Hydrogen depth profiling in DLC films using RNRA

I. BURDUCEA[a,b*], M. STRATICIUC[a,b], P. M. RACOLTA[a], C. C. SURDU-BOB[c], M. BADULESCU[c], A. ANGHEL[c], AL. JIPA[b], C. LUCULESCU[c]

[a]*Horia Hulubei National Institute of Physics and Nuclear Engineering (IFIN-HH), 30 Reactorului St., Magurele, Ilfov, 077125, Romania*

[b]*Faculty of Physics, University of Bucharest, 405 Atomistilor St., Magurele, Ilfov, 077125, Romania*

[c]*National Institute for Lasers, Plasma and Radiation Physics (INFLPR), Atomistilor No.409, PO Box MG-36, Magurele-Bucharest, Romania*

A series of Diamond-Like Carbon (DLC) films were obtained using Thermionic Vacuum Arc (TVA) method at INFLPR and were assumed to be hydrogen free. Resonant Nuclear Reaction Analysis (RNRA) using ^{19}F ions was used for hydrogen depth profiling in DLC films. We have found that a hydrogen content less than 5% is present within the DLC films deposited by TVA plasma, although no H-containing gas was used. This result can be explained by the dissociation of water molecules desorbed from the chamber walls during deposition. A larger percentage (around 20%) of H was found within the outermost surface of the films which is probably due to the water adsorbed from the ambient air.

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1. Introduction

Diamond-Like Carbon (DLC) is an amorphous carbon material containing a mixture of sp3, sp2 and sp1 hybridized carbon which displays physical and mechanical properties quite similar to diamond [1]. DLC is commonly used in a large variety of applications such as coating of different materials with direct applications in electronics, medicine, aerospace and industrial equipment [2, 3].

The DLC containing up to 50 at. % hydrogen (a:C-H) is the hydrogenated form of C while DLC with less that 1% hydrogen (a-C) is the so called "H-free DLC" [2]. In the paper of Robertson [4] a delimitation of H-containing from H-free DLC films concerning the amount of hydrogen of about 7% is given.

Hydrogen plays an important role in these materials, their interesting properties being related to its concentration. Hydrogenated forms of DLC are used in applications that take advantage of the low friction coefficients and high wear-resistance of these films [2]. The detection of H and its depth profiling is of great interest in DLC materials.

There are a limited number of non-destructive techniques with the ability to measure hydrogen concentration as a function of depth into the coating material. Hydrogen detection and profiling methods include Time of Flight (TOF) with neutron scattering, Secondary Ion Mass Spectroscopy (SIMS), Resonant Nuclear Reaction Analysis (RNRA) and Elastic Recoil Detection Analysis (ERDA) [5].

The most used nuclear reactions involve the use of ^{15}N, ^{19}F and ^{7}Li accelerated beam ions, each of these reactions having advantages and disadvantages. The reaction using ^{19}F is the most sensitive one, but has a smaller depth in the sample. This technique is based on the $^{1}H(^{19}F, \alpha\gamma)^{16}O$ resonant nuclear reaction [6, 7, 8], which shows a strong resonance at 16.44 MeV.

In this study RNRA using a ^{19}F ion beam is used for hydrogen depth profiling in DLC films [6].

The analysis of DLC films using RNRA technique provided useful information for the material manufacturers regarding the unexpected presence of H in their samples.

2. Experimental

2.1 Sample deposition

In this work DLC thin films have been prepared using Thermionic Vacuum Arc (TVA) [9, 10]. BK7 optical glass was used as substrate. The main parameters used for obtaining the DLC films were the following: the filament current was set to 100 A, the anode voltage varied between 700 and 900 V and the anode current varied from 2.6 to 3 A. The distance anode-substrate was increased from 2.5 to 15 cm. The working pressure inside the deposition chamber was 3×10^{-5} Torr. Table 1 presents the main parameters of the deposition.

Table 1. Deposition parameters of the DLC samples.

Sample number	Anode-substrate distance [cm]	Deposition time [min]	Thickness [nm]
DLC_1	10	5	47
DLC_2	15	20	67
DLC_3	2.5	0.5	100
DLC_4	5	2.5	167

Film thickness values were measured in cross-section using Scanning Electron Microscopy (SEM). The samples are assumed to be "H-free DLC". Investigations concerning hydrogen content are not usually considered necessary for the characterization of these films due to the fact that the method to produce this type of DLC do not use H-containing precursors. However to be certain that this is the case, one should measure if H is present or not in the samples. RNRA method can give information regarding the H presence in the samples. Thus a set of four samples, namely DLC_1, DLC_2, DLC_3 and DLC_4 were analyzed using RNRA method.

2.2 RNRA measurements

RNRA is an accelerator-based analytical technique used in materials science for light elements profiling. It is used also to determine the hydrogen content of materials. RNRA used for the hydrogen profiling in DLC samples was $^{1}H(^{19}F, \alpha\gamma)^{16}O$.

The $^{1}H(^{19}F, \alpha\gamma)^{16}O$ reaction has a narrow resonance at 16.44 MeV (laboratory system). The reaction takes place only at this particular energy with a cross section of 0.5 barn and a width of about 89 keV, producing 6.1, 6.9 and 7.1 MeV γ-rays coming from the deexcitation of the residual ^{16}O nucleus [11]. Increasing the ^{19}F beam energy with a few keV above the resonance, the cross section for the production of the high-energy γ-rays is negligible. Thus, if the surface of a material containing hydrogen is irradiated with ^{19}F ions at energies greater than the resonance energy, the ^{19}F ions will be continuously slowed down until at a depth d_R. When the resonance energy will be reached the reaction will occur at a yield proportional to the hydrogen concentration. At greater depths, the ^{19}F beam energy will be below the resonance energy where the cross section is again negligible [6].

The samples used in this work were irradiated at the tandem Van-de-Graaff accelerator of the Horia Hulubei Institute of Physics and Nuclear Engineering (IFIN-HH), using a $^{19}F^{+3}$ ion beam by increasing its energy in steps of few tens of keV in the 16-18 MeV range.

The detection of γ-rays was done with an Ortec HPGe detector having an energetic resolution of 14 keV for the 6.1 MeV γ-rays coming from the resonant nuclear reaction. Data analysis was performed offline using Origin software [12].

3. Results and discussion

The nuclear reaction used to profile the H in the samples is a threshold reaction, having a first resonance at the 16.44 MeV energy of the ^{19}F beam. From Fig. 1 it can be clearly seen that no γ-rays are emitted at the 16 MeV beam energy while for the 17 MeV the 6.1 MeV γ-rays are present in the spectrum. The first two peaks from Fig. 1 are 511 keV single and double escape peaks. A second resonance, at the 17.56 MeV energy of the ^{19}F beam limits the use of this reaction to 320 nm for the DLC with mass density of 3 g/cm^3 and to 720 nm for the DLC with mass density of 1.3 g/cm^3.

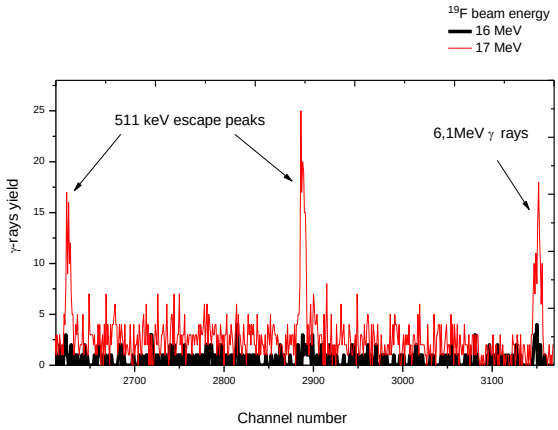

Fig. 1. The 6.1 MeV γ-rays yield for the ^{19}F beam energy at 16 MeV(black line) and 17 MeV(red line) for sample DLC_3.

The background between 5 and 7 MeV energy is due to cosmic-ray-induced secondary radiation components from the atmosphere and the beam-induced background, but in our case this has a rather small value of ~ 4 counts/min [13]. Under energetic ion bombardment of materials the effect of hydrogen migration is present [14] and a small fraction of hydrogen is also lost. In order to minimize these effects a large collimator of the ion beam (~ 8 mm in diameter) and a small beam current (~ 2-3 nA) were used. A DLC reference material with a known hydrogen content was used to obtain quantitative results. DLC reference material is a:C-H type containing 30% H, having a mass density of 1.3 g/cm^3 and a thickness of ~ 510 nm. This sample was produced at the IPP Max-Planck-Institute für Plasmaphysik. Using SRIM-2008 code [15], it was calculated that 100 keV energy loss in the DLC reference sample corresponds to a depth value of 65 nm. Taking this into account it means that the reference sample is completely depth profiled.

Fig. 2 presents the H depth profile for the DLC reference sample. H content given by the γ-ray yield is represented in arbitrary units (a.u.) for an accumulated charge of 4 μC. The first two points from Fig. 2, at 0 nm and at 33 nm, respectively corespond to the hydrogen present at the surface, the other points are related to the known H content of 30%.

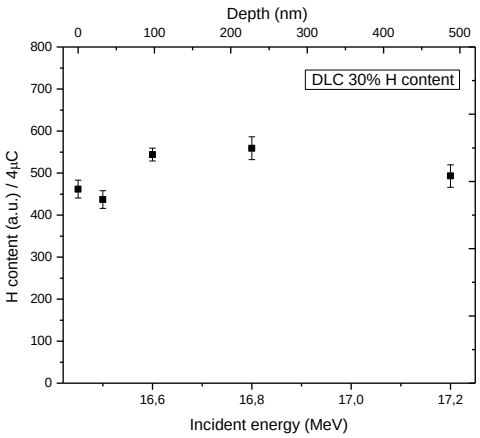

Fig. 2. The hydrogen profile for the DLC reference sample (30% H).

Two possible sources of H – contamination can be the dissociated water during film growth and the adsorbed water molecules from the ambient air after deposition. Fig. 3 shows the results of the hydrogen depth profile of the DLC films. The H content in % was calculated using the gamma ray yield of the reference sample. In principle the energy scale can be converted into a depth scale, provided the mass density of the film is known. In our case the mass density of the deposited samples was not determined. It is known that mass densities of *a*-C:H DLC fall in one range between 1.4 g/cm^3 and 2.0 g/cm^3 whereas mass densities of *a*-C DLC typically exceed 2.0 g/cm^3 [16]. Because the density of the DLC samples is not known the following discussion will be made for two cases: for an assumed density of 1.6 g/cm^3 and 3 g/cm^3.

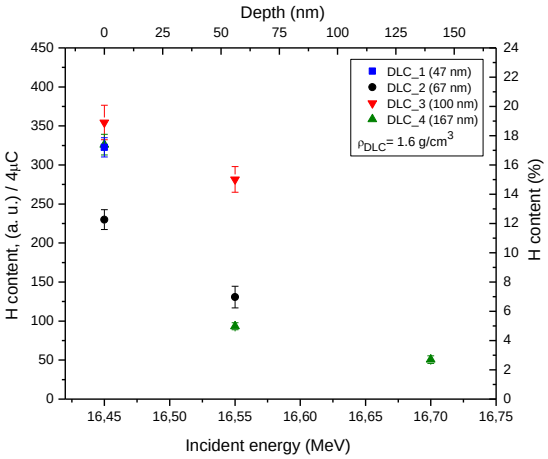

Fig. 3. Distribution of the hydrogen in DLC films deposited on BK7 optical glass obtained by RNRA, ρ= 1.6 g/cm^3.

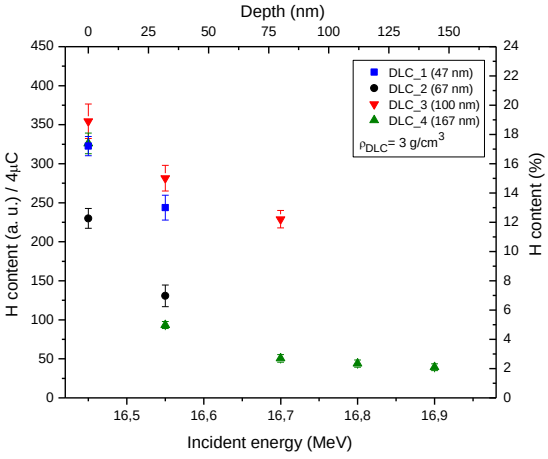

Fig. 4. Distribution of the hydrogen in DLC films deposited on BK7 optical glass obtained by RNRA, ρ= 3 g/cm^3.

Using SRIM-2008 code [15], for the DLC density of 1.6 g/cm^3 every 100 keV of energy absorbed in the samples will depth probed them for ~ 57 nm while for the 3 g/cm^3 density it will be ~ 32 nm.

For the density value of 1.6 g/cm^3 it can be seen that hydrogen is present at the surface in about 20% in all samples (0 nm in Fig. 3). At approximately 60 nm depth, the amount of H in DLC_4 and DLC_2 decreases down to 5%, this shows that the films fall into the "H-free" classification [4]. The higher amount of H observed in the DLC_3 sample may be due to the fact that, within the short deposition time of 30 seconds, the water desorbed from the chamber walls is not completely pumped down, thus providing hydrogen to the carbon plasma.

Fig. 4 shows hydrogen depth profiles of the DLC films for the assumed density value of 3 g/cm^3. The hydrogen content at the surface is quite high compared to the bulk. This is most probably due to the water adsorbed from the ambient air. This gives an indication about their hydrophilicity.

The H presence in the bulk of the samples could be atributed to the H adsorbed on the walls of the deposition chamber. To avoid these water vapors, a solution can be to heat the walls of the deposition chamber before igniting the plasma.

4. Summary and conclusions

RNRA of DLC films deposited onto BK7 optical glass by TVA method gave useful information for materials manufacturers regarding the presence of hydrogen in their materials. We have found that hydrogen is present within the DLC films although no H-containing gas was used. The surface of the films has a higher H content than the bulk. This is most probably due to the water adsorbed from the ambient air. The H presence in the bulk of the films could be atributed to the H adsorbed on the walls of the deposition chamber.

The results obtained are potentially useful for the DLC manufacturers to make them aware of the importance of outgassing before ignition of the plasma.

In future experiments, complementary methods will be employed, such as Rutherford Backscattering Spectrometry, ERDA, X-Ray Reflectivity and contact angle measurements for obtaining more complete information for these structures [17, 18, 19, 20].

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*Corresponding author: bion@nipne.ro