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Electron spectroscopy studies of the diamond like carbonic thin films

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Thin films of diamond-like (DLC) and graphitic materials are characterized by low thermal expansion coefficients, high thermal and electrical conductivities and chemical inertness. DLC, in addition, exhibits extreme hardness. The problem of DLC thin films characterization by electron spectroscopy is presented. The outstanding problem is the determination of the ratio of carbon atoms with diamond-like sp^3 tetrahedral bonding to carbon atoms with carbon graphitic sp^2 trigonal boding. This ratio results from the quantitative percentage composition of the DLC thin films. We report the characterisation by XPS and XAES of the diamond vs. graphite nature of several amorphous carbon thin films deposited by Laser Ablation of PMMA (poly methyl methacrylate).

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1. Introduction

Carbon exists in nature in different allotropic forms. The bond of carbon atoms can hybridize in three different ways: sp^3 hybridization is a typical structure of diamond; sp^2 hybridization is a two-dimensional graphite layered structure; sp^1 hybridization is a one-dimensional structure. The stable trigonally π bonded crystal structure graphite is soft, optically opaque, electrically conducting and chemically active; the metastable tetragonal bonded σ crystal structure diamond is the hardest material, transparent from far-ultra violet to the far infrared, insulating and chemically inactive. Carbon, with the dilution of hydrogen, can also form polymer like structures.

Aisenberg and Chabot [1] found that the films deposited from carbon ion beams were very hard, electrically insulating and wear resistant i. e. with properties very close to diamond and used the term "*diamond like carbon*" to describe these films.

These films were found to have mixed phases of diamond and graphite but **no long**-range **order**; they were **amorphous** in nature.

So, the term "*diamond like*" emphasizes a set of properties akin to diamond and at the same time implies the absence of crystalline diamond order.

The various forms of carbonaceous amorphous films may be divided into two broad categories:

1. DLC films formed by carbon only are called amorphous carbon or amorphous diamond (i-C);
2. Carbonaceous films containing a mixture of hydrogen, and carbon are called hydrogenated amorphous carbon (a-C: H) or hydrogenated DLC.

By controlling the amount of graphite, diamond and polymer phase an a-C: H or hydrogenated DLC type material can be formed.

All diamond like carbon films are amorphous, but not all-amorphous carbon films are diamonds like. Thin films of hydrogenated amorphous carbon present a mixing of sp^2 and sp^3 hybridisation and the structure and macroscopic properties of such thin films depends strongly on the percentage of sp^2 and sp^3 contained in the films.

In this paper we report the results of electron spectroscopy study of amorphous carbon structures obtained by PLD from PMMA targets. The evaluation of the sp^2 / sp^3 ratio was carried out by Photoelectron Spectroscopy (XPS), and X-ray Auger Electron Spectroscopy (XAES).

The Pulsed Laser Deposition (PLD) method for preparing thin films from organic polymers is of interest due to its simplicity and good control of the deposition process [2].

The polymer fragmentation during ablation and subsequent deposition leads to a new structure which can be exploited for applications. Excimer laser ablation is an efficient technique for deposition of PMMA films.

2. Experimental

XPS and XAES data were obtained using a Vacuum Generators spectrometer model ESCALAB MK II. Specimens were irradiated with an AlKα source ($h\nu$=1486.6 eV) and the vacuum in the analysis chamber was maintained at 10^{-9} mbar. Spectra were collected in the analyzer constant energy mode, with pass energy Ep of

10eV or 50 eV. The calibration of the instrument was obtained taking as reference the silver line Ag 3d $_{5/2}$ at 368.2 eV.

Derivative spectra were obtained using a 23 point Savitzky- Golay convolution array. A second order polynomial was used in the Savitzky – Golay analysis.

Thin films of PMMA were deposited by PLD [5], by using a pulsed KrF* excimer laser (at 248 nm wavelength, pulse duration ≥ 20 ns, 1Hz repetition rate and maximum output energy of 85 mJ/pulse). The laser radiation was focused on the target through an MgF_2 cylindrical lens with focal length 30-cm. The incidence angle to the target was 45^o. The laser spot area was set within 4.2 and 6.4 mm^2. The incident fluency varied in the range 0.8- 1.6 J/cm^2.

The target was a PMMA pellet 15×15×2 mm^3 made from high purity ICI DIAKON powder and moulded at 190^{o}C. The holder with the PMMA target was placed in stainless vacuum chamber, which was subsequently evacuated down to 1-7 × 10^{-3} Pa The target was rotated with 0.4 rot/min during the PLD process. The substrate for film deposition was a (100) oriented silicon wafer on a molybdenum heating block, parallel to the target surface. A heating device was used in order to keep the deposition substrate at a pre-selected temperature in the range 25-200 ^{o}C.

The following samples have been prepared and investigated:

a) The film deposited on the silicon substrate held at room temperature, by using a laser fluence of 1.4 J/cm^2 and 30000 laser pulses;

b) The film deposited on the silicon substrate held at 200 ^{o}C, by using a laser fluence of 0.8 J/cm^2 and 20000 laser pulses;

c) The film deposited on the silicon substrate held at 200 ^{o}C, by using a laser fluence of 1.2 J/cm^2 and 10000 laser pulses.

3. Results and discussion

XPS is a chemical-sensitive technique and the XPS chemical shift has proven to be a valuable method for understanding the local environment of an atom in a solid and for investigating whether a carbon film is sp^3 or sp^2 bonded.

Apart from the chemical shift, the XPS technique can provide other useful information, such as film composition, plasmon loss for conducting materials and valence band density of states.

The XPS survey spectra for carbonaceous films show only oxygen as a surface contaminant, in addition of the main peak of carbon.

The C1s spectra of carbonaceous films and of PMMA ablated target, corresponding to different experimental conditions were recorded and the contribution of the different components was evaluated using a peak-synthesis procedure.

Fig. 1 shows a typical analysis of the C1s peak of a carbonaceous film obtained by PLA method.

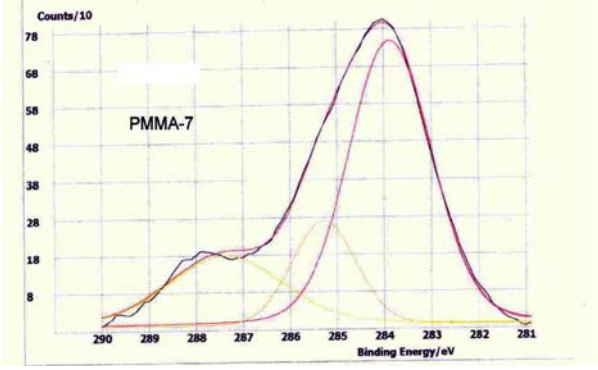

Fig. 2. A typical analysis of the C1s peak of a carbonaceous film obtained by PLA method.

According to literature [6], the peaks located at binding energies of ~284, 285 and 287 eV are assigned to graphite, hydrocarbon and diamond. The 285 eV component is usually due to hydrocarbon contamination from the vacuum system [7].

The higher energy components of C1s peak can be assigned to some C-O bonds.

According with ref. [7], oxygen induces shifts to higher binding energies by about 1.5 eV per C-O bond (for example a =C=O bond induce a 3eV chemical shift and a O-C=O bond induces a 4.5 eV chemical shift to higher energies).

The sp^3 carbon atom was then determined as the ratio of the corresponding peak area over the sum of the sp^3 peak aria and sp^2 peak aria.

XAES provide a relatively sensitive analysis of the sp^3 and sp^2 bonding in the carbonaceous thin films, by the study of the fine structure of the carbon Auger peak.

The energy of the main feature of C KLL in the N(E) spectra ranges from 250 to 280 eV for DLC films. It is known [3,4] that the main feature for graphite occurs at 269 eV, for diamond at 262 eV, and for a-C:H films at ~265 eV.

A secondary feature at ~241 eV is generally identified as an energy loss peak. Some of the samples contaminated by oxygen present an additional peak at 247 eV.

One important difference between the diamond spectra and the spectra of all other carbonaceous sample is the presence in the latter of two peaks located at ~275 and ~280 eV [3].

In the derivative spectra the maximum (at ~253 eV) is quite fixed for all samples, whereas the variation of the minimum could be associated to the presence of the features discussed above. From these observations, in [3] was indicated as a fingerprint of the different arrangement of carbon atoms the distance D between the maximum of the positive-going excursion and the minimum of the negative-going excursion in the derivative XAES spectra.

Typical XAES derivative spectrum for different carbon samples are presented in Fig. 3 and Fig. 4.

Carbon with sp^2 bonding gives a wide energy separation of D~22.5 eV, and with sp^3 bonding it yields a narrow energy separation of D~14.3 eV.

The a-C:H films present an sp^3 and sp^2 hybridization and the method proposed by Lascovich et al. [3] can be used to calculate the ratio of the two.

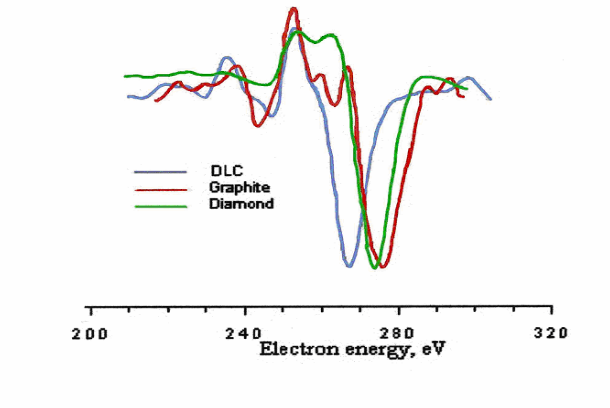

Fig. 3. Typical XAES derivative spectrum for different carbon samples [3].

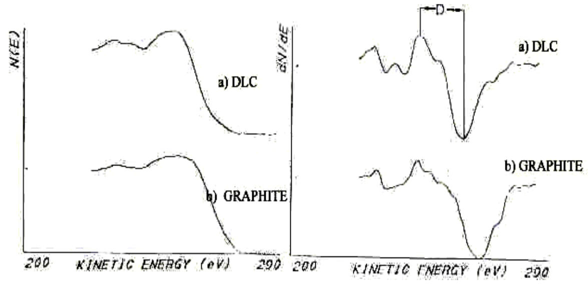

Fig. 4. Integral N(E) and derivative dN/dE XAES spectra of a DLC film compared with graphite [3].

The results of XAES and XPS analysis are presented in Table 1.

Table 1. XPS and XAES evaluation of the sp^3 content in DLC.

Sample	FLUENCE [J/CM^2]	SP^3 %	
		XPS	***XAES***
PMMA 5	0.8	20	22
PMMA 7	1.2	27	25
PMMA 11	1.4	30	32

The results correlated with the Raman spectra, and XRD patterns [5] suggest that a DLC configuration could be produced in these films.

The XPS and XAES methods provide the same qualitative variation of the sp3 content with laser fluence.

4. Conclusions

XPS and XAES techniques can be used for the direct evaluation of the sp3 content in DLC films.

The XPS and XAES methods produce comparable results.

Homogeneous, defect-free thin films have been obtained by excimer laser pulsed deposition from a PMMA bulk material. XAES and XPS analysis shows the growth of the contribution of sp^3 bonded carbon in the films deposited when the fluence of the ultraviolet laser pulses is growing.

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