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Plasma Characterization of Pulsed-Laser Ablation Process Used for Fullerene-like CN_x Thin Film Deposition

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An *in situ* Optical Emission Spectroscopy (OES) characterization was performed on Pulsed-Laser Ablation (PLA) process used for fullerene-like CN_x thin film deposition at nitrogen pressures within the 5 – 100 mTorr range. Plumes were generated by ablation of pyrolytic graphite (99.99%) target using a (500 mJ, 7 ns, 1064 nm) Nd: YAG-pulsed laser. The spectra from the plume show, essentially, the presence of the band heads of CN Violet vibrational/rotational B²Σ⁺ - X²Σ⁺ system and the characteristic C₂ emission lines, belonging to the Swan A³Π_g - X³Π_u system. These excited CN and C₂ molecules were generated by laser ablation and by collisions of the plume with the substrate surface. Their vibrational temperatures were strongly dependent on nitrogen pressure during the deposition process and presented a decrease between 2.64 and 1.23 eV, as pressure increased from 5 to 100 mTorr. Synthesis of fullerene-like structures required high molecular temperatures at the condensation surface. High concentrations of CN radicals in the plasma promoted nitrogen incorporation into the films. The OES plasma characterization allowed for a correlation of the concentration and vibrational temperatures of CN and C₂ species present in the plasma with the fullerene-like CN_x film composition and bonding, determined by XPS, IR, and Raman spectroscopy.

1 Introduction

Pulsed Laser Deposition (PLD) technique has attracted much attention in recent years for the synthesis of thin films of different materials, such as: high temperature superconductors, ferroelectrics, nitride and metal compounds, and fullerene carbon molecules. On the other hand, because the average energy of laser-ablated species is much higher than kT and a certain fraction of these species is ionized, it is possible to form metastable phases such as diamond-like carbon (DLC) and fullerene-like amorphous carbon nitride, CN_x, materials from a graphite target in nitrogen atmospheres [1,3]. For this reason, laser-ablated carbon plumes have been widely characterized. Since the dynamic behaviour of species in the laser-ablated plasma plume affects the characteristic of deposited thin films, many publications aim to understand the PLD process and the correlation between composition, structure, and properties of deposited films, plasma parameters, and chemical state of species present in the plasma [1-3]. Different techniques such as Optical Emission Spectroscopy (OES) [1,3,4], time-of-flight mass spectroscopy [1,3,5], laser-induced fluorescence spectroscopy [6], interferometry [7], and Langmuir probe method [8] have been used in order to understand and control the deposition process. Among the various diagnostic techniques, which are convenient tools in the detection of different chemical species, the OES has remarkable advantages pertaining to high spatial and temporal resolution for *in situ* characterization without perturbation of the plasma. From the intensities and contour forms of the observed emis-

sion spectra in the OES, useful plasma parameters such as: electron temperature and density [9], kinetic energy of ablated species, and vibrational temperature of molecules can be estimated [1-4]. This work analyzes plasma chemistry, physics, and vibrational temperature of CN and C₂ species present in the plume close to the target surface. Results permit a possible optimization of plasma ionization and molecular excitation for fullerene-like CN_x thin film deposition at different nitrogen pressures.

2 Experimental details

The experimental set up is shown in Fig. 1. CN_x films were deposited by pulsed-laser ablation of high purity (99.99%) pyrolytic graphite target in a nitrogen atmosphere using an INDI-30 Spectra-Physic Q-switched Nd YAG-pulsed laser (energy 500 mJ, wavelength 1064 nm, and pulsed width 7 ns) operated at 10 Hz. Laser-ablated carbon fragments were deposited onto silicon substrates and combined with active nitrogen species present in the plasma. Films were deposited at a substrate temperature near 300 °C. The target was placed 25 mm from the substrate and oriented 45° with respect to the substrate. The vacuum chamber was evacuated down to an approximate pressure of 2x10⁻⁴ mTorr, before each deposition. Nitrogen gas pressure was varied in the 5-100 mTorr range. The angle of laser incidence on the target was 45° and focused onto such by means of a glass lens to give fluency around 10 - 12 J/cm². Under these conditions, the growth rate was 10-12 nm/min.

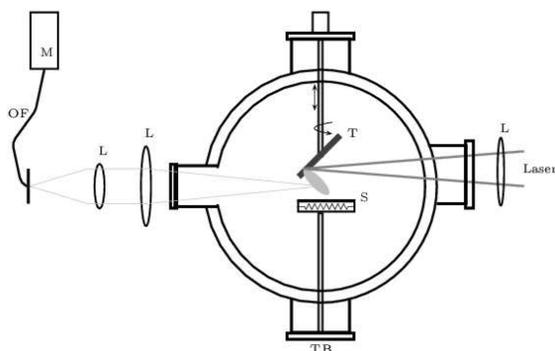


Figure 1. Experimental Setup: M-monochromator, OF-optical fiber, L-focusing lens T-target, S-substrate, TB-turbomolecular pump.

Plasma chemistry was determined by spectroscopy analysis of the emitted light. Optical emission from the ablation plasma plume, generated by the Nd YAG laser irradiation of the carbon target in nitrogen, was collected by a bundled optical fiber (diameter 2 mm) placed outside the quartz window, approximately 20 cm from the target surface, and fixed in such manner as to permit detection of the maximum light emission. The 4:1 ratio corresponding to the observed area of the plasma plume and images, gives a spatial resolution of 4 mm in diameter. The other end of the fiber is coupled to the entrance slit of a 0.55 m spectrograph (Triax 550, Jobin Yvon-Spex, f/6.4) equipped with a CCD camera for multi-channel detection and a 1200 l/mm grid with spectral resolution of 0.025 nm. The grid was moved in 20 nm sequences and the collected spectra were “assembled” to obtain a spectra in the 300-700 nm range.

3 Results and discussion

Characteristic emission spectra collected over 350-650 nm during the laser ablation of graphite at 12 J/cm² and 30 mTorr of nitrogen background pressure is illustrated in Fig. 2. The emission sampling point was nearly 1 cm away from the target and spectra collection time was 1 s, providing integration over several complete laser ablation events at the laser repetition rate of 10 Hz. In Fig. 2 we observe that emission spectra at 30 mTorr is dominated by very strong peaks of excited neutral, C(I), and single ionized, C(II), atoms. Additionally, we evidence much weaker CN emission lines of band heads from the Violet vibration/rotational B²Σ⁺ - X²Σ⁺ system, characteristic for carbon plasma in the presence of reactive nitrogen [1-4,10]. The most dominant CN sequences had head positions at 385-391 and 415-422 nm. Another result was the detection of C₂ molecular species in the nitrogen atmosphere, evidenced from characteristic emission lines belonging to the Swan A³Π_g - X³Π_u system. Detection of C₂ molecules is related to plume thermalization caused by collisions with background nitrogen molecules, promoting recombination of C to form C₂ [11]. Fullerene-like CN_x films have predominantly graphite-like structures and require sp² electron hybridization. Plume thermalization and a greater availability of C₂ species provide a large

fraction of sp² hybridization as opposed to sp³ hybridization, also observed in high-quality DLC films produced from laser plumes in PLD processes.[2].

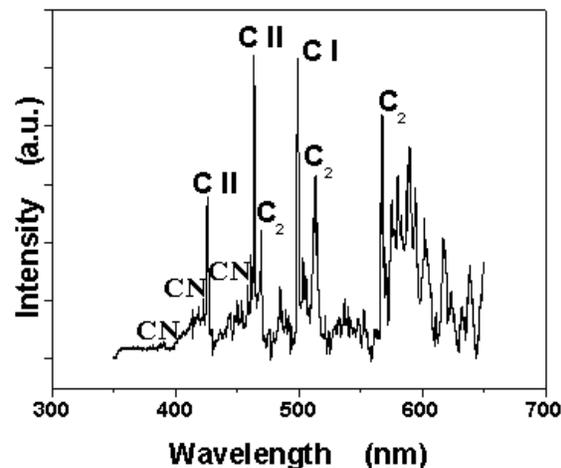


Figure 2. Typical optical emission spectrum of the plume of graphite ablation in nitrogen atmosphere at 30 mTorr and 3.03 x 10⁹ Watts/cm².

The expanded spectra near the violet band emission of the CN molecule (B²Σ⁺ - X²Σ⁺) and the C₂ Swan band emission (A³Π_g - X³Π_u), are shown in Figs. 3a and 3b. As illustrated in these figures, the CN Δν = 0 sequence is degraded to the UV with its (0,0), (1,1), (2,2), (3,3), and (4,4) vibrational transitions; while the 382-390 nm range and the bands of the C₂Swan system Δν = +1 is degraded to the red with its (1,0), (2,1), (3,2), (5,4), and (6,5), dominating the spectral region from 460 to 480 nm. The observed emission lines are identified using the information consigned in Ref. 3. The variation of the emission intensities of 391.1 (11,11), 388.34 (0,0), and 387.14 (1,1) nm lines associated to the CN Violet system, and 467.8 (5,4), 471.5 (2,1) nm lines from the Swan system, and C⁺⁺ 464.7 nm line, are observed, in Figs. 4a and 4b, for nitrogen pressure up to 5 mTorr at ~10 J/cm². The emission intensities of all CN, C₂, and C⁺⁺ increase with increased nitrogen pressure. Furthermore, the intensities of C₂ lines are stronger than CN molecules, indicating that plume thermalization, caused by collisions of C species with background nitrogen molecules promote a larger recombination of C to form C₂. This result can be correlated to the N/C ratio of deposited CN_x films, calculated using the ratio between the N 1s and C 1s peaks obtained through X-ray Photoemission Spectroscopy (XPS). We found that nitrogen content decreased from 23% to 18%, as pressure was increased from 5 to 30 mTorr [12].

In order to determine formation mechanisms, we have estimated the vibrational temperature of CN molecules using a relative emission intensity method. Assuming a Boltzmann distribution in the density of excited molecular levels, the emission intensity of vibrational transition (I_{ν₁ν₂}) is related to the vibrational temperature (T_{vib}) by expression [13]:

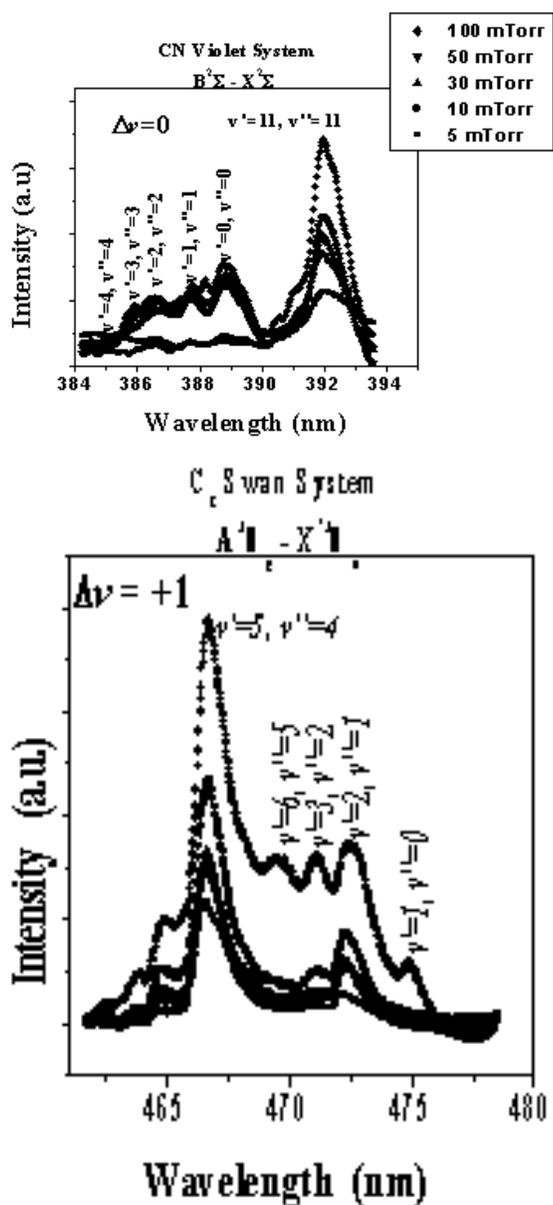


Figure 3. Spectra at different pressures of Nitrogen background: a) CN Violet system $B^2\Sigma^+ - X^2\Sigma^+$ with $\Delta\nu=0$; b) C_2 Swan system $A^3\Pi_g - X^3\Pi_u$ with $\Delta\nu = +1$.

$$\ln \sum_{\nu''} (\lambda^4 I_{\nu'\nu''}) = C_1 - G(\nu') \left[\frac{hc}{\kappa T_{vib}} \right] \quad (1)$$

where ν' and ν'' are the vibrational quantum number of upper and lower levels, respectively; λ is the wavelength corresponding to the transition (ν', ν''); $G(\nu')$ is the upper vibrational level; C_1 is a constant; h is Planck's constant; κ is Boltzmann's constant; and c is the speed of light. Vibrational energy levels and the emission wavelength of the diatomic CN ($B^2\Sigma^+ - X^2\Sigma^+$) molecule were calculated using molecular constants given in Ref. 14.

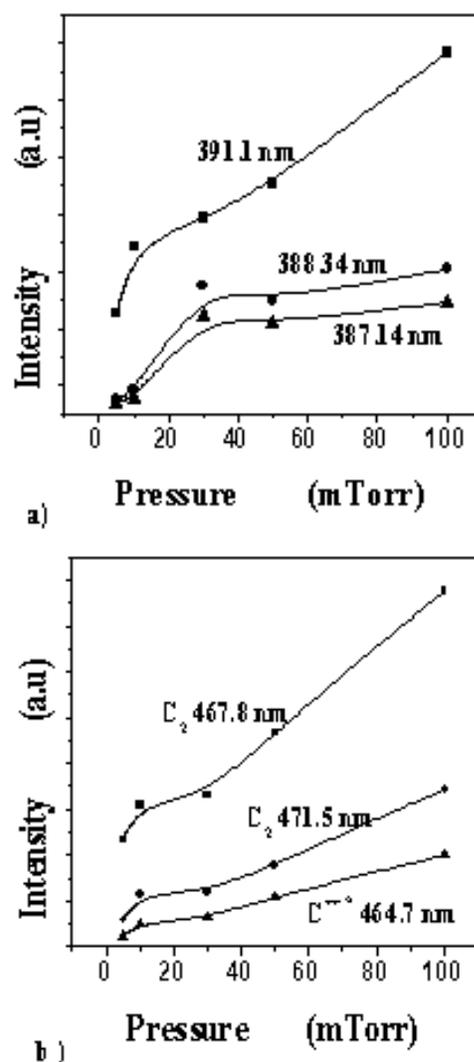


Figure 4. Emission intensities of: a) 391.1 (11,11), 388.34 (0,0) and 387.14 (1,1) nm lines associated to the CN Violet system; b) 467.8 (5,4), 471.5 (2,1) nm lines of Swan system and C^{++} 464.7 nm line from graphite plasma plume as a function of nitrogen pressure. Power density 12 J/cm^2 . Lines are guide to the axis.

Figure 5a plots data for CN emission peaks at 388.3 nm (0,0), 387.1 nm(1,1), 386.2 nm (2,2), 385.1 nm (4,4) according to equation (1), for different nitrogen pressures. Slopes are inversely proportional to T_{vib} , demonstrating a decrease in vibrational temperature from 2.64 to 1.23 eV, as pressure increased from 5 to 100 mTorr (see Fig. 5b). This behavior agrees with previously reported results [1,3,15] for fullerene-like CN_x films obtained by laser ablation of graphite in nitrogen using an excimer laser. At 5 mTorr, we observe strong increase of vibrational temperature, due to the occurrence of fewer plume collisions on the way to the substrate. Vibrational temperature at 5 mTorr (2.64 eV) is sufficiently close to the bonding energies of CN molecules (3.8 eV) to influence composition and film structure. In fact, films grown at 5 mTorr presented the highest N content (23%) and P₂/P₃ ratio (1.41), for N 1s nitrogen bonding and the highest Raman I(D)/I(G) ratio (2.45), related to the

lowest G-peak position (1548.1 cm^{-1}). These results indicate highest fullerene likeness under our experimental conditions [12].

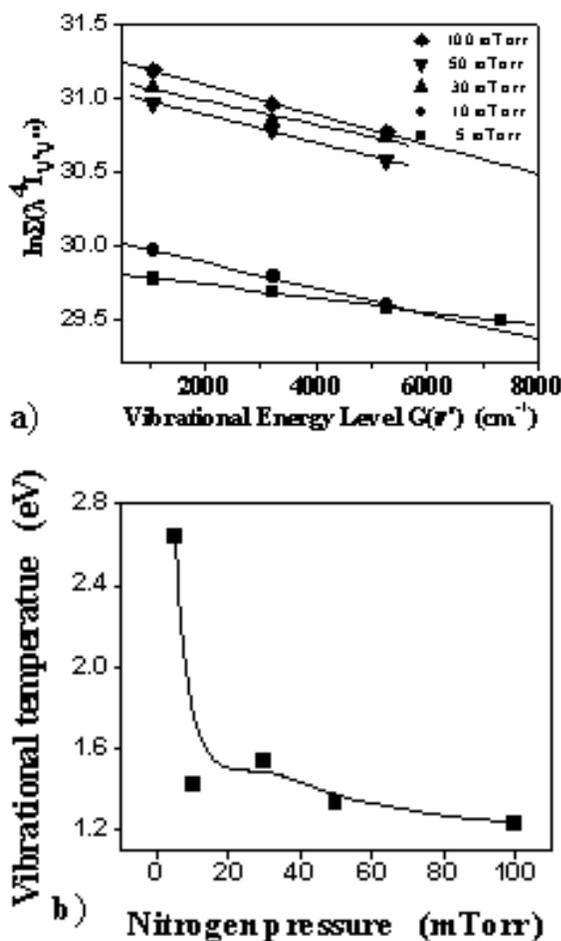


Figure 5. a) Boltzmann plots emission intensities of CN vibrational spectra for different nitrogen pressures. b) Vibrational temperature as a function of Nitrogen pressure. Lines are guide to the axis.

4 Conclusions

Plasma produced by laser ablation of graphite at low nitrogen pressures by using an Nd: YAG-pulsed laser, were analyzed for synthesis of fullerene-like CN_x films. Plasma composition and vibrational temperature was correlated to film composition and bonding. We concluded that:

Close to the target, plasma is dominated by strong peaks of excited neutral, C(I), and single ionized, C(II), atoms, CN radicals, and C_2 molecules, characteristic of carbon plasma in the presence of reactive nitrogen.

Detection of C_2 and CN molecules is related to plume thermalization caused by collisions with background nitrogen molecules, promoting recombination of C to form C_2 and provide a large fraction of sp^2 hybridization, thus favoring fullerene-like CN_x formations.

The intensities of C_2 lines are stronger than the intensities of CN lines. This result was correlated with the nitrogen content in the deposited CN_x films. We have found that nitrogen content decreases from 23% to 18%, as pressure increases from 5 to 30 mTorr.

Vibrational temperature decreases from 2.64 to 1.23 eV, as pressure increases from 5 to 100 mTorr. Vibrational temperature at 5 mTorr (2.64 eV) is sufficiently close to the bonding energies of CN molecule (3.8 eV) to influence composition and film structure. These results agree with the composition and structure of deposited fullerene-like CN_x films.

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