

Preliminary results on comparative study of three methods for nanocarbon films deposition: thermionic vacuum arc, magnetron sputtering and cathodic arc

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The aim of this paper is to make a comparative analysis of the properties of the nanostructured carbon thin films deposited by three PVD type methods: an original one: Thermionic Vacuum Arc (TVA), Filtered Cathodic Vacuum Arc (FCVA) and Magnetron Sputtering (MS). In the TVA method, the deposition takes part in the vapors of the anode materials, the deposited film containing only the ions of this material and therefore the energy of ions could achieve values up to 500 V. The structures of the films have been characterized by X-ray Photoelectrons Spectroscopy (XPS), Auger electron spectroscopy AES, Raman spectroscopy and Transmission Electron Microscopy (TEM).

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1. Introduction

The peculiarity of the development of the high tech area researches in the last decades was without doubts the continuous miniaturization, both of the final products, as well as its parts. Micron size elements and more - nanostructured materials, started to be real dimensions of the components on production lines. For example, nanosmooth and very thin (<50 nm, even <10 nm) Diamond Like Carbon (DLC) films are used as corrosion and wear-protective coatings for both the magnetic disks and the magnetic heads.

The nanostructured carbon thin films contain significant fractions of sp^3 type C bonds, which give them distinguished properties, like high hardness (3000-5000 kg mm^{-2}), low friction coefficients (0.1-0.2), chemical inertness, wear resistance (1.6×10^{-9} mm^3/mN) and prefigured electrical properties, all these being strongly dependant on the deposition methods and parameters [1, 2].

There are many methods, reported until today, used for the deposition of nanostructured carbon thin films. [3-6]. The diversity of methods used for the deposition of diamond-like carbon films provides the flexibility to tailor their properties according to specific needs and potential applications.[7,8] Some of them have been created as a combination of sounding performances of two methods, as in the case of LASER – ARC, a method which puts together the advantages of the high deposition rate of the arc methods with the a precise control by a pulsed laser of the arc ignition [9]. This is the reason why it is of great interest to compare the properties of nanostructured carbon

films obtained by three methods of deposition: an original one - Thermionic Vacuum Arc (TVA), and two other well-known methods: Filtered Cathodic Vacuum Arc (FCVA) and Magnetron Sputtering (MS).

2. Experimental

The TVA deposition method consists from an externally heated cathode surrounded by a Wehnelt cylinder that concentrates the high voltage accelerated electrons on the anode material – carbon – in this case. Due to the high applied voltage, the continuously evaporated material from the anode ensures within the inter-electrodes space the formation of a steady state carbon vapors with enough density in order to ignite and to maintain a bright discharge. Because the discharge plasma is formed only by electrons and carbon ions/neutrals, the films are deposited in high purity conditions.[10] The thin film is bombarded during its growth by the energetic carbon ions having energies up to 500 eV [11].

In the case of MS deposition, the energy of the carbon ions impinging onto the growing film was controlled by the substrate bias value.. The incorporation of Ar used as sputtering gas in MS devices can be minimized by heating the substrate during or after deposition [12]. By the MS method can be obtained films with a roughness about ~1 nm, much lower as compared with the other two deposition methods.

In the FCVA method, as well as in the TVA method, there is no need for a buffer gas. The energy of the carbon ions ejected by the boiling points in the cathode surface

can be controlled by the negative substrate bias, the total pressure values being about 10^{-2} Pa.

A number of investigations have been performed in order to identify the microstructure of the amorphous carbon films deposited onto silicon using a variety of techniques. The X-ray photoelectron spectroscopy (XPS) analyses were done using using a VG ESCA 3 MK II spectrometer. The Auger electron spectroscopy (AES) was used to identify the elemental films composition, by using a PHI Auger electrons spectrometer model 3017. Before investigation the surface of the samples was sputter-cleaned with 3 keV Ar ions for 20 minutes, using an ion gun PHI Model 04-191.

Raman spectroscopy has been carried out to identify the carbon phases in the deposited films, using a LabRAM HR UV-VIS-NIR Horiba Jobin-Yvon spectrometer.

Transmission electron microscopy (TEM) analyses were performed on a Philips CM 120 ST (120 kV) TEM provided with HR-TEM facility capable of obtaining a resolution of 1.4 \AA and a magnification of 1.2 M.

3. Results and discussions

The elementary composition of the obtained carbon layers were investigated by mean of photoelectrons spectroscopy (XPS) and by Auger electrons spectroscopy (AES).

The full XPS spectra of carbon films obtained by the three above presented methods - TVA, MS and FCVA, are presented in the following figures (Figs. 1, 2 and 3).

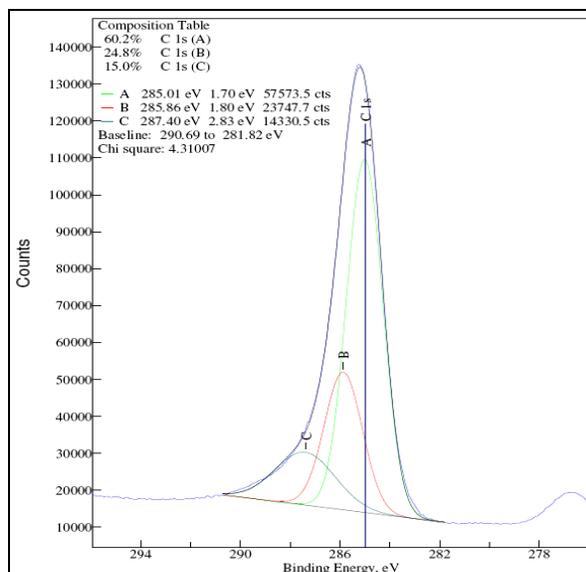


Fig.1. Deconvoluted XPS C1s spectra for MS sample
A: $C sp^2$, B: $C sp^3$, C: C-O-H.

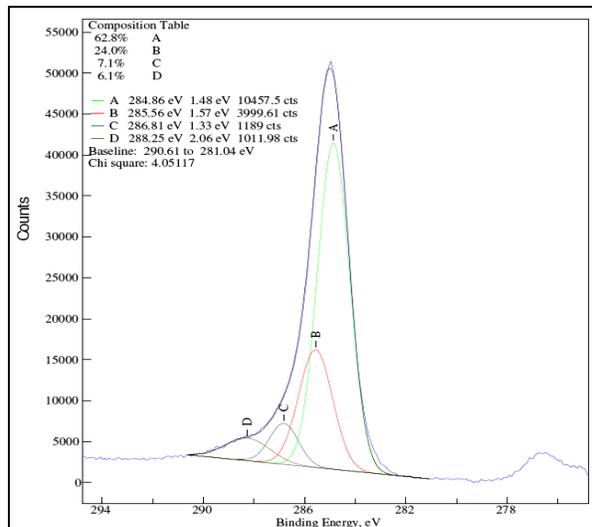


Fig. 2 Decomposed XPS C1s spectra for FCVA sample
A: $C sp^2$, B: $C sp^3$, C: C-O, D: C-O-H.

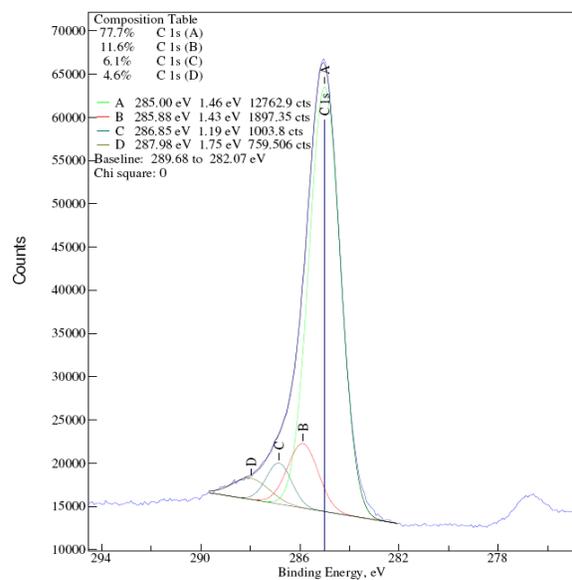


Fig. 3. Deconvoluted XPS C1s spectra for TVA sample
A: $C sp^2$, B: $C sp^3$, C: C-O.

XPS analyses indicated that over 87% of the deposited material is composed of carbon; the rest of 13% is made of impurities including C-O and C-O-H bonds. It is interesting to notice that in the case of TVA, there are no C - O - H bonds, which indicates the expected non hydrogenated character of the deposited films by this method. Also the XPS data showed that sp^2 type bonds for these samples are more abundant (60% - 78%) than the sp^3 type bonds (12% and 25%). The results of the quantification of the decomposed XPS Carbon spectra and the elementary composition from the AES investigation of the samples deposited by the mentioned three methods are presented in Table 1 and 2.

Table 1. Data of the sp^2 and sp^3 bonds.

No. sample	Deposition method	Fraction of sp^2 and sp^3 bonds		
		sp^2	sp^3	sp^3/sp^2
MS	Magnetron Sputtering	60.2	24.8	41 %
FCVA	Cathodic Vacuum Arc	62.8	24.0	38 %
TVA	Thermionic Vacuum Arc	77.7	11.6	14 %

Table 2. The elementary composition of the obtained carbon films (investigated by AES).

No. sample	Deposition method	Elementary composition	
		C [%]	O [%]
MS	Magnetron Sputtering	90.6	9.4
FCVA	Cathodic Vacuum Arc	88.2	11.8
TVA	Thermionic Vacuum Arc	93.4	6.6

The superposed Raman spectra of the samples obtained by the three deposition methods are presented in Fig 6.

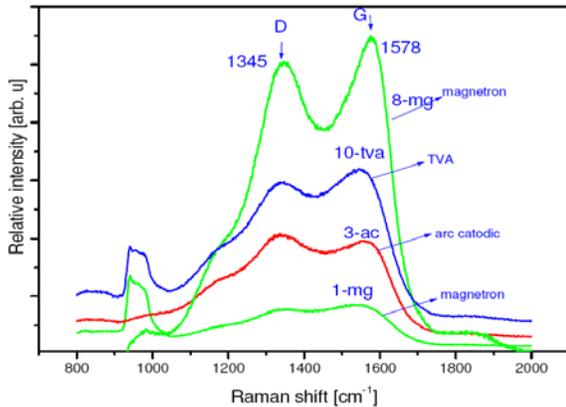


Fig. 4. Raman spectra of DLC films produced by the three deposition methods: TVA, MS and FCVA.

Raman spectra were obtained in a back scattering configuration using the 632.5 nm line of a He-Ne laser. The fitted peak shape, have two maxima at 1570 cm^{-1} and at 1340 cm^{-1} , which correspond to G band (graphite-peak) and respectively D band (disorder-peak).

A large number of crystalline inclusions embedded into the amorphous Carbon films were revealed by TEM images, in the case of TVA samples and also in the case of MS samples.

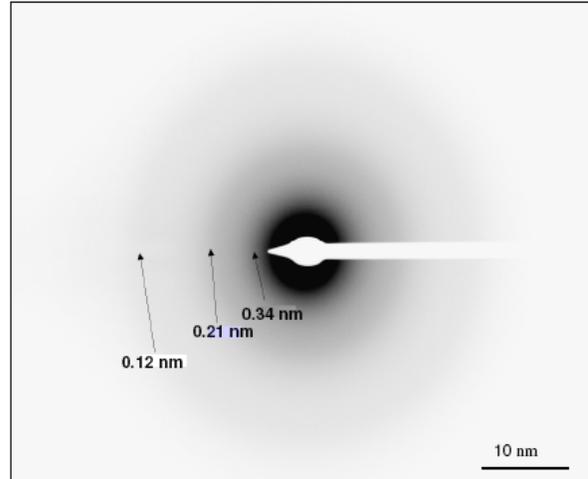


Fig. 5. Electron diffraction pattern of the film deposited by TVA method.

According to the SAED diffraction pattern (given in Fig. 5 and Fig.6) using a 420 mm camera light and 200 mm spot size these shape are made of diamond structured nanoparticles with diamond specific orientation (220) and (110). We also calculate the mean diameters assuming a log-normal distribution of experimental data. The mean value of measured diameters from BFTEM images is 4.1 nm in the case of TVA samples, while the maximum frequency of appearance is for 19.4 nm diameter in the case of MS, as can be derived from the histograms. (Fig.7 and Fig. 8)

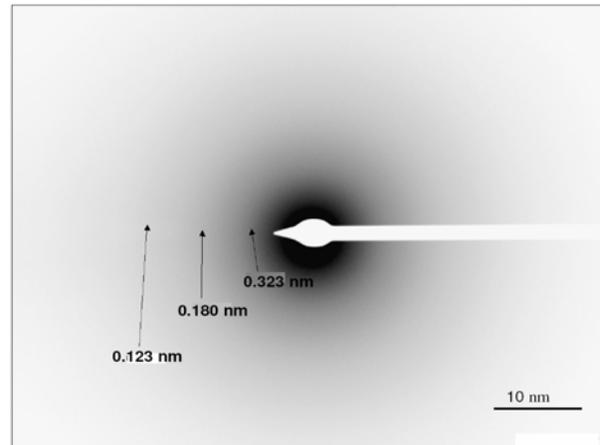


Fig. 6. Electron diffraction pattern of the film deposited by MS method.

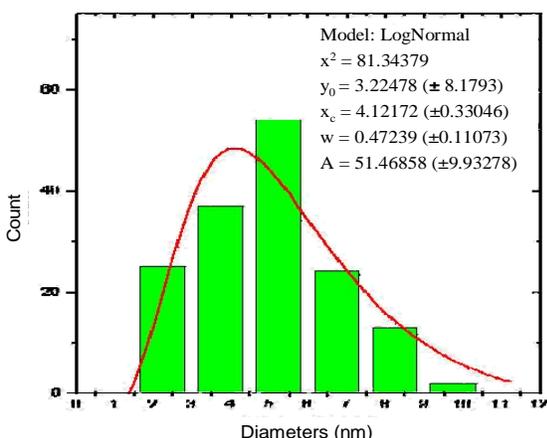


Fig. 7. Grain size distribution in the case of TVA sample.

A higher number of uniformly spread diamond crystallites at higher ion energies, but of a lower size (<10 nm) were observed in the DLC films prepared by TVA method.

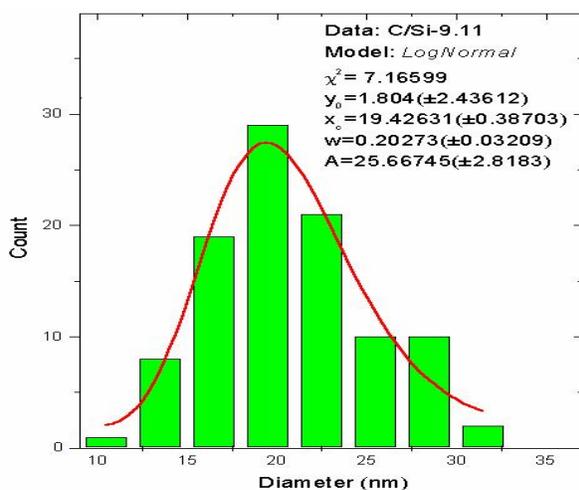


Fig. 8. Grain size distribution in the case of MS sample

4. Conclusions

Preliminary results on characterization of nanostructured carbon thin films deposited by three methods - as a comparative study - are reported. XPS, AES and Raman spectra as well as TEM analyses were conducted in order to investigate the properties of the nanostructured carbon thin films. Amorphous films were obtained with sp^3/sp^2 abundance ranges between 14 and 41 % by MS, FCVA and TVA methods. Crystalline inclusions embedded into the amorphous Carbon films were revealed by TEM images in cases of TVA and MS deposited samples, which indicate possible applications in wear-protective coatings for magnetic devices.

Further systematic studies have to be conducted to carry out how the physical and chemical properties of amorphous carbon coatings vary as a function of deposition techniques.

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