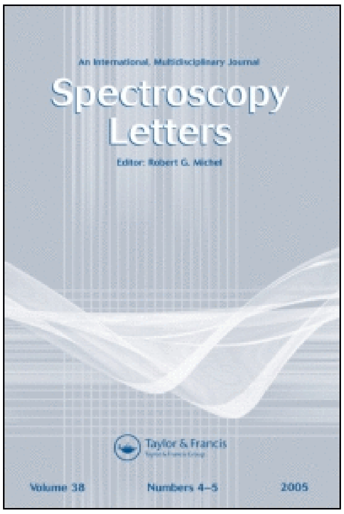

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# Structural Characterization of RF-Sputtered a-C:N Thin Films by Raman, IR, and X-ray Reflectometry Spectroscopies

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# Structural Characterization of RF-Sputtered a-C:N Thin Films by Raman, IR, and X-ray Reflectometry Spectroscopies

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**ABSTRACT** Amorphous carbon nitride thin films (a-C:N) were deposited from a carbon target, at room temperature onto silicon substrates, by reactive RF sputtering in a gas mixture of argon and nitrogen. The structural properties of these films have been studied by Raman, infrared (IR), and X-ray reflectometry spectroscopies. Both the IR and Raman spectra of the a-C:N films reveal the presence of C–C, C=C, C=N, and C≡N bonding types. The Raman spectra analysis shows, an increase of the C≡N triple bonds content when the concentration of nitrogen $C(N_2)$ in the gas mixture is increased. The Raman intensities ratio between the disorder (D) and graphitic (G) bands increases with $C(N_2)$ suggesting an increased disorder with the incorporation of nitrogen in the carbon matrix. The effect of $C(N_2)$ on the density of a-C:N films was also investigated by X-ray reflectometry measurement. The increase of the nitrogen concentration $C(N_2)$ was found to have a significant effect on the density of the films: as $C(N_2)$ increases from 0 to 100%, the density of the a-C:N films decreases slightly from 1.81 to 1.62 g/cm$^3$. The low values of density of the a-C:N films were related (i) to the absence of C–N single bonds, (ii) to the increase of disorder introduced by the incorporation of nitrogen in the carbon matrix, and (iii) to the presence of the bands around 2350 cm$^{-1}$ and 3400 cm$^{-1}$ associated with the C–O bond stretching modes and the O–H vibration, respectively, suggesting a high atmospheric contamination by oxygen and water. The presence of these bands suggests the porous character of the studied samples.

**KEYWORDS** amorphous carbon nitride, IR spectroscopy, Raman spectroscopy, RF sputtering, X-ray reflectometry

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## INTRODUCTION

Carbon nitride ($CN_x$) thin films have received great interest in the past few decades, and many related works have been reported.[1–11] The crystalline phase $\beta$-$C_3N_4$ of this material is theoretically characterized by hardness greater than that of diamond as described by Liu and Cohen.[1] The structure of this material is not well-known, and different attempts have been made to prepare it experimentally. The synthesis of carbon nitride films with a structure similar to that of $\beta$-$Si_3N_4$ remains at the moment an important goal for most laboratory research in the advanced materials science, and investigation in this field requires more effort. In most cases, the attempts have resulted in amorphous films (a-C:N) with a nitrogen content not exceeding 50%. The a-C:N films can be deposited by chemical vapor deposition (CVD)[2–4] or by physical vapor deposition (PVD)[5] techniques. As in the case of other materials, it is well-known that the structure of the material depends strongly on both the deposition technique and the deposition parameters. This dependence is due principally to the fact that carbon atoms can be bonded to nitrogen in many configurations: C–N single bonds, C═N double bonds, and C≡N triple bonds. The a-C:N films are relatively easy to grow, and they have become potential candidates for eventual use in mechanical applications as a protective coating.[6,7] As has been reported by Torng et al.,[8] a-C:N films have better wear resistance than do the usual hard carbon films used as protective overcoats in magnetic thin film rigid disks. In addition to their mechanical properties, a-C:N films have a great promise in optical,[9] electrical,[10] and electronic[11] applications.

In this work, we present the results of the structural properties study of a-C:N thin films deposited by reactive radio-frequency (RF) sputtering. The influence of the concentration of nitrogen in the reactive gas mixture on the structural characteristics of these films is studied by Raman, infrared, and X-ray reflectivity spectroscopies techniques.

## MATERIALS AND METHODS

The amorphous carbon nitride (a-C:N) thin films used in this study were prepared by RF sputtering in an ALCATEL SCM 451 deposition system described in detail elsewhere and equipped with an ALCATEL ARF 601 RF generator operating at 13.56 MHz.[12] Prior to each deposition, the vacuum chamber was evacuated down to a low pressure of $5 \times 10^{-5}$ Pa. The a-C:N films were deposited onto polished silicon substrates at ambient temperature, from a graphite target, in a gas mixture of argon and nitrogen. The total pressure in the deposition chamber was adjusted to be maintained at 1 Pa, and the RF power was fixed at 250 W. The concentration of nitrogen $C(N_2)$ in the gas mixture was varied from 0 to 100%. Before any deposition, the graphite target was presputtered for 15 min in order to eliminate superficial contamination resulting from the exposure of the target in air.

Raman spectra were obtained using a Renishaw Raman 1000 spectrometer with an excitation wavelength of 514 nm. The scanning resolution was 1 $cm^{-1}$, and the scans were performed at room temperature and normal atmospheric conditions. The IR spectra were recorded at room temperature by a Hitachi 270–50 IR spectrophotometer in the range 4000–400 $cm^{-1}$ with a resolution of 2 $cm^{-1}$. The structural properties of the films were investigated also by X-ray reflectometry measurements with $CuK_\alpha$ source ($\lambda = 1.5418$ Å). The structural studies were performed in a station equipped with a SIEMENS M386-X-A3 goniometer and an INEL XRGI/2 X-ray tube powered by an INEL XRG 3000 generator. The goniometer and the acquisition of the data were controlled by a computer.[13]

## RESULTS AND DISCUSSION

### Raman Spectroscopy

Raman spectroscopy is a powerful technique that is widely used to study the structural properties of carbon-containing films. Figure 1 shows the Raman spectra of amorphous carbon nitride thin films deposited with different nitrogen concentrations $C(N_2)$. The thickness of the films was determined by X-ray reflectometry measurements and ranged between 500 and 650 Å. The Raman spectra of amorphous carbon (a-C) and a silicon substrate are also presented in the same graph as references.

The Raman spectra of a-C:N films resemble closely that of a-C film ($C(N_2) = 0\%$). This similarity between the Raman spectra of the a-C:N and a-C films points out that the carbon network in a-C:N films is arranged in the same manner as in a-C films. All the spectra present a main band located between 1000 and 1800 $cm^{-1}$, which is commonly attributed to C═C bonds in different configurations, a small bump centered at 720 $cm^{-1}$ attributed to the C–C bonds,[14] a weak band at 2224 $cm^{-1}$ associated with C≡N groups,[15] and finally a wide band centered

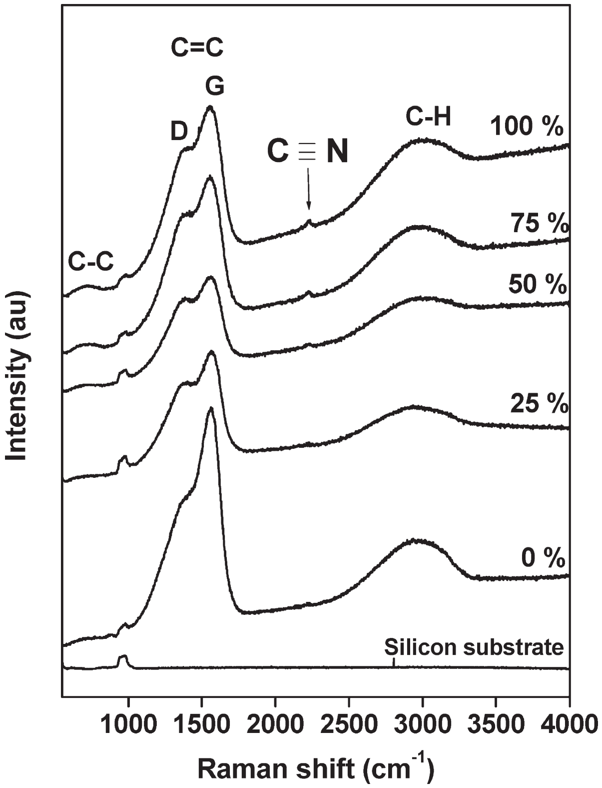

**FIGURE 1** Raman Spectra of a-C:N Thin Films Deposited at Different Concentration of Nitrogen C($N_2$).

at 2900 cm$^{-1}$ attributed to C–H bonds. The weak band at 960 cm$^{-1}$ is due to the silicon substrate as can be seen in the Si substrate spectrum. The presence of the C≡N band indicates that the nitrogen atoms are well incorporated in the bonding network of amorphous carbon as can be confirmed by the IR measurements in the following section. The presence of C–H radicals is probably due to the absorption of water vapor by the films during their exposure in the air atmosphere before the analysis.

It has been reported in previous work by Bousetta et al.[3] that the Raman spectrum of carbon nitride thin film with a high nitrogen content, obtained by cyclotron resonance plasma assisted vapor deposition, is characterized by a well-resolved peak at 1275 cm$^{-1}$ characteristic of C–N single bonds. In our Raman spectra of a-C:N films, there is no evidence of this band; thus we can conclude that the nitrogen atoms in a-C:N thin films are bonded to carbon atoms mainly as C=N double bonds and C≡N triple bonds. The C=N band is not explicitly mentioned among the Raman bands assigned above because it is masked by the wide and strong C=C band.

Additional information on the bonding structure of the a-C:N films can be obtained from the deconvolution of the wide band (1000–1800 cm$^{-1}$) characteristic of C=C bonds. Indeed, this band is clearly composed of two overlapping bands: the first band (G) centered at 1570 cm$^{-1}$ is due to the graphite-like carbon bonds, and the second one (D) centered at 1390 cm$^{-1}$ is due to the disordered C=C bonds.[16] The D band should not be confused with the sharp Raman line of diamond usually observed at 1332 cm$^{-1}$.[17] The variation of the intensity ratio of the G and D bands I(D)/I(G), with the concentration of nitrogen C($N_2$) in the gas mixture, is presented in Figure 2. This figure shows clearly that the I(D)/I(G) ratio increases, from 1.3 to a saturation value of about 1.7, with increasing C($N_2$) at around 50%. The I(D)/I(G) ratio is lightly higher in samples containing nitrogen compared with the a-C films. This result can be explained in terms of structural disorder induced by the incorporation of nitrogen into carbon matrix, leading to more structural disorder.[18,19] Jung et al.[20] reported, for a-C:N films obtained by magnetron sputtering, that the incorporation of nitrogen atoms induces disorder in the carbon nitride films through the breaking of medium or long-range order of the sp$^2$ bonded carbon structure. Jacobshon et al.[21] observed for a-CN:H that the increase of I(D)/I(G) can be ascribed to the increase of the number and/or the size of sp$^2$ bonded carbon clusters in the film. Zheng et al.[22] reported that the graphite becomes

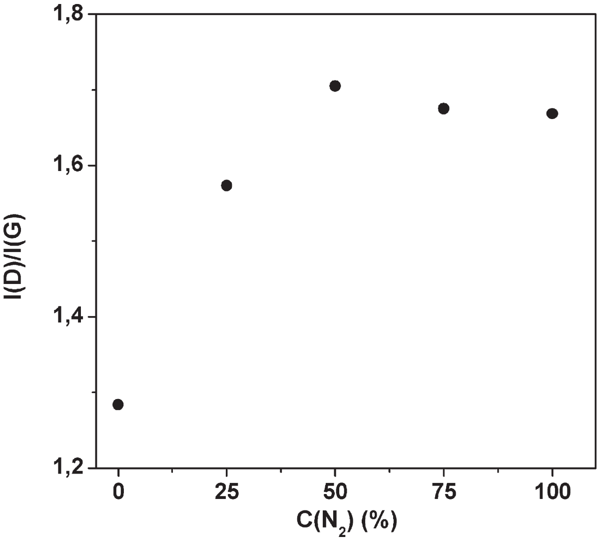

**FIGURE 2** Raman Intensity Ratio I(D)/I(G) of D and G Bands as a Function of the Concentration of Nitrogen C($N_2$).

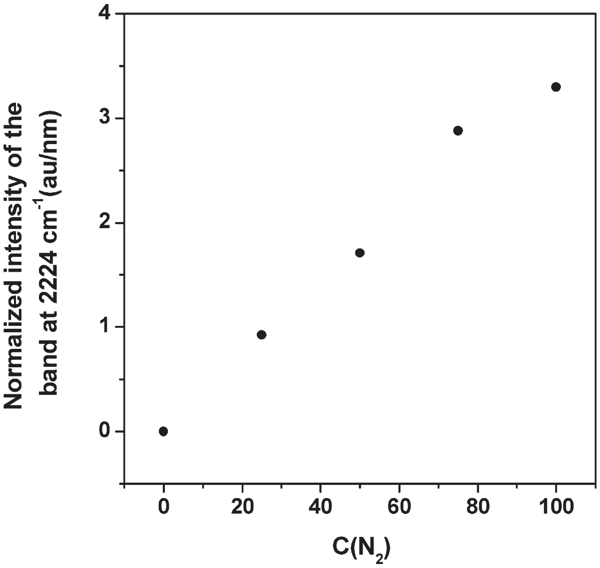

**FIGURE 3** Variation of the Raman Intensity of the $C\equiv N$ Band, Normalized to the a-C:N Films Thickness, with the Nitrogen Concentration C($N_2$).

more disordered after implantation by high-energy nitrogen ions.

Figure 3 shows the overall intensity of the Raman band at 2224 cm$^{-1}$ ($C\equiv N$ triple bonds) normalized to film thickness as a function of C($N_2$). This figure shows that the intensity of this band increases progressively with increasing C($N_2$) in the deposition chamber. This behavior suggests that the incorporation of nitrogen in the a-C:N films increases with the nitrogen concentration in the gas mixture.

## Infrared Spectroscopy

The structural properties of the a-C:N films were studied also using infrared (IR) spectroscopy measurements. Figure 4 shows the IR absorption spectra of the a-C:N thin films obtained at different nitrogen concentrations C($N_2$) in the gas mixture. The IR spectra of amorphous carbon (a-C) and a silicon substrate are also presented in the same graph as references. As can be observed in Figure 4, a broad band in the 1000–1800 cm$^{-1}$ range becomes more apparent with increasing C($N_2$). This result suggests a pronounced influence of nitrogen on the structure and composition of the deposited a-C:N films. This broad band is associated with the $C{=}N$ bonds, according to results of He et al. results,[23] and $C{=}C$ bonds that become active after the sp$^2$ symmetry break by the incorporation of nitrogen.[24] However, Ferrari et al.[25] reported that this band is due to the presence of a system of conjugated $C{=}N/C{=}C$ bonds and the subsequent delocalization, even in small domains, of the $\pi$ electrons. Because of the weak values of the film thickness, no contribution of $C\equiv N$ bonds was visibly detected. The sharp band at 610 cm$^{-1}$ is due to the Si–Si bonds in the silicon substrate as can be seen in the spectrum of the silicon substrate.

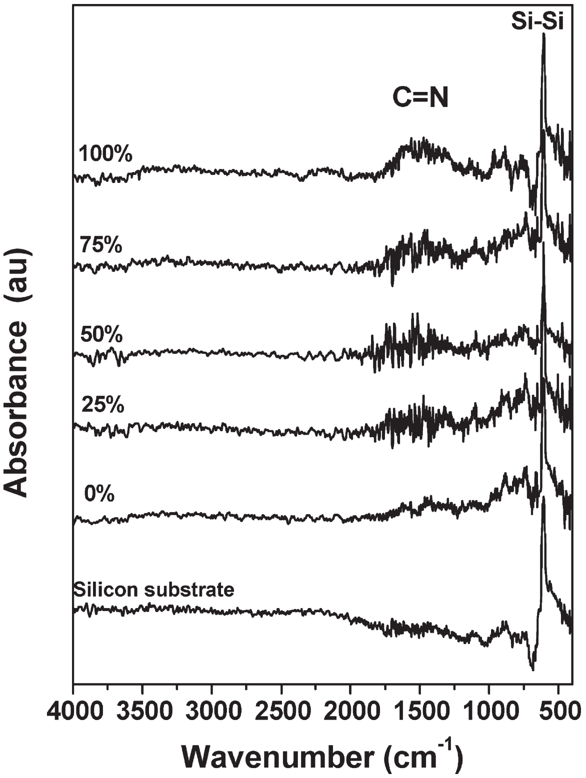

**FIGURE 4** Infrared Absorption Spectra of a-C:N Thin Films Deposited at Different Concentrations of Nitrogen C($N_2$).

To obtain more information from the IR spectroscopy measurements, we have prepared a relatively thick sample (0.5 μm) of a-C:N with C($N_2$) = 100%. The IR spectrum of this sample is reported in Figure 5. This spectrum is dominated by the broad and asymmetric band in the 1000–1800 cm$^{-1}$ range with a maximum at approximately 1590 cm$^{-1}$, which corresponds with the $C{=}N$ double bonds stretching mode. This broad band is predicted to contain also some other absorption modes such as $C{=}C$ and C–C stretching vibrations,[9] and also the deformation modes of $NH_x$ and $CH_x$ groups. Unfortunately, it has been impossible to deconvolute this main band and to identify the contribution of each absorption mode. Comparing the feature of this IR absorption band to that of Raman in the 1000–1800 cm$^{-1}$ region, there is a remarkable resemblance in the shape between these bands (Fig. 6) and, in particular, the presence of two main bands at almost similar wavenumbers to

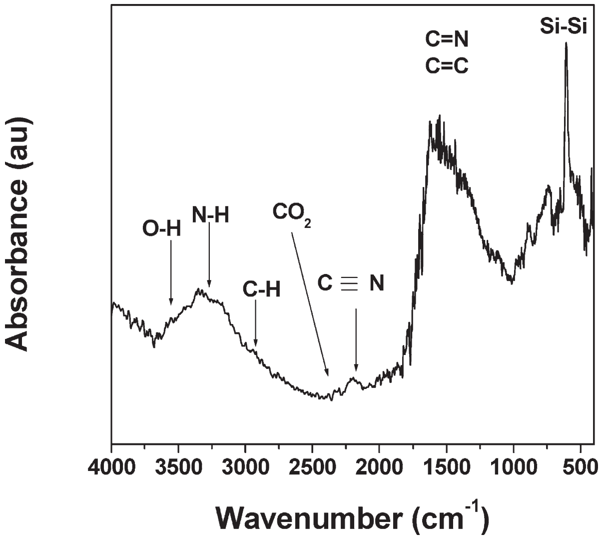

**FIGURE 5** Infrared Absorption Spectrum of a Relatively Thick (0.5 μm) a-C:N Film Deposited at $C(N_2) = 100\%$.

those observed in Raman spectrum. Indeed, the IR band is characterized by two peaks centered at 1380 ($D_{IR}$) and 1600 ($G_{IR}$) cm$^{-1}$. The IR $G_{IR}$ and $D_{IR}$ peaks are related with sp$^2$ carbon groups or with groups mainly containing carbon.[26–28] These authors pointed out that the $G_{IR}$ and $D_{IR}$ peaks cannot be attributed either to symmetry breaking due to direct nitrogen incorporation in the sp$^2$ aromatic clusters or to vibrations of graphite, nor simply assimilated to Raman vibrations (G, D). These authors have also proposed an alternative interpretation by indicating that the infrared activity does not primarily result from nitrogen breaking the symmetry but is a purely electronic effect.

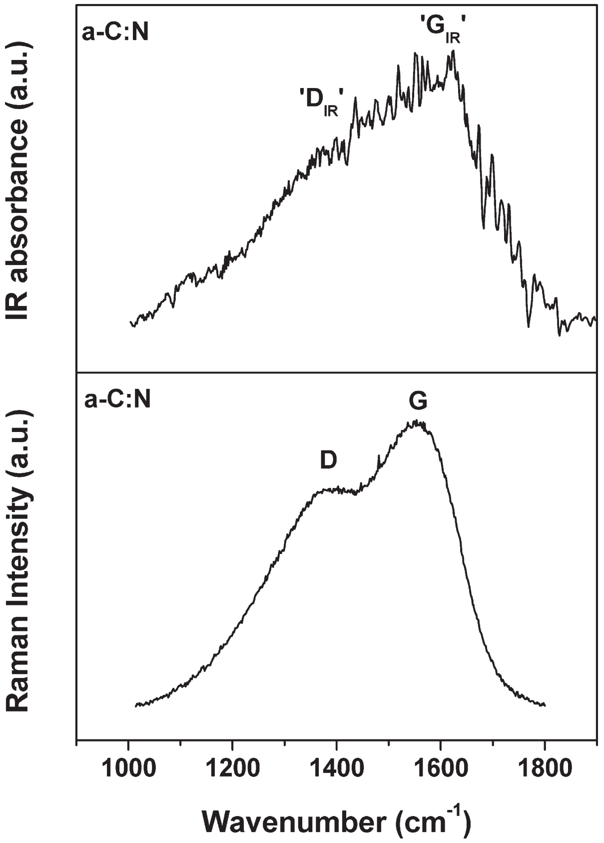

**FIGURE 6** IR Absorption and Raman Spectra in the 1000–1800 cm$^{-1}$ Region for the a-C:N Film Deposited in Pure Nitrogen Gas.

The IR spectrum shows also a relatively narrow and weak absorption band in the 2100–2300 cm$^{-1}$ range. This broad absorption band is asymmetric indicating the presence of different bands. A best deconvolution of the experimental data of this band necessitates at least tree Gaussian components located around 2148, 2195, and 2235 cm$^{-1}$ (Fig. 7). These bands can be attributed, respectively, to isocyanate groups (N=C=O),[29] to isonitrile (–N≡C) groups,[30] and to nitrile groups (–C≡N)[30] indicating the presence of sp bonded carbon. This result suggests that C and N atoms are chemically bonded in the film. This type of bonding produces bond-terminating sites and induces the loss of connectiveness of the amorphous carbon network. This correlation has been discussed in more detail by different authors.[31,32] The presence of C≡N triple bonds has also been shown in the previous section by Raman spectroscopy. In addition to the bands signaled above, the presence of a broad and asymmetric band from 2500 to 3650 cm$^{-1}$ should be noted. This band can be attributed to the superposition of different bands such as N–H, C–H, and O–H stretching modes.[33] The appearance of these bands is surprising because hydrogen and

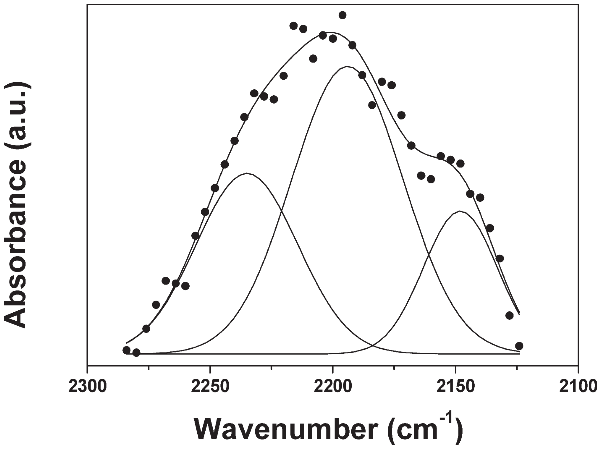

**FIGURE 7** The IR Absorption Spectrum in the 2100–2300 cm$^{-1}$ Region for the a-C:N Film Deposited in Pure Nitrogen Gas: (······) Experimental Spectrum; (———) Deconvolution Results.

oxygen were not intentionally introduced during the deposition of films. The presence of hydrogen-containing radicals in a-C:N films can be due to the contamination of the films after the exposure in air before their analysis. Finally, the weak absorption band at around 2350 $cm^{-1}$ can be associated with the C–O bond stretching modes suggesting a high atmospheric contamination by oxygen.[34]

## X-ray Reflectometry

Figure 8 shows the experimental reflected intensity spectra as a function of the incidence angle $\alpha$ of a-C:N films deposited onto glass substrates (a-CN films/glass substrate) at different nitrogen concentration $C(N_2)$: (b) 0, (c) 50%, and (d) 100%. For comparison, in the same figure we represent the intensity of the reflected beam obtained from the glass substrate (curve (a)). The reflectivity curve of the glass substrate reveals one X-ray penetration and consequently only one critical angle $\alpha_{C,S} = 0.22°$. The critical angle corresponds approximately with the angle at which the reflected intensity dropped by half (inflection point) from its maximum value at the onset of the penetration front. The curves of the a-C:N films onto glass substrate show two critical angles $\alpha_{C,F}$ and $\alpha_{C,S}$. The first angle ($\alpha_{C,F}$) is attributed to the less dense material (a-C:N) and the second ($\alpha_{C,S}$) to the heavy material, which in this case corresponds with the glass substrate. The values of $\alpha_{C,F}$ obtained for the different a-C:N films are presented in Table 1.

**TABLE 1** **Parameters Obtained from the X-ray Reflectivity Spectra: Critical Angle $\alpha_C$, Mass Density $\rho$, and Thickness of a-C:N Films at Different $C(N_2)$**

| $C(N_2)$ (%) | $\alpha_C$ (°) | $\rho$ (g/cm$^3$) | Thickness (Å) |
|---|---|---|---|
| 0 | 0.195 | 1.81 | 650 |
| 50 | 0.190 | 1.72 | 530 |
| 100 | 0.181 | 1.62 | 503 |

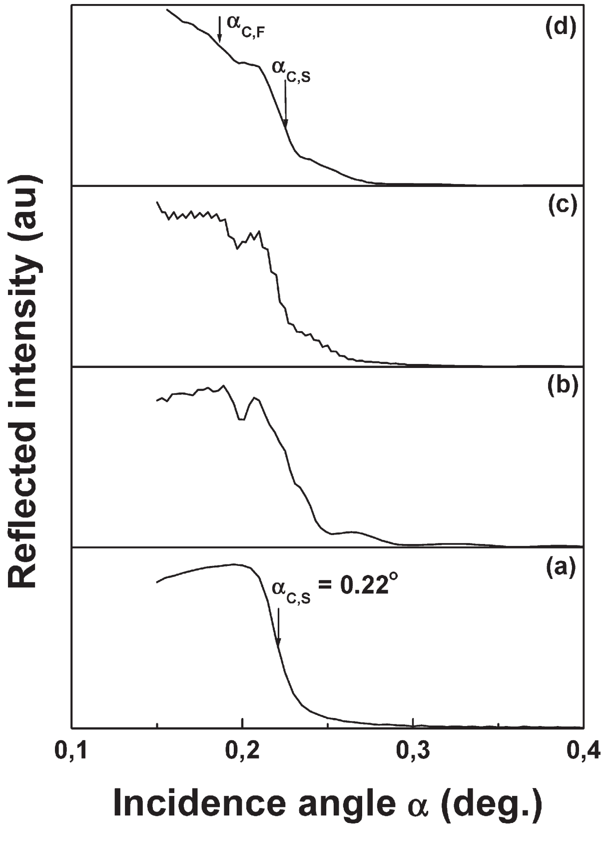

**FIGURE 8** **The Linear Variation of the Specular Reflected X-ray Intensity versus the X-ray Incidence Angle α of a-C:N Thin Films Obtained at Different Experimental Conditions: (a) Glass Substrate as Reference; (b) Amorphous Carbon ($C(N_2)$ = 0%), (c) 50%; (d) 100%.**

The mass density $\rho$ of a-C:N thin films as calculated from the corresponding critical angle is also presented in Table 1. Our densities values are similar to those reported in the literature. Nakayama et al.[29] reported values of 1.9 g/$cm^3$, as deduced from Rutherford backscattering spectroscopy (RBS) analysis, for a-C:N films prepared by magnetron sputtering. Hu et al.[35] reported a sharp decrease in density from 3.3 to 2.1 g/$cm^3$ as the nitrogen composition increases from 10% to 15% in carbon nitride films and ascribed this transition to the change in the local carbon coordination from $sp^3$ to $sp^2$. The low values obtained are in accordance with Raman and IR analysis shown in the previous section indicating that our a-C:N films are composed mainly of C═N and C≡N bonds.

It can also be observed in Table 1 that the density diminishes slightly from 1.81 to 1.62 g/$cm^3$ as $C(N_2)$ increases from 0 to 100%. The decrease in density of a-C:N, as $C(N_2)$ increases, can be related with the increase in the disorder induced by the incorporation of nitrogen in the carbon matrix as shown by Raman spectroscopy. The low density in the carbon nitride material has also been associated with the increase in the concentration of voids.[36] The low value of density of the studied films can be correlated with the bands around 2350 $cm^{-1}$ and 3400 $cm^{-1}$, associated with the C–O bond stretching modes and the O–H vibration, respectively, suggesting a high atmospheric contamination by oxygen and water. The presence of these bands suggests the porous character of the samples.

## CONCLUSIONS

Amorphous carbon nitride thin films were obtained by reactive RF sputtering at room temperature using a graphite target in an atmosphere composed of a gas mixture of argon and nitrogen. The influence of the concentration of nitrogen $C(N_2)$, in the gas mixture, on structural characteristics of these films was investigated by Raman, IR, and X-ray reflectometry spectroscopies. In addition to C–C and C═C bonds, Raman and IR techniques reveal that the nitrogen atoms are bonded to the carbon atoms in N═C and N≡C bonding types. The C≡N triple bonds content increases with $C(N_2)$, and the incorporation of nitrogen in the carbon network produces more structural disorder in the a-C:N films as deduced from Raman spectroscopy measurements. From X-ray reflectometry analysis, we have shown that as the nitrogen concentration $C(N_2)$ increases, the density of a-C:N films decreases slightly. The lower density values of a-C:N films were related to the absence of C–N single bonds and to the disorder introduced by the incorporation of nitrogen in the carbon matrix. IR spectroscopy reveals the presence of O–H and C–O stretching bands suggesting a high atmospheric contamination of the studied samples by water and oxygen. The identification of these bands exhibits a porous structure of the amorphous carbon nitride films. This is also consistent with the lowest value of density (about 1.6 $g/cm^3$).

## REFERENCES

1. Liu, A. Y.; Cohen, M. L. Prediction of new low compressibility solids. *Science* **1989,** *245*, 841–842.
2. Wixom, M. R. Chemical preparation and shock wave compression of carbon nitride precursors. *J. Am. Ceram. Soc.* **1990,** *73*, 1973–1978.
3. Bousetta, A.; Lu, M.; Bensaoula, A.; Schultz, A. Formation of carbon nitride films on Si(100) substrates by electron cyclotron resonance plasma assisted vapor deposition. *Appl. Phys. Lett.* **1994,** *65*, 696–698.
4. Ricci, M.; Trinquecoste, M.; Auguste, F.; Canet, R.; Delhaes, P.; Guimon, C.; Pfister-Guillouzo, G.; Nysten, B.; Issi, J. P. Relationship between the structural organization and the physical properties of PECVD nitrogenated carbons. *J. Mater. Res.* **1993,** *8*, 480–488.
5. Hellgren, N.; Johansson, M. P.; Broitman, E.; Sandström, P.; Hultman, L.; Sundgren, J.-E. Effect of chemical sputtering on the growth and structural evolution of magnetron sputtered CNx thin films. *Thin Solid Films* **2001,** *382*, 146–152.
6. Li, D.; Chung, Y.-W.; Wong, M.-S.; Sproul, W. D. Nanoindentation studies of ultra-high strength carbon nitride thin films. *J. Appl. Phys.* **1993,** *74*, 219–322.
7. Vlcek, J.; Rusnak, K.; Hajek, V.; Martinu, L. New approach to understanding the reactive magnetron sputtering of hard carbon nitride films. *Diamond Relat. Mater.* **2000,** *9*, 582–586.
8. Torng, C. J.; Sivertsen, J. M.; Judy, J. H.; Chang, C. Structure and bonding studies of the C:N thin films produced by RF sputtering method. *J. Mater. Res.* **1990,** *5*, 2490–2496.
9. Han, He-X.; Feldman, B. J. Structural and optical properties of amorphous carbon nitride. *Solid State Commun.* **1988,** *65*, 921–923.
10. Cuomo, J. J.; Leary, P. A.; Yu, D.; Reuter, W.; Frisch, M. Reactive sputtering of carbon and carbide targets in nitrogen. *J. Vac. Sci. Technol.* **1979,** *16*, 299–302.
11. Zhang, Z. J.; Huang, J. L.; Fan, S. S.; Lieber, C. M. Phases and physical properties of carbon nitride thin films prepared by pulsed laser deposition. *Mater. Sci. Eng. A* **1996,** *209*, 5–9.
12. Khaidar, M.; Essafti, A.; Bennouna, A.; Ameziane, E. L.; Brunel, M. RF-sputtered tungsten-amorphous silicon Schottky barrier diodes. *J. Appl. Phys.* **1989,** *65*, 3248–3252.
13. Ijdiyaou, Y.; Hafidi, K.; Azizan, M.; Ameziane, E. L.; Outzourhit, A.; Dreesen, L.; Benai, K. Grazing incidence X-ray reflectometry studies of CdTe(1 1 1) surfaces and a-Si thin films. *Solar Energy Mater. Solar Cells* **1998,** *52*, 27–36.
14. Chowdhury, A. K. M. S.; Cameron, D. C.; Hashmi, M. S.J. *Hard Coatings Based on Borides, Carbides & Nitrides*; Kumar, A., Chung, Y.-W., Chia, R. W. J., Eds.; The Minerals, Metals & Materials Society: Warrendale, PA, 1998; p. 61.
15. Chowdhury, A. K. M. S.; Cameron, D. C.; Hashmi, M. S. J.; Gregg, J. M. Evidence for continuous areas of crystalline $\beta$ -$C_3N_4$ in sputter-deposited thin films. *J. Mater. Res.* **1999,** *14*, 2359–2363.
16. Chen, M. Y.; Li, D.; Lin, X.; David, V. P.; Chung, Y.-W.; Wong, M.-S.; Sproul, W. D. Analytical electron microscopy and Raman spectroscopy studies of carbon nitride thin films. *J. Vac. Sci. Technol. A* **1993,** *11*, 521–524.
17. Zou, X. R.; Lu, H. W.; Xie, J. Q.; Feng, J. Y. Raman characteristics of hard carbon-nitride films deposited by reactive ionized cluster beam techniques. *Thin Solid Films* **1999,** *345*, 208–211.
18. Jin, Y.-S.; Shibata, T.; Matsuda, Y.; Fujiyama, H. Structural bonding properties of carbon nitride films prepared by dc magnetron sputtering. *Thin Solid Films* **1999,** *345*, 18–22.
19. Kaltofen, R.; Sebald, T.; Schulte, J.; Weise, G. Plasma substrate interaction effects on composition and chemical structure of reactively r.f. magnetron sputtered carbon nitride films. *Thin Solid Films* **1999,** *347*, 31–38.
20. Jung, Hae-Suk; Park, Hyung-Ho. Correlation between deposition parameters and structural modification of amorphous carbon nitride (a-CNx) film in magnetron sputtering. *Appl. Surf. Sci.* **2003,** *216*, 149–155.
21. Jacobsohn, L. G.; Freire, F. L.; Franceschini, D. F.; Lacerda, M. M.; Mariotto, G. Growth kinetics and relationship between structure and mechanical properties of a-C(N):H films deposited in acetylene–nitrogen atmospheres. *J. Vac. Sci. Technol. A* **1999,** *17*, 545–551.
22. Zheng, W. T.; Cao, P. J.; Li, J. J.; Wang, X.; Jin, Z. S. Chemical bonding of CNx films synthesized by nitrogen ion implantation into diamond and graphite. *Surf. Coat. Technol.* **2003,** *173*, 213–218.
23. He, X.-M.; Shu, L.; Li, W.-Z.; Li, H.-D. Structure and properties of carbon nitride films synthesized by low energy ion bombardment. *J. Mater. Res.* **1997,** *12*, 1595–1602.

24. Kaufman, J. H.; Metin, S.; Saperstein, D. D. Symmetry breaking in nitrogen-doped amorphous carbon: Infrared observation of the Raman-active *G* and *D* bands. *Phys. Rev. B* **1989,** *39*, 13053–13060.
25. Ferrari, A. C.; Rodil, S. E.; Robertson, J. Interpretation of infrared and Raman spectra of amorphous carbon nitrides. *Phys. Rev. B* **2003,** *67*, 155306–155325.
26. Fanchini, G.; Tagliafero, A.; Ray, S. C. Electronic and vibrational structures of amorphous carbon nitrides. *Diamond Relat. Mater.* **2003,** *12*, 208–218.
27. Fanchini, G.; Tagliaferro, A.; Messina, G.; Santangelo, S.; Paoletti, A.; Tucciarone, A. Vibrational properties and microstructures of reactively sputtered hydrogenated carbon nitride. *J. Appl. Phys.* **2002,** *91*, 1155–1165.
28. Fanchini, G.; Messina, G.; Paoletti, A.; Ray, S. C.; Santangelo, S.; Tagliaferro, A.; Tucciarone, A. Relationship between composition and position of Raman and IR peaks in amorphous carbon alloys. *Surf. Coat. Technol.* **2002,** *151–152*, 257–267.
29. Nakayama, N.; Tshuchiya, Y.; Tamada, S.; Kosuge, K.; Nagata, S.; Takahiro, K.; Yamaguchi, S. Structural properties of amorphous carbon nitride films prepared by reactive RF-Magnetron sputtering. *Jpn. J. Appl. Phys.* **1993,** *32*, L1465–L1468.
30. Mutsukura, N.; Akita, K-ichi. Infrared absorption spectroscopy measurements of amorphous CNx films prepared in $CH_4/N_2$ r.f. discharge. *Thin Solid Films* **1999,** *349*, 115–116.
31. Lejeune, M.; Durand-Drouhin, O.; Charvet, S.; Grosman, A.; Ortega, C.; Benlahsen, M. Correlation between plasma parameters, microstructure and optical properties of sputtering magnetron $CN_x$ films. *Thin Solid Films* **2003,** *444*, 1–8.
32. Durand-Drouhin, O.; Benlahsen, M.; Clin, M.; Zellama, K. Atomic rearrangement of sputtered amorphous carbon nitride thin films during growth. *Diamond Relat. Mater.* **2004,** *13*, 1854–1858.
33. Zocco, A.; Perrone, A.; Luches, A.; Relle, R.; Klini, A.; Zergioti, Y.; Fotakis, C. Optical characterisation of CNx thin films deposited by reactive pulsed laser ablation. *Thin Solid Films* **1999,** *349*, 100–104.
34. Li, D.; Chung, Y.-W.; Yang, S.; Wong, M.-S.; Adibi, F.; Sproul, W. D. Infrared absorption and nuclear magnetic resonance studies of carbon nitride thin films prepared by reactive magnetron sputtering. *J. Vac. Sci. Technol. A* **1994,** *12*, 1470–1473.
35. Hu, J.; Yang, P.; Lieber, C. M. Nitrogen-driven $sp^3$ to $sp^2$ transformation in carbon nitride materials. *Phys. Rev. B.* **1998,** *57*, R3185–R3188.
36. Rossi, F.; Andre, B.; van Veen, A.; Mijnarends, P. E.; Schut, H.; Labohm, F.; Delplancke, M. P.; Dunlop, H.; Anger, E. Physical properties of nitrogenated amorphous carbon films produced by ion-beam-assisted deposition. *Thin Solid Films* **1994,** *253*, 85–89.