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Full Length Article

# Diamond-like carbon layers modified by ion bombardment during growth and researched by Resonant Ultrasound Spectroscopy

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ABSTRACT

Biocompatible Diamond-Like Carbon (DLC) films were prepared by Pulsed Laser Deposition technique using the laser energy density of 10 J cm$^{-2}$ on the graphite target. The surface of the grown film was modified during the deposition by bombardment with argon, xenon, nitrogen or oxygen ions. The ion energy (up to 150 eV) was changed by gun voltage and by ionic current. The films with high and low diamond/graphite content were prepared. Physical and mechanical properties of biocompatible DLC thin layers prepared by hybrid laser technology were studied. The composition of layers and the content trace elements were determined by the methods of Rutherford Backscattering Spectrometry and Particle Induced X-ray Emission. The content of $sp^2$ and $sp^3$ bonds was measured using X-ray Photoelectron Spectroscopy. For different energy of argon and oxygen ions the maximum of $sp^3$ bonds content was found (83.63% of $sp^3$ bonds for argon ions). All films were smooth, which was confirmed by profilometry and Atomic Force Microscopy measurements. Maximum roughness Ra and RMS was did not exceed 1 nm. The Youngís and shear moduli were studied by Resonant Ultrasound Spectroscopy. The Young's Modulus attained the value of 601 GPa and the shear Modulus attained the value of 253 GPa at the energy of 30 eV of Ar ions. The influence of ion bombardment on DLC film properties is discussed.



## 1. Introduction

Diamond-like carbon (DLC) is one of the most interesting films with high hardness, optical transparency in the visible and infrared regions, electrical and thermal conductivities, wear resistance, low friction coefficient, and excellent biocompatibility [1,2]. The main aim for utilization of ion bombardment during deposition process was the $sp^3$ bonds content increase and the improvement of elastic properties of the layers. As a result, we have expected general improvement in practical use of DLC coating, namely for medical implants. The goal of this work was achieving optimal deposition conditions of DLC layers modified by ion bombardment, and the study of elastic properties by newly developed method Resonant Ultrasound Spectroscopy (RUS), which has potential to be widely used because of its non-destructiveness [3].

Ion beam assisted processing can be used for direct deposition films, such as Ion Beam Assisted Deposition technology (IBAD) or for modification of the fabricated or grown films [4,5]. In the case of IBAD, usually ions energy higher than 1 keV (typically up to 2 keV) and gases or precursors such as methane, ethylene/ethane, acetylene, $CH_4/H_2$, HMDSO, fluorinated carbon, $H_2S$, $O_2$ and $N_2$ are used. For modification, especially for a-C and a-C:H DLC films, the Kaufmann source or Van der Graaf accelerator using gases as Ar, Xe, $N_2$ and Kr were applied [6–9]. For surface modification (or graphene synthesis) also bias voltage was used [10,11]. Ion bombardment of DLC films strongly affects the film properties, such as crystallinity, density, $sp^3$ content and surface morphology. By bombardment the mobility of adatoms is increased and weak carbon–carbon bonds are removed. The processes that are under way in ion bombarded growing film are not yet fully understood. Publications indicates the importance of other parameters than ion energy, such as the ion mass and possible chemical activity of the ion. Even though ions with higher energy deposit more energy into growing layer, reported results show that there are optimal energy values (tenths

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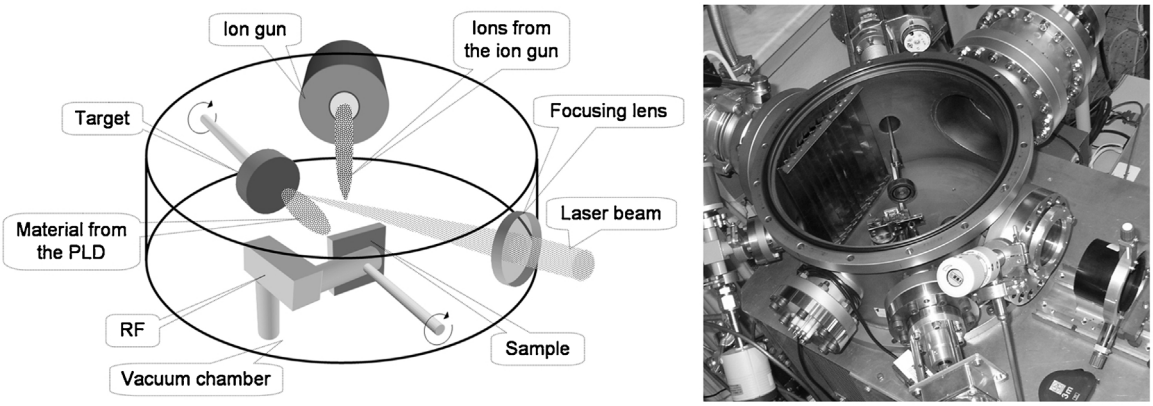


**Fig. 1.** Scheme of the PLD deposition system with ion bombardment and a photo of the chamber.

of eV) that are most efficient in influencing the growth. The same is valid for ion mass [12–15].

In our study we combine PLD technique with in situ ion bombardment of growing DLC films to produce films of higher $sp^3$ content. We use KrF excimer laser, Kaufman ion source and gases as argon, xenon, nitrogen and oxygen. For analysis (composition, bonds, and morphology) of thin films following methods were used: Rutherford Backscattering Spectrometry (RBS), Particle Induced X-ray Emission (PIXE), X-ray Photoelectron Spectroscopy (XPS), profilometric and Atomic Force Microscopy (AFM). And for determination of elastic properties (Young's and shear modulus) we used the method RUS.

## 2. Experimental

The DLC layers were prepared using PLD with simultaneous bombardment of growing film with Ar, Xe, $O_2$ or $N_2$ ions of various energies (see Fig. 1.). The laser (KrF excimer; $\lambda = 248$ nm; pulse duration $\tau = 20$ ns) energy density was 10 J cm$^{-2}$ (spot size $2 \times 1$ mm) and the repetition rate was 10 Hz. The number of pulses was adjusted to reach approximately the same layer thickness (1500 nm for layers on Ti6Al4V cylindrical substrate (for RUS measurement) and 100 nm on Si (111) substrate). The graphite target was rotated (0.5 Hz) and the target-substrate distance was 45 mm. DLC films were created with substrate at room temperature. Base vacuum of the coating system was $1 \times 10^{-4}$ Pa. Films were deposited in Ar ambient of 0.25 Pa. Before the deposition process the substrates were cleaned by RF discharge (13.56 MHz) in 5 Pa of argon for two minutes. The layers were created with or without ion bombardment. The ion gun eH200 (Kaufman and Robinson, Inc.) was used for the bombardment. The operating parameters of the ion gun were held at a working pressure of 0.25 Pa (for gases: Ar, Xe, $O_2$, $N_2$) and at a cathode current of 0.15 A. The ion energy was varied from 30 eV to 150 eV for Ar and Xe, and from 50 eV to 150 eV for $O_2$ and $N_2$.

A standard measurement set for determination of DLC layers physical properties was conducted, i.e.: thickness, roughness, elemental composition, bonds. Then on selected layers the elastic properties were evaluated to determine the optimal fabrication conditions.

Thickness and surface roughness were measured by mechanical profilometer Tencor AlphaStep 500.

The layers topography was characterized by the atomic force microscopy type Solver NEXT (NT-MDT) in a dynamic regime with HA_NC tips (tip radius ~6 nm). The roughness average ($R_a$), adapted from ISO 4287/1, was calculated from 100 μm$^2$ area with software NOVA P9.

X-ray photoelectron spectra were measured by an ADES-400 photoelectron spectrometer (VG Scientific, UK) using Mg Kα radiation (1253.6 eV). The spectra were recorded for wide-survey and narrow scans in C 1 s and O 1 s regions with a pass energy of 100 eV or 20 eV (C 1 s line). Inelastic electron background was subtracted using Shirley's procedure [2,16].

The composition of layers and the content of trace elements were determined by Particle Induced X-ray Emission, and Rutherford Backscattering Spectrometry methods using 3 MV Tandetron 4130MC accelerator at INP Řež with the energy of protons equal to 2.94 MeV.

Elastic properties of DLC layers were evaluated by Resonant Ultrasound Spectroscopy. This method is based on comparison of the frequency spectra of free vibration of the substrate measured before and after layer deposition, and determines in-plane elastic properties of the layer from frequency shifts of the individual resonant peaks [17]. Plane stress state is assumed in the vibrated layer and takes into account the elastic and mass contributions of the layer as a small perturbation to the elasticity and mass of the substrate. Thus only six independent elastic coefficients $Q_{ij}$ describing in-plane elasticity in a general case can be obtained by this method. Assuming isotropic elasticity of the deposited layers, only two parameters ($Q_{11}$, $Q_{33}$) were iteratively refined by matching of calculated and measured frequency shifts. Subsequently, they were recalculated [17] to G (shear) and E (Young's) modulus. Vibration of the samples was excited by a thermoacoustic source with infrared pulsed laser. The resonant frequencies and shapes of individual modes were evaluated from signals recorded by the scanning laser vibrometer implemented in the optical microscope (Polytec Micro System Analyzer MSA 500). For each sample, 20–30 resonance modes were detected in the frequency range 0.3–2 MHz.

## 3. Results and discussion

### 3.1. The thickness and roughness

The thickness of all DLC layers was in the region from 60 nm to 140 nm for Si (111) substrates and from 1200 nm to 1540 nm for Ti6Al4V substrates. The lowest growth rate of the layers was for energy of ions from 30 eV to 50 eV for all the gases. Surface roughness Ra and RMS was not higher that 1 nm (measured on the Si substrates by mechanical profilometer). The layer topography was characterized by AFM, too. The layers were smooth with a small number of small droplets. (see Fig. 2.) The average surface roughness Ra was not higher than 0.4 nm (calculated from 10 μm × 10 μm area).

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