks were rather small between the samples, indicating that all MWCVD films were quite similar. The broad bands at about 1345 and 1560 cm^{-1} are assigned to the D and G bands of sp^2 -bonded carbon (graphite), respectively. The other two bands are situated around 1160 and 1470 cm^{-1} . Some authors attributed these bands to diamond nanocrystals [18,19] or their precursor structures [20]; others assigned them to trans-polyacetylene situated at the grain boundaries of diamond nanocrystallites [21,22]. Irrespective of the final assignment, however, the peak at 1160 cm^{-1} has never been observed in amorphous carbon films (ta-C, DLC, a-C, a-C:H) nor in polycrystalline diamond coatings with large crystals, but appeared only in films containing NCD [23]. It may stem either from the crystallites themselves or from the boundary material (which then must be unique to NCD) but can, in our opinion, be used as a fingerprint for the existence of NCD. The Raman spectra suggest a mixture of diamond nanocrystallites (with a size of 3-5 nm as determined by XRD [23]), and an amorphous carbon matrix including some sp^2 -bonded graphitic phase, as shown from the AES results discuss above.

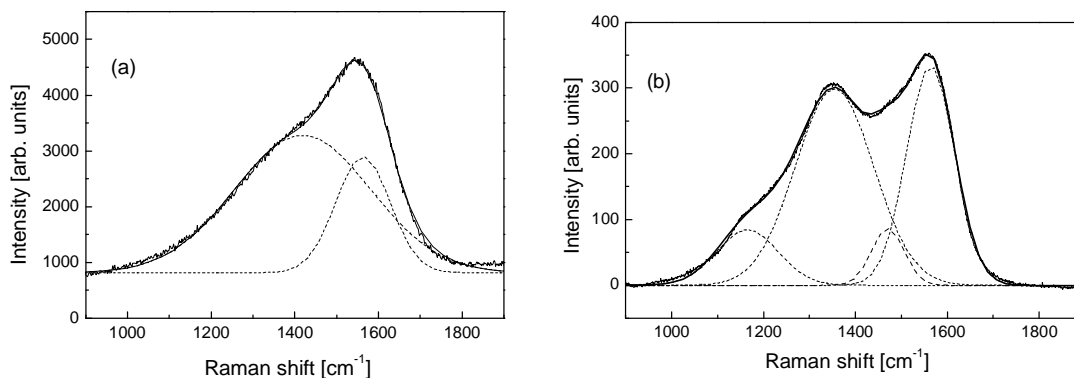


Fig. 3. Typical deconvoluted Raman spectra of (a) DLC and (b) NCD/a-C films.

The Raman cross-section of sp^2 -bonded carbon is 50-100 times higher than that of sp^3 -carbon for an excitation wavelength of 514 nm [24], that of amorphous carbon (a-C) is even 233 times greater than that of diamond [25]. This means that a Raman study of NCD/a-C composite films will predominantly give insight into the nature and the chemical bonding structure of the amorphous matrix. On the other hand, the matrix is the phase that can determine a number of application relevant properties (mechanical, optical, electrical), which makes its investigation rather important for the optimization of the basic properties (fraction in the composite material, composition, sp^3/sp^2 ratio, etc.).

Transmittance spectra were taken only for DLC films deposited on glass substrates (Fig. 4). They showed high transparency (up to 90%) of the films prepared in presence of CH_4 . In contrast, DLC films deposited in pure Ar ambient possess a lower transmittance in the investigated spectral region due to higher absorption as a result of the higher content of sp^2 -bonded carbon atoms.

The reflectance curves of DLC films prepared with methane and of a NCD/a-C film given in Fig. 5, were similar, suggesting a similar nature of the DLC films and the matrix of the NCD/a-C coatings. Their spectra are almost featureless, neither interference effects nor peaks hinting at distinct absorption bands can be observed; R reaches 10% (DLC) and 14% (NCD/a-C) at 1000 nm. The reflectance spectrum of DLC prepared with argon exhibits a quite different behaviour as compared with the other films; in this case R is much higher (ca. 35% at 1000 nm). This is in agreement with the higher absorption observed for this films (Fig. 4).

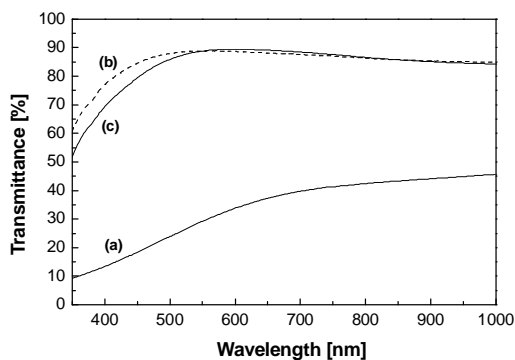


Fig. 4. Transmittance spectra of DLC films prepared with (a) 100% Ar, (b) 98% Ar + 2% CH_4 and (c) 50% Ar + 50% CH_4 .

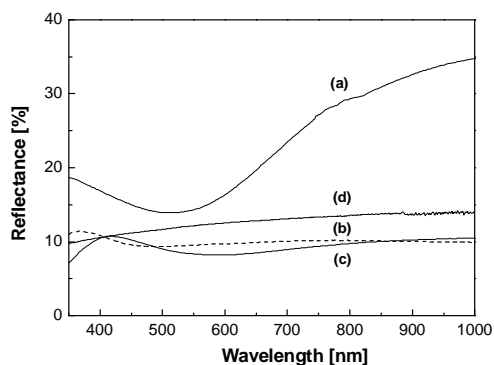


Fig. 5. Reflectance spectra of DLC films prepared with (a) 100% Ar, (b) 98% Ar + 2% CH_4 , (c) 50% Ar + 50% CH_4 and (d) NCD/a-C film.

The refractive index n of a DLC film prepared with pure Ar varies between 1.85 and 1.95 and possesses a pronounced broad maximum at about 500 nm (Fig. 6 (a)), while n of the NCD/a-C

film is in the range of 2.0-2.1 (Fig. 6 (b)). The refractive index of the NCD/a-C films is higher than that of the entirely amorphous DLC films, reflecting the presence of a crystalline phase, but still relatively low as compared to that of diamond (2.41 at 633 nm [26]). The extinction coefficients k of both types of films, increase from the IR to the UV region reaching values of 0.19 (DLC) and 0.13 (NCD/a-C) at 400 nm. The higher absorption, especially at shorter wavelengths, can be expected as both types of film contain considerable amounts of sp^2 -bonded carbon. These results indicate that the optical properties of the NCD nanocomposite films are determined by the features of the amorphous matrix rather than those of the crystalline fraction.

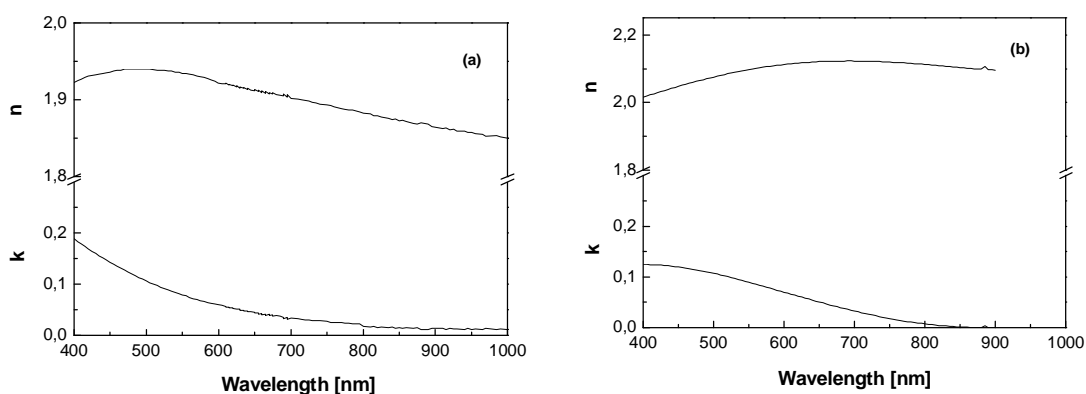


Fig. 6. Dispersion of the refractive index n and the extinction coefficient k of (a) DLC film prepared with Ar and (b) NCD/a-C film.

4. Conclusions

Smooth and uniform DLC and NCD/a-C films were prepared by magnetron sputtering and microwave plasma chemical vapour deposition, respectively. The presence of sp^2 -bonded carbon atoms with considerable fractions, estimated by analyses of the carbon Auger peak, predetermines their optical properties: refractive indexes below 2.1 and relatively high extinction coefficients. The properties of the amorphous phase in both types of films have to be improved by variation of the deposition conditions in order to optimize their optical properties and to allow application of these films e.g. as protective optical coatings.

Acknowledgements

The authors gratefully acknowledge the financial support of NATO under the Collaborative Linkage Grant Program (CBP.EAP.CLG 981519). They would like to thank Dr. V. Vorlicek (Institute of Physics, ASCR, Prague) for the Raman measurements. This research was supported by the Marie-Curie EIF within the 6th EC Framework Programme (MEIF-CT-2004-500038).

References

- [1] M. C. Angus, C. C. Hayman, *Science* **241**, 913 (1988).
- [2] J. Robertson, *Surf. Coat. Technol.* **50**, 185 (1992).
- [3] T. Sharda, M. Umeno, T. Soga, T. Jimbo, *J. Appl. Phys.* **89**, 4874 (2001).
- [4] D.M. Gruen, *Annual Rev. Mater. Sci.* **29**, 211 (1999).
- [5] C. Popov, W. Kulisch, *Proceedings of the CVD XVI and EUROCVI-14 Conference, Paris*, Eds. M. Allendorf, F. Maury, F. Teyssandier, The Electrochemical Society, Pennington, NJ, 2003, p. 1079.

-
- [6] C. Popov, M. Jelinek, S. Boycheva, V. Vorlicek, W. Kulisch, J. Metastable Nanocryst. Mater. **23**, 31 (2005).
- [7] H. Liddell, *Computer-Aided Techniques for Design of Multilayer Filters*, Bristol, Adam Hilger, 1981, p. 19.
- [8] Tz. Babeva, S. Kitova, I. Konstantinov, Appl. Opt. **40**, 2682 (2001).
- [9] V. Panayotov, I. Konstantinov, Proc. SPIE **2253**, 1070 (1994).
- [10] I. Konstantinov, Tz. Babeva, S. Kitova, Appl. Opt. **37**, 4260 (1998).
- [11] V. Panayotov, I. Konstantinov, Appl. Opt. **30**, 2795 (1991).
- [12] I. Montero, L. Galan, A. Laurent, J. Perriere, J. Sposta, Thin Solid Films **228**, 72 (1993).
- [13] S. T. Jackson, R.G. Nuzzo, Appl. Surf. Sci. **90**, 195 (1995).
- [14] J. C. Lascovich, S. Scaglione, Appl. Surf. Sci. **78**, 17 (1994).
- [15] C. Popov, W. Kulisch, S. Boycheva, K. Yamamoto, G. Ceccone, Y. Koga, Diamond Relat. Mater. **13**, 2071 (2004).
- [16] B. Marchon, J. Gui, K. Grannen, G.C. Rauch, J.W. Ager, S.R.P. Silva, J. Robertson, IEEE Trans. Magn. **33**, 3148 (1997).
- [17] A. C. Ferrari, J. Robertson, Phys. Rev. B **61**, 14095 (2000).
- [18] R. J. Nemanich, J. T. Glass, G. Lucovsky, R. E. Shroder, J. Vac. Sci. Technol. A **6**, 1783 (1988).
- [19] S. Praver, K. W. Nugent, D. N. Jamieson, J. O. Orwa, L. A. Bursill, J. L. Peng, Chem. Phys. Lett. **332**, 93 (2000).
- [20] P. K. Bachmann, D. U. Wiechert, Diamond Relat. Mater. **1**, 422 (1992).
- [21] A. C. Ferrari, J. Robertson, Phys. Rev. B **63**, 121405 (2001).
- [22] R. Pfeiffer, H. Kuzmany, N. Salk, B. Günther, Appl. Phys. Lett. **82**, 4149 (2003).
- [23] C. Popov, W. Kulisch, P. N. Gibson, G. Ceccone, M. Jelinek, Diamond Relat. Mater. **13**, 1371 (2004).
- [24] N. Wada, P. J. Gaczi, S.A. Solin, J. Non-Cryst. Solids **35/36**, 543 (1980).
- [25] S. R. Sails, D. J. Gardiner, M. Bowden, J. Savage, D. Rodway, Diamond Relat. Mater. **5**, 589 (1996).
- [26] P. Koidl, C. -P. Klages, Diamond Relat. Mater. **1**, 1065 (1992).