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Characterization of the bonding structure of nanocrystalline diamond and amorphous carbon films prepared by plasma assisted techniques

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ABSTRACT Thin nanocrystalline diamond/amorphous carbon (NCD/a-C) composite films and amorphous diamond-like carbon (DLC) films were prepared by three methods: microwave plasma chemical vapour deposition (MWCVD) from methane/nitrogen mixtures (NCD/a-C), RF magnetron sputtering of a pure graphite target in argon/methane ambients, and pulsed laser deposition (PLD) in vacuum or argon atmosphere (DLC). The films prepared by the three techniques were comprehensively characterized with respect to their bonding structure by Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS).

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1 Introduction

Nanocrystalline diamond (NCD) films, either in pure form or as a composite with an amorphous carbon (a-C) matrix, and diamond-like carbon (DLC) films have attracted great research interest, due to their properties approaching those of diamond in terms of hardness [1, 2], low friction coefficient, high wear resistance [3, 4], optical transparency [5, 6], chemical stability, thermal conductivity, biocompatibility [7, 8], etc. The properties of DLC films can vary over a wide range depending on the chemical bonding nature, namely the sp^3/sp^2 carbon ratio and the content of hydrogen, from soft polymer-like carbon to hard coatings with predominantly tetrahedrally coordinated ("diamond-like") carbon atoms. In a similar way the nature of the amorphous carbon matrix can influence to a large extent the properties of the NCD/a-C nanocomposite films, a problem which has been somewhat neglected in the literature up to now.

In the present work DLC and NCD/a-C films were investigated with respect to their growth rate, morphology, topography, and especially their chemical bonding structure, and some conclusions concerning the influence of the process peculiarities on the film properties were drawn.

2 Experimental

Nanocrystalline diamond/amorphous carbon (NCD/a-C) composite films were prepared by MWCVD from CH_4/N_2 mixtures with 9 and 17% methane in a deposition set-up described in detail elsewhere [9]. All deposition experiments were performed at substrate temperatures up to 770 °C, a working pressure of 2.6 kPa and a MW plasma input power of 800 W. The duration of the deposition processes was 420 min. The films were grown onto monocrystalline (100) silicon wafers, etched in NH_4F/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. Polycrystalline diamond (PCD) films deposited by hot-filament CVD (0.9% CH_4 in H_2, 825–850 °C substrate temperature and 2250 °C filament temperature) were used as a reference for the analyses as well as substrates for the growth of NCD without additional pretreatment.

DLC films were deposited by RF magnetron sputtering (MS, in the following DLC-MS) from a target of isostatically pressed graphite (5N) with a bulk density of 2.17 g/cm^3; the power applied to the target was 1000 W. The process was carried out in Ar/CH_4 mixtures with methane concentrations up to 70% at a working pressure of 0.4 Pa. The films were deposited onto monocrystalline (100) silicon substrates, chemically cleaned before charging into the deposition reactor, and placed on a rotating holder 45 mm from the target. The rotation improved the homogeneity and morphology of the layers. The substrates were kept at room temperature.

DLC films were also prepared by PLD (DLC-PLD) using a KrF excimer laser ($\lambda = 248$ nm, $\tau = 20$ ns, f = 13 Hz) for the ablation of a high purity graphite target (GoodFellow) with an energy density of 20 J/cm^2. The layers were deposited in vacuum or Ar ambient with working pressures up to 1 Pa. The deposition time was 3.9–5.8 min, correspond-

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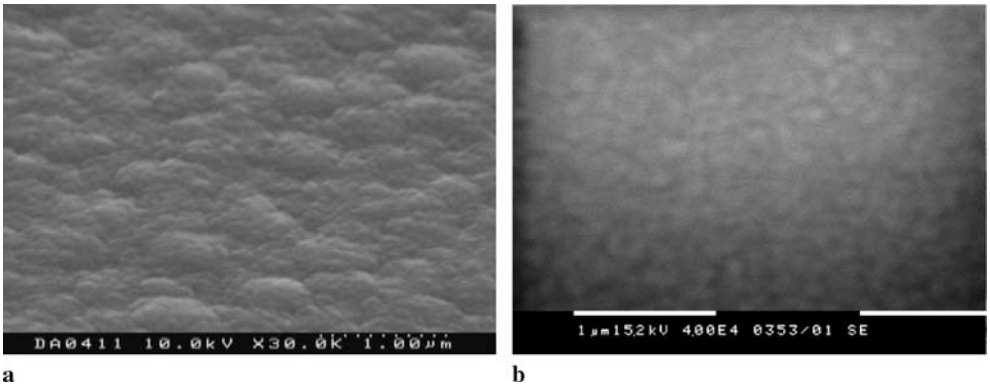

FIGURE 1 Top view SEM micrographs of (**a**) NCD/a-C film and (**b**) DLC-MS film (scale *bar* 1 µm)

ing to 3000–4500 laser pulses. Silicon wafers were used as substrates; they were initially cleaned for 2 min. by a RF discharge (4 Pa Ar, 100 W) in the chamber. The substrates were not additionally heated during the deposition; the target-substrate distance was kept constant at 40 mm.

The film thickness, from which the growth rates for each process were calculated, was determined by profilometry and cross-section scanning electron microscopy (SEM). SEM and atomic force microscopy (AFM) provided information about the morphology and topography of the films. The chemical bonding structure of the NCD/a-C and DLC films was investigated by Auger electron spectroscopy (AES, Las3000, Riber) with a primary electron energy of 3 keV, and by X-ray photoelectron spectroscopy (XPS, ADES-400 VG Scientific) with Al K_α radiation and 20 eV pass energy. The AES and XPS analyses were performed without sputter cleaning of the samples in order to prevent their amorphisation and/or graphitisation.

3 Results and discussion

3.1 *Growth rates, morphology, topography*

The thicknesses of the films deposited by MWCVD varied between 700 nm and 4 µm whereas those of the films prepared by MS and PLD were in the range of 40–180 nm and 50–120 nm, respectively, depending on the deposition conditions. In the case of MWCVD, the growth rate was influenced by the substrate temperature and the methane concentration in the gas phase. The growth rate increased when increasing the temperature suggesting a kinetic control of the process; it shows that surface reaction(s) are the rate-limiting step of the deposition process. Higher CH_4 concentrations also resulted in an increase of the growth rate due to higher concentrations of film-forming species (1.8 nm/min. for 9% CH_4 and 9.5 nm/min. for 17% CH_4 at 770 °C). An increase of the methane concentration on the growth rates of the DLC-MS films had a similar effect; the rate raised from 10 nm/min. (5% CH_4) to 68 nm/min. (70% CH_4). This result shows that methane plays an active role in the deposition process, either via enhanced sputtering of the target or by co-deposition of carbon species originating from the CH_4 molecules. The growth rate of the DLC-PLD films showed a week dependence only on the working pressure, varying between 20 nm/min. (vacuum 2×10^{-4} Pa) and 12 nm/min. (1 Pa Ar); the slight decrease is probably due to the decreased mean free path of the ablated species with the increase of the pressure.

XRD measurements revealed that the NCD films are composed of diamond nanocrystallites with a diameter of 3–5 nm, embedded in an amorphous carbon matrix (a-C) [10], while the DLC films were completely amorphous.

All films under investigation were uniform as seen from the SEM images in Fig. 1. AFM analyses showed that the NCD films were smooth with rms roughnesses down to 12 nm. In addition, a sub-structure of the films due to the relatively low nucleation density achieved by the ultrasonic pre-treatment of the substrates could be observed [11]. The DLC films possess even smoother surfaces with rms roughnesses on the order of 2–5 nm. No distinct trend concerning the influence of the deposition conditions on the surface roughness was observed.

3.2 *Chemical bonding structure – Auger electron spectroscopy*

The bonding structure of the NCD/a-C and DLC films was investigated by AES; by analysis of the derivative Auger C_{KLL} spectra the sp^3-carbon fraction was evaluated. The kinetic energy width *D* between the most positive maximum and the most negative minimum (the so-called *D* value) was determined for all samples under study,

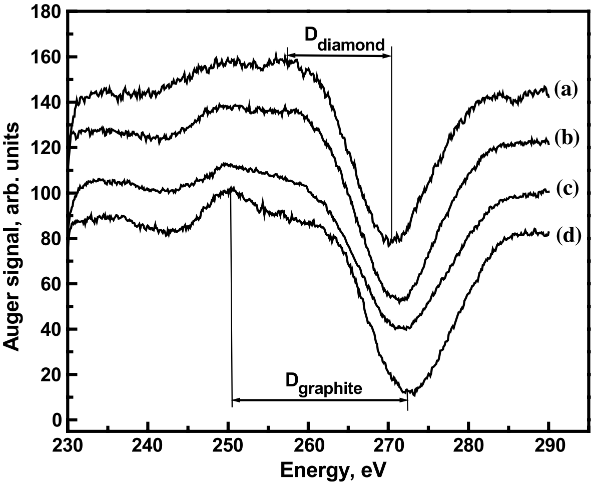

FIGURE 2 Auger C_{KLL} spectra of (a) PCD, (b) NCD/a-C, (c) DLC-MS and (d) graphite films

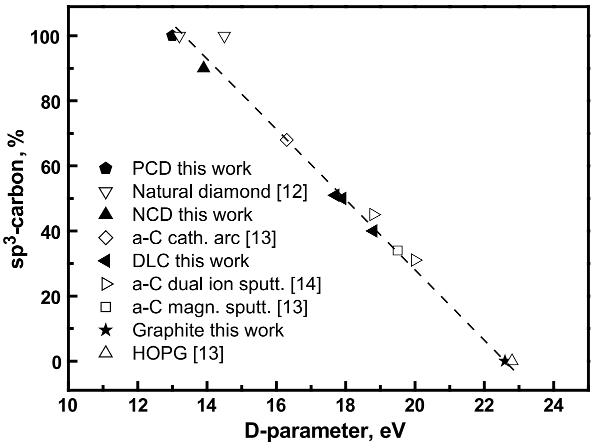

FIGURE 3 Fraction of sp^3 atoms in different carbon films vs. the D value determined from the analyses of the Auger spectra

as well as for graphite and polycrystalline diamond films, which were measured under the same conditions and used as references (Fig. 2).

Taking into account the two extreme cases – diamond (100% sp^3-bonded carbon atoms) and graphite (100% sp^2-bonded carbon atoms) – one can use a linear interpolation of the D values to determine the fraction of sp^3-hybridized atoms in any carbon film [12–14]. For the PCD films D was 13.0 eV, the same value as reported for natural diamond [12]. It should be mentioned that the D values of diamond in the literature vary between 13.0 and 14.5 eV depending on the type and facets of the examined material [13, 14]. In the case of graphite, we found a value of 22.6 eV, which is within the range reported in the literature (up to 22.8 eV for highly oriented pyrolytic graphite, HOPG) [13, 14]. The difference of D for diamond and graphite in our measurements was 9.6 eV. The D values for the NCD/a-C and DLC films under investigation fall between these two extremes; assuming a linear relation between D and the fraction of sp^3 carbon atoms, the bonding structure was determined. For the DLC films prepared by sputtering D decreases from 18.8 to 17.7 eV when the CH_4 concentration in the gas phase is increased from 30 to 70%, corresponding to an increase of the sp^3-carbon fraction from 40 to 51%, while the NCD/a-C films ($D = 13.9$ eV) are composed predominantly of sp^3-bonded atoms (90%). All results discussed above are summarized in Fig. 3, together with data taken from literature.

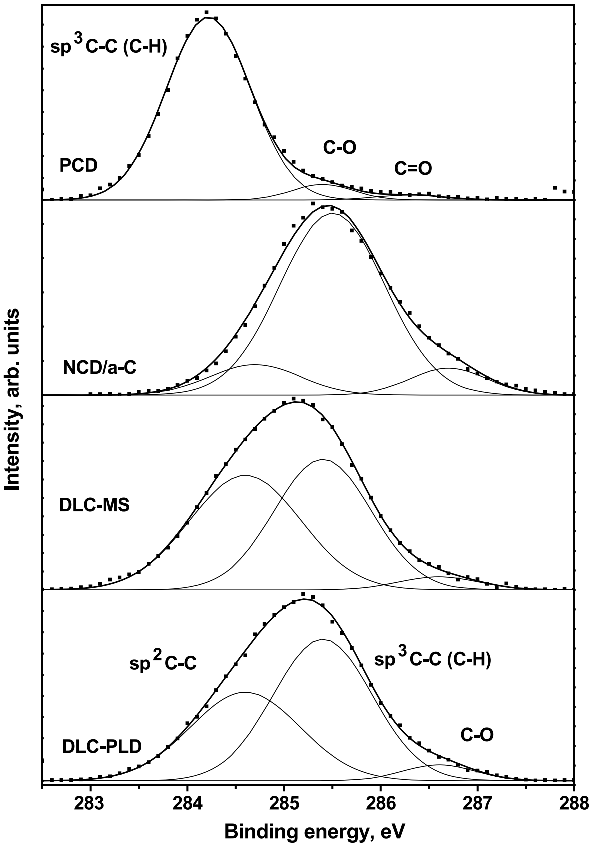

FIGURE 4 Deconvoluted C 1s X-ray photoelectron spectra of PCD, NCD/a-C, DLC-MS and DLC-PLD films. The spectra are given without correction of the charging effect

3.3 *Chemical bonding structure – X-ray photoelectron spectroscopy*

XPS measurements have been performed with nine samples (two NCD/a-C, three DLC-MS and four DLC-PLD); a PCD film was used as a reference. Representative and deconvoluted C 1s spectra for each type of films are shown in Fig. 4. From the figure it is evident that three contributions have to be taken into account for the C 1s peak (exception PCD). A summary of the deconvolution analysis is given in Table 1. The major peak (PCD, NCD) or that with higher binding energy when two peaks with similar intensities appeared (DLC), can be attributed to sp^3 bonded car-

Sample	Deposition conditions	FWHM sp^3 peak [eV]	ΔBE1 [eV]	FWHM sp^2 peak [eV]	sp^3 content from XPS [%]	ΔBE2 [eV]	Oxygen content [at %]	sp^3 content from AES [%]
PCD		0.87	–	–	100	1.2	7.7	100
NCD/a-C1	600 °C on Si	1.08	0.8	0.93	87	1.2	8.7	90
NCD/a-C2	600 °C on PCD	1.09	0.8	0.90	88	1.2	8.9	–
DLC-MS1	30% CH_4	1.09	0.8	1.18	37	1.1	5.1	40
DLC-MS2	40% CH_4	1.10	0.8	1.13	48	1.1	6.6	51
DLC-MS3	70% CH_4	1.10	0.8	1.10	55	1.1	3.6	50
DLC-PLD1	1.0 Pa Ar	1.07	0.8	1.18	44	1.2	3.0	–
DLC-PLD2	0.5 Pa Ar	1.00	0.8	1.15	50	1.2	3.8	–
DLC-PLD3	0.25 Pa Ar	0.99	0.8	1.14	53	1.2	4.6	–
DLC-PLD4	vacuum	1.02	0.8	1.13	59	1.2	4.7	–

TABLE 1 Results of the deconvolution of C 1s XPS peaks of PCD, NCD/a-C, DLC-MS and DLC-PLD prepared at different conditions

bon. In the case of NCD/a-C films it is impossible to distinguish between sp^3 carbon in diamond nanocrystals and sp^3 C−C and C−H bonds in the amorphous matrix. The FWHM of the sp^3 peak of all samples was 1.0–1.1 eV with the exception of the PCD sample (0.9 eV). Owing to charging effects, the position of the peak varied considerably in different samples. Therefore, for the remaining two peaks the binding energies are given with respect of that of the first peak. The contribution at $\Delta E_1 \approx -0.8$ eV can be identified with sp^2 carbon [15]. Since the sp^2 related peak was absent for the measurement of the reference PCD film, it can be concluded that adventitious carbon from surface contaminations has no influence on the results. The FWHM of the sp^2 peak was 0.9 eV for NCD films, and 1.1–1.2 eV for the DLC films prepared by both techniques. The content of sp^3 carbon in all films under investigation was evaluated from the corresponding peak area, weighted by the sum of the $sp^3 + sp^2$ areas; the results are summarized also in Table 1. Areas of the peaks were determined following Shirley's inelastic background subtraction mode. An increase of the sp^3 fraction was observed with the increase of the methane concentration for DLC-MS and with the decrease of Ar pressure for DLC-PLD, while NCD/a-C films possessed constant content of sp^3 bonded carbon atoms. Comparison of the sp^3 fraction determined by XPS shows good agreement with the results from AES.

The third peak at $\Delta E_2 \approx 1.1$–1.2 eV can be identified with C−O bonds, which are due to surface contamination after exposure to the air. Results of the XPS survey analyses showed that all samples under discussion contain up to 10% of surface oxygen.

4 Conclusions

NCD/a-C and DLC films prepared by different techniques were investigated with respect to their growth rate, morphology, topography and chemical bonding nature. The content of the sp^3 carbon atoms was evaluated by analysing the carbon AES and XPS peaks. The results from both analyses showed good agreement revealing that the bonding nature of the DLC films can be varied by the process parameters. In case of NCD/a-C films although impossible to distinguish between sp^3 carbon in diamond nanocrystallites and in the amorphous matrix, the sp^3/sp^2 ratio was constant for the investigated samples.

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REFERENCES

1 S.A. Catlegde, Y.K. Vohra, J. Appl. Phys. **86**, 698 (1999)
2 A.A. Voevodin, M.S. Donley, Surf. Coat. Technol. **82**, 199 (1996)
3 C. Zuiker, A.R. Krauss, D.M. Gruen, X. Pan, J.C. Li, R. Csencsits, A. Erdemir, C. Bindal, G. Fenske, Thin Solid Films **270**, 154 (1995)
4 A. Grill, Surf. Coat. Technol. **95**, 507 (1997)
5 T. Sharda, T. Soga, T. Jimbo, J. Appl. Phys. **93**, 101 (2003)
6 J. Kaplan, F. Jansen, M. Machonkin, Appl. Phys. Lett. **47**, 750 (1985)
7 S. Mitura, A. Mitura, P. Niedzielski, P. Couvrat, Chaos Soliton. Fract. **10**, 2165 (1999)
8 C. Dumkum, D.M. Grant, I.R. McColl, Diam. Relat. Mater. **6**, 802 (1997)
9 C. Popov, M. Novotny, M. Jelinek, S. Boycheva, V. Vorlicek, M. Trchova, W. Kulisch, Thin Solid Films **507**, 297 (2006)
10 C. Popov, W. Kulisch, P.N. Gibson, G. Ceccone, M. Jelinek, Diam. Relat. Mater. **13**, 1371 (2004)
11 W. Kulisch, C. Popov, Phys. Stat. Solidi A **203**, 203 (2006)
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 J.I.B. Wilson, J.S. Walton, G. Beamson, J. Electron. Spectrosc. Relat. Phenom. **121**, 183 (2001)