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Radiation induced changes in amorphous hydrogenated DLC films

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ABSTRACT

Amorphous hydrogenated diamond-like carbon (DLC) films synthesized at room temperature from acetylene gas on quartz glass wafers by means of the direct ion beam deposition method and irradiated with X-ray photons of different energy were investigated. Ionizing radiation induced changes of bonding structure in a-C:H films of different thickness and different density were studied using Raman and infrared spectroscopy and atomic force microscopy. Optical transmittance spectra of the DLC films in UV–vis range were measured as well. The influence of technological deposition characteristics on the optical properties of irradiated amorphous DLC films and the role of the hydrogen in the DLC films were estimated and discussed with the purpose to assess possible application of amorphous hydrogenated DLC films as the protective coatings in radiation detectors. All investigated DLC films showed some increasing tendency of the optical transmittance in the visible and infrared range after the irradiation. Low density PLCH films irradiated with high energy X-ray photons were highly transparent in the whole UV–vis range and indicated possible changes in the bonding structure of the irradiated samples, which have been discussed on the basis of the results obtained during this investigation.

1. Introduction

Diamond-like carbon (DLC) films are widely used in different technological applications due to their excellent optical, electrical and mechanical properties [1–3]. Tissue equivalence, chemical inertness, high indentation hardness, absolute non-toxicity makes this material attractive for medical applications [4,5]. Outstanding characteristics of amorphous a-C films, containing significant fraction of sp^3 C bonds depend on the film growth conditions and its microstructure [6–11]. a-C films can contain up to 85% sp^3 bonds, while sp^3 fraction in hydrogenated amorphous a-C:H films is usually less than 50% [2]. Increased hydrogen content corresponds to the polymer-like soft carbon films, while reducing of the hydrogen content leads to the harder and denser films and may deteriorate optical properties [1].

Characteristics of a-C:H films depend mainly on the technological parameters and methods which were applied for their synthesis and may be modified via interaction with different particles [12,13]. Gamma or X-ray in the induced changes in polycrystalline CVD carbon films are widely investigated [14,15], however, there is a lack of studies on the radiation induced modification of amorphous DLC films synthesized using direct ion deposition method.

The aim of this work was to investigate the structural changes in the X-ray photon irradiated a-C:H films and to study the influence of ionizing radiation on their optical properties with a scope to assess the possibility of film application as passive layers or protective coatings.

2. Experimental

2.1. Samples

Amorphous diamond-like hydrogenated carbon films synthesized from acetylene (C_2H_2) gas on quartz glass wafers at room temperature using direct ion beam deposition method were chosen for this investigation. Working pressure of 2×10^{-2} Pa was kept during the whole deposition process. Deposition time varied from 20 to 30 min. Details on deposition method and deposition conditions have been described in Refs. [16,17].

Two groups of samples were prepared. Samples of the first group were deposited at ion beam energy of 800 eV using different ion beam current density: No. 1—50 $\mu A/cm^2$; No. 2—100 $\mu A/cm^2$; No. 3—150 $\mu A/cm^2$. Samples produced with the lowest ion beam current density of 20 $\mu A/cm^2$ and deposited at 240 eV were attached to the second group (No. 4). Index E next to a sample number was used

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Table 1
Charcteristics of investigated a-C:H films

Sample	Thickness (nm)	*H* (at%)	Density (g/cm^3)	Refractive index	*E*(tauc) (eV)	E_{04} (eV)	E_U (eV) [32]	Sp^3 [31]
1E	109	31	1.60	2.1	1.85	2.40	0.22	<20
1	102	30 [27]	1.79	2.2	1.59	2.12	0.21	25
2E	116	28	1.72	2.2	1.64	2.10	0.25	∼22
2	112	24 [27]	1.96	2.4	1.29	1.74	0.20	39
3E	142	26	1.86	2.3	1.46	1.93	0.23	27
3	139	25 [27]	2.00	2.4	1.33	1.85	0.21	40
4GM/E	∼200	36	1.42	1.9	2.34	3.12	0.28	
4M	182	27 [27]	1.82	2.3	1.51	2.05		26
4G	173	24 [27]	2.12	2.5	1.21	1.55	0.18	45

Methods which were used for the evaluation of certain parameters can be found in indicated reference sources.

for the identification of the initial samples. The main characteristics of as grown films were described in previous papers: sp^3 content and density of the films were evaluated from the results of Raman spectroscopy [18] and the hydrogen concentration was obtained by elastic recoil detection (ERD) method [19]. According to Robertson [2] all initial samples from the first group (1E, 2E, 3E) were classified as diamond-like a-C:H (DLCH) films, and the samples from the second group (4GM/E) as polymer-like a-C:H (PLCH) films. Summary of the main characteristics of initial samples is provided in Table 1.

The size of all prepared samples was approximately the same (∼1 cm^2), however, the samples from the second group were cut in two equal pieces and indexes 4G and 4M were assigned to each piece with the purpose to distinguish between the low (32 kV) and high (15 MV) X-ray photon energy, which was applied for the irradiation of the samples.

2.2. Irradiation conditions

Samples No. 1, No. 2, No. 3 and No. 4G were placed at the central position of the exposure field of medical linear accelerator Clinac (VARIAN) and irradiated all at the same time with X-ray photons generated at the X-ray tube voltage of 15 MV. Irradiation was processed under the real exposure conditions, which are present during medical treatment, and the dose of 2 Gy was transferred to the samples, which is usual for one treatment. Irradiation dose rate was 35 mGy/s. The similar procedure was performed to the 4 M samples, which were irradiated with the low energy X-ray photons, generated in mammography unit Alpha RT (INSTRUMENTARIUM) at the X-ray tube voltage of 32 kV. Maximal absorbed dose in the irradiated samples was 62 mGy at the dose rate of 12 mGy/s. Low energy X-ray photon spectrum was calculated using IPEM code [20], based on Monte Carlo method taking into account the special geometry of the irradiation as it was described in Ref. [21]. Estimated average photon energy was 17.6 keV for 32 kV X-ray tube voltage. Average photon energy of 10.8 MeV for 15 MV X-ray tube voltage was approximated from the results presented in Ref. [22]. Since the exposure fields (30 cm × 30 cm) for high energy photons and (12 cm × 18 cm) for low energy photons were larger as compared to the irradiated area of the samples, it was assumed, that there was no distortion of the X-ray beam in our experiment.

2.3. Experimental methods

Bonding structure and optical properties of irradiated carbon films were analysed using Fourier transform infrared (FTIR) and Raman scattering (RS) spectroscopy. The Raman spectra were recorded on a PC-operated Raman spectrometer described in Ref. [23]. Spectra Physics Stabilite 2017 argon laser operating at 514.5 nm wavelength with 800 mW power excitation was employed as a light source for Raman scattering. The Raman spectra were recorded with a 10-cm^{-1} spectral resolution in the Raman shift range from 900 to 2100 cm^{-1}. The overlapped background corrected Raman spectral bands were fitted with two Gaussian contours, using Least Square Fitting software.

The FTIR spectra from radiation-modified samples were obtained using Spectrum GX FT-IR (PerkinElmer) spectrometer. FTIR transmittance and reflectance spectra were detected in the range of 1400–4000 cm^{-1} at spectral resolution of 0.3 cm^{-1}.

Optical transmittance spectra of samples were measured by ultraviolet and visible absorption spectrometer SPECORD UV–vis. Absorption coefficient was calculated from UV–vis transmittance spectra using Lambert–Beer law and the E_{04} values (photon energy where the optical absorption is 10^4) for different DLC films were estimated.

Laser ellipsometer Gaertner 117 operating with a He–Ne laser (λ = 632.8 nm) was used for the estimation of the thickness and refractive index of the irradiated films.

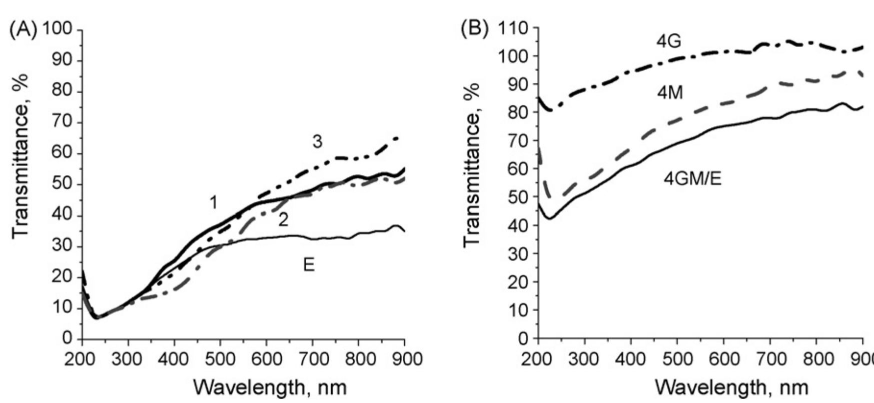

Fig. 1. Optical trasmittance spectra of the investigated a-C:H films: (A) samples from the first group; (B) samples from the second group.