Influence of nitrogen gas pressure on plume-plasma and chemical bonding of carbon nitride films synthesized by pulsed laser deposition

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The effect of nitrogen gas pressure on the atomic structure of Carbon Nitride (CN\textsubscript{x}) thin films synthesized by pulsed laser deposition has been studied. CN\textsubscript{x} thin films were deposited from a graphite target in a nitrogen atmosphere on silicon substrates at a temperature of 300 °C at laser fluences of 2 and 10 J/cm\textsuperscript{2}, and at a gas pressure between 1 and 50 mTorr. The nitrogen to carbon (N/C) atomic ratio, bonding state, and microstructure of the deposited carbon nitride films were investigated by means of X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy, respectively. Raman spectra show that the intensity ratio of the D peak over the G peak increases with increasing deposition gas pressure. XPS analysis revealed a strong dependence of the amount of structurally incorporated nitrogen upon the gas pressure; the increase of deposition gas pressure results in an increase in the N/C ratio. Further analyses of the XPS N 1s core level spectra of the CN\textsubscript{x} films revealed a typical double peak arrangement, which is most pronounced for the highest laser fluence at low pressures. These two peak components indicate that the nitrogen bonded into a graphitic structure dominates over the two-fold coordinated pyridine-like bonding configuration. This favors the growth of intersecting corrugated graphene structures that may be considered to have a "fullerene-like" microstructure. The results were understood in combination with the optical emission of the plasma plume. It was found that the increase in pressure reduces the leading edge energies of the species in the plasma and increases the thermalization of the plasma due to a higher collision possibility.

Keywords: Thin films; ablation film deposition; Raman spectroscopy; fullerenes-like

Se estudia la influencia del gas de nitrógeno sobre la estructura atómica de las películas delgadas de CN\textsubscript{x}, sintetizadas mediante Deposición por Láser Pulsado. El láser se hizo incidir sobre un blanco de grafito (de alta pureza) a 2 y 10 J/cm\textsuperscript{2} en una atmósfera de nitrógeno y las películas crecieron sobre silicio calentado a 300 °C. Se investigó la razón atómica de nitrógeno a carbono (N/C), los enlaces químicos y la microestructura de las películas mediante Espectroscopía Raman y Espectroscopía fotoelectrónica de Rayos-x (XPS). Los espectros Raman muestran una fuerte dependencia de la cantidad de nitrógeno estructuralmente incorporado con la presión del gas de trabajo. El pico N 1s muestra la estructura típica de doble pico, característicos de compuestos a-CN, indicando que la configuración dominante en los enlaces del nitrógeno dentro de la estructura gráfica es tipo piridina de doble coordinación, lo cual favorece el crecimiento de estructuras grafeniformes corrugadas que se intersecan y que se puede considerar con microestructuras tipo fulereno. Los resultados presentados aquí fueron analizados en combinación con el diagnóstico de la pluma del plasma.

Descriptores: Películas delgadas; depósito por ablación; espectroscopia Raman; estructuras tipo fulereno.

PACS: 73.50.Gr; 81.15.Fg; 78.30.-j; 61.48.+c

1. Introduction

Pulsed-laser deposition (PLD) has been broadly used to grow a variety of carbon-containing refractory films, such as diamond-like carbon [1, 2], carbon nitride [3, 4] and silicon carbide [5]. In particular, since the theoretical study by Liu and Cohen [6], extensive work has been done to deposit β-phase carbon nitride, known as superhard material, by laser ablation of a graphite target in a nitrogen atmosphere. Deposition of CN\textsubscript{x} materials has proven to be particularly challenging because of the difficulty of incorporating nitrogen in the growing amorphous carbon matrix. In most cases, the nitrogen content is reported between 30 and 40 at.% [7], considerably lower than the concentration of 57 at.% required for C\textsubscript{3}N\textsubscript{4}. For that material, several groups [7] have opted for performing ion- or plasma-assisted PLD in an attempt to increase nitrogen incorporation in the material.

In general, CN\textsubscript{x} films contain a mixture of carbon sites characterized by diamond sp\textsuperscript{3}, graphite sp\textsuperscript{2} and, to a lesser extent, nitrile sp\textsuperscript{1} hybrid configurations. Amorphous CN\textsubscript{x} thin films are currently being extensively studied as to their potential tribological application-owing to their favourable mechanical and tribological properties [8]. Deposited under appropriate deposition conditions, hard and elastic CN\textsubscript{x} films with outstanding elastic recovery can be synthesized [4, 9]. The beneficial properties are most evident in films having a, so called, “fullerene-like” microstructure, consisting
of nitrogen containing corrugated and frequently intersecting graphene sheets [9]. These are commonly synthesized by magnetron sputtering [9], where the structure formation mechanisms have been under recent investigation [10]. Interestingly, Voevodin et al. [4] uncovered striking similarities between sputtering and PLD with respect to the existence of preformed CN species in the deposition flux, which can serve as building blocks for the formation of corrugated sheet-like structures [10].

In PLD, film growth properties are mostly affected by the plasma obtained during the laser ablation process, the so-called “plume” is produced by irradiation of a target by using high-power laser pulse. For instance, inclusion of nitrogen atoms is achieved by supplying nitrogen via reactive laser ablation of a graphite target in a nitrogen atmosphere. On the other hand, dynamic properties like the kinetic energy of each species in the plume also have significant effects upon the PLD-grown films. In this context, we performed plasma diagnostics using space resolved emission spectroscopy during the deposition of CNx thin films by Nd:YAG laser ablation of graphite in low-pressure N2 atmospheres.

The aim of this work is to describe the plasma chemical processes that take place during deposition of CNx films and their effect on the local microstructure. The carbon nitride films (a-C:N) were deposited by laser ablation of a graphite target in pure nitrogen, under different pressure. The composition and chemical bonding of the deposited films were studied using X-ray photoelectron spectroscopy (XPS) measurements and Raman spectroscopy.

2. Experimental setup

The experimental setup and experimental procedure were described previously [3, 11]. We used a short-pulse, Q-switched Nd:YAG laser which provided 7-ns, 500-mJ laser pulses at a wavelength of 1064 nm with a 10-Hz repetition rate. The experimental took place in a stainless steel vacuum chamber configured as a six-way cross of 10 cm inner diameter tubes forming a central 10-cm diameter target chamber evacuated to 10−5 mTorr, and flushed with pure nitrogen (99.999%) at different flow rates during experiments. The laser beam was focused with a 20-cm focal length lens on a graphite target (99.99%) with a 45° angle of incidence, giving an energy density of approximately 10 J/cm2. Nitrogen gas (99.999%) was injected to the chamber as a reactive gas, and the flow of such was accurately controlled by a needle valve. During laser ablation, nitrogen pressure was varied from 1 to 90 mTorr as measured by a vacuum gauge. The substrate was placed at a distance of 30 mm from the target. The films were deposited on silicon substrates that had previously been ultrasonically cleaned in acetone.

Emission spectra were collected, imaged onto spectrograph TRIAX 550 with 1200 grooves/mm grating and a resolution of 0.025 nm using two 10 and 13 cm focal length lenses positioned outside the reactor. For time-integrated spectra measurements, the spectrograph was equipped with a CCD sensor (1024 × 256). Most of the spectra were collected with integration times of 1 s.

Raman spectra were obtained using a laser confocal Raman Spectrometer with He-Ne (632 nm) laser, made by Jobyn Ivon, equipped with a 600 lines/mm grating. To minimize the damage during the measurement, a laser input power was fixed at 2.0 mW. XPS employed an Mg Ka 1253.6 eV X-ray (VG Microlab 310F) source. The samples were analyzed without initial sputter cleaning to avoid influencing the sensitive bonding structure in the uppermost atomic layers with the high-energy Ar ion bombardment. Analysis of the core levels of C and N, characteristic of the chemical bonding, was carried out by multiple Gaussian fitting of the experimental spectra.

3. Results and Discussion

3.1. Raman spectroscopy and XPS analysis

It is well known that the growth rate decreases as a function of the nitrogen background pressure, producing variations in the thickness of the CNx films grown during the same deposition time. This variation in the thickness produces changes on the Raman intensity. We have normalized our spectra before any fitting. The usefulness of normalizing a set of spectra is that one can visualize changes in the shape and position of the D and G bands as a function of nitrogen concentration and a trend of the Raman parameters can be drawn. Figure 1 shows normalized Raman spectra as a function of nitrogen pressure of the carbon nitride films deposited at the laser fluences of 2 and 10 J/cm2, respectively.

The spectra showed a broad asymmetric band between 900 and 1900 cm−1, which is similar to the typical Raman signal of amorphous carbon. This broadband was deconvoluted into two Gaussians showing that the G peak lies approximately at 1560 cm−1 and the D peak is located at around 1400 cm−1. The G peak is connected to the presence of all sp2 structures, both olefinic (chains) and aromatic (rings), while the D peak is related to the presence of aromatic rings only [12]. The change of intensity ratio of D and G bands, I_D/I_G, the full width at half maximum (FWHM) of G and D bands, the G and D bands position with laser fluence, and nitrogen gas pressure is shown in table (1). These parameters are sensitive to the structural change of sp2 hybridized carbon domains and reflect the number and/or the size of graphitic domains for amorphous carbon materials [12].

Except for the case of low fluence (2 J/cm2) and low pressure (1 mTorr), for both fluences the I_D/I_G ratio increases, the G peak position slightly moves to higher values, and the FWHM of peak G decreases when the nitrogen pressure increases. Also the G band and D band position shifted upward with increasing nitrogen gas pressure. Generally, the downward shift of the D band can be attributed to the strained or curved graphite plane [13]; when the materials are strained, the spacing between the atoms will change, leading to a change in vibration frequency. The reduction in G and D
et al. used [14]. According to Ferrari bon ions between these systems, even when low fluences are form an amorphous carbon, given the high energy of the car- bon with a high content of sp$^3$ bonds, but to the increase of sp$^2$-type cluster size.

All this indicates that what is being carried out in this experiment is introducing order to the material; thus, diminishing its hardness. Additionally, in terms of the fluence, no defined tendency is observed.

According to XPS analysis done in our previous work [11] the N content in the film increases with the gas pressure, corroborating an increase in sp$^2$ content. It seems that N atoms play a significant role in sp$^2$ hybridized C network. N atoms are incorporated either by substituting C atoms in the aromatic rings or connecting these sp$^2$ microdomains. Hence, we may infer from Table (1) that the lowering of FWHM of G band with N content indicates an increase of cluster size. The increase of cluster size at higher N content films is attributed to the thermalization of the laser ablated species, leading to the formation of structures with reduced three dimensional cross linking.

The typical XPS N 1s core level spectra shown in Fig. 2 present two main peaks (i.e. the Peak I at 398-399 eV and Peak II at 400.0-400.8 eV. These peaks are usually assigned to bonding structure of a-CN thin films [15]. The Peak I is related to two-fold coordinated sp$^2$ -hybridized nitrogen (sp$^2$ C-N) bonds-attributed to electrons originating from nitrogen atoms having two neighbors; just like in Pyridine. Nitro- gen atoms can also be bonded substitutionally for carbon in a graphite ring system. The Peak II corresponds to the respective sp$^2$ C-N bonds, originating from nitrogen atoms having three neighbors. The others peaks III and IV are smaller compo- nents; the latter can be assigned to N atoms bonded to sp

In the first case, what is noted is that the general trend of the I$_D$/I$_G$ ratio increases when pressure is increased (for both fluences used), or, in other words, increases upon increasing the nitrogen content in the samples. The position of the G peak is practically kept constant (the variation is very subtle). The half width of the G peak decreases upon increasing pressure or nitrogen content in the samples. This situation corresponds to the nitriding process of ta-C:N type samples. That is, the starting material is an amorphous carbon with a high content of sp$^3$ bonds between the carbons, which typically occurs when the PLD technique is used to form an amorphous carbon, given the high energy of the carbon ions between these systems, even when low fluences are used [14]. According to Ferrari et al. [12], in this case the position of the G peak - when measured with irradiation on the visible (our case) - practically does not move upon varying nitrogen quantity in the samples, and this is related to the fact that the nitrogen substitutes the C=C groups with aromatic groups. The diminishing of the G half width is directly related to the loss of disorder, i.e., the introduction of N to the samples generates more order, more sp$^2$-type clusters. Also, the increase in the I$_D$/I$_G$ ratio is not necessarily linked to the increase in the number of sp$^2$ bonds, but to the increase of sp$^2$-type cluster size.

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The general structure of the spectra does not vary much with addition, an intense line of first positive of N observed under our specific experimental conditions. In addition, emissions from the First Negative system N\(^+\) Violet (B \(^2\)Σ\(^+\) → X \(^2\)Σ\(^+\)\), \(\Delta \nu = 1\), (0, -1) systems, and ionic emissions from the First Negative system N\(^2\) were faintly observed under our specific experimental conditions. In addition, an intense line of first positive of N\(_2\) was observed. The general structure of the spectra does not vary much with the N\(_2\) pressure, while the intensities of the specific emissions do. Figure 3 shows emission spectra of the plume, taken at a distance of approximately 1 cm from the target, for CN Violet and C\(_2\) Swan systems at a fluence of 10 J/cm\(^2\) at a wavelength of 1064 nm and 7 ns energy pulse.

Electron temperatures (Te) can be determined from the optical emission spectroscopy analysis by using the relative atomic line intensities from a particular ionization \([16]\), assuming Local Thermodynamic Equilibrium (LTE) and that the collision processes predominate on the radiative and recombination processes. The LTE is fulfilled if electron density is sufficiently higher. Bekefi \([18]\) and McWhirter \([19]\) have derived a necessary criterion for the compliance of LTE according to the following expression for electron density:

\[
\frac{n_e (cm^{-3})}{10^{14}} \geq 1.4 \times 10^{3} [Te (eV)]^{1/2} [\Delta E mn (eV)]^{3}.
\]

Where \(E_{mn}\) is the energy difference between the upper and lower levels.

In our conditions for electron temperature Te = 0.33 eV and \(\Delta E_{mn} = 2.51 \text{ eV, the } n_e \text{ is } 1.37 \times 10^{15} \text{ cm}^{-3}\). For this reason, the LTE is sufficiently fulfilled.

The vibrational temperatures (Tv) at different nitrogen pressures for bands C\(_2\) Swan (\(\Delta \nu = 1\), in the 467-474 nm range) and CN Violet (\(\Delta \nu = 2\), in the 450-460 nm range) systems respectively, were obtained from Boltzmann plot of the sums of the band-head strengths measured in various \(\nu'\) (upper vibrational level) and \(\nu''\) (lower vibrational level) progressions against the vibrational term values G (\(\nu''\)). The Te and Tv slightly decrease with nitrogen pressure, although we observe that the CN vibrational temperature is higher for C\(_2\), as shown in Table II. This is probably because the nitrogen atmosphere cooled the hot electrons as well as excited states of molecules by collisions leading to a more efficient thermalization; thereby decreasing the vibrational temperature.

The addition of nitrogen, and hence the increase of the pressure, improved the confinement of the plasma, which in turn enhanced the emission from molecular and atomic nitrogen species.

The type of bonds in the film determines to a great extent its properties. However, the correlation between the type of bonds and the plume properties is not straightforward. The study undertaken in this work on the relation between the different plasma parameters and bonding types should therefore be considered as explorative. The increase of the gas pressure causes a slight increase of the plasma density (calculated in previous work Ref. 17 at the time when the formation of CN...
radicals was increased. The maximum of PII/PI ratio of 1.27 is observed at 30 mTorr, the sample with the highest N content, while its plasma parameters and I_D/I_G presented middle values. It was also shown that a high concentration of CN radicals having high vibrational temperature in the ablation plume is necessary for the production of fullerene-like structures. Fullerene-like CN_x films have predominantly graphite like structure and require sp^2 electron hybridization.

4. Conclusions

We have found a shift of position of the G peak towards a higher wavenumber from 1570 to 1580 cm^{-1} and an increase of its intensity with an increase of nitrogen content. This shift of the G peak position to a higher frequency combined with the fall of the G linewidth is a signature of the increase of the sp^2 fraction in the sample [17]. The lowering of FWHM of G band with N content indicates an increase in cluster size. The increase in cluster size at higher N content films is attributed to the thermalization of the laser ablated species, leading to the formation of structures with reduced three dimensional cross linking. Our results are in good agreement with the earlier results of similar measurements [4].

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