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Diamond and polymeric-like films prepared by PECVD method

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Plasma Enhanced Chemical Vapours Deposition (PECVD) is a versatile method which allows for the preparation of amorphous hydrogenated carbon films with different structures by varying the deposition parameters. We have prepared carbonic structures by PECVD technique onto quartz and silicon substrates in atmospheres of argon and methane mixtures. These films were characterized by the UV-VIS, FTIR, Raman, Ellipsometry and AFM methods. The total RF power, gas pressure (0.1 mbarr) and substrate temperatures ($<100^0$C) were kept constant for all the depositions. Diamond-like carbon structures were obtained for a wide range of methane dilutions between 100% ÷ 20% and a narrow transition from diamond-like (DLC) to polymer-like carbon (PLC) structures between 20% ÷ 10% dilutions was found.

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1. Introduction

Carbonic structures represent a wide family of materials with a high potential for research and applications. Their properties are mainly influenced by the carbon atoms hybridization state. Depending on the prevailing hybridization state one can speak about diamond-like films (sp^3) graphitic films (sp^2) and polymeric films (sp^1) [1].

These structures can be prepared by various methods such as ion beam deposition, magnetron sputtering, pulsed laser deposition and plasma enhanced chemical vapor deposition [2]. PECVD is a frequently used method as it makes possible the preparation of different carbonic structures by varying the energy of the bombarding species upon the growing films. This was performed by modifying the DC_{bias} values in the range 20÷1000 V [1] or by varying the dilution of methane in argon for a PECVD (13.56 MHz) deposition system [3].The last receipt was also studied by us using a PECVD-RF deposition system at a frequency 1.78 MHz.

2. Methods

2.1. Deposition of diamond-like and polymeric films

We have used a deposition system (YBN-75P-I) equipped with a rotary - diffusion pumping system which reaches a base pressure of 2×10^{-6} mbarr. The system is equipped with two magnetron cathodes and a PECVD assembly. The deposition substrates were soldered with silver paint onto the water-cooled PECVD cathode. This ensured a temperature of 15^0C for substrates previous deposition and an expected temperature below 100^0C in plasma conditions. Quartz and silicon substrates were used for transmittance measurements in UV-VIS, respectively IR. Previous deposition these substrates were cleaned in ethanol in an ultrasonic bath for 5 minutes. Amorphous carbon hydrogenated films were prepared at 100%, 80%, 60%, 40%, 20%, 10% methane dilutions in argon at the same deposition pressure of 0.1 mbarr, using deposition times of respectively 15, 20, 30, 40, 50 and 240 min. The RF plasma power was kept constant corresponding to high values of DC_{bias} between 330÷400 V.

2.2. Morphological and structural characterizations of the DLC and PLC structures

2.2.1. AFM measurements

Atomic Force Microscopy have been used to characterize the surfaces morphology and estimate surface roughness (R_{rms} - root mean square roughness and R_{abs} - absolute roughness) for DLC and PLC structures on glass surfaces.

Our AFM system works in the tapping mode in air [5] with a commercial standard silicon nitride cantilever (NSC35) having a force constant of 7.5 N/m, 240 kHz resonance frequency and tips with radius less than 10 nm. The AFM images cover various areas, from 30 μm × 30 μm to 3 μm × 3 μm. An image consists of multiple scans displaced laterally from each other in the y direction; all surfaces have 256 × 256 pixels. A low-pass filtering was performed in order to remove the statistical noise without loss of information. AFM measurements were performed on different points of the sample, keeping the same conditions of room temperature and ambient atmosphere.

2.2.2. Spectrophotometric measurements

The values of the refractive index (n) and extinction coefficient (k) for DLC and PLC structures on glass surfaces were obtained from the ellipsometric measurements of Φ, Δ according to homogeneous thin layer optical theory [4]. A high precision ellipsometer (EL X-01R) with a He-Ne laser at 632.8 nm wavelength and 70° angle of incidence was used. The complex refractive index values resulted from 6 different simulations algorithms (based on harmonic analysis and minimum search) with different accuracy and computing time.

The transmission measurements in UV-VIS (10000-30000 cm^{-1}) were performed using a Perkin Elmer Lamda 20 spectrophotometer. From the positions of maximum and minimum values of the transmission spectra we have estimated the films thickness using the formula:

$$2nd=k\lambda \qquad (1)$$

where the n values were used those estimated at 632.8 nm. For some depositions these thickness values were compared with those obtained from interferential microscopy measurements (microscope Carl Zeiss Jena). The absorption coefficient was obtained from the formula:

$$\alpha = \left(\frac{1}{d}\right) \times \ln\left(\frac{1-R}{T}\right) \qquad (2)$$

where d is the film thickness and R the average reflection estimated in the region of low absorption.

Optical measurements in IR (400÷8000 cm^{-1}) were performed using a Perkin Elmer BX Spectrophotometer. We have studied the absorption in the region 2700÷3100 cm^{-1} corresponding to the stretching region of C-H bonding.

In order to characterize the structure of the carbonic matrix, Raman spectroscopy measurements were performed. An Ocean Optics TM-2001 spectrometer with a 500 mW laser radiation source operating at a wavelength of 785 nm was used. For every sample a set of 10 measurements of 5 sec. integration time were performed.

3. Results and discussion

3.1 Deposition rate

Fig. 1 displays the dependence of deposition rate for the carbonic films prepared in methane- argon mixtures in a wide range of dilutions. Between 100% and 20% a relatively monotonous decreasing was obtained from 23 nm/min to 9.5 nm/min, while from 20% to 10% an abrupt decrease from 9.5 nm/min to 0.6 nm/min was evidenced.

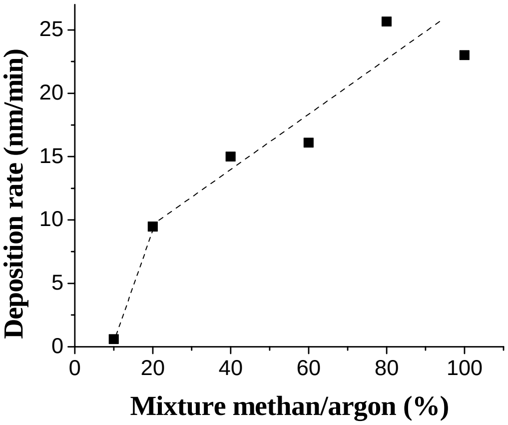

Fig. 1. Deposition rate for the DLC and PLC sample vs. methane dilution. The lines are drawn for visual help.

3.2 Spectro-ellipsometric measurements

The graphical representation for the refractive index vs. methane dilution (Fig. 2) displays values higher than 2 for the DLC films (except 80% sample) in agreement with the results reported in literature. A strong decreasing from 2.05 up to 1.41 was measured from 20% la 10 % dilution corresponding to the transition from DLC to PLC films.

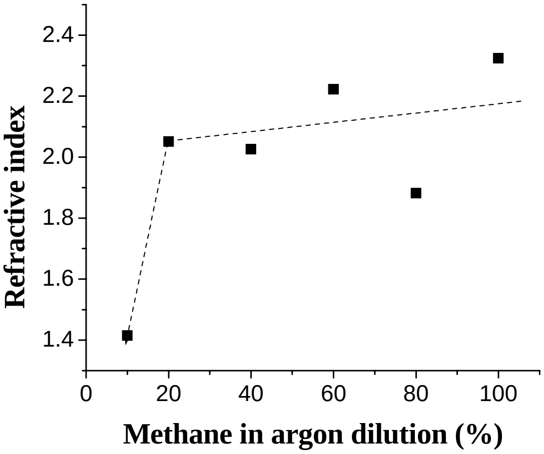

Fig. 2. The refractive index at 628.3 nm vs. methane dilution; The lines are drawn for visual help.

3.3 NIR, UV-VIS measurements

Fig. 3 displays the optical transmittance in the 4000 ÷ 30000 cm^{-1} range for the DLC and PLC samples prepared onto quartz substrates.

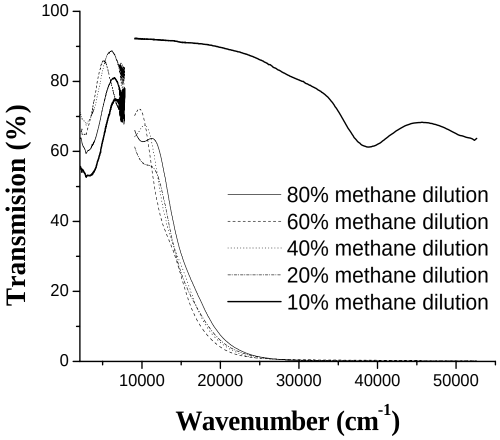

Fig. 3. NIR UV-VIS measurements for DLC and PLC films onto quartz substrate.

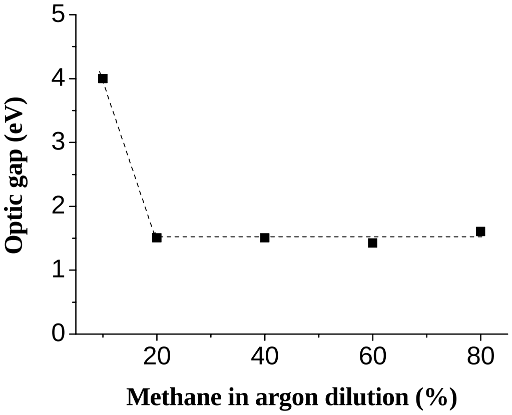

Fig. 4. Optical gap values for the DLC and PLC films vs. methane/argon dilution. The lines are drawn for visual help.

Transmission values around 100% are noticed for the polymeric sample which is in agreement with the similar values of the refractive index for the substrate (1.47) and carbonic film (1.41). The transmission of DLC films shows maxima and minima of interference in the region 4000 ÷ 10000 cm^{-1} and decreases due to the inter-band absorption at higher wave number values.

The absorption coefficient in the region of band to band absorption was used for estimating the value of Tauc optical gap using the representation:

$$(\alpha E)^{1/2} = B(E-E_0)$$

(where E is the photon energy) the optical gap E_0 and the slope B (a constant proportional to the joint density of states) were determinate. The values obtained for the Tauc gap (Fig. 4) shows similar values around 1.5 eV for the DLC films and a high value of 4 eV for the PLC layer. For the PLC film the value of E_{04} was considered.

3.4 Raman spectroscopy

As shown in Fig. 5 all prepared samples reveal two maxima around 1420 and 1150 cm^{-1}. The peak at 1420 cm^{-1} can be understood as a convolution of D (disorder) and G (graphitic) peaks which are present in the DLC structures (Fig. 5). For the hard DLC films [8] the presence of a broad band between 1100 and 1200 cm^{-1} is a fingerprint for the existence of diamond nanocrystals. In case a narrow peak at 1332 cm^{-1} is evidenced, the diamond crystals have micrometric dimensions. For our samples the band at 1150 cm^{-1}, indicating the presence of diamond nanocrystals, has a maximum intensity at a 40% CH_4 concentration. One can notice (Fig. 6) that the values of I_D/I_G ratio have a minimum at average CH_4 (40 ÷ 60%) concentrations, which corresponds to a maximum percent of sp^3C bonds [8]. Using the evaluations of S. Zhang and all [6, 7] we have estimated a 65% sp^3 C-bonds concentration for our best DLC structures, prepared in 40% methane in argon dilution.

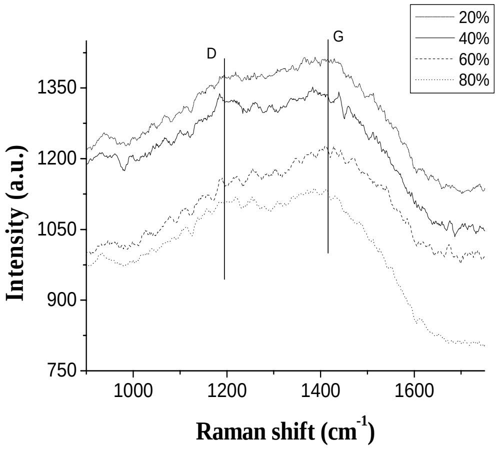

Fig. 5. Raman spectra for the DLC films.

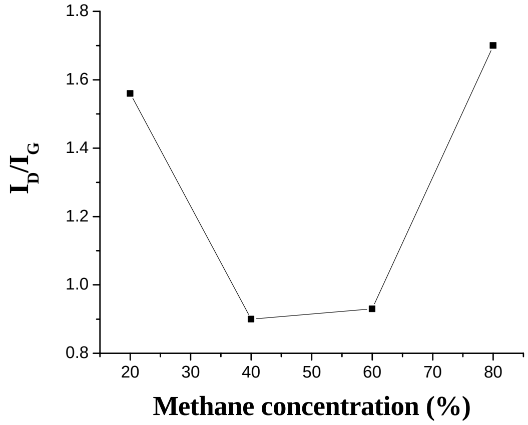

Fig. 6. I_D/I_G ratio for the DLC films.

3.5 Infrared spectroscopy

Fig. 7 displays the absorption coefficient in the range 2700 ÷ 3100 cm^{-1} for the DLC and PLC films prepared in 40 % respectively 10% methane dilutions. We have chosen this type of DLC film as it has the highest sp^3/sp^2 ratio as demonstrated by the Raman results. The absorption coefficient was estimated from the transmission measurements using, as a baseline, the extrapolation of the zero absorption regions (below 2800 cm^{-1} and above 3000 cm^{-1}) in the range of the stretching band. FTIR results display the typical vibration modes for amorphous carbonic hydrogenated structures. The difference between the absorption spectrum on DLC and PLC films in the range 2700 ÷ 3100 cm^{-1} consists in different intensities and widths bands for the similar stretching lines. As an overall characteristic property, the intensity of the stretching band of the PLC film is higher then that of DLC one denoting a higher concentration of bonded hydrogen atoms.

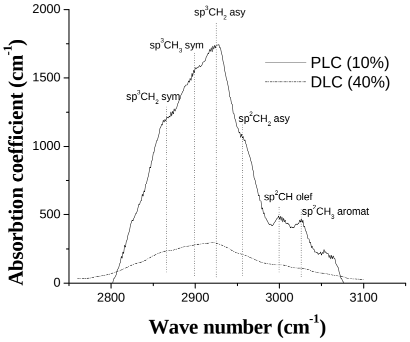

Fig. 7. IR absorption coefficient for the DLC (40%) and PLC (10%) films.

3.6 AFM measurements

Fig. 8 and 9 display the AFM images for the two types of carbonic structures. One can notice important differences of the surface peaks features as height and diameter values. They are more homogeneous for the PLC films comparative to the DLC ones. However both types of films are rather smooth with R_{rms} values around 4 nm.

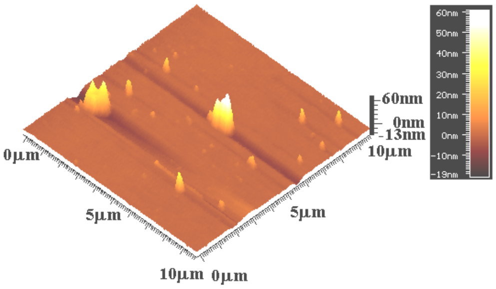

Fig. 8. 3D AFM topographic image for DLC (20%) structures on glass substrate (10 μm × 10 μm), R_{rms}=3.9 nm, R_{abs}=1.3 nm.

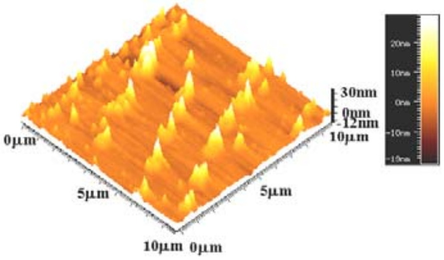

Fig. 9. 3D AFM topographic image for PLC (10%) structures on glass substrate (10 μm × 10 μm), R_{rms}=4.2 nm, R_{abs}= 2.5 nm.

The AFM results demonstrate once again the abrupt transition of films structures and morphology at the modification of methane dilution from 20% to 10%.

4. Conclusions

We have prepared amorphous hydrogenated carbon structures by RF (1.78 MHz) – PECVD in various atmospheres of methane diluted in argon. Diamond-like carbon films have been obtained in the range 100% ÷ 20% CH_4/Ar dilutions. The DLC structures with the highest sp^3 carbon atoms concentrations, corresponding to a minimum value of the I_D/I_G ratio, were prepared at a 40% dilution. A further increasing for the methane dilution, from 20% to 10%, drastically changed the character of the carbonic films from DLC to PLC. The refractive index dropped from 2.05 to 1.41, while the optical gap increased from 1.51 eV to around 4 eV. This transition was also accompanied by a major modification of the films topography as demonstrated by AFM images.

References

[1] J. Ristein, R. T. Stief, L. Ley, W. Beyer, J. Appl. Phys. **84**, 3836-3847 (1998).
[2] P. K. Chu, L. Li, Materials Chemistry and Physics, **96**, 253-277 (2006).
[3] L. Valentini, J. M. Kenny, G. Mariotto, P. Tosi, G. Carlotti, G. Socino, L. Lozzi, S. Santucci Journal of Vacuum Science & Technology A: Vacuum, Surfaces and Films, **19**(4) 1611-1616 (2001).
[4] R. M. A. Azzam, N. M. Bashara "Ellipsometry and Polarized Light), North-Holland, Amsterdam, (1987).
[5] N. Dumitrascu, G. Borcia, N. Apetroaei, G. Popa, Plasma Sources Sci. Technol. **11**, 127-134 (2002).
[6] A. Zeng, E. Liu, P. Hing, S. Zhang, S. N. Tan, I. F Annergren, J. Gao, Annerg. and J. Gac, International Journal of Modern Physics B, **16**, 1024 (2002).
[7] S. Zhang, X. T. Zeng, H. Xie, P. Hing, **123**, 256–260 (2000).
[8] J. Schwan, S. Ulrich, V. Batori, H. Ehrhardt, S. R. P. Silva, J. Appl. Phys. **80**, 440–447 (1996).

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