

Synthesis and characterization of a-CNx thin films prepared by laser ablation

A. Arrieta[a, b], L. Escobar-Alarcón, E. Camps
[a] *Departamento de Física, Instituto Nacional de Investigaciones Nucleares*
Apartado postal 18-1027, México DF 11801, México
[b] *Departamento de Física, Universidad Autónoma Metropolitana Iztapalapa*
Apdo. Postal 55-534, México D. F. 09340, México

S. Muhl
Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México
Apdo. Postal 364, México DF 01000, México
(Recibido 23 de octubre de 2003; Aceptado 13 de agosto de 2004)

Amorphous carbon nitride (a-CNx) thin films were synthesized by laser ablation on silicon (100) and glass substrates. The plasma was produced using the fundamental line of a Nd:YAG laser with 28 ns pulse duration focused on a graphite target. Deposition of a-CN films was carried out in a nitrogen atmosphere in the range of pressures from 3 x 10^{-3} to 1.5 x 10^{-1} Torr. The laser fluences used in this work were varied from 9 to 46 J/cm^2. We have carried out the characterization of the optical properties, composition and morphology of the thin films as a function of the nitrogen pressure and the laser fluence used for deposition. The study of the optical properties showed that the optical band gap diminishes as the pressure is increased. The compositional characterization showed the presence of carbon, nitrogen and oxygen in the deposited films; the nitrogen content increased as the pressure increases reaching a value of 29% in atomic concentration at a pressure of 7.5 x 10^{-2} Torr. The surface morphology of the deposited films was characterized by a roughening of the surface as the pressure increases; it is observed also that the roughness diminished as the laser fluence increased.

Keywords: Laser ablation; Carbon nitride; CN_x; Optical band gap; Compositional characterization; Surface morphology.

1. Introduction

Amorphous carbon nitride thin films have attracted the attention of many research groups because of their potential applications in a great variety of technological fields. The properties of the deposited a-C:Nx thin films such as density, hardness and internal stress depend mainly on the sp^3/sp^2 carbon bonding ratio. For thin films deposited by laser ablation, these characteristics are strongly dependent on the nitrogen working pressure and laser energy density used during deposition, which have an important influence on the energy of the plasma species and on the plasma density. It is worth noting that an appropriate selection of the deposition parameters is important in order to obtain materials with the desired properties. In this work we report the synthesis and characterization of a-CNx thin films prepared by laser ablation. This deposition technique has been extensively used in the last few years to produce a wide variety of materials in thin film form owing to its advantages over other deposition techniques. Particularly, laser ablation has been used successfully for the preparation of carbon based thin films, such as: diamond like carbon (DLC), a-CNx and a-CNx:H [1-3].

2. Experimental

The experimental set up used in this work has been described elsewhere [4]. Briefly, laser ablation was performed using a Q-switched Nd:YAG laser with emission at the fundamental line (λ = 1064 nm) with a 28 ns pulse duration at a repetition rate of 20 Hz. The laser beam was focused on a rotating target, at an incidence angle of 45°. The target was a graphite disk, 99.99% purity, 25 mm diameter and 2 mm thick. The substrates used in the present experiments were pieces of silicon cut from (100) wafers and glass microscope slides. The films were deposited simultaneously onto the different substrates that were placed next to each other. This was performed in order to use the most suitable substrate for characterization purposes. Prior to deposition the substrates were ultrasonically cleaned in an acetone and ethyl alcohol bath following standard procedures. In all the experiments the substrates were placed at 50 mm from the graphite target.

The deposition chamber base pressure was of the order of 7x10^{-6} Torr and was backfilled with nitrogen (99.99% purity) to the working pressure from 3 x10^{-3} Torr to 1.5 x10^{-1} Torr. The energy density delivered on the target was varied from 9 J/cm^2 to 46 J/cm^2 by keeping the spot size constant on the target surface and adjusting the energy per pulse. All the films were grown at room temperature.

The compositional analysis was performed by Energy Dispersive Spectrometry (EDS). The optical band gap was determined from Tauc plots obtained from optical absorption measurements using an UV-Vis spectrometer (Philips PU8710). Surface morphology was studied using a scanning electron microscope (Phillips XL-30) equipped with the EDS probe. Finally, the film thicknesses were measured with a Sloan Dektak IIA profilometer.

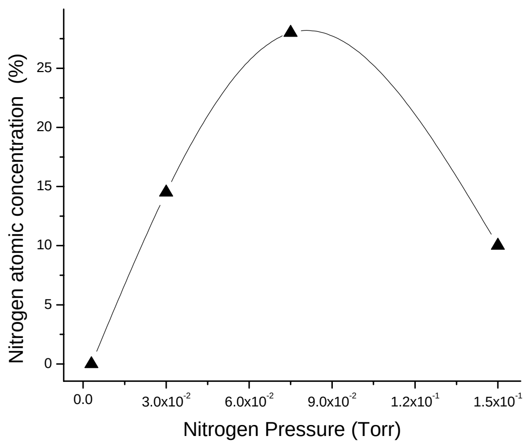


Figure 1. Nitrogen atomic concentration as a function of the nitrogen working pressure at laser fluence of 15 J/cm^2. The lines are guides to the eye.

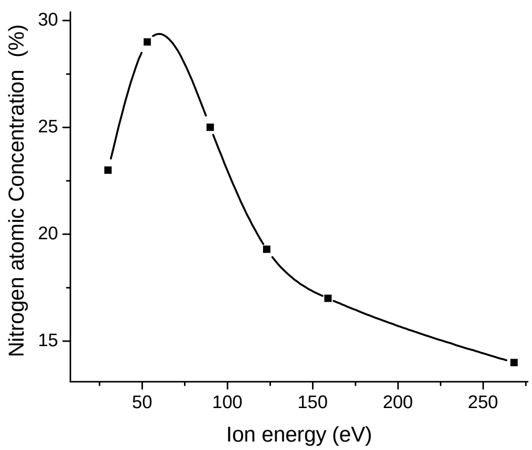


Figure 2. Nitrogen atomic concentration as a function of the ion energy at pressure of 7.5 x 10^{-2} Torr. The lines are guides to the eye.

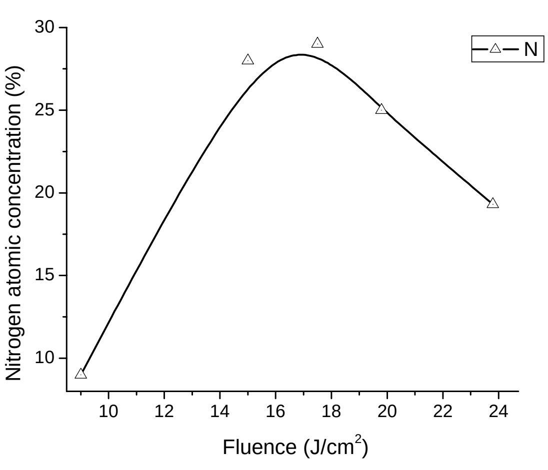


Figure 3. Nitrogen atomic concentration as a function of the laser fluence at pressure of 7.5 x 10^{-2} Torr. The lines are guides to the eye.

3. Results

The EDS results showed that the deposited films are composed of carbon, nitrogen and oxygen. In table 1 some of the EDS results are shown for different samples deposited at a pressure of 7.5 x 10^{-2} Torr. It is important to point out that no oxygen was intentionally introduced, however as one can observe in table 1 the films contain an appreciable quantity of this element. The incorporation of oxygen and even of hydrogen in a-CNx thin films has already been reported [3] although their origin has not been completely explained.

Figure 1 shows that the nitrogen content in the films increases as the nitrogen pressure increases keeping the laser fluence at 15 J/cm^2. At a pressure of 3 x 10^{-3} Torr no N was detected. For a pressure value of 3 x 10^{-2} Torr approximately 14.5% of N is incorporated, a maximum of 29% N is found for a pressure of 7.5 x 10^{-2} Torr, and this diminished for higher pressures (1.5 x 10^{-1} Torr). These results indicate that there exists an optimum pressure around 7.5 x 10^{-2} Torr at which the maximum nitrogen incorporation is obtained. This result can be attributed to the fact that at this pressure a higher quantity of atomic nitrogen is produced and this readily reacts with the carbon species in the plasma, favoring the formation of CN. At the highest pressure (1.5 x 10^{-1} Torr), although there is more N_2 in the plasma species this is no longer dissociated such that less N is produced and consequently there is less incorporation of this element into the film. It is worth noting that the processes responsible for the incorporation of N in the a-C network also include the N adsorbed in the target, as well as superficial reactions on the film during growth, and therefore the net process is very complex.

In figure 2 we show the variation of the atomic concentration of nitrogen incorporated in the films as a function of the energy of the carbon ions present in the plasma. The mean kinetic energy of the carbon ions was determined according to the procedure described in ref. [5] and its variation as a funcion of the laser fluence at constant pressure. As it can be observed there is also an optimal energy value (approximately 52 eV) at which the maximum incorporation of N is obtained. It is interesting to point out that this energy coincides with the pressure to which one also the maximum nitrogen content is obtained. The observed behavior could be due to the chemical sputtering of the nitrogen incorporated in the film that increases at higher energies. The figure 3 shows the nitrogen content as a function of the laser fluence used to ablate the target keeping the pressure at 7.5 x 10^{-2} Torr. As can be observed, the nitrogen content reaches a maximum value of approximately 29% at a fluence close to 17.5 J/cm^2, whereas the lowest value, 8%, corresponds to a fluence of 9 J/cm^2. This result can be attributed to an increase in the kinetic energy of the ions as the laser fluence is increased. As was shown in figure 2, the maximum nitrogen incorporated in the films is obtained at an ion energy of around 52 eV that corresponds to a fluence value close to 17 J/cm^2, this result is consistent

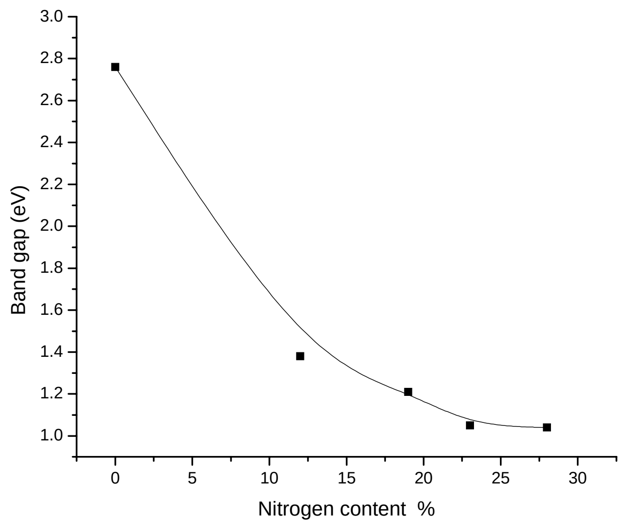
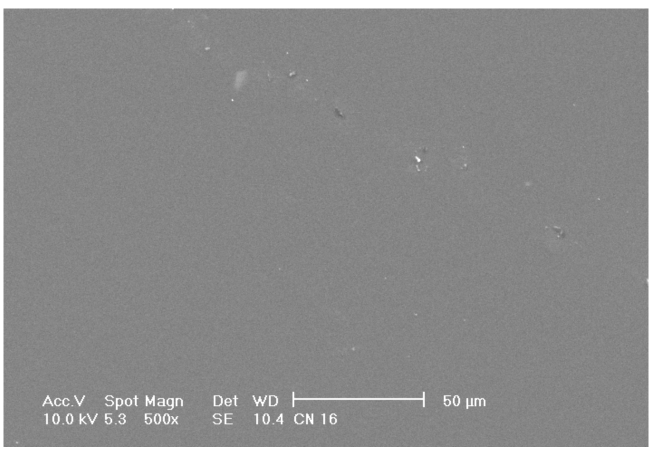
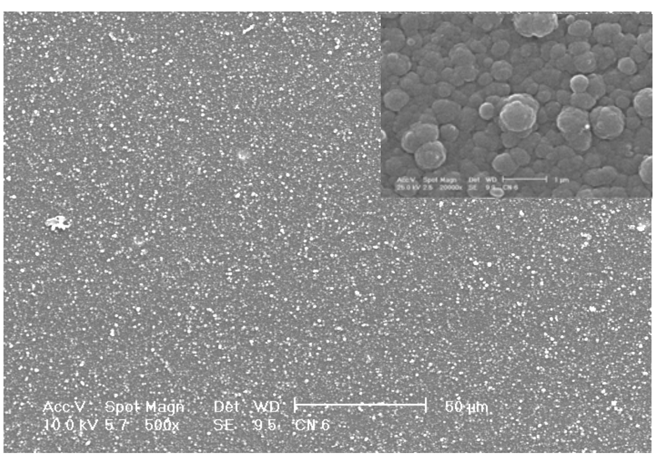


Figure 4. Optical band gap as a function of the nitrogen incorporated in the films. The lines are guides to the eye.



a)



b)

Figure 5. Thin film surface morphology at two different pressures at a laser fluence at 15 J/cm^2: a) 3 x 10^{-3} Torr and b) 1.5 x 10^{-1} Torr.

with the results discussed previously. These results suggest that the nitrogen incorporated into the a-CNx films could be controlled by the ion energy of the plasma ions.

From the spectrophotometer measurements the absorption coefficients were calculated using the equation:

$$\alpha = \frac{2.3 \quad OD}{d}$$

where *d* is the thickness of the film and *OD* is the optical density. The optical band gap of the films was determined using the Tauc relation:

$$\left(E\,\alpha\right)^{1/2} = \beta\left(E - E_0\right)$$

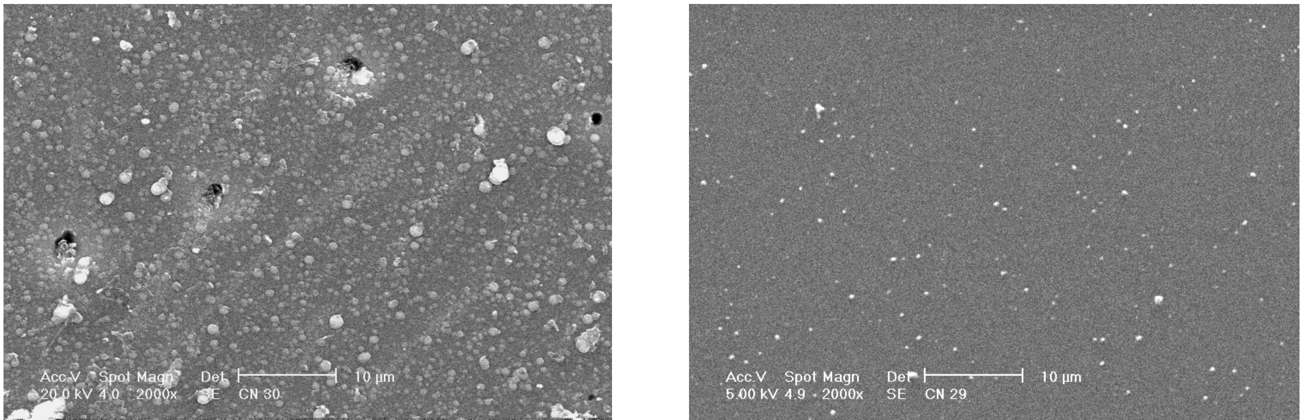
Where E is the energy of the incident light, E_0 is the optical band gap and β is a constant [6]. The obtained results, shown in figure 4, clearly indicate that the optical band gap decreases with the nitrogen content, from 2.7 eV for no nitrogen incorporated into the film, to 1.04 eV for 29 % nitrogen concentration. It has been proposed that when nitrogen is incorporated in the a-C network it can act as a bridging atom between sp^2 clusters and this results in an increment in the sp^2 cluster size, inducing the formation of larger graphitic domains [7]. From this idea, it can be concluded that the low values of the optical band gap correspond to large graphitic clusters with more sp^2 bonded carbon.

In figure 5 the effect of the pressure on the surface morphology of the deposited films is shown. As can be observed at pressures of 3 x 10^{-3} Torr the surface of the deposits is smooth with very few micro-particles dispersed on the surface (figure 5a), this effect is characteristic of the laser ablation technique and in some cases it is considered an undesirable effect. As the pressure increases, the surface of the deposits becomes more and more rough, in fact the morphology changes drastically at pressures of 1.5 x 10^{-1}

Torr as shown in the figure 5b, the insert shows that the deposit is formed by clusters with sizes ranging from 0.5 µm to 1 µm. This image reveals that low-density films with high porosity are produced at high nitrogen pressures. Furthermore, the presence of H and O can be attributed to the fact that in these porous films moisture can easily be absorbed from the environment. This change in topography may be attributable to a reduction in the energy of the species in the plasma as the pressure of gas increases due to collisions between the plasma species and the background gas, since the mean free path is reduced. It is worth mentioning that such processes favor coalescence in gas phase which might be responsible for the formation of the clusters.

4. Conclusions

The results of this work show that nitrogen incorporation in a-CNx thin films prepared by laser ablation depends on the laser fluence used for deposition and reaches a maximum value close to 29 % at 17.5 J/cm^2. For higher



a) 9.1 J/cm^2 b) 46 J/cm^2

Figure 6. Thin film surface morphology at two different laser fluences at a pressure of 7.5 x 10^{-2} Torr: a) 9 J/cm^2 and b) 46 J/cm^2.

fluences the nitrogen content diminishes. Nitrogen content also depends on the kinetic energy of plasma species used for the growth film and it shows a maximum at approximately 55 eV. The compositional results show the presence of oxygen in spite of the fact that no oxygen was deliberated introduced during deposition. The optical band gap decreases with the nitrogen content and this suggests the formation of large graphitic clusters with more sp^2 bonded carbon as the pressure is increased. Additionally, the surface morphology characterization reveals that low-density films with high porosity are produced at higher nitrogen pressures and the same result is obtained for low fluences.

Figure 6 shows the effect of the laser fluence on the surface morphology of the deposited films. For the lowest fluence used in this work, 9 J/cm^2, very rough surfaces are obtained while for the highest fluence, 46 J/cm^2, a smoother surface is obtained as reveal the figure 6b. This might be due to a higher kinetic energy at high fluence that increases the surface mobility and allows the growth of a film continuous and smooth.

References

[1] D.L. Pappas, K.L. Saenger, J. Bruley, W. Krakow, J.J. Cuomo, T. Gu, R. W. Collins; J. Appl. Phys. **71**, 5675 (1992)

[2] C. Niu, Y.Z. Lu, C.M. Lieber, Science. **261**, 334 (1993)

[3] L. Escobar-Alarcón, J. E. Villarreal Barajas, E. Camps, S. Muhl, E. Haro-Poniatowski, S. Romero, B. Salinas; Materials Science and Engineering B. **90**, 81 (2001).

[4] O. Olea-Cardoso, E. Camps, L. Escobar-Alarcón, S. Muhl, M. A. Camacho-López, E. Haro-Poniatowski, Thin Solid Films. **433,** 27 (2003).

[5] Nadezhda M. Bulgakova, Alexander V. Bulgakov, Oleg, F. Bobrenok, Phys. Rev. E. **62**, 5624 (2000).

[6] N. F. Mott, E.A. Davis, Electronic properties in non-crystalline materials, Oxford University Press, London, (1971).

[7] D. Mendoza, J. Aguilar-Hernández, G. Contreras-Puente; Solid State Comm. **84,** 1025 (1992).