

ELECTRON SPECTROSCOPY OF NANOCRYSTALLINE DIAMOND SURFACES

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Thin, fully optically transparent nanocrystalline diamond (NCD) films prepared at growth temperatures from 400 °C to 1100 °C were well characterized by SEM, AFM, and by angular-resolved x-ray photoelectron spectroscopy (ARXPS). The ARXPS spectra were applied for estimating the extent of sp³ hybridization of carbon atoms in a surface region of the NCD films. Elastic peak electron spectroscopy (EPES) was used for assessment of the inelastic mean free path (IMFP) values of electrons in NCD films in the electron energy range 200 eV – 2400 eV. The resulting IMFPs were compared to the IMFPs calculated from the optical data and from the TPP-2M predictive formulae.

Keywords: Nano-crystalline diamond, Electron spectroscopy

1. Introduction

The nanocrystalline diamond (NCD) films have recently attracted considerable interest due to possible important technological applications [1]. Such films can be used for various tribological coatings and as hard, wear resistant biocompatible materials [2] exhibiting a low friction coefficient. A major advantage in comparison to polycrystalline diamond films is, in particular, their relative low surface roughness.

In the present contribution we used this unique material for determination of the inelastic mean free path (IMFP) values of electrons by means of the Elastic peak electron spectroscopy (EPES). The EPES method combines the measurement of the electron elastic backscattering probability from an investigated sample and a standard material (so-called method with a standard) with the relevant Monte Carlo (MC) calculation. Note, a single crystal or polycrystalline diamond sample surface with large grains are less convenient for assessment of the IMFPs than the NCD samples since no coherent effects are expected in the recorded spectra. Their occurrence makes calculations of electron transport in a solid difficult.

The IMFPs are especially important in quantitative electron spectroscopy methods, i.e. XPS, AES, etc., for determining the surface composition, the overlayer thickness, the non-destructive depth profiling of elements found near solid surfaces, and for calculations of electron transport in a solid. The methods for evaluating the IMFPs for selected elements, inorganic and organic compounds in the electron energy range 50 eV – 10000 eV have been extensively reviewed [3]. The IMFPs are available in the NIST database [4].

Recently, the IMFPs for diamond and graphite have been calculated from the optical data by Tanuma et al. [5] and from the TPP-2M predictive formulae [6]. Surprisingly large root-mean-square (RMS) deviations were found between the IMFPs calculated from TPP-

2M and those evaluated from the optical data for diamond (71.8%) [5]. At present, the number of reliable experimental IMFP data obtained with the EPES spectroscopy for diamond [3] is very limited. Up to the best present authors knowledge, the first attempt to determine the IMFPs for a NCD film has been done very recently by the EPES method using a Cu standard [7]. Therefore, the aim of the present work is to compare the IMFPs determined from the EPES method to theory.

2. Characterization

The NCD films deposited from the methane/hydrogen plasma are undoped, fully optically transparent below 5.4 eV, photosensitive, with Raman signature of predominant diamond bonding. More details about the film preparation and basic characterization (Raman, SEM, optical transmittance) can be found elsewhere [8]. The *RMS* value of the surface roughness, estimated by AFM, ranged from 10 nm to 30 nm depending on the NCD film thickness. At the pristine NCD film surfaces 2-3 at. % of oxygen was found. Diamond grains of nanometric dimensions, illustrated in Fig. 1, would be surrounded by differently bonded carbon atoms, e.g. by the sp^2 hybridized carbons [9].

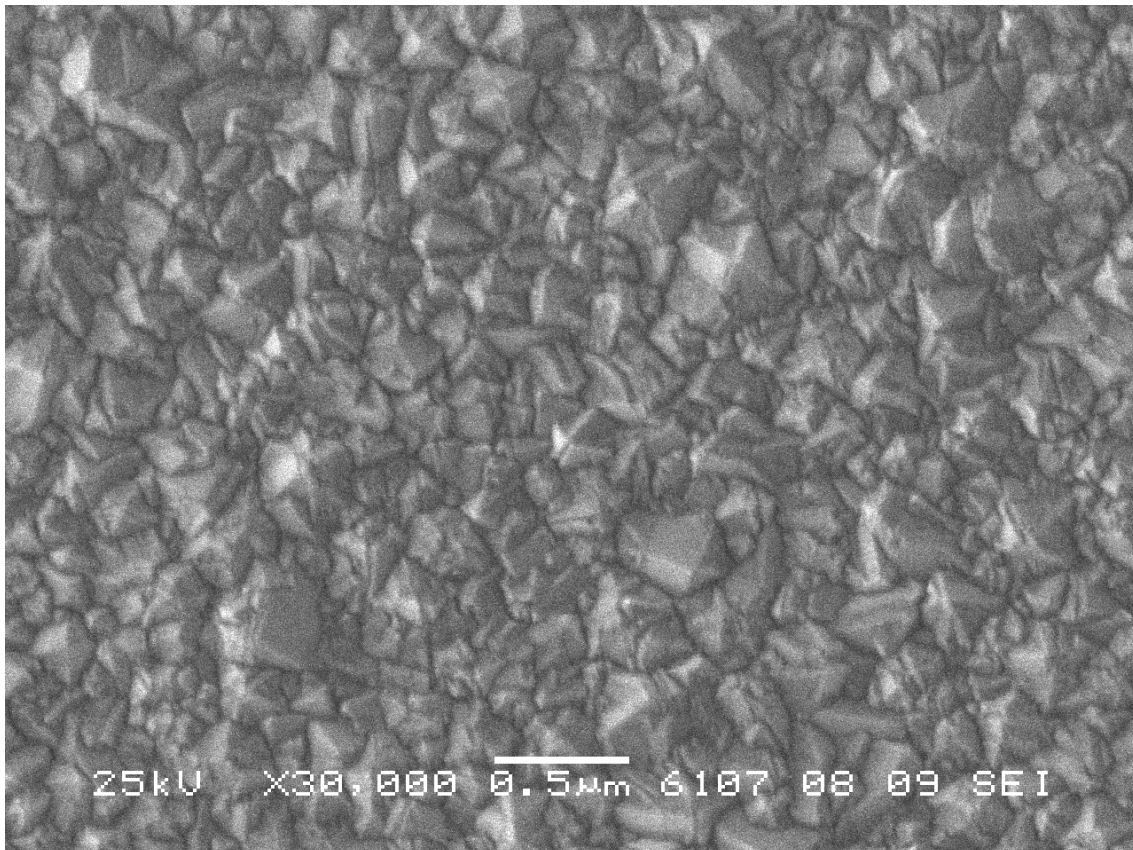


Fig. 1: Typical SEM image of the pristine NCD film 900 nm thick grown on Si(100) at 800 °C.

The surface composition and the sp^2 and sp^3 percentage has been elucidated by angular-resolved X-ray induced photoelectron spectroscopy [7] (ARXPS) using a curve fitting of the C 1s spectrum [10,11]. In the present analysis of chemical bonds, we rely on the theoretical support predicting the chemical shift of ~ 1 eV. Haerle et al. [10] calculated the C 1s shift between the sp^2 and sp^3 contributions to the C 1s peak in amorphous carbon systems by molecular dynamics simulations. The shift was found to be about 1.0 eV. The recent first-principles calculations of the C 1s core-level shift between the C sp^2 and C sp^3 contributions for a series of amorphous carbon density revealed almost the same value 1.1 ± 0.2 eV [11]. The calculations agree well with the measured and fitted C 1s lines [10,12,13]. These calculations provide strong support for decomposing the XPS spectra into two peaks resulting from sp^2 and sp^3 hybridized carbon atoms [14].

The exemplary high-resolution C 1s spectra recorded from the NCD film grown at 500 °C, measured at emission angles of 0° and 60°, and the results of the non-linear fitting procedure are shown in Figs 2 (a) – (b), respectively. Comparison of the resulting percentage of sp^3 hybridized carbon atoms, calculated from C 1s (sp^2) and C 1s (sp^3) peaks for the NCD films, and the parameters of the applied fitting procedure are listed in Table 1.

Table 1.

Comparison of parameters characterizing preparation conditions: thickness, oxygen content, and carbon atoms bonding at the NCD film surfaces. Notation: T_s - substrate temperature during the NCD film growth. FWHM – C 1s full width at half maximum.

Sample	T_s (°C)	Thickness (nm)	Emission angle (°)	Oxygen (at %)	FWHM	C 1s fitting C sp^3 (%)
1	400	130	0	2.6	1.1	96.8
			60	-	1.2	92.9
2	500	106	0	2.3	1.0	98.5
			60	-	1.2	94.7
3	890	1230	0	2.5	1.0	95.3
			60	-	1.2	95.2
4	890	490	0	2.3	1.0	96.3
			60	-	1.1	93.9
5	1100	470	0	2.1	1.0	96.9
			60	-	1.1	92.7

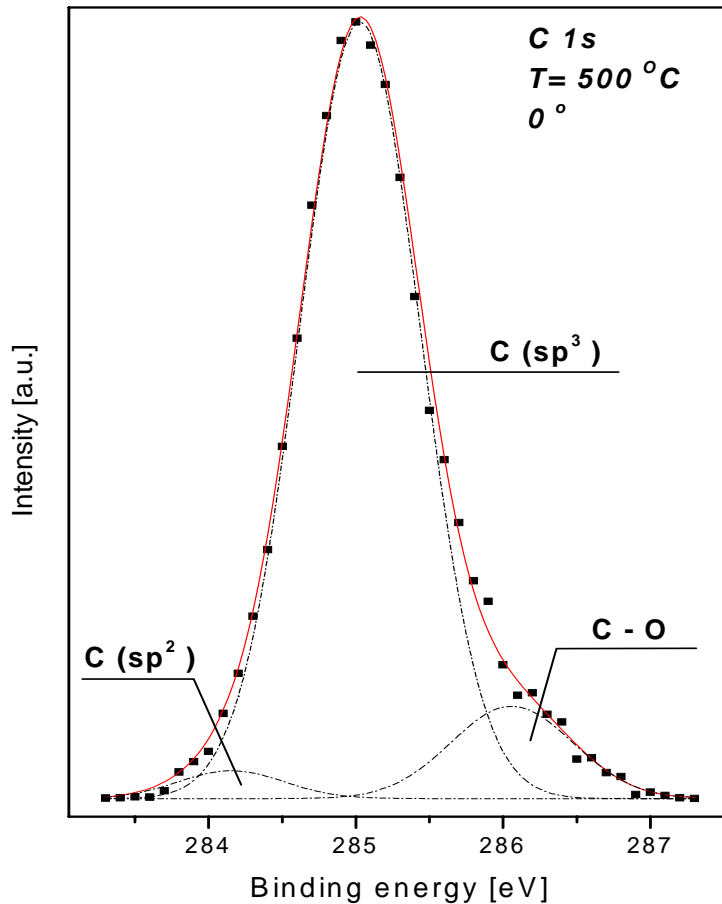


Fig. 2(a): The exemplary high-resolution C 1s spectrum of the NCD film grown at 500 °C with 98.5 % of sp^3 hybridized carbon atoms in the analyzed volume as measured at emission angle of 0° with respect to the surface normal.

The resulting percentage of sp^3 hybridized carbon atoms for all grown NCD films is above 90 %. The percentage is larger below the surface region (from 95.3 % to 98.5 %) than at the surface region (from 92.7 % to 95.2 %). No remarkable differences in the sp^3 percentage among the five NCD films prepared in the temperature range $400^\circ\text{C} - 1100^\circ\text{C}$ were observed (Table 1), which indicates an excellent quality of the film grown also at the lower temperature. The difference in the measurement geometry of C 1s lines leads to variation of the mean photoelectron probing depths. Specifically, the mean probing depth, given as a product of the IMFP and cosine of the emission angle [15], resulted in 1.6 nm and 0.8 nm for emission angles of 0° and 60° , respectively. The differences evaluated from two geometries of the measurement of the C 1s line (Figs 2 (a) – (b), Table 1) are consistent and indicate the surface slightly contaminated with oxygen, as well as slightly enriched with carbon atoms in trigonal configuration. Similar observations have recently been published by Birrell et al. [9].

3. Inelastic mean free paths

The electron backscattering intensities (elastic peak areas) were recorded for all NCD samples and gold standard in the primary electron kinetic energy range from 200 eV to 2400 eV. The geometry of the EPES analysis was the following: (i) the primary beam normal to the sample surface, (ii) the electron emission angle 35° with respect to the surface normal and (iii) the half-cone acceptance angle of the analyzer 4.1° . The typical half-width (FWHM) of the elastic peak spectra recorded in the applied energy range was ~ 0.5 eV. The MC algorithm of electron transport in a solid was described in details elsewhere [16]. The model assumes smooth surface, uniform atomic composition and density, the elastic scattering events along the trajectory length following the Poisson stochastic distribution with the distribution of distances between elastic collisions as a function of the electron elastic mean free path and the polar scattering angles with respect to the initial direction described by the probability density function dependent on the total mean free path and the electron differential elastic scattering cross-sections. The EPES measurements and the MC calculations were carried out for the same geometry of measurement and electron kinetic energies. In the MC calculations, the recommended IMFP was selected for the Au standard [3], whereas for the investigated sample, the calculations proceeded assuming a set of the IMFPs ranging from 0.1 to 30 nm. From the calculated dependences of the electron elastic backscattering ratio as a function of the IMFP, called the calibration curves, and the respective EPES measured ratio, the IMFP values for the sample are evaluated. The kinetic energy dependence of the electron IMFPs obtained with the EPES method and Au standard averaged over the five NCD films is shown in Fig. 3. These are compared to the IMFPs calculated by Tanuma et al. and the IMFPs resulting from the TPP-2M predictive formula IMFPs for diamond and graphite [5,6].

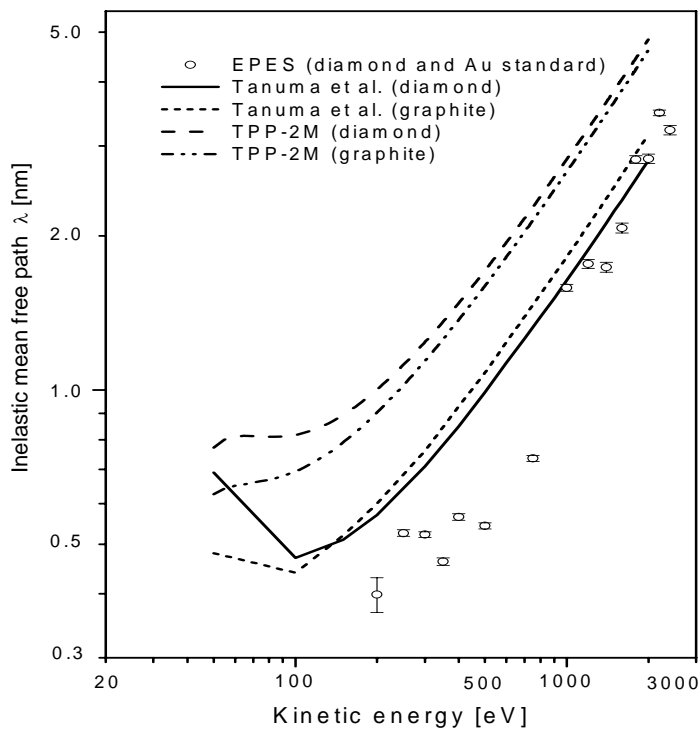


Fig. 3: Comparison of IMFP values and their energy dependence in the NCD films, diamond and graphite. Circle: the EPES IMFPs obtained with the Au standard averaged over the five NCD films. Solid line: diamond - Tanuma et al. [5]. Short-dashed line: graphite - Tanuma et al. [5]. Long-dashed line: diamond - TPP-2M [6] predictive formula. Double-dotted dashed line: graphite - TPP-2M [6] predictive formula.

The deviations between the IMFPs observed for the five NCD films are of the order of few percent indicating no remarkable differences between the evaluated IMFPs for five NCD films exhibiting different percentage of sp^3 carbon hybridization. Large discrepancies between Tanuma et al. optical IMFPs and the TPP-2M predictive formula IMFPs for graphite and diamond are observed. The EPES IMFPs for NCD are closer to Tanuma et al. optical values, with better approximation to the relevant values for diamond.

4. Summary and conclusions

Nanocrystalline diamond films deposited from the methane/hydrogen plasma were successfully grown at low substrate temperature (400 °C) as well at high temperature (>800 °C). The C 1s lines recorded at two different emission angles and therefore at two different information depths were used to estimate the extent of sp^3 hybridized carbon atoms at the analyzed surfaces. Results indicate that (i) NCD surfaces are dominantly composed from the sp^3 hybridized carbon atoms with a slight enrichment of the top surface by the sp^2 hybridized carbon atoms, (ii) surface quality of all samples was found to be the same irrespective of the growth temperature. The latter property is extremely technologically important for numerous applications necessitating low temperature treatments. Assessment of IMFP values for NCD films by measurements of the electron elastic backscattering probability combined with the Monte Carlo calculations of electron transport facilitated testing two procedures used to calculate the IMFP in diamond. Results showed better agreement of the present IMFP data to those calculated from the optical data.

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