FORMATION OF CARBON NITRIDES CN_x FILMS ASSISTED BY T.E.A. CO_2 LASER ABLATION GRAPHITE IN A REMOTE NITROGEN PLASMA

C. Jama+, O. Dessaux+, N. Duez+, C. Dupret+, P. Goudmand+, L. Gengembre* and J. Grimblot*.

+Laboratoire de Physicochimie de l'Energétique et des Plasmas EA MRES 1761
* Laboratoire de Catalyse Homogéne et Hétérogéne URA CNRS 04020
Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq cedex, France

Abstract:
Hard thin films of carbon nitride CN_x were prepared on a non heated substrate in the pressure range 100 - 1000 Pa. The film is obtained only after few pulses of T.E.A. CO_2 focalised laser on silicon targets. IRTF spectra of the deposit films show a very efficient nitrogen fixation with CN bands characteristic of tetraedric carbon. These results are confirmed by Raman and XPS spectroscopies. The effect of the distance of deposition zone from the discharge is also discussed.

I - Introduction

In the few last years, there has been a surge of activity in the synthesis of carbon nitride thin films. This interest originates from the theoretical work by Liu and Cohen on predicting the extreme hardness, comparable to or greater than diamond, of a hypothetical material β-C_3N_4 structurally analogous to β-Si_3N_4 /1/. These films have been synthetized by several deposition techniques, such as reactive rf sputtering of carbon in nitrogen at 2-10 mtorrs /2, 3/. Niu and al reported to have synthetized films using laser ablation of graphite at wavelength λ=532 nm under an atomic nitrogen beam created by rf discharge within a nozzle at pressure of 100 hPa /4/.

In a previous preliminary work on the synthesis and characterization of carbon nitride films CN_x, using T. E. A. CO_2 laser ablation under a plasma denoted cold remote nitrogen plasma (CRNP), we have evidenced the important effect of atomic nitrogen $N(^4S)$ /5/. In the deposition chamber, the CRNP appeared like a yellow afterglow and was characterized by a very low charged particles concentration and an important thermodynamic non-equilibrium /6/. In this paper, we present results on maximized nitrogen content of the films by optimizing the process parameters.

II - Experimental

1°) Substrates

The deposition of CNx films were studied for two kinds of substrates : polished silicon wafers, and high glossy aluminium plate initially protected by an adhesive polymer film. These samples were used without previous cleaning.

2°) Film preparation

The experimental set up is shown Fig. 1. The pulsed CO_2 laser (T. E. A. 203 LUMONICS) parameters used were the wavelength λ=10,56 µm and the pulse duration of 50 10^{-9} s. The carbon nitride (CN_x) films were deposited by pulsed CO_2 laser ablation of carbon molecular fragments from a graphite sample in a gaseous flow of pure or doped nitrogen. Films were also obtained under a CRNP plasma at 0,9m from discharge zone. The energy per laser irradiation pulse was 10 joules, and the laser beam was properly focused on the graphite substrate. The nitrogen flow was excited in an electrodeless discharge by mean of a microwave generator. The transmitted power was about 800 W. The discharge was produced in a quartz tube, and, by a continuous pumping, the plasma was led to the reaction chamber. Sputtered graphitic carbon or pyrocarbon fragments combined with nitrogen reactive species were used for CNx thin films deposition. The nitrogen partial pressure range was equal to 100-1000 Pa.

3°) Film characterization

The films were characterized by IRTF (Perkin Elmer spectrometer) and Raman (Dilor spectrometer using 160 mW laser ray at wavelength 541,5 nm) spectroscopies. The thickness measurements were measured with a profilometer Alpha-Step instrument. The surface composition of the deposited films were characterized by XPS (LHS 10 spectrometer). The Al Kα X-Ray source operated at 13 kV and 20 mA current emission. The atomic stoichiometries were determined by the ratio :

$$n_A/n_B = I_{A_i}/I_{B_j} \cdot K_{B_j}/K_{A_i}$$

where $I_{A_i}(B_j)$ is the i(j) photopeak intensity of the element A(B) and $K_{A_i}(B_j)$ is the result term between the cross section of the i(j) core level orbital, the inelastic mean free path and the transmission factor of the analyser, both of the latter being kinetic energy-dependent. The efficiency of the electron detector was considered to be constant.

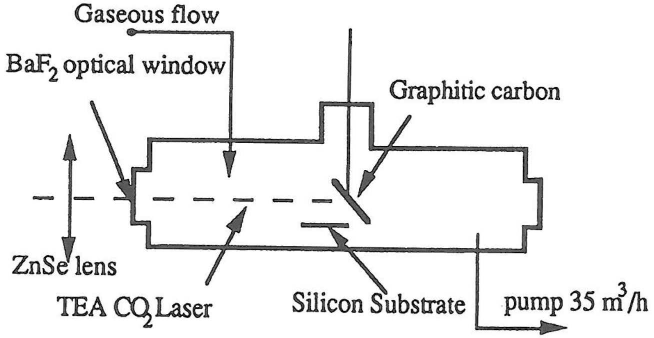

Figure 1 : Experimental set up for CN_x deposition.

III - General film characteristics

Figure 2 shows for two nitrogen pressures, the film thickness as a function of the number of the laser irradiation repetition, denoted N_{ir}, prepared under molecular nitrogen atmosphere. In the same conditions, the film thickness (deposition rate) decreases and the nitrogen composition ratio relative to carbon N/C (denoted X_N) incorporated in the films increases (fig.3) with increasing nitrogen pressure. At a pressure of 500 Pa nitrogen fixation is negligeable under non excited Helium/nitrogen mixture flow, while no deposit is obtained when Helium is substitued by Argon. Hydrogenated films are formed under a static non excited nitrogen environment.

No nitrogen fixation is observed when graphite is substituted by pyrocarbon. This result shows the important role of the graphitic structure in the nitrogen fixation mechanism.

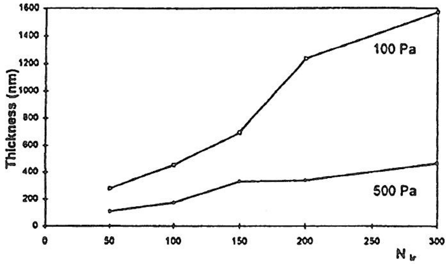

Figure 2 : Film thickness of the deposit versus the laser irradiation number.

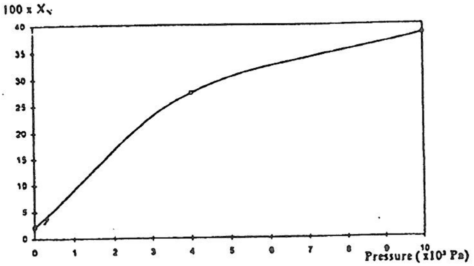

Figure 3 : X_N atomic ratio from XPS as function of the CRNP pressure.

IV- Results and discussion

1°) Infrared spectroscopy

The IR spectra obtained under a nitrogen pressure show variation of peak area and height depending on the deposition atmosphere (fig. 4). At a pressure of non excited nitrogen of 1 hPa, the CNx films show one broad absorption band in the region of 1000-1700 cm^{-1} which may be related to the diamond like structure /7/ and could correspond to C-N in a tetraedric environment. A weak peak is present between 2000-2350 cm^{-1}, which is attributed to a triple bonded C≡N stretching mode /8/. At 500 Pa, an intensification of this last and a decrease of the width of the band 1000-1700 cm^{-1} are observed. A complete disappearence of the band 2000-2350 cm^{-1} is observed when a pressure of 500Pa of a CRNP plasma is used . A spectacular intensification of the C≡N stretching mode is evidenced at a pressure of 500 Pa under non excited Helium 90 %/10% nitrogen mixture environment.

2°)Raman spectroscopy

Raman spectra of crystalline and amourphous carbon are well known /9-11/. Graphite shows a single peak at 1582 cm^{-1} for single cristals and two peaks at 1351 and 1556 cm^{-1} for polycrystals. Diamondlike amorphous carbon films show two major peaks at 1575 cm^{-1} (G peak, for graphite) and 1360 cm^{-1} (D peak, for disorder). Figure 5 shows the Raman spectra of CNx films deposited at 500 Pa on silicon wafers under CRNP plasma or a non excited helium 90 %/10% nitrogen flow. For films deposited in helium / nitrogen, two main Raman bands at 1363,3 (D peak), 1583,7 (G peak). When deposited with CRNP, the films show Raman bands at 1353,9 (D peak) and 1584,5 (G peak). A peak of a very low intensity at 2324,1 cm^{-1} , characteristic of triple bonded CN stretch, could also indicate that nitrogen is chemicaly bonded to carbon in the CN_X film. In figure 5, we can observe the variation of the D and G intensities, CNx films tend to have an intense D peak when they are prepared under CRNP atmosphere. This can be explain in term of structural disorder induced by nitrogen fixation as C-N in tetraedric environment by energetic particles such as nitrogen atoms $N(^4S)$ and long live excited nitrogen molecules.

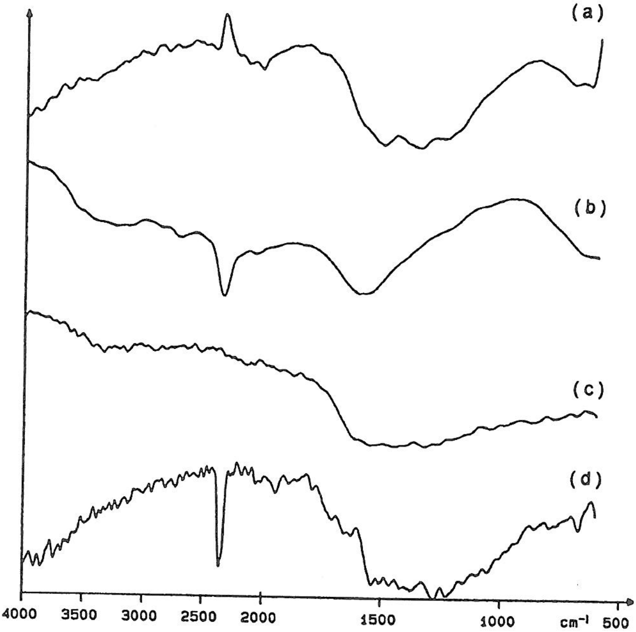

Figure 4 : IRTF transmission spectra of CN_x film deposited in non excited nitrogen at : 100Pa (a); 500Pa (b); in CRNP at 500Pa (c) and in non excited Helium90%/10% nitrogen mixture at 500Pa (d).

3°)XPS spectroscopy

The XPS analysis of CNx deposited films unambiguously provides evidence of nitrogen incorporation. Variation of this incorporation versus nitrogen pressure is evidenced in figure 2. Moreover XPS analyses indicate the N 1s peak at 399,6 eV C 1s peak at 285 eV and a low intensity peak O 1s at 532,4 eV. The XPS results are similar to that for covalent carbon nitrogen bond /12/. Nitrogen fixation increases when the CRNP plasma is used instead of a non excited nitrogen flow. At 600 Pa nitrogen atomic ratio X_N=0,31 is obtained with the non excited nitrogen flow and X_N=0,38 when the CRNP is used. This result demonstrates the important role of CRNP energetic species on nitrogen fixation. Figure 6 and figure 7 show respectively the XPS spectra of C 1s and N1s films deposited under CRNP environment at 1000 Pa. The carbon 1s may be curve-resolved into four separate carbon environments. It shows a broad peak of graphite structure at 284,6 eV with a shoulder due to C-N in tetraedric environment called diamondlike covalent bonding at 285,5 eV. The part of the spectrum corresponding to the carbon atoms positively polarized by neigbouring nitrogen appears on the high energy side of the peak. This part is composed in two peaks, at 287,5 eV and 289,3 eV and correspond respectively to C=N and C≡N groups. On the other hand, the N 1s spectrum can be resolved in three peaks at 399,4 eV, 400,8 eV and 402,3 eV which correspond respectively toC-N, C=N (and/or) C≡N, and N-O groups.

Effect of the substrate distance from the discharge.

Table 1 presents the results of the effect of distance between discharge and the deposition zones. The nitrogen fixation in the films increases when the distance decreases. This result can be explain by the presence of high energetic species near the discharge. At 0,4 m the specimen is subjected to some ionic specises/13/ while at 0,9 m the yellow Lewis-Rayleigh afterglow is observed /14/. The most important variation between these two afterglows is the presence of ionic species in the pink afterglow.

Distance (m)	X_N
0,4	0,47
0,9	0,38

Table 1 : X_N evolution versus the distance between the discharge and the deposition zone.

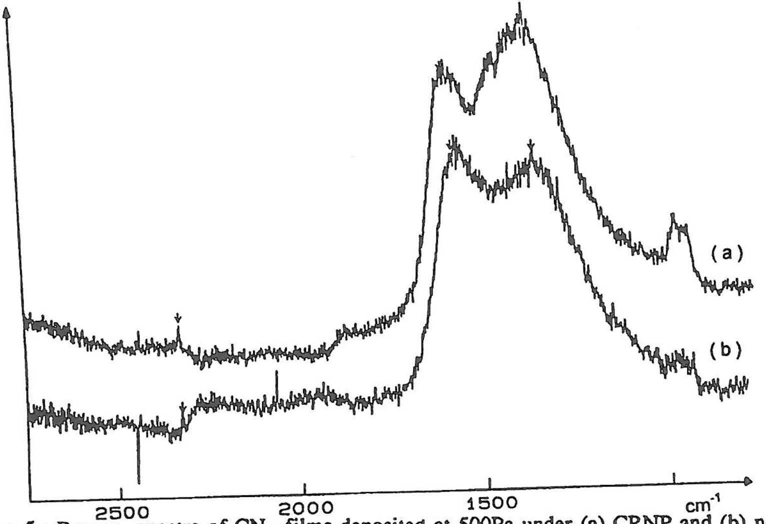

Figure 5 : Raman spectra of CN_x films deposited at 500Pa under (a) CRNP and (b) non excited Helium90%/10% nitrogen mixture.

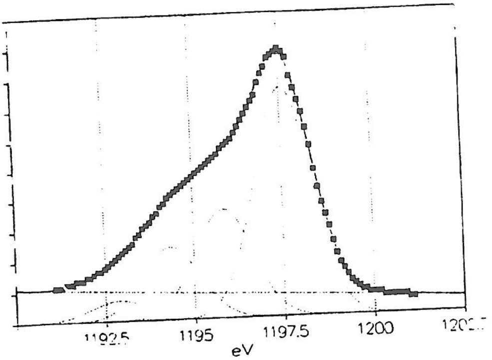

Figure 6 : C1s decomposition of CNx film

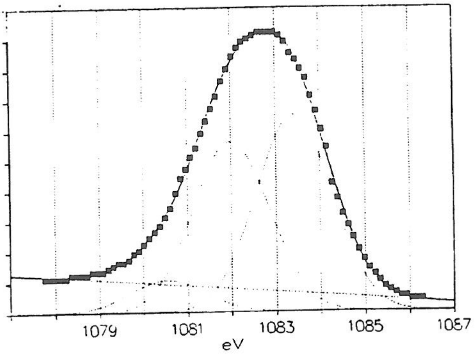

Figure 7 : N1s decomposition of CNx film

V. Conclusion

Carbon nitride films CNx are synthetized by TEA CO_2 laser under different atmosphere : a non excited nitrogen/helium mixture, pure nitrogen or CRNP plasma and are characterized by IRTF, X- Ray photoelectron and Raman spectroscopies. No deposit is obtained under nitrogen / argon atmosphere. The important role of the graphitic structure in the nitrogen fixation mechanism is evidenced. The important role of CRNP energetic species on nitrogen fixation is also demonstrated. Nitrogen atomic ratio X_N=0,31 is obtained with the non excited nitrogen flow and X_N=0,38 when the CRNP plasma. A spectacular increase of this last has been noticed when the distance between discharge and deposition zones decreases. X_N increases from 0,38 to 0,47 when the distance decreases from 0,9 to 0,4 m. Structural analysis shows nitrogen fixation. C≡N, C=N and C-N are evidenced. These two last forms of nitrogen fixation are favorised when the CRNP plasma is used.

References

/1/ A. Y. Liu and M. L. Cohen Phys. Rev. B 41, 10117 (1990).
/2/ J. J. Cuomo, P. A. Leary, D. Yu, W. Reuter and M. Frish, J. Vac. Sci. Technol.,16 299 (1979).
/3/ C. J. Trong, J. M. Silvertsen, J. H. Judy and C. Chang, J. Mat. Res. 5, 2490 (1990).
/4/ C. Niu, Y. Z. Lu, and C. M. Lieber, Science 261, 334 (1993).
/5/ O. Dessaux, N. Duez, C. Dupret, P. Goudmand and C. Jama, 10th C. I. P., Antibes (1995)
/6/ B. Mutel, M. Bridoux, M. Crunelle-Cras, O. Dessaux, F. Grase, P. Goudmand and G. Moreau, *Chem. Phys. Lett.* 2 (3), (1984) 290.
/7/ P. V. Nagarkar, K. E. Sichel, J. Electrochem. 136, 2979 (1982).
/8/ H. X. Han and B. J. Feldman. Solid State Commun. 65, 921 (1988).
/9/ R. O. Dillon, J. A. Dillon and V. Katkanant, Phys. Rev. B29, 3482 (1984).
/10/ D. Beeman, J. Silverman, R. Lynds and M. R. Anderson, Phys. Rev. B30, 970 (1984).
/11/ F. Parmigiani, E. Kay and H. Seki, J. Appl. Phys. 64, 3031 (1988).
/12/ C. Jama, O. Dessaux, P. Goudmand, L. Gengembre and J. Grimblot, Surf. Inter. Anal. 18, 751 (1992).
/13/ P. Supiot, thesis n° 1200, Lille (1993).
/14/ B. Mutel, thesis n° 704, Lille (1986).