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Journal of Physics: Conference Series **370** (2012) 012013 doi:10.1088/1742-6596/370/1/012013

Pulsed laser deposition of carbon films in low pressure neutral gas background

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Abstract. We have investigated Pulsed Laser Deposition (PLD) of thin carbon films using a graphite target, in a low pressure Argon gas background. Raman spectroscopy based structural analysis of the films shows a correlation between films properties and pressure of the buffer gas background. The morphology of the resulting thin films was characterized with Raman spectroscopy. Time resolved Optical Emission Spectroscopy (OES) observations indicate that, at the substrate position, and for background pressures above 80 mTorr, the dominant species in the expanding carbon plasma are C_2 molecules. This is also consistent with Faraday cup observations, which show a strong decrease in the carbon ions content, as the pressure is increased. Our main result is the observation of a sharp transition in the film morphology, around 300 mTorr, from Diamond like Carbon (DLC) at lower pressures, to amorphous Carbon at higher pressures.

1. Introduction

Pulsed laser deposition (PLD) is a well established technique used for deposition of different materials, including metals, semiconductors and polymers [1]. Particular attention has been given to PLD of carbon coatings, due to their morphological, structural, mechanical and electrical properties [2], which lead to potential biomedical applications. In this context we report on the characterization of thin carbon films obtained by PLD in an argon background and discuss the resulting morphology in correlation with properties of the laser produced carbon plasma.

2. The experiment

The experiments were performed in a vacuum chamber at Argon background gas pressures between 0.5 and 700 mTorr. A Nd:YAG laser pulse, 370 mJ, 3.5 ns, at 1.06 μm, operating at 10 Hz was applied to a rotating graphite target, at approximately 45° to the normal, with a fluence of 6.7 J/cm^2. A Silicon (100) substrate was located 5 cm from the laser spot, and the exposure time was fixed at 1.5 min. To characterize the plasma composition we used time integrated and time resolved visible spectroscopy, using a spectrometer combined with a 15 ns gated OMA. Axial Faraday cup measurements were performed to characterize the ionic content and dynamics of the laser plasma plume. The morphology

and composition of the resulting thin carbon films was investigated with Raman spectroscopy, atomic force microscopy (AFM) and secondary ion mass spectroscopy (SIMS).

3. Plasma properties

Figure 1 shows a 20 ms, time integrated spectrum of the Carbon plasma emission collected from a point on axis, 20 mm from the target surface, with 50 mTorr Argon background. The spectrum shows emission lines associated with single ionized Carbon, and molecular bands. Additional spectroscopic observations, closer to the target surface, show also single ionized Argon lines. These emission lines are either not observed or not resolved at this distance. Here the spectrum is dominated by emission corresponding to vibrational states of the $d^3\Pi_g \rightarrow a^3\Pi_u$ Swan band, of the neutral C_2 molecule [3]. Further observations of the laser plasma plume, with 15 ns time resolution, published elsewhere [4], show an increase in the molecular content of the laser plume, as pressure increases.

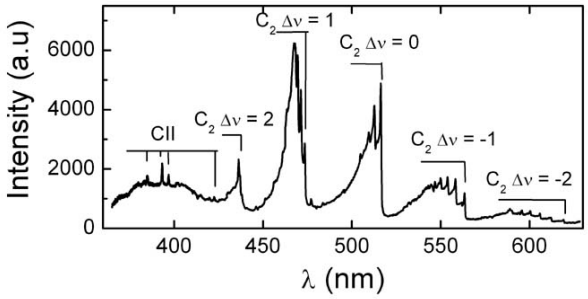

Figure 1. Time integrated spectrum of the carbon plasma emission from a point on axis, 20 mm from the target surface, at 50 mTorr Argon background.

Figure 2 shows signals from Faraday cups located at 7 and 10 cm from the graphite target, for three different pressures. The distinctive feature is the observation of two well defined plasma fronts, in agreement with previous observations [5]. Characteristic velocities of the order of $4 \bullet 10^4$ m/s and $3 \bullet 10^3$ m/s are inferred from the Faraday cup data for the fast and slow plasma fronts.

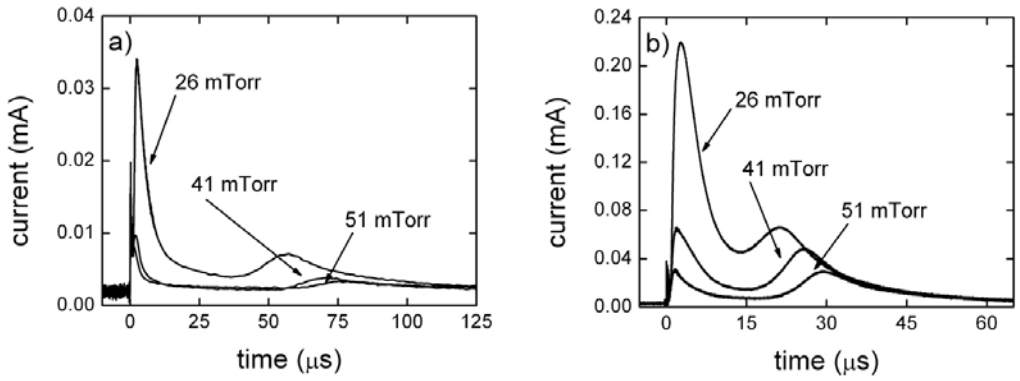

Figure 2. Characteristic signals of Faraday cups, as a function of pressure, located at (a) 10 cm, and (b) 7 cm, from the target surface.

On inspecting the leading edge or peak value of the fast component in the Faraday cup signals, an apparent reduction in the characteristic time of flight might be observed, as the Argon background

pressure increases. This might imply an increase in the ions characteristic velocity, as the pressure increases, which is unlikely. The observed effect is explained by the fact that an increase in background pressure also increases the collision rate of lower energy ions. As a result of this process, a significant fraction of lower energy ions are scattered in the radial direction, thus resulting in a shift to higher energies of the peak value of the Faraday cup signals. The trend in the slow component, increase in the time of flight with increasing pressure, is also consistent with a global higher collision rate. In this case, the lower characteristic energy results in a global energy loss, which can also be seen along the axial direction, due to the much lower ion flux, in comparison with the fast component.

On the base of the spectroscopic observations [4] it is reasonable to assume that the dominant species in the Faraday cup signals is CII ions. Under these conditions, the characteristic energy of the carbon ions in the fast component is estimated to be around 250 eV. A species composition for the slow component can not be established, as it might be a mixture of slow CII ions and ionized C_2 molecules.

4. Raman analysis of carbon films

The Raman analysis of DLC-films can be performed following a general procedure proposed by Ferrari *et al.* [6]. Raman spectra of thin carbon films are characterized, in the 1000 to 1800 cm^{-1} range, by two distinctive peaks, namely D and G peaks. Relative intensity and position of peaks depend on film morphology. Usually, the G peak is fitted whit a single skewed Lorentzian peak described by the Breit-Wigner-Fano (BWF) lineshape, and the D peak is fitted with a Lorentzian.

Figure 3 shows characteristic Raman spectra, with deconvoluted D and G peaks, at 170 and 380 mTorr Argon background pressure, together with the evolution of the peak intensity ratio, as a function of the Argon background pressure.

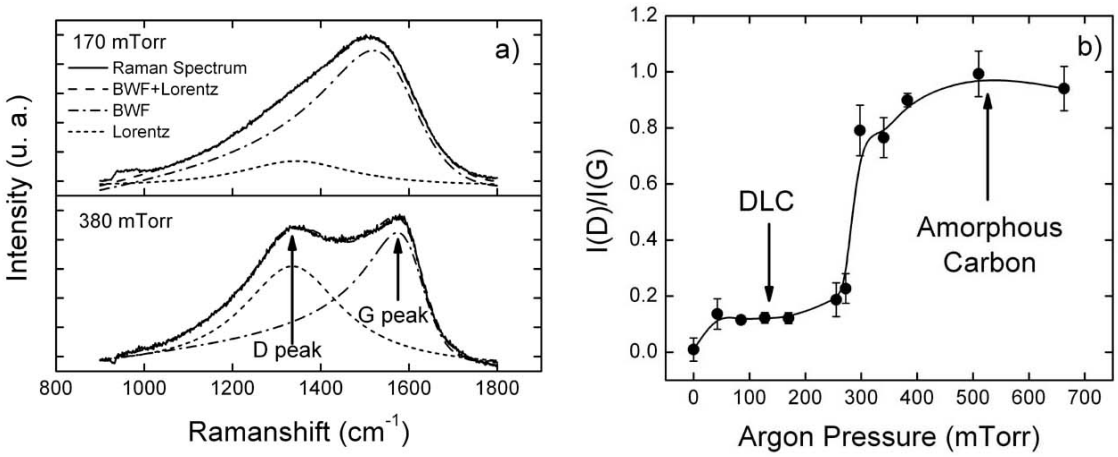

Figure 3. (a) Characteristic Raman spectra at two different pressures, showing D and G peaks deconvolution, (b) Intensity ratio of D and G peaks, as a function of pressure.

The intensity ratio, $I(D)/I(G)$, is determined by the degree of graphitization of the films. The Raman spectrum at 170 mTorr is characteristic of a diamond like film (DLC), whereas that at 380 mTorr corresponds to amorphous carbon [6][7]. The $I(D)/I(G)$ ratio was found to change with Argon pressure, in the ~0.1 to ~1.0 Torr range, thus indicating a transition from DLC to amorphous carbon, as pressure increases. The small peak in the Raman spectra around 900 cm^{-1} is due to a vibrational state of the Silicon substrate. It can be used, together with peak G, to estimate the film thickness, if an independent thickness measure is available. This was done using SIMS, to find that as pressure increases, the characteristic thickness of the carbon films decreases from 90 to 20 nm.

5. Discussion

The evolution of the $I(D)/I(G)$ ratio shows a sharp transition from DLC to amorphous carbon films. The OES observations [4] show that as the Argon background pressure is increased the laser plasma plume dominant species are C_2 molecules. On the other hand, the Langmuir probe measurements indicate that as pressure increases the relative intensity of the second plasma front, as compared with the first. On the base of these observations it can be conjectured that above the transition pressure of ~170 mTorr Argon, the main contribution to Carbon film growth is due to the second front, with low energy ions and dominant C_2 molecules, being the film growth process closer to a traditional deposition process. At lower pressure the dominant species are high energy CII ions. The characteristic high energy of the ions might lead to transient heating, followed by C_2 deposition.

6. Conclusions

We have characterized the carbon ions content of a laser produced Carbon plasma produced in low pressure Argon background, and the morphological properties of thin Carbon films resulting from laser Carbon plasma deposition on Silicon substrates. We have found that the structural properties of the Carbon films depend on the Argon background, with a sharp transition from DLC to amorphous Carbon around 300 mTorr. Further analysis and parameter scan is required to explain the observed transition, which will be reported elsewhere.

Acknowledgements

This work has been funded by FONDECYT project 1110380. F. Guzmán and H. M. Ruiz acknowledge doctoral studies scholarships from CONICYT and MECESUP, respectively.

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