Mechanical and Vibrational Properties of Carbon Nitride Alloys

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A study of ultraviolet and visible Raman spectroscopy was made in amorphous carbon nitride (a-C:N$_x$) and amorphous hydrogenated carbon nitride (a-C:N$_x$:H) thin films. Two growth techniques were used: 1) glow discharge was used for depositing hydrogenated films with diamond-like (at -200V of bias) and graphite-like (-800V of bias) structure and 2) ion beam assisted deposition (IBAD) to deposit non-hydrogenated films and to obtain high nitrogen concentrations ($\sim$30%). The difference in energy between the visible and UV Raman, the so called G dispersion parameter, was investigated for both series of films. This parameter brings additional information concerning the structure of the films regarding size and concentration of graphitic clusters, and qualitative information on the sp^2/sp^3 concentration. The characterization of the structural properties in these films indicates an increase of graphite clusters with the incorporation of nitrogen.

Keywords: Mechanical and vibrational properties; Carbon nitride alloys; Raman spectroscopy

I. INTRODUCTION

The prediction of Liu and Cohen [1] of a C$_3$N$_4$ phase with a bulk modulus and hardness higher than those for diamond has led to considerable research on carbon nitrides. Despite these efforts, there has been no success on the synthesis of crystalline β-C$_3$N$_4$ [2-4]. However, a number of research has addressed the development of its counterpart a-C:N$_x$. The results have shown promising tribological properties [5-6]. Indeed, amorphous carbon nitride is presently used as a protective coating for hard disks and read heads.

Raman spectroscopy has been largely used in the study of the structural characterization of amorphous carbon due to fact that it is a non-destructive technique. In particular, the application of resonant Raman spectroscopy to determine the structure and composition of carbon films with and without nitrogen is highlighted. Using visible and ultraviolet excitation, the G peak dispersion can be derived and correlated with key parameters, such as density, sp^3 content, elastics constants and chemical composition [7-10]. Complementary results have also been supplied by infrared spectroscopy [11,12]. In this work, we present a study of vibrational properties of a-C:H:N$_x$ and a-C:N$_x$ films using ultraviolet (244 nm) and visible (514.5nm) Raman spectroscopy.

II. EXPERIMENTAL

Vibrational modes related to carbon-hydrogen, carbon-nitrogen and nitrogen-hydrogen bonds were investigated through Raman spectroscopy performed using two excitation energies named: visible (514nm) and ultraviolet UV (244nm). This study was focused on the investigation of the vibration energy and energy shifts associated with the G ($\sim$1580 cm^{-1}) and D ($\sim$ 1350 cm^{-1}) bands. These measurements were made in 3 series of samples. Two series of a-C:H:N$_x$ films were prepared by glow discharge using a mixture of methane (CH$_4$) and N$_2$ under different condition: (a) at 1 Pa total gas pressure and bias voltage of -200 V; and (b) at 12 Pa and bias voltage of -800 V. In both cases the deposition temperature (measured with a shielded thermocouple buried in a piece of copper placed closed to the substrate) was approximately 100 °C, and the base pressure was 2×10^{-6} Torr. The use of these two different conditions was adopted for obtaining carbon-nitrogen alloys with different structural properties [13,14]. The incorporation of nitrogen was obtaining by adding N$_2$ gas into the chamber, but keeping constant the total CH$_4$ + N$_2$ pressure. The concentration of nitrogen was obtained by nuclear reaction analysis [14]. Another series of a-CN$_x$ films was prepared by ion beam assisted deposition where a high purity graphite target was sputtered by a 1500 eV argon ion beam. Simultaneously, a 100 eV nitrogen ion beam was used to bombard the film, while it was growing. Under these conditions, non-hydrogenated films of a-C:N$_x$ and with high nitrogen concentrations ($\sim$33%) was deposited. Additional experimental details on the deposition of this series of film can be found elsewhere [15]. Nuclear reaction and XPS were performed to found the nitrogen concentration. Stress measurements were taken from films deposited on $4\times25\times0.4$ mm^3 (111) c-Si bars, using the bending beam method to determine the radius of curvature (see Ref. [16] for further details). The stress isn't in document was then calculated using the Stoney's equation [17]

III. RESULTS AND DISCUSSION

Figures 1 and 2 show the ultraviolet Raman spectroscopy for the series of films named graphite-like (deposited at -800V) and diamond-like (-200V) as a function of nitrogen content. The visible spectra are reported elsewhere [16]. In both cases, we can observe the G and D peaks characteristic of amorphous carbon. The G peak is due to the bond stretching of all pairs of sp^2 atoms in rings and chains. The D peak is due to the breathing modes of sp^2 atoms in rings. A third peak is observed at about 2200cm^{-1}. It is associated with C≡N sp^1 stretching bonds, also observed by infrared [8-13]. Observe that this peak increases with the nitrogen content in both series of films (Figs. 1 and 2). The enhancement of the sp^1 CN groups in UV excitation occurs because this groups has a

$\pi - \pi^*$ band gap of 5-6 eV. The gap is relatively constant; it does not display the wide range of local gaps found for sp^2 bonded groups, so it is resonant for UV excitation [9].

In Fig. 3 it is shown the Raman spectra of non-hydrogenated films (a-C:N$_x$). In this case the peak related to sp^1 bonds, at ~2200 cm^{-1}, is much smaller than that appearing in the films prepared by glow discharge. When the excitation energy is varied the Raman spectra change. However, contrary to single wavelength excitation, the variation of the Raman spectra with photon energy allows us to gain important information on the sp^2 configuration. Thus, using the UV and visible Raman spectra, we concentrate on the G peak, which position increases as the excitation wavelength decreases from IR to UV [7-10]. The G peak dispersion is defined as the rate of change of the peak position as a function of the excitation wavelength [11], that is: G disp(cm^{-1}/nm)=[Gpos(244nm)-Gpos(514.5nm)]/(514.5-244)nm where Gpos is the G peak position to the UV (244nm) and visible (514.5nm) Raman.

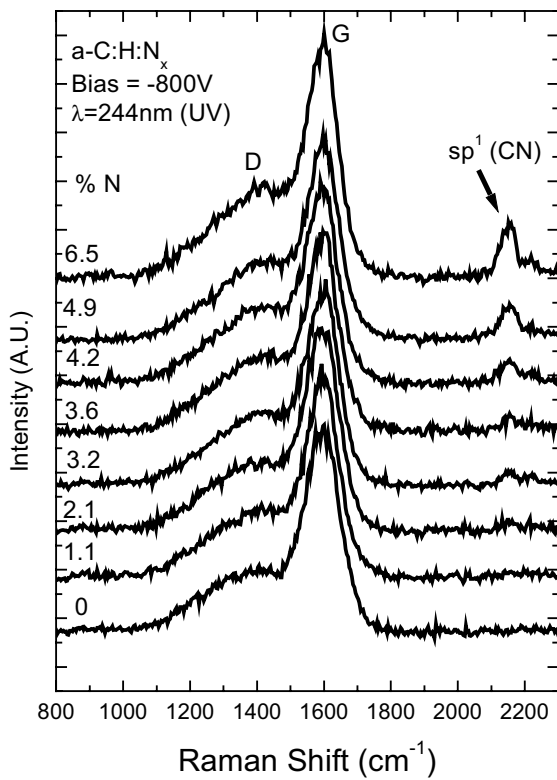FIG. 2: UV Raman spectra from a-C:H:N$_x$ (-200V) alloys.

FIG. 1: UV Raman spectra from a-C:H:N$_x$ (-800V) alloys.

Ferrari has shown a linear variation of the G peak with excitation wavelength [9]. In their study it was sufficient to consider only two wavelengths to obtain the G dispersion parameter. In Fig. 4, the G dispersion is shown as a function of nitrogen concentration for diamond-like a-C:H:N$_x$ (-200V), graphite-like (-800V) and a-C:N$_x$ (IBAD) films. We observed that this parameter decreases with nitrogen concentration and is very high (~0.28 cm^{-1}/nm) for pure diamond-like samples (a-C:H (0 at.%N)), decreasing as the nitrogen concentration increases. In the case of non-hydrogenated a-C:N$_x$ films, the
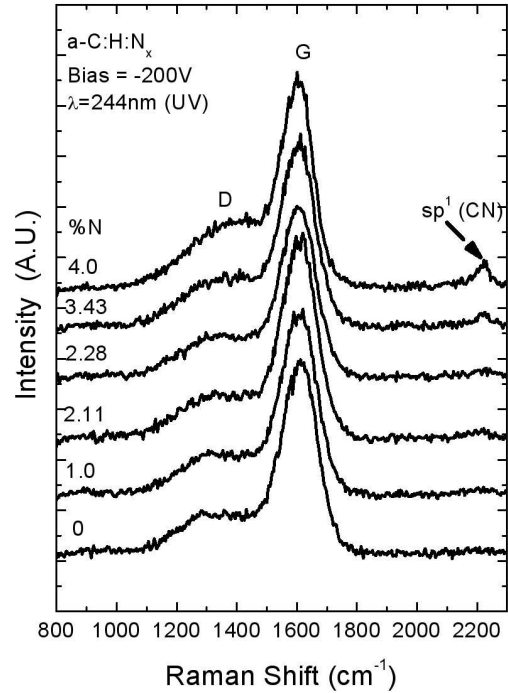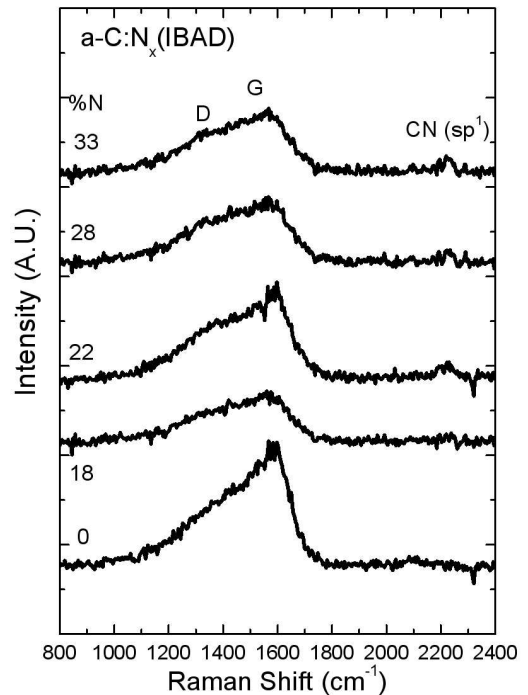

FIG. 3: UV Raman spectra from a-C:N$_x$ films (IBAD).

G dispersion is much smaller, varying from 0.06 cm^{-1}/nm, for 0 at.%N, to 0.04 cm^{-1}/nm, for 33 at.%N.

Ferrari reports that the G dispersion increases with disorder and vice-versa and it is not dispersive in graphite itself, nanocrystalline graphite or glassy carbon [18]. The G peak only disperses in more disordered carbons, where the dispersion is proportional to the degree of disorder. In materials with only sp^2 rings, the G peak dispersion saturates at a maximum of 1600cm^{-1}, corresponding to the G position in nc-graphite. In contrast, in those materials also containing sp^2 chains, particularly ta-C and ta-C:H, the G peak continues to rise past 1600cm^{-1} and can reach 1690 cm^{-1} at 229 nm excitation in ta-C.
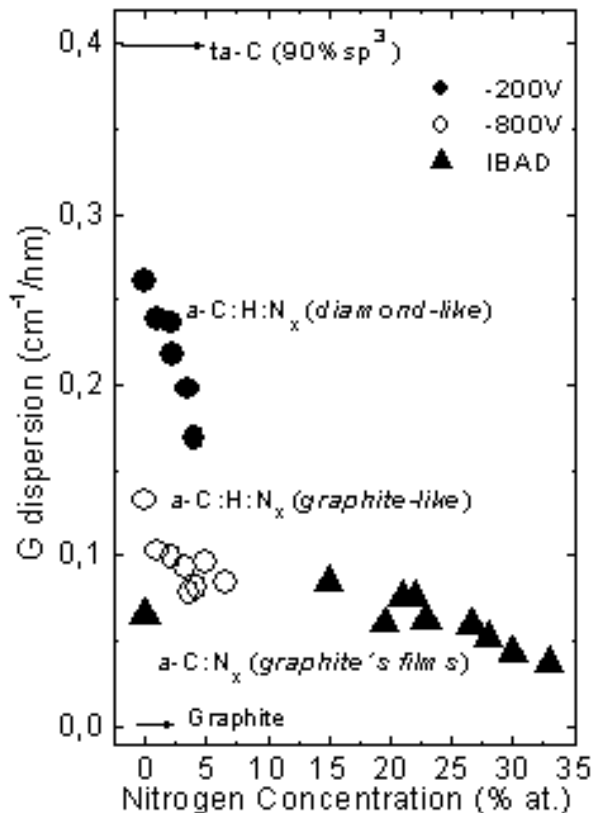

FIG. 4: G dispersion parameter as a function of the nitrogen concentration for a-C:H:N$_x$ (-200V), a-C:H:N$_x$ (-800V) and a-C:N$_x$ alloys.

Thus, ta-C has the largest dispersion. In this case, the nitrogen incorporation in the matrix of hydrogenated carbon favors the increase of sp^2 bonds and graphite clusters. On the other hand, the nitrogen addition in a-C may increase its hardness and elastics recovery, as is the case of the IBAD samples [15]. In this case, N does not cause more clustering of sp^{2}sites, but more cross-linking structures and thus increases disorder, even though not necessarily through an sp^3 increase [19,20]. The G dispersion is thus a simple, direct way to characterize amorphous carbons in terms of optical, structural and mechanical properties [9].

In Fig. 5 we observe the behaviour of G dispersion with the intrinsic stress for hydrogenated (a-C:H:N$_x$) and non-
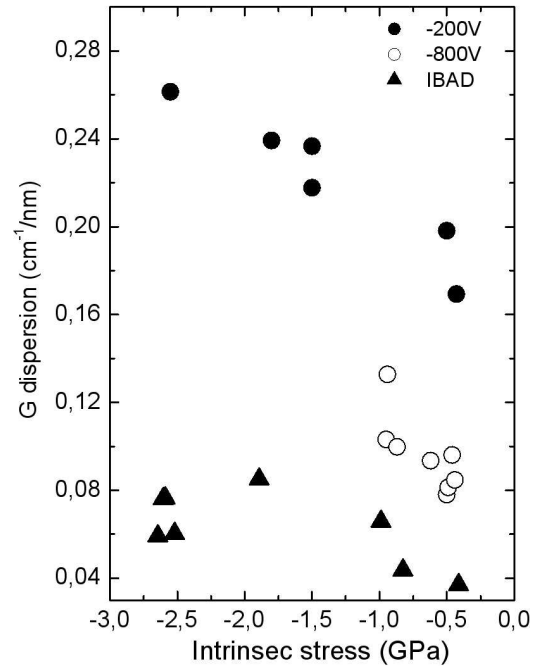

FIG. 5: G dispersion as a function of the intrinsic stress for a-C:H:N$_x$ (-200V), a-C:H:N$_x$ (-800V) and a-C:N$_x$.

hydrogenated amorphous carbon nitride (a-C:N$_x$). A decrease of the G dispersion is observed as the stress decreases. This indicates that the relaxation of the matrix due to nitrogen favors the order of graphite clusters. On the other hand, the nitrogen incorporation also increases the sp^1 bonds in all series of films reported here. That contributes to the disorder of the graphite clusters [8], due to the break of the sp^2 rings to form CN sp^1 chains. However, as can be observed in Fig. 4, the G dispersion decreases with nitrogen. Thus, apparently the increase in disorder due to sp^1 bonds seems to be small compared to other contributions.

IV.   CONCLUSION

In conclusion, hydrogenated and non-hydrogenated amorphous carbon nitride films were studied by visible and ultraviolet Raman spectroscopy. The results indicated that small incorporation of nitrogen ($\sim$6.5%) in hydrogenated films favors the order of the matrix, deduced from the behavior of the G dispersion parameter. For the case of non-hydrogenated films the nitrogen incorporation has little influence in the G dispersion parameter, even for concentration as high as 33 at.% nitrogen.

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