Effects of deposition parameters on the properties of amorphous carbon nitride thin films prepared by laser ablation

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Abstract. The properties of amorphous carbon nitride thin films, such as the composition, density, optical band gap, microstructure ($sp^3/sp^2$ ratio), have been investigated as a function of the working gas pressure and the laser fluence used for deposition by pulsed laser ablation. The compositional characterization showed the presence of carbon, nitrogen, oxygen and hydrogen in the deposited films; the nitrogen content increased as the fluence increased reaching a maximum saturation value of 30.0 at. % at a nitrogen pressure of $7.5 \times 10^{-2}$ Torr. A similar behavior was observed when the fluence was kept constant and the gas working pressure was varied. The study of the optical properties showed that the optical band gap increased as the pressure and fluence were increased. The density of the deposits diminished as the nitrogen content increased suggesting the formation of a more porous material at higher N contents. The Raman results revealed that the $I_D/I_G$ ratio increased monotonically with the increase of nitrogen content in the films indicating a rise in either the number or the size of the $sp^2$ clusters.

1. Introduction

In recent years there has been great interest in trying to synthesize amorphous carbon nitride thin films owing to their potential applications as hard coatings [1], as protective overcoats for magnetic storage disks [2], in field emission devices [3], gas sensors [4] and radiation detectors [5], to mention some. In general terms it has been shown that the physical properties of the deposited thin films such as microstructure, optical band gap, density, and internal stress can be varied depending on the $sp^3/sp^2$ carbon bonding ratio, the nitrogen content of the film and the type of bonding between carbon-carbon and carbon-nitrogen atoms. For thin films deposited by laser ablation, these characteristics are strongly dependent on the nitrogen working pressure and the laser fluence used during deposition because these parameters...
influence significantly the plasma properties and therefore the physical processes involved in the thin film growth. Although carbon nitride thin films have been prepared using a variety of deposition techniques under different experimental conditions [6], more work is still needed to understand the mechanisms involved in the carbon nitride formation. From this point of view it is of interest to characterize the physical properties of a-C:N thin films deposited by laser ablation, as a function of the laser fluence and the nitrogen gas pressure. In this work the composition, density, optical band gap, and microstructure ($sp^3/sp^2$ ratio) of a-CNx thin films as a function of the gas working pressure and the laser fluence used for deposition are reported.

2. Experimental

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 at a repetition rate of 10 Hz. The target was a 99.99% purity graphite disk. The substrates used in the present experiments were pieces of silicon (100) and glass microscope slides. The deposition chamber base pressure was of the order of $7.5 \times 10^{-6}$ Torr and was backfilled with nitrogen (99.99% purity) up to the working pressure. Experiments were carried out at different working pressures, from $3.0 \times 10^{-3}$ Torr to $7.5 \times 10^{-1}$ Torr. For each pressure the laser fluence used to ablate the target was varied from $5.0 \ J/cm^2$ to $39.0 \ J/cm^2$ keeping the target-substrate distance at 5.0 cm. The thin films were grown at room temperature for the same deposition time for all samples. The elemental analysis was performed by Elastic Forward Analysis (EFA) [7] using a 4.0 MeV $^7$Li ion beam from a Tandem Van de Graff accelerator. The angle between the ion beam and the sample surface was fixed at $30^\circ$ while the angle between the detected particles and the incident ion beam was fixed at $45^\circ$. The optical band gap was obtained from a Tauc plot of the ultraviolet/visible spectrometry measurements with an UV/Vis spectrometer (Philips PU8710). The Raman spectra were recorded with a high resolution micro-Raman system (HR LabRam 800) using the 632 nm line of a He-Ne laser in a backscattering configuration. The film thicknesses were measured with a Sloan Dektak IIA profilometer. The elemental analysis was also performed by EDS using an EDAX system coupled to a scanning electron microscope (Philips XL30).

3. Results and discussion

Initially several samples were prepared, firstly to determine the optimal growing conditions and secondly to test the reproducibility of the system.

3.1 Composition

The concentration (at. %) of the different elements present in the samples was determined from the Elastic Forward Analysis and from EDS measurements. Figure 1a shows the nitrogen content as a function of the laser fluence. As it can be observed the nitrogen content increased as the laser fluence increased (at a fixed working pressure) reaching a saturation value at a laser fluence value close to $16.0 \ J/cm^2$. It is interesting to note that a similar tendency was observed for each pressure in spite of the fact that the nitrogen concentration in the background atmosphere is different at different pressures. At $3.0 \times 10^{-2}$ Torr there is only 40 % of nitrogen available to form the nitride in comparison with that at $7.5 \times 10^{-2}$ Torr. For a nitrogen pressure of $7.5 \times 10^{-2}$ Torr the saturation value was approximately 30.0 at. %, whereas at $3.0 \times 10^{-2}$ Torr the N content saturate close to 25.5 at. %. An analogous behavior was observed when the fluence was kept constant ($23.0 \ J/cm^2$) and the gas working pressure was varied (figure 1b). In this case the nitrogen content reaches a saturation value in the order of 30.0 at. %, at a nitrogen pressure of approximately $7.5 \times 10^{-2}$ Torr.

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. These results seem to indicate that the H and O, absorbed from the moisture atmosphere, can diffuse throughout the thin film suggesting the formation of a porous material. The thin films deposited at the same pressure (7.5 x 10^{-2} Torr) and fluences greater than 16.0 J/cm² had a composition of C_{0.46}N_{0.22}O_{0.08}H_{0.24}, whereas at the lowest fluence of 6.1 J/cm², the composition was C_{0.69}N_{0.06}O_{0.08}H_{0.17}.

Figure 1. a) Nitrogen content as a function of the laser fluence at different gas pressures, b) the nitrogen content as a function of the nitrogen pressure. (Lines are only a guide to the eye).

Figure 2. a) Density as a function of the nitrogen pressure, b) density as a function of the laser fluence. (Lines are only a guide to the eye).

When the gas pressure was varied keeping the laser fluence at 23.0 J/cm², the film density, obtained from the EFA measurements, showed that the density reaches its highest value, 3.7 g/cm³, for a pressure of 7.5 x 10^{-2} Torr (figure 2a). Values of density of approximately 1.0 g/cm³ were obtained at pressures greater than 1.0 x 10^{-1} Torr indicating the formation of a more porous material at these pressures. Furthermore, as it is shown in figure 1b the nitrogen content in the films reaches its saturation value at a pressure close to 1.0 x 10^{-1} Torr, so that the more porous films are those with the maximum N content. A similar behavior was observed when the fluence was varied keeping the nitrogen pressure at 7.5 x 10^{-2} Torr (figure 2b), in this case the density was almost constant at 1.25 g/cm³ for fluences greater than 16.0 J/cm², whereas for fluences lower than 16.0 J/cm², the density slightly increases up to values close to 1.77 g/cm³. Again, the lower density corresponds to samples with the higher N content, as it can be seen from figure 1a.
3.2 Raman Spectroscopy
The Raman spectra of amorphous carbon nitride thin films are similar to those previously reported for DLC films being characterized by an asymmetric band composed of two sub-bands in different proportions [8]. One of these in the range of 1560-1600 cm\(^{-1}\), the G band associated with the in-plane stretching motion of pairs or chains of C sp\(^2\) bonded atoms. The second band around 1350 cm\(^{-1}\), the D band, is associated with a breathing mode of sixfold aromatic rings and only becomes active in presence of disorder [8]. In order to perform the data analysis, the Raman spectra were simulated using a Breit-Wigner-Fano (BWF) line shape for the G peak and a Lorentzian line shape for the D peak. The interpretation of the Raman results was performed following the three stage model proposed by Ferrari [9]. The results showed that as the laser fluence increased the G peak position was seen to shift to higher frequencies for the background atmospheres used. According to the three stage model such a shift of the G peak can be interpreted as an increase in clustering. In fact the \(I_D/I_G\) ratio increased monotonically 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. Additionally, even though a shift in the G peak was observed as a function of the laser fluence and gas pressure when these data were expressed in terms of the N at.% it was clear that the shift and the clustering are determined by the concentration of incorporated nitrogen in the deposit.

3.3 Optical bandgap
In figure 3a and 3b the variation of the optical Tauc gap as a function of the laser fluence and nitrogen content is presented. In general terms these results indicate that the optical band gap increases with the laser fluence and the nitrogen content. In particular figure 3b shows that the gap increases with increased nitrogen concentration but the rate of increase is different at low and high gas pressures. It is clear that unlike the clustering the Tauc property is not uniquely dependent on the N at.\%, and therefore these two characteristics are not completely dependent.

4. Conclusions
The results of this work show that amorphous carbon nitride thin films with the same composition but different microstructure and optical properties could be obtained. The Raman and band gap results suggest that the incorporation of nitrogen into the carbon network produces some ordering in the material associated with sp\(^2\) phase clustering but that the experimental conditions, gas pressure, also strongly affect the film properties. Additionally, the density characterization reveals that low-density films with high porosity are produced at higher nitrogen contents.
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