Available online at www.sciencedirect.com

ScienceDirect

Diamond & Related Materials 16 (2007) 1291 – 1294

DIAMOND AND RELATED MATERIALS

www.elsevier.com/locate/diamond

a-CN thin film properties as a function of laser ablation plasma parameters

L. Escobar-Alarcón [a,d], A. Arrieta [a,b], E. Camps [a,d,*], S. Romero [a],
S. Muhl [c], M.A. Camacho-López [d]

[a] *Departamento de Física, Instituto Nacional de Investigaciones Nucleares, Apartado Postal 18-1027, México DF 11801, México*
[b] *Departamento de Física, Universidad Autónoma Metropolitana, Apartado Postal 55-534, México DF 09340, México*
[c] *Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Apartado Postal 364, México DF 01000, México*
[d] *Facultad de Química, Universidad Autónoma del Estado de México, Paseo Colón y Tollocan, Toluca, México, 50110, México>*

Abstract

In this work the laser ablation plasma parameters (mean kinetic ion energy, plasma density and type of excited species) were studied as a function of the laser fluence under different working atmospheres. Amorphous carbon nitride thin films were deposited using the plasma conditions previously diagnosed in order to establish a correlation between plasma parameters and thin film properties. The plasma was produced using the fundamental line of a Nd:YAG laser with 28 ns pulse duration focused on a high purity graphite target. A single planar probe was used to determine the mean kinetic energy of ions and their density. Time and space resolved optical emission spectroscopy was used to identify the excited species present in the plasma. It could be established that the film nitrogen content as a function of the ion energy has an abrupt increase for low ion energies and for greater energies saturation was observed. The saturation value depended on the working pressure, with a maximum value of 30 at.% at 10 Pa. A similar trend was observed for the band gap, which also reached a saturation value, which depended on the working pressure. The density of the material and its microstructural properties showed different behaviors. It was observed that a-CN thin films with the same composition but different microstructural and optical properties could be obtained.

Keywords: Amorphous carbon; Carbon nitride; Pulsed laser deposition

1. Introduction

When laser ablation is used for deposition of thin films, the material is evaporated from a solid target and transferred to the substrate in the form of plasma consisting of various species including neutrals, ions and clusters [1]. This technique can work under reactive atmospheres, and has been used successfully to deposit complex oxides and nitrides [2,3]. Additionally, the kinetic energy of plasma species can be varied in a very wide range. Particles with high energies have been used to produce films with good adhesion and high density [4]. These features make this technique a good candidate to grow amorphous carbon nitride thin films (a-CN), as has been shown in the last years in which the preparation of amorphous carbon nitrides such as a-CN*x* and a-CN*x*:H has been reported [5,6].

The physical properties of these nitrides depend mainly on the sp^3/sp^2 carbon-bonding ratio and on the nitrogen content incorporated into the film [7]. These characteristics are strongly dependent on the nitrogen working pressure and the laser energy density used during deposition because these parameters influence significantly the plasma properties, and therefore the characteristics of the deposited material. From this point of view it is of interest to characterize the plasma parameters and try to correlate such parameters with the physical properties of the deposited material in order to gain insight in determining the role of the plasma parameters on the properties of the deposited films.

2. Experimental setup

The laser ablation was performed using a Q-switched Nd:YAG laser with emission at the fundamental line ($\lambda = 1064$ nm) with a 28 ns pulse duration. The laser beam was focused on a

---

* Corresponding author. Departamento de Física, Instituto Nacional de Investigaciones Nucleares, Apartado Postal 18-1027, México DF 11801, México. Tel.: +52 55 5329 7200; fax: +52 55 5329 7234.
E-mail address: ecc@nuclear.inin.mx (E. Camps).

0925-9635/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.diamond.2006.11.022

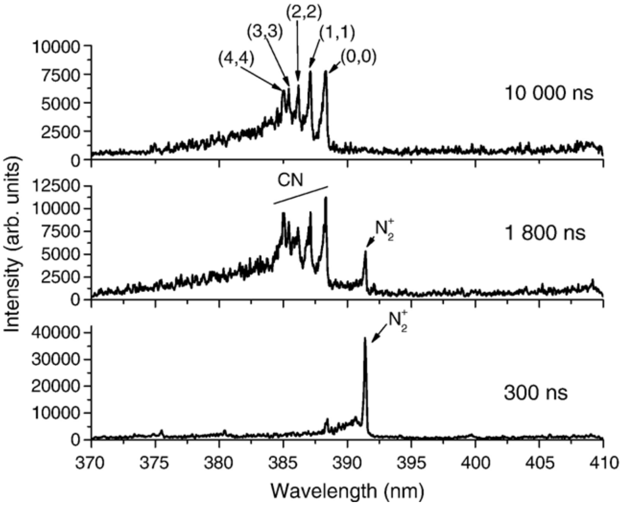

Fig. 1. Optical emission spectra acquired at different time delays after the start of the laser-target interaction. The transition from N_2^+ to CN species is clearly observed for longer times.

rotating target, at an incidence angle of 45°. The target was a graphite disk, 99.99% purity, 25-mm diameter and 5-mm thick. The deposition chamber base pressure was of the order of 7×10^{-4} Pa and was backfilled with nitrogen (99.99% purity) or with a N_2/Ar (40/60) mixture. Experiments were carried out at the following pressures: for the nitrogen atmosphere, 4 Pa and 10 Pa, whereas for the N_2/Ar mixture the pressure was set at 10 Pa. For each pressure the laser fluence used to ablate the target was varied from 6 J/cm^2 to 39 J/cm^2. In all the experiments the target-substrate distance was 5.0 cm.

The mean kinetic energy of ions and the plasma density were determined from the Time of Flight (TOF) curves [8], obtained using a 6-mm diam Langmuir planar probe. In all the experiments the probe was biased at −20 V, where saturation of the ion current to the probe was evident. The signal from the probe was monitored through a 15 Ω resistor, connected to a fast digital oscilloscope. The plasma density was determined from the ion current values across the resistor. Measurements were performed under the experimental conditions used for thin film deposition in order to establish a correlation between plasma parameters and thin film properties. Additionally, the optical emission spectroscopy (OES) technique was used in order to determine the kind of excited species present in the plasma. OES was performed using a 0.5 m spectrometer (Spectra Pro 500i) equipped with a fast-intensified charge coupled device (ICCD) (Princeton Instruments model 1024E) with a 150 ns gate for photon detection. The light was collected by a UV–Vis fiber bundle placed at a side quartz window of the vacuum chamber approximately 25 cm from the plasma. Synchronization between the laser pulse and ICCD was ensured using a fast detector.

The film thicknesses were measured with a Sloan Dektak IIA profilometer. Compositional analysis was performed by Energy Dispersive Spectrometry (EDS) using a scanning electron microscope (Phillips XL-30) equipped with an EDS probe, in this case prior to the measurements the signal was calibrated using a standard for low Z elements with an excitation energy of 5 keV. Some samples were studied by elastic forward analysis (EFA) [9], in this case a 4.0 MeV ^{7}Li ion beam from a Tandem Van de Graff accelerator was used. The angle between the ion beam and the sample surface was fixed at 30° while the angle between the detected particles and the incident ion beam was fixed at 45°. Microstructural characterization was performed by Raman spectroscopy; the Raman spectra were recorded with a high-resolution micro-Raman system (LabRam HR 800) using the 632.8 nm line of a He–Ne laser in the backscattering configuration.

3. Plasma diagnostics

Optical emission spectroscopy measurements with temporal resolution were performed in order to study the temporal evolution of the excited species present in the plasma. Measurements were performed at 5 cm from the target, under a N_2 atmosphere at a pressure of 10 Pa, varying the laser fluence. The OES results reveal that the main emitting species for times up to 800 ns, were: C$^+$ (283.66, 290.6, 299.2 and 426.65 nm), C^{2+} (406.89 and 418.66 nm), atomic excited nitrogen N$*$ (427.8 nm), and N_2^+ (391.39 nm), with the C$^+$ (426.65) being the most abundant specie in the plasma at these times. For longer times, typically greater than 1 μs, it was observed the formation of excited CN species that eventually could become the precursors for the CN thin film formation. Fig. 1 shows three OES spectra acquired at different time delays after the start of the laser-target interaction. As it can be observed, for times up to 300 ns, in this spectral region the main emission is due to N_2^+ excited species (Fig. 1a), but for longer times (greater than 1.8 μs) the spectral emission is dominated by the CN emission corresponding to the CN violet system. These results could be interpreted in terms of a high interaction

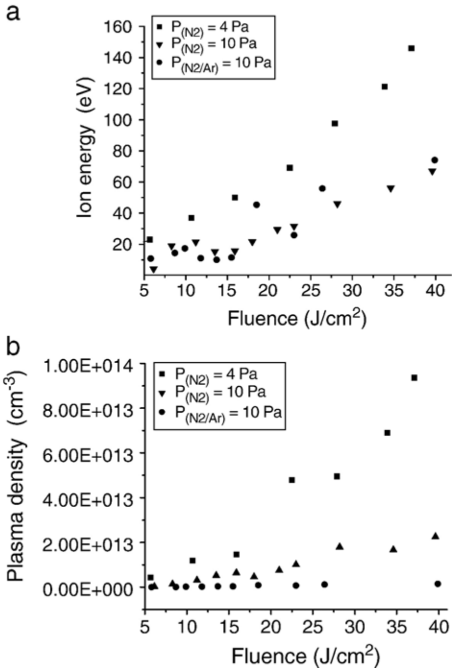

Fig. 2. Effect of the laser fluence on: (a) the mean ion kinetic energy, (b) the plasma density as a function of the laser fluence, under different background atmospheres.

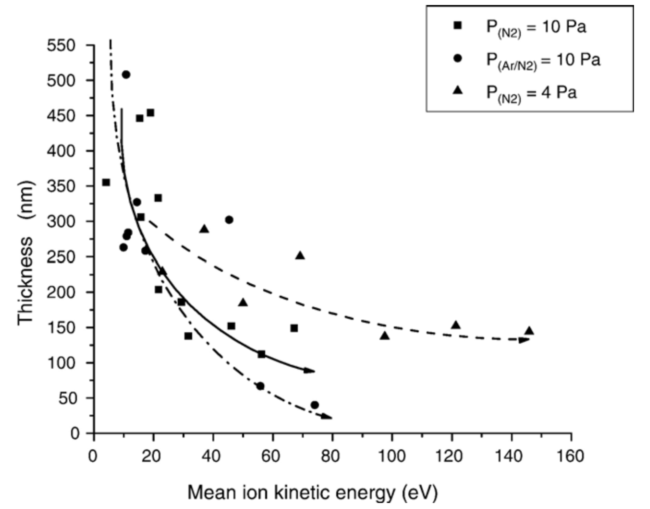

Fig. 3. Influence of the mean ion kinetic energy on the thickness of films deposited under different working atmospheres (lines are a guide for the eye).

between carbon and nitrogen species that favors the CN formation and excitation. It is worth mentioning that at longer times the CN emission bands are the only characteristics observed in the OES spectra, suggesting that an important contribution of the nitride formation is originated in the gas phase.

The Langmuir probe measurements reveal that the mean kinetic energy of ions increases with the laser fluence from low values such as 4 eV, up to 150 eV in our experimental conditions as it is observed in Fig. 2a. At the lower pressure (4 Pa) the increase of energy was faster than at the highest one (10 Pa), and could be 80 eV greater than at the higher pressure for the case of the highest fluence. When the N_2/Ar mixture was used, the mean ion energy detected is practically the same than that obtained when pure nitrogen was used (at the same pressure), 4 eV at 6 J/cm^2 and 74 eV at 39 J/cm^2, for a total pressure of 10 Pa. This behavior suggests that the probe detects fundamentally C ions probably with a small N ion contribution and the only effect of the argon gas is to favor the processes of multiple scattering of the plasma species, which is reflected as greater data dispersion.

Fig. 2b shows that the plasma density grows with the laser fluence, achieving a maximum value of 9.4×10^{13} cm^{-3} at a fluence of 39 J/cm^2 and a N_2 pressure of 4 Pa. At 10 Pa the plasma densities lied within the interval from 2.9×10^{11} to 2.2×10^{13} cm^{-3} (for a N_2 atmosphere) and within the interval from 2.9×10^{10} to 1.4×10^{12} cm^{-3} (for a N_2/Ar atmosphere), for the same variation of the laser fluence. The increase of plasma density can be explained in terms of a greater amount of material ablated when increasing the fluence. Multiple dispersion processes are favored when Ar is used in the working atmosphere, so that less particles can reach the probe (the substrate), therefore films grown under a pure nitrogen atmosphere are subjected to a greater bombardment. The same amount of N_2 is available when pure nitrogen is used at the lowest pressure or when the N_2/Ar mixture at 10 Pa is used; nevertheless as shown above, there are considerable differences in ion energy and plasma density for both cases. These results suggest that the major contribution to the plasma density could be attributed to carbon ions. Therefore deposition of carbon thin films in such experimental conditions, in principle, will allow us to study the effect of the plasma parameters keeping the same amount of N_2 available to form the nitride.

4. Thin film deposition and characterization

Carbon nitride thin films were deposited under the previously characterized plasma conditions, so that for each deposited sample the values of plasma density and ion energy were known and controlled.

Fig. 3 shows the film thickness as a function of the mean kinetic ion energy. The film thickness diminishes as the ion energy increases. However, this behavior depends on the working pressure; this effect is stronger for higher pressures where the plasma density has the lowest values. High values of plasma density compensate the loss of material due to the energetic ion bombardment. Probably combinations of chemical and collisional sputtering, which depend on the ion energy, are the responsible for the film thickness variation observed. It is worth mentioning that this type of behavior has been observed for different materials and even in some cases has been reported no film deposition for higher fluences.

The nitrogen content as a function of the ion energy for the different atmospheres used in this work is shown in Fig. 4. A very similar tendency no matter what pressure or type of gas is used was observed, i.e. an abrupt increase in the nitrogen content for low ion energy values up to a certain saturation value for high ion energy values. It is observed that depending on the type of gas and pressure used, a different nitrogen content saturation value was reached, at 10 Pa (N_2 atmosphere) it was about 30.0 at.%, whereas at 4 Pa the corresponding value was approximately 25.0 at.%. The difference in the nitrogen content (5%) can not be attributed to the reduction of nitrogen in the background atmosphere, because at 4 Pa there is 60% less nitrogen present than at 10 Pa. This result suggests again that

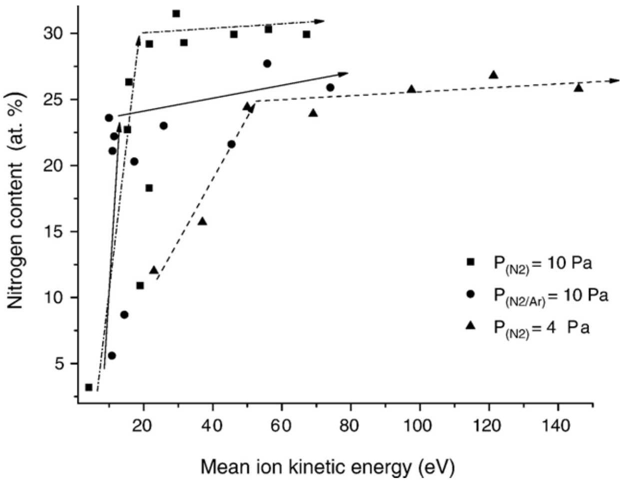

Fig. 4. Nitrogen content in CN*x* films deposited at different pressures, as a function of the mean ion kinetic energy at (lines are only a guide to the eye).

the plasma-background gas interaction plays an important role in thin film growth.

The EFA measurements revealed the presence of carbon, nitrogen, hydrogen and oxygen incorporated into the film. It is important to note that the concentrations of H and O are almost constant over the film thickness. Thin films deposited at the same pressure (10 Pa) and plasma ion energies greater than 15 eV had a composition of $C_{0.46}N_{0.22}O_{0.08}H_{0.24}$, whereas at the lowest energies (5 eV), the composition was $C_{0.69}N_{0.06}O_{0.08}H_{0.17}$. It is worth mentioning that a good agreement between nitrogen content measured by EDS and EFA was observed. The density of the a-CN*x* films as a function of the plasma ion energy showed an increase as the ion energy decreases, which is due to a decrease of the nitrogen content in the films as the ion energy decreases. In these conditions the density reaches its highest value of 1.75 g/cm^3, at 4 eV, while a density of approximately 1.2 g/cm^3 was obtained at 67 eV. These results indicate that with the increase of ion energy a more porous material is obtained and therefore H and O can be absorbed from the moisture atmosphere.

Micro-structural characteristics of the deposited materials were studied by Raman spectroscopy. The results showed that as the ion energy is increased the G peak position was seen to shift to higher frequencies for the three background atmospheres used. According to the three-stage model [10] such a shift of the G peak can be interpreted as an increase in clustering. In fact the I_D/I_G ratio was found to increase with the increase of nitrogen content in the films, indicating also a rise in either the number or the size of the sp^2 clusters. Both results indicate that even when the nitrogen content saturates, the structure of the films is changed by the ion bombardment.

The optical characterization reveals a variation of the optical Tauc gap as a function of the plasma ion energy. In general terms these results indicate that the optical band gap increases with the ion energy up to a certain value where saturation begins. This behavior is directly related with the increase of nitrogen content in the films as a function of ion energy. Moreover, films with the same composition can have different gaps, depending on the working pressure, or in other words depending on the plasma density and ion energy.

5. Conclusions

In laser ablation experiments for deposition of a-CN thin films, the variation of the working parameters, laser fluence and/or pressure, both induce changes in the plasma density and the energy of the ions incident on the substrate. As the bombardment of the growing film is increased the nitrogen content in the substrate rapidly saturates. However, even though the nitrogen content does not increase, the density of the material, its structure and its optical gap can change with further increases in the degree of ion bombardment.

Acknowledgments

This work was partially supported by the National Council for Science and Technology of Mexico (CONACYT) under project number 46344F.

References

[1] G.K. Hubler, in: D.B-. Chrisey, G.K. Hubler (Eds.), Pulsed Laser Deposition of Thin Films, Chap. 13, John Wiley & Sons, 1994.
[2] C. Julien, M.A. Camacho-Lopez, L. Escobar-Alarcón, E. Haro-Poniatowski, Mater. Chem. Phys. 68 (2001) 210.
[3] L. Escobar-Alarcón, E. Camps, M.A. Castro, S. Muhl, J.A. Mejía-Hernández, Appl. Phys., A 81 (2005) 1221.
[4] S. Metev, in: D. Bauerle, K.L. Kompa, L. Laude (Eds.), Laser Processing and Diagnostics (II), E-MRS Symposia Proceedings, vol. XI, Les Editions de Physique, Les Ulis, 1986, p. 143.
[5] D.L. Pappas, K.L. Saenger, J. Bruley, W. Krakow, J.J. Cuomo, T. Gu, R.W. Collins, J. Appl. Phys. 71 (1992) 5675.
[6] L. Escobar-Alarcón, J.E. Villarreal Barajas, E. Camps, S. Muhl, E. Haro-Poniatowski, S. Romero, B. Salinas, Mater. Sci. Eng., B 90 (2001) 81.
[7] S. Muhl, J.M. Méndez, Diamond Relat. Mater. 8 (1999) 1809.
[8] M.N. Bulgakova, A.V. Bulgakov, O.F. Bobrenok, Phys. Rev., E 62 (2000) 5264.
[9] S. Romero, M. Fernández, G. Murillo, H.M. Berdejo, Nucl. Instrum. Methods Phys. Res., B 194 (2002) 164.
[10] A.C. Ferrari, J. Robertson, Phys. Rev., B 61 (2000) 14095.