Measurements of the mechanical properties and structure of a DLC film before and after ^{19}F irradiation

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Amorphous hydrogenated carbon (a-C:H) coated silicon wafer, also known as diamond like carbon (DLC), was irradiated using fluorine (^{19}F) beam at the 9 MV Tandem Van de Graaff accelerator, IFIN-HH Bucharest. Investigations of possible changes that appear following exposure to irradiation are presented in this work as a new atomic force microscopy (AFM) application. Nanoindentation coupled with AFM technique has been used to measure the hardness of the DLC film before and after the irradiation. Twenty-four indentations were made at four different points on the DLC film (thickness 510 nm) using the same diamond tip, force and under the same conditions. The results show that the values for the roughness and hardness increased for the irradiated DLC film the with respect to the unirradiated one. This film was also characterized by Fourier Transform Attenuated Total Reflectance (FT-ATR).

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1. Introduction

The nanoindentation atomic force microscopy (AFM) is one of the most useful techniques for thin films [1] nanomechanical properties characterization. This technique was first developed in 1970s from the need to measure the mechanical properties of small volumes of material using a small force. Microhardness instruments available in the early 1980s could not apply low enough forces to give penetration depths less than the required 10% of the film thickness in order to avoid influence of the hardness measurement from the presence of the substrate [2]. Regarding nanoindentation the forces involved for a typical cantilever are in the range of 1-100 μN, resolution better than 0.5 μN [3] small enough for the indentation to not be influenced by substrate. Having such a small indentation force this technique leaves only a small mark on the surface and usually is consider to be a nondestructive one [4,5]. An indentation test consists of touching the material of interest whose mechanical properties are unknown with a hard diamond tip whose properties are known. The length scale of the tip penetration is measured in nanometers rather than microns or millimeters used common in conventional hardness tests. [2].

A typical AFM – nanoindentation experiment consist of several steps: first engage in Tapping Mode to find a good area for indentation; then select from the software Indentation Mode, this halts the lateral scanning of the cantilever and lifts the tip slightly off the surface; then the desired parameters are selected and the indentation is executed [3]. Nanoindentation, compared to other hardness techniques, is a relatively simple method with a simple setup as well as ease in sample preparation.

Diamond like carbon (DLC) coatings are a mixture of sp2 and sp3 bonded carbon atoms containing from less than 1at% to about 50 at% hydrogen [6]. DLC has remarkable properties such as: high electronic resistivity, high hardness and low coefficient of friction. This material has received an overwhelming interest from both the scientific and industrial community first of all due to its interesting applications in the field of automotive and machining, biomedical, industrial equipment.

It is known that a material under energetic ion bombardment changes its mechanical, electrical and optical properties. Sometimes these modifications are wanted or unwanted. To gain information regarding the changes produced by irradiation nanoindentation AFM it is used. For other applications the precise surface topography and a smooth surface are critical [7]. AFM is an ideal tool to do such types of characterization [8].

In the present work a comparison on the unirradiated/irradiated DLC film is made. The film was characterized by Atomic Force Microscopy (AFM) and Fourier Transform Attenuated Total Reflectance (FT-ATR). Noticeable hardness increase was observed, while the FT-ATR spectra do not show any considerable variation.

2. Experimental

2.1 a-C:H coated silicon

For this experiment amorphous hydrogenated carbon (a-C:H) coated silicon wafer from IPP Max-Planck-Institute für Plasmaphysik was used. The properties of this film are: H content 30%; carbon density $\rho = 9 \cdot 10^{22}$ cm^{-3}; refractive index (632 nm) n = 2.13 – i*0.08; thickness ≈ 510 nm.

2.2 ^{19}F irradiation

The irradiation was conducted using the 19F ion beam delivered by the 9 MV Tandem Van de Graaff accelerator at IFIN-HH Bucharest [9]. The DLC sample was irradiated under high vacuum (10^{-6} Torr) using ^{19}F beam at different energies (16.4 – 17.4 MeV) and a current beam of aproximatively 3 nA. Sample was fixed on a target holder and introduced in the reaction chamber. The sample was placed at 45° with respect to the incident beam. The DLC film was irradiated for 10 hours, at an estimated dose of ≈ 2.3×10^{14} ions.

2.3. Atomic force microscopy nanoindentation

Nanoindentation measurements were performed using a MultiMode NanoScope III Controller atomic force microscope (Digital Instruments Veeco Metrology Group, Santa Barbara, CA, USA). The DLC film was indented by a three sided pyramidal diamond tip stainless steel cantilever. This tip has a height of about 50 μm, a total angle of 141° [10]. Other characteristics of this diamond tip were describe elsewhere [11]. All the measurements were obtained at room temperature at a scan rate of about 0.5 Hz. Images were taken at 512 x 512 pixels resolution. The acquisition and analysis of the images were performed using the NanoScope 531r1 software and SPIP 5.1.11 analysis software [12].

2.4 Fourier Transform Attenuated Total Reflectance

Sample structure characterization was performed with a FT-IR/Raman Bruker Vertex 70 instrument equipped with ATR (Attenuated total reflection using infrared Fourier transform - ATR-IR). FT-ATR spectra were recorded between 600 and 4000 cm^{-1}. Spectral acquisition was made with 64 scans at 4 $cm^{-}1$ resolution. All the spectra were manipulated and analyzed with the OPUS software [13]. Atmospheric compensation, vector normalization of whole spectra and baseline correction using straight lines and one iteration additional concave rubber band correction were applied to the spectra. The ability of infrared spectroscopy is to identify peaks corresponding to various types of C-H stretching vibrations (sp^3 – CH_3 / CH_2 / CH and sp^2 - CH). [14]

3. Results and discussion

3.1. AFM-nanoindentation

For the AFM analysis DLC sample was mounted onto the piezoelectric scanner and with the help of a video camera the areas of interest were located. Figure 1 shows the 3D surface topography of the DLC sample before and after ^{19}F irradiation. It can be seen that the DLC film is densely and homogeneously distributed. In order to characterize the roughness of the film and have a representative value, four different areas of 10 μm^2 were analyzed in Tapping Mode using a RTESP tip (Phosphorus (n) doped Si- cantilever). From these images using the AFM software the root mean square (RMS) roughness was measured. The initial roughness, average of the four measurements, is about 3.99 nm while the RMS roughness after the irradiation becomes 6.56 nm. In general the roughness depends on the parameters of the deposition methods such as substrate temperature, substrate material and film composition. In our study the roughness increased due to the ^{19}F irradiation.

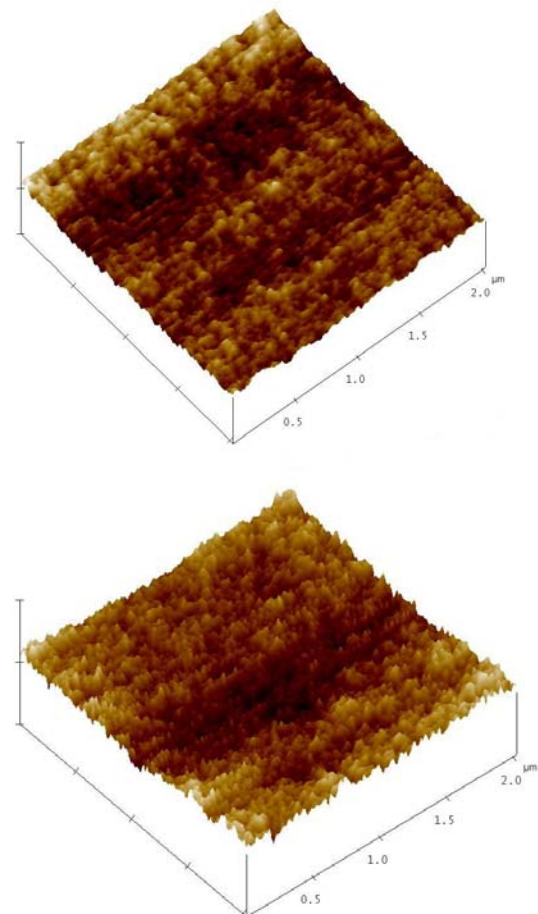

Fig. 1. AFM 3D topography images of DLC sample before (up) and after 19F irradiation (down); [z 4.000 nm/div].

Fig. 2 shows the 3D AFM nanoindentations on DLC film (a - d) unirradiated, (e - h) ^{19}F irradiated. Matrices of 3 x 2 nanoindentations were carried out in four different regions on the diamond like carbon film at the same tip force and under the same conditions. The original scan size of the DLC sample was 4 x 4 μm^2. In order to see better the diamond tip tracks a smaller surface was chosen.

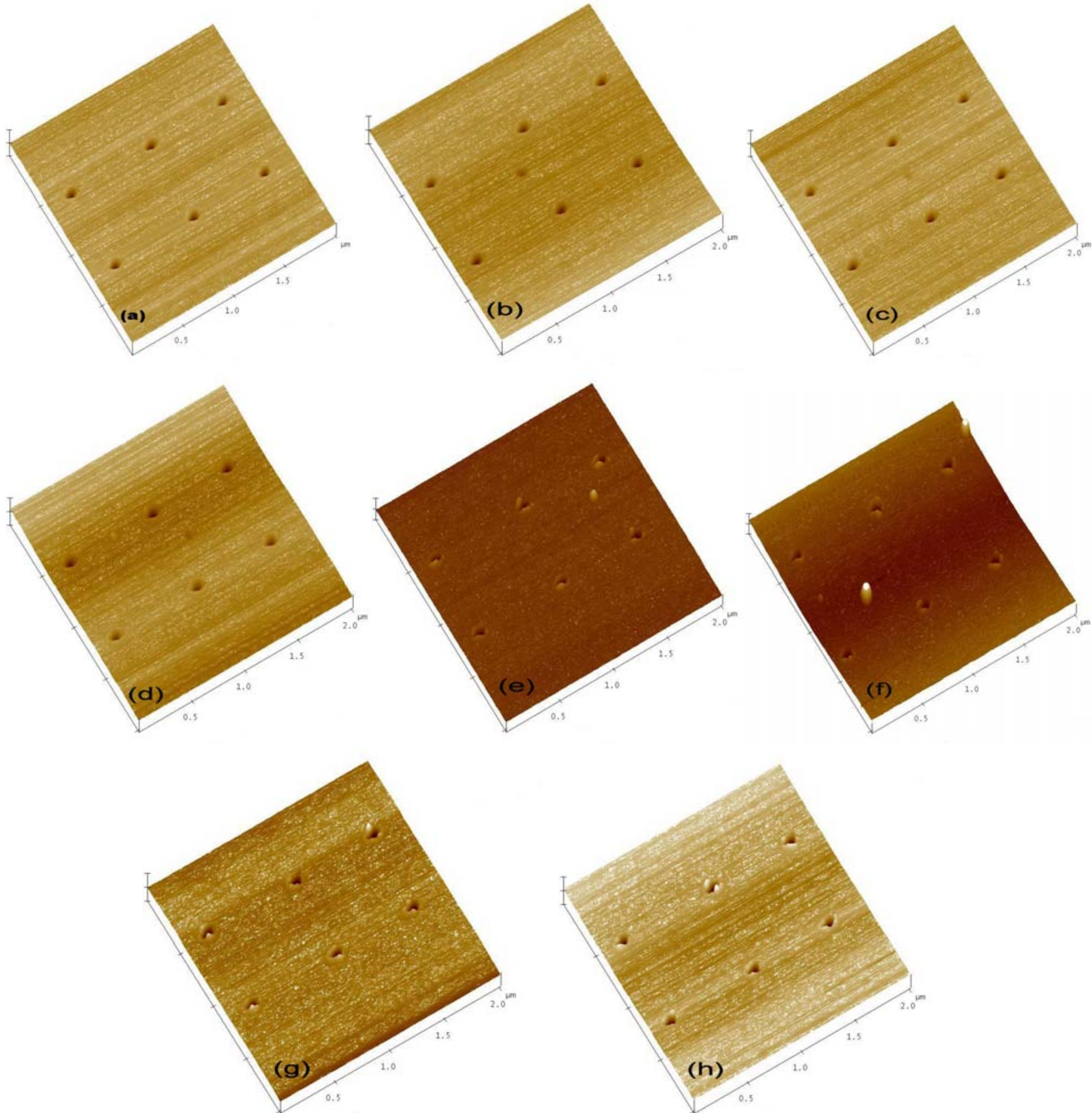

Figure 2. 3D AFM nanoindentations on DLC unirradiated (a - d); ^{19}F irradiated obtained using the same force 197 μN in order to compare hardness (e - h). The pile-up phenomenon is visible only for the irradiated DLC film [z 20.000 nm/div].

The image shown in the Figure 3 is a good illustration of the pile-up phenomenon. This is visible only for the irradiated film, see Figure 2 (e-h). The presence of the pile-up has a negative influence on the accurate determination of the projected area and lead to inaccurate hardness value. Unfortunately the pile-up phenomenon is inherent and cannot be prevented [15]. The pile-up of material around the indent tends to underestimate the

actual contact depth and consequently underestimate the contact area (A) between the indenter and the sample, resulting in an overestimation of the hardness [16].

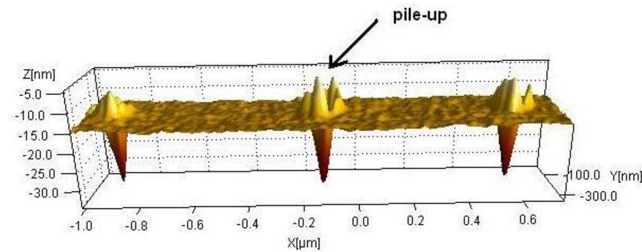

Fig. 3. Pile-up phenomenon's around the irradiated DLC film

Hardness was calculated according to the relation:

$$H = F_{max} / A$$

where F is the maximum force applied to the sample and A is the projected area between the diamond tip and the material surface.

The projected area, summation of the pixel area elements inside the surface outline that are in the same plane as the virgin sample surface, was determined with the image analysis software SPIP 5.1.11 [17]. This software automatically locates the indent in the AFM image and knowing the indentation force - calculated using the formula: Force (N) = Spring constant (N/m) x Trigger threshold (V) x Sensitivity (nm/V) x units conversion factor ($1x10^{-9}$m/nm) [11] - measures its projected area and then calculates the hardness. In determining the projected area the pile-up effect was not taking into consideration.

It was found that mechanical properties were affected significantly after the irradiation. The calculated average value of the hardness for the unirradiated/irradiated film was calculated is in the order of 33 GPa, respectively 46 GPa, which represents a 39.39% increase. The hardness value of the unirradiated DLC film is in good agreement with those reported in the literature [18,19]. Because the sample is deposited on a substrate care must be taken because the results could be influenced by it [1]. The maximum indentation depth for the unirradiated/irradiated DLC film is 17 nm and 35 nm respectively. Thus the measured hardness is obtained from the DLC film only, there is no substrate influence.

3.2. FT - ATR studies

Fig. 4 and Table 1 show the FT-ATR spectra of DLC film before and after irradiation.

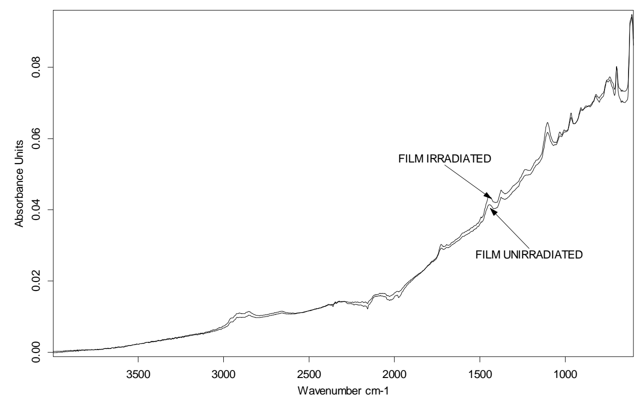

Fig. 4. FT-ATR spectra of DLC film unirradiated / DLC film irradiated

Table 1. FT-ATR band wavenumber of unirradiated / irradiated DLC film

No.	Band wavenumber of unirradiated DLC film (cm^{-1})	Band wavenumber of irradiated DLC film (cm^{-1})	Assignment
1	3060	3060	sp^2 - CH
2	3021	3022	sp^2 – CH_2
3	3005	2999	sp^2 - CH
4	2956	2956	sp^3 – CH_3
5	2921	2921	sp^3– CH/CH_2
6	2879	2879	sp^3 – CH_3
7	2865	2865	sp^3 – CH_3
8	2852	2853	sp^3 – CH_2
9	882	877	sp^3 – C-C
10	820	821	sp^2 – C=C
11	758	756	sp^2 – C-H
12	739	740	sp^2 – C-H

In general, very small band variations are observable in the FT-ATR spectra of unirradiated/irradiated DLC film. The low frequency range FT-ATR spectrum range 900 – 700 cm^{-1} (Fig. 5) and high frequency range 3100 – 2700 cm^{-1} (Fig. 6) contain the major C-H and C-C absorbance peaks.

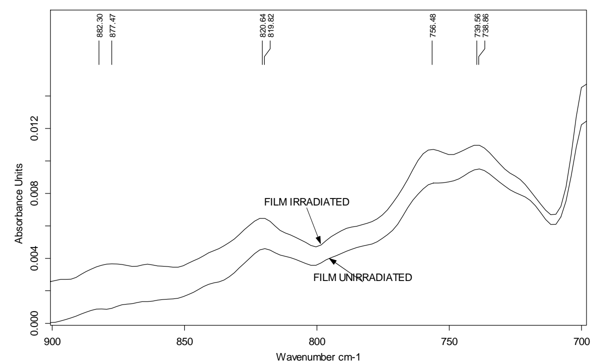

Fig. 5. FT-ATR spectra in the low frequency range from unirradiated / irradiated DLC film.

In the wavenumber region 900 – 700 cm^{-1}, all the spectra are quite similar. The investigated samples display a peak around 750 cm-1, assigned to sp2 C-H, peak 720 cm^{-1} assigned to sp^2 C=C and peak 750 cm^{-1}, assigned to sp^3 C-C.

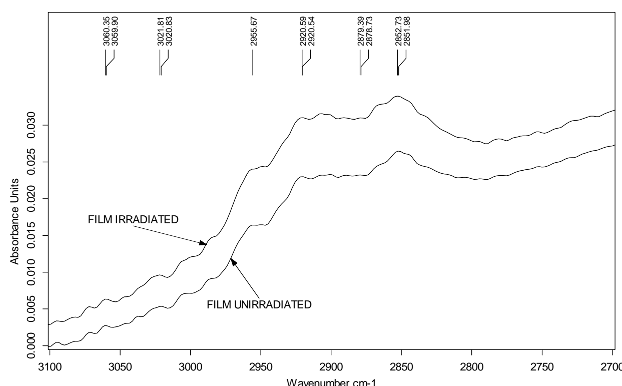

Fig. 6. FT-ATR spectra in the high frequency range from unirradiated / irradiated DLC film.

By examining the 3100 – 2700 cm^{-1} wavenumber region, the samples (unirradiated/ irradiated) were found to be peaks of CH_x ($3 \leq x \leq 1$) in the bonding preference of H for sp^3 and sp^2 C.

4. Conclusion

Using AFM nanoindentation method the roughness and hardness of the DLC film, before and after irradiation with a ^{19}F beam having energy in the 16-18 MeV range, were measured. The ^{19}F beam was delivered by the 9 MV Tandem Van de Graaff accelerator. It was observed that ^{19}F beam induced changes in the mechanical properties of DLC film, while results of FT-ATR show very small band variations of the unirradiated/irradiated DLC film. The average value of the hardness for the unirradiated/irradiated film was calculated is in the order of 33 GPa and 46 GPa respectively, which represents a 39.39% increase. Changes in the roughness of the irradiated DLC film are observed. The RMS roughness after the irradiation is 6.56 nm while the roughness of the unirradiated film is about 3.99 nm. In conclusion, it should be noted that AFM nanoindentation is a versatile tool for characterization of nanostructures.

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