

## Thin film deposition of nitrated amorphous carbon by laser ablation

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Thin films of amorphous carbon (a-C) were grown by laser ablation in a nitrogen atmosphere at pressures from  $4.5 \times 10^{-4}$  Torr to  $7.5 \times 10^{-2}$  Torr. The structural properties of the films were studied by Raman spectroscopy. The obtained spectra were similar to those reported for Diamond-Like Carbon (DLC) films. The study of the behavior of the optical band gap and the nitrogen/carbon (N/C) ratio in the films, showed that the optical band gap reduced its values when the nitrogen content in the films is increased.

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### 1. Introduction

Pulsed laser deposition (PLD) has been extensively used in the last few years in the deposition of thin films due to its advantages over other techniques. Particularly the possibility of growing films under reactive atmosphere in a wide pressure range, leading to a plasma composition with different excited and energetic species [1], with an average energy higher than the thermal evaporation energy plus the inherent PLD features of high adhesion and low substrate temperatures during film growth, make this technique suitable to grow nitrated a-C thin films (a-C:N) [2].

a-C:N thin films have attracted the attention of many researchers, due to their possible applications as protective coatings of microelectronic devices, as the incorporation of nitrogen into a-C reduces the compressive stress giving to the a-C:N better mechanical properties [3]. As the optical and electrical properties of a-C can be changed by the incorporation of nitrogen this material has important potential applications. The properties of the deposited a-C:N depend on the  $sp^3/sp^2$  carbon bonding ratio, density, hardness and internal stress, which strongly depend on the deposition pressure, as the energy of the plasma particles varies with the pressure. From this point of view it is of interest to characterize the structural and optical properties of a-C:N thin films deposited by laser ablation as a function of the nitrogen gas pressure. This is the aim of the present work.

### 2. Experimental procedure

#### Experimental setup

A schematic diagram of the experimental setup is presented in figure 1. The system consists of a vacuum chamber evacuated by a diffusion pump. A pirani and a cold cathode gauge were used to measure the total pressure of the vacuum chamber. The energy source used in these

experiments was a Q-switched Nd:YAG laser with emission at the fundamental line ( $\lambda = 1064$  nm) with 28 ns pulse duration at a repetition rate of 20 Hz. The laser beam was focused on the target at an incidence angle of  $45^\circ$ . The target was a graphite disk 50 mm in diameter and 2 mm thick, it was rotated with an electric motor in order to avoid laser damage of the material. The substrates used in the present experiments were silicon (100) wafers and glass microscope slides. Prior to deposition the substrates were ultrasonically cleaned in an acetone and ethylic alcohol bath. Previously to the ultrasonic bath the glass substrates were washed in an extran (5%) solution. Substrates were placed at 60 mm approximately from the graphite target.

Films were deposited simultaneously onto silicon and glass substrates placed next to each other. The use of this configuration is an attempt to grow films with similar properties on different substrates. However owing to the different properties of the substrates some differences in the film properties are possible.

The deposition chamber base pressure was of the order of  $5 \times 10^{-6}$  Torr and was filled with nitrogen (99.99% purity) at working pressures between  $4.5 \times 10^{-4}$  Torr and  $7.5 \times 10^{-2}$  Torr. This pressure corresponds to the total pressure of the system. The nitrogen pressure was controlled by a needle valve.

Thin films were grown at room temperature and the deposition time was the same for all the samples corresponding to 36, 000 pulses approximately, with this time the samples thickness was of the order of 100 nm. All films were deposited at the same power density close to  $5 \times 10^8$  W/cm<sup>2</sup>.

#### Film Characterization

The obtained thin films were characterized by various techniques. Raman spectroscopy was used in order to study structural properties. Raman spectra were recorded with a

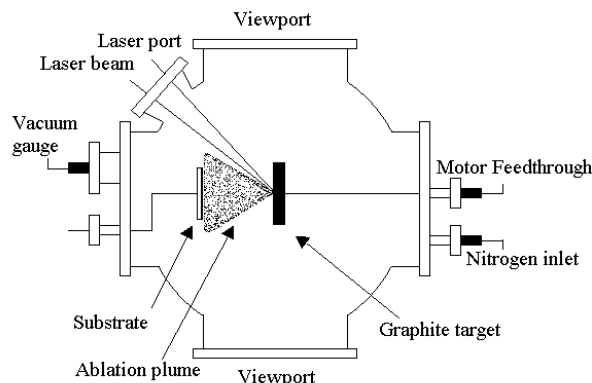


Figure 1. Schematic diagram of the experimental setup used in this work.

Spex 1403 double monochromator using the 514.5 nm line of an argon laser in a backscattering configuration. The signal was detected with a photomultiplier and a standard photon counting system. Surface chemical analysis was performed using energy dispersive X-ray analysis (EDX). The optical band gap was obtained from ultraviolet/visible spectrometry measurements with an UV/Vis spectrometer (Philips PU8710). Refractive index was determined from ellipsometry measurements. Thickness were measured with a Sloan Dektak IIA profilometer. The surface morphology of the films was observed with a scanning electron microscope (Philips XL30). The films deposited on silicon substrates were used for Raman, EDX and ellipsometry measurements. On the other hand the films deposited on glass substrates were used for optical measurements.

### 3. Results

#### Raman Spectroscopy

Raman spectroscopy has been used extensively for characterize  $sp^2$  and  $sp^3$  bonds of carbon films. It is well known that polycrystalline graphite exhibits two peaks at  $1350\text{ cm}^{-1}$  and  $1580\text{ cm}^{-1}$  [4,5]. On the other hand Raman spectrum of amorphous carbon thin films (diamond like carbon (DLC) for example) consist of an asymmetric band composed of two bands in different proportions. One of them at  $1560\text{ cm}^{-1}$ , the so-called G band, can be interpreted in terms of scattering by  $sp^2$  bonded carbon associated with graphite and a second band at  $1340\text{ cm}^{-1}$ , the so-called D band associated with the disorder due to the formation of  $sp^3$  bonds between graphitic adjacent planes. Theoretical studies have reported that a shift of the polycrystalline graphite bands towards low frequencies, can be interpreted as indicative of an increase in the fraction of the  $sp^3$  bonds [6]. Also has been suggested that the intensity ratio  $I_D/I_G$  can be related with the  $sp^3/sp^2$  bonding ratio [7]. However it's worth noting that this procedure is still subject of controversy.

In figure 2 the Raman spectrum of the graphite target is shown. Two peaks at  $1347\text{ cm}^{-1}$  and  $1581\text{ cm}^{-1}$  compose this spectrum. The position of these peaks and their

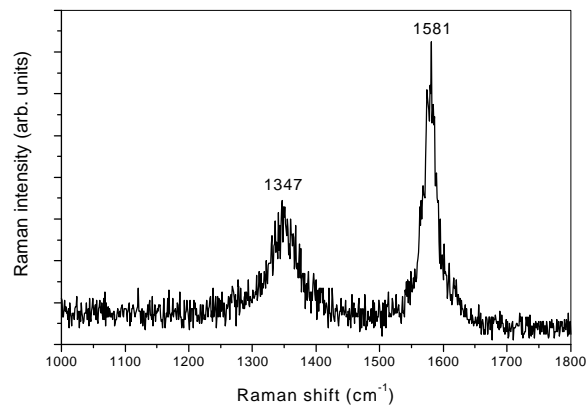


Figure 2. Raman spectrum of the graphite target used in the present experiments.

corresponding attribution has been reported before [4,5] and corresponds unambiguously to pyrolytic graphite.

In figure 3 the Raman spectrum of a film grown in vacuum at a pressure of  $2.5 \times 10^{-6}$  Torr is shown. This is similar to previously reported spectra for DLC films [1,8]. One can clearly observe an asymmetric band with its maximum pointing at  $1529\text{ cm}^{-1}$ . For deeper analysis this spectrum was fitted with gaussian functions using a commercial fitting computing program. The fitted peak shapes are shown in figure 3. These have their maximum value at  $1331\text{ cm}^{-1}$  and at  $1529\text{ cm}^{-1}$  and correspond to D and G bands respectively.

Carbon thin films deposited in nitrogen atmosphere, showed a Raman spectra similar to the spectrum presented in figure 4. In this case the D band is more intense which is an indicative of a more graphitic-like material. This can be explained by a loss of energy due to a more intensive collisional process between the carbon species and the nitrogen particles. This effect is more important at higher nitrogen pressures. For this spectrum the D and G bands have their maximum at  $1368\text{ cm}^{-1}$  and at  $1568\text{ cm}^{-1}$  respectively.

Figure 5 shows the Raman peak position of the D and G bands versus the nitrogen pressure. From this figure it is clear that an increase in the  $N_2$  pressure results in a shift

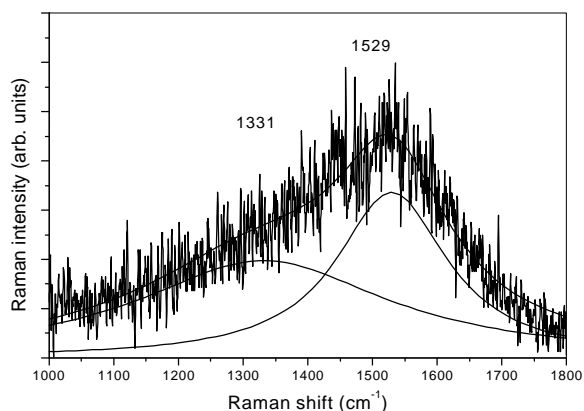


Figure 3. Raman spectrum of a film grown at base pressure.

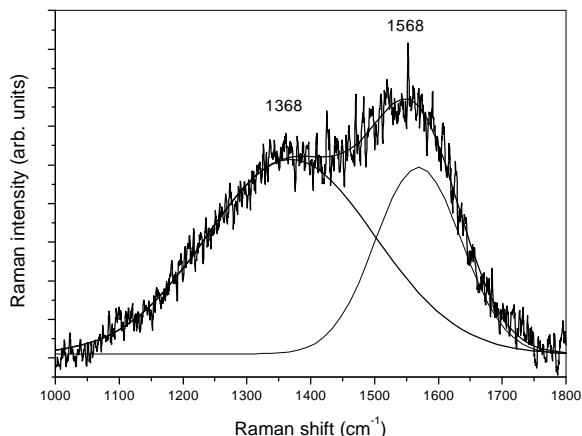


Figure 4. Raman spectrum of a thin film deposited in a nitrogen atmosphere at  $7.5 \times 10^{-2}$  Torr.

toward higher frequencies of the peak positions that can be interpreted as an increase in the  $sp^2$  bonding fraction. Therefore an increase in the pressure will induce a more graphitic structure in the film.

Figure 6 shows the  $I_D/I_G$  ratio as a function of the nitrogen gas pressure. It was found that when the nitrogen pressure increases from  $2.5 \times 10^{-6}$  Torr to  $7.5 \times 10^{-2}$  Torr the ratio  $I_D/I_G$  decrease from 2.8 to 1.9. It has been shown that the ratio can be related with the  $sp^3/sp^2$  bonding ratio, then the  $sp^3/sp^2$  ratio decreases with the  $N_2$  pressure and therefore this result confirm the growth of more graphitic-like films at high  $N_2$  pressures.

**UV/Vis spectrometry**

The optical absorbance of the obtained thin films was measured in a wavelength range of 280-700 nm with an UV-Vis spectrometer. From these measurements and the refractive index values obtained from ellipsometry measurements the absorption coefficients were calculated. The optical band gap of the a-C:N thin films was

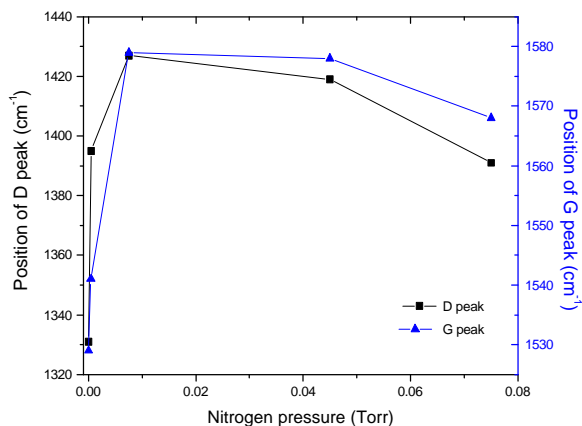


Figure 5. Raman peak position of the D and G bands versus the nitrogen pressure

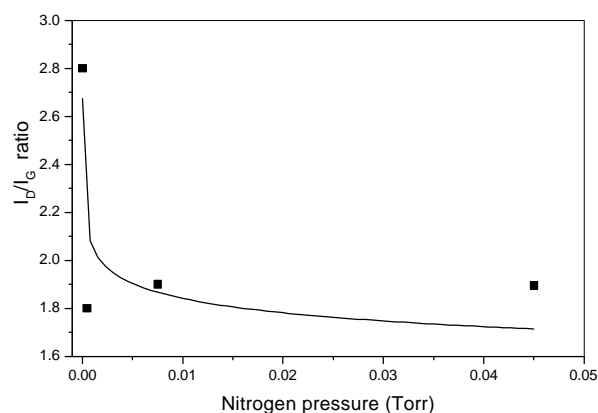


Figure 6.  $I_D/I_G$  ratio as a function of the nitrogen gas pressure

determined by the Tauc relation [9,10]. In figure 7 the optical band gap as a function of the nitrogen pressure is presented. These results clearly indicate that the optical band gap decrease as the nitrogen pressure increase. From the fact that the optical band gap can be related to the  $sp^2$  bonded carbon contents, one concludes that low values of the optical band gap correspond to a large graphitic clusters with more  $sp^2$  bonded carbon. This is indicative of graphitization in films deposited at higher nitrogen pressures. This tendency is consistent with the Raman results.

**Scanning Electron Microscopy Composition**

The ratio N/C of the thin films deposited was estimated from EDX measurements. Figure 8 shows the N/C ratio as a function of the nitrogen pressure. This result shows clearly that a major percentage of  $N_2$  is incorporated in the film when deposition is performed at a high  $N_2$  pressure.

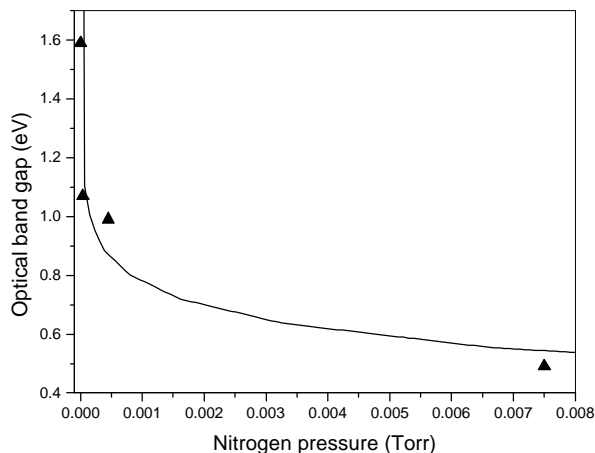


Figure 7. Optical band gap of amorphous carbon as function of the nitrogen pressure

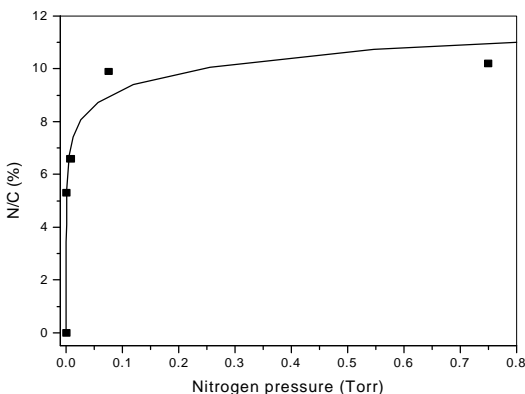


Figure 8. N/C ratio of a-C:N thin film versus nitrogen pressure

### Morphology

Typical SEM images of the deposited thin films are similar to the micrograph presented in figure 9. These reveal smooth surfaces in some cases with mirror-like appearance but with some spherical particles scattered on the surface. These particles have been ejected from the target due to surface heating above the melting point with the subsequent fusion of the surface. This effect has been observed before for a variety of materials deposited by laser ablation and it is generally an undesirable feature of this technique. Additionally the nitrogen pressure has an important effect on the surface morphology because as  $N_2$  pressure increases the surface of the deposited films exhibits more splashing. This can be due to collisions between vapor species that can favor coalescence that form particles before their arrival at the substrate.

### Conclusions

We have deposited amorphous carbon thin films using laser ablation from a graphite target. Raman spectroscopy results showed that an increase in the nitrogen pressure induces a more graphitic-like structure with more  $sp^2$  bonded carbon. This can be related to a greater incorporation of the nitrogen in the film and to a reduction of the energy of the plasma particles, as the mean free path is reduced. In these low energy conditions a maximum value of 10% was obtained for the N/C ratio, with this value being enough to alter significantly the optical band gap which is reduced from 1.6 eV to 0.5 eV.

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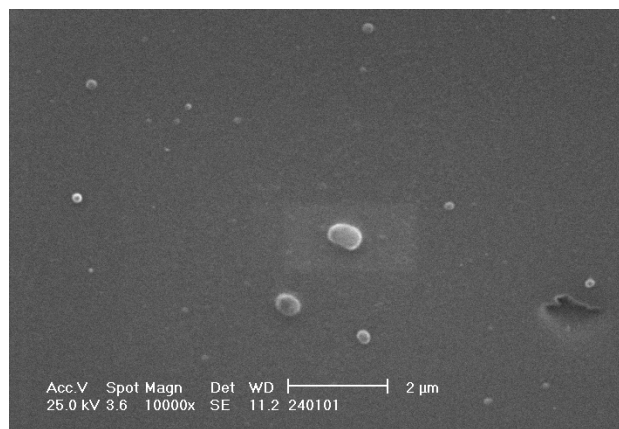


Figure 9. Typical surface morphology of the a-C:N thin film deposited by laser ablation

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