Influence of precursor gases on the structure of plasma deposited amorphous hydrogenated carbon–nitrogen films

D. F. Franceschini[a] and F. L. Freire, Jr.
Departamento de Física, Pontifícia Universidade Católica do Rio de Janeiro, Caixa Postal 38071, 22452-970, Rio de Janeiro, Brazil

S. R. P. Silva[b]
Engineering Department, Cambridge University, Trumpington Street, Cambridge CB2 1PZ, United Kingdom

(Received 17 November 1995; accepted for publication 27 February 1996)

The atomic structure of amorphous hydrogenated carbon–nitrogen films was studied by electron energy loss spectroscopy (EELS). The films were deposited onto Si(100) substrates by rf plasma decomposition of CH_4–NH_3 and CH_4–N_2 mixtures, with substrates placed on the powered electrode of a diode glow-discharge system. The sp^2 fraction of C and N atoms as a function of the nitrogen content in the films was obtained by EELS analysis. An increase of the carbon sp^2 fraction with increasing fraction of NH_3 and N_2 feed gases was observed. The variation in the atomic structure of the *a*-C(N):H thin films is correlated to the internal compressive stress. © *1996 American Institute of Physics.* [S0003-6951(96)01319-8]

In the last few years there has been an increasing interest in the study of nitrogen incorporation into hard amorphous hydrogenated carbon (*a*-C:H) films. Research into the search for the proposed β-C_3N_4 phase, which is predicted to be harder than diamond was initiated by Liu and Cohen.[1] As a result of nitrogen incorporation into carbon films it was found that both optical and electrical properties,[2–4] as well as their mechanical properties[5–7] can be modified. Particularly with respect to the mechanical properties, it was found that nitrogen incorporation results in a substantial reduction of the compressive internal stress of the films. The improvement in adhesion that resulted from the stress reduction has made it possible to use amorphous hydrogenated carbon–nitrogen [*a*-C(N):H] films as antireflective coatings in Ge based IR sensors.[7]

One of the key factors in determining the structure and properties of hard amorphous carbon films is the hybridization state of the atoms that form the amorphous network.[8] Previous results on *a*-C(N):H films[9] allude to an increase in the graphitic clustering (sp^2 bonding) upon nitrogen incorporation, which may be correlated to the observed internal stress reduction.[5] A similar reduction in stress is observed for highly tetrahedral C:N films[10,11] in which nitrogen incorporation above 1 at. % resulted in both stress reduction and increase in the sp^2 carbon fraction.

All of the above-cited deposition studies on *a*-C(N):H films are based on addition of N_2 to the deposition atmosphere, in the deposition of the *a*-C films. To date, few researchers have studied the use of ammonia as the source gas for nitrogen.[12,13] Contrary to the above research, Seth *et al.*[12] reported an increase in the sp^3 carbon atoms fraction upon nitrogen incorporation in *a*-C(N):H films deposited by PECVD in C_4H_6–NH_3 atmospheres. In order to clarify the role of the nitrogen precursor gas on the structure and properties of *a*-C(N):H films, we report a study on the influence of the precursor gases NH_3 and N_2 in the determination of they hybridization state of carbon and nitrogen atoms in *a*-C(N):H films, as a function of the nitrogen content. The compressive internal stress was also measured and correlated with the other results.

The *a*-C(N):H films were produced by plasma decomposition of CH_4–NH_3 and CH_4–N_2 mixtures, with the NH_3 partial pressure in the plasma ranging from 0% to 12.5%, and that of N_2 ranging from 0% to 50%. The films were deposited on single-crystal Si(100) substrates, which were placed on the water-cooled, rf (13.56 MHz) powered electrode of a diode configured glow-discharge system. The depositions were performed at a total pressure of 8 Pa and a dc self-bias of -370 V. In order to control the dc self-bias during depositions, a rf power of 52 ± 2 W was applied. The chemical composition of the films was obtained from nuclear techniques—RBS, ERDA and nuclear reactions—as described previously.[14] Results from the nuclear technique analysis, combined with film thickness measurements with a stylus profilometer, were used to calculate the density of the films. Profilometry was also used to determine the internal compressive stress by measuring the curvature of the substrate.

The hybridization states of carbon and nitrogen atoms were determined by electron energy loss spectroscopy (EELS), which was carried out on a Philips CM30 transmission electron microscope (TEM) fitted with a Gatan 666 EELS spectrometer operated at 100 keV at a collection angle of 10 mrad. Samples were prepared by lifting off the films by dissolving the Si substrate in HF:HNO_3 diluted in deionized water and then floating them onto Cu TEM grids. The EELS C and N *K* edge spectra contain a peak corresponding to the 1*s* to π^* transition followed by a step ($\approx$5 eV above) which arises due to the 1*s* to σ^* transition. Figure 1 shows the carbon *K* edge EELS spectra taken from films obtained by

[a]Electronic mail: dante@fis.puc-rio.br
[b]Permanent address: Department of Electronic Engineering, University of Surrey, Guildford, Surrey GU2 5XH, United Kingdom.

Downloaded¬20¬Sep¬2010¬to¬131.227.178.118.¬Redistribution¬subject¬to¬AIP¬license¬or¬copyright;¬see¬http://apl.aip.org/about/rights_and_permissions

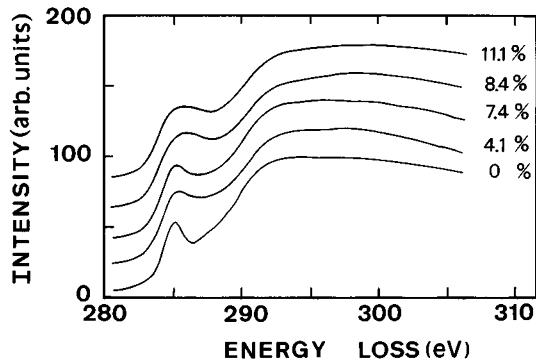

FIG. 1. The C K edge electron energy loss spectra of a-C(N):H films deposited using gas mixtures of CH_4-N_2. The figures in percent at the right of the curves are the amount of nitrogen incorporated into the film.

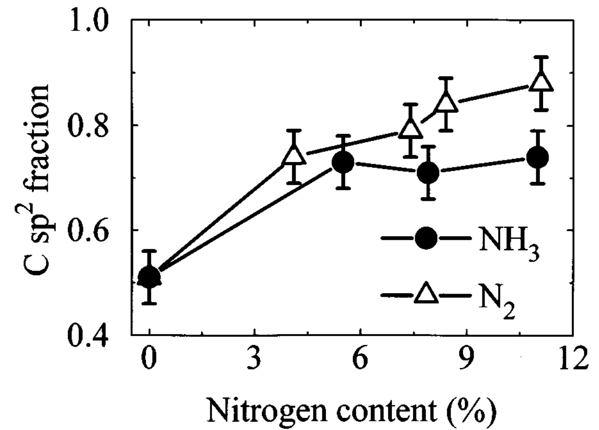

FIG. 2. Carbon atoms sp^2 fraction $f_C(sp^2)$ as a function of nitrogen content in the film, for N_2 and NH_3-derived films.

using CH_4-N_2 mixtures. The nitrogen K edge spectra are similar in shape and have the N $1s-\pi^*$ and $1s-\sigma^*$ transitions, at energies around 399 and 407 eV, respectively. The sp^2 fraction of carbon and nitrogen atoms is calculated using the normalized area under the π^* peak and then comparing this to that of a 100% sp^2 bonded graphite standard.[15]

The chemical composition as a function of the partial pressures of N_2 and NH_3 in the plasma is listed in Table I. The nitrogen incorporation level—up to 11 at. % for both series of films—lies within the range of values reported in the literature for plasma deposited a-C(N):H films, which are always smaller than 20 at. %.[2,3,5–7,16,17] The hydrogen content as well as the atomic density show different behavior for the two series of samples. For the same amount of incorporated nitrogen, the hydrogen content is higher for the NH_3-derived films. The atomic density is almost constant for both series of nitrogenated films. For the films deposited from CH_4-N_2 mixtures, the density shows the same value that was obtained from the nitrogen free sample. For the NH_3-derived films a density decrease of about 20% is observed.

The dependence of the sp^2 fraction of the carbon atoms $f_C(sp^2)$ as a function of the nitrogen content in the film is plotted in Fig. 2. The $f_{C(sp^2)}$ value that we obtained for the nitrogen-free sample ($\approx$0.5) lies within the range normally observed in a-C:H films.[8] For the nitrogenated samples, in both cases, there is a steeper initial increase in the carbon sp^2 fraction for nitrogen contents smaller than 5 at. %. For higher nitrogen incorporation, the carbon sp^2 fraction shows a slow variation for N_2-derived films, and a nearly constant behavior with $f_C(sp^2)\approx 0.75$, for films obtained using NH_3 as the nitrogen source. The dependencies of the sp^2 fraction of nitrogen atoms $f_N(sp^2)$ of the films obtained using both nitrogen precursors are plotted on Fig. 3. Taking into account the experimental error bars present in the analysis, for the N_2 series $f_N(sp^2)$ maybe taken to be constant at about 0.65 $\pm$0.10. The NH_3-derived films show a variation that is difficult to resolve from that observed for N_2-derived films.

The above discussed variation in $f_C(sp^2)$ contrasts with the results reported by Seth *et al.*[12] on a-C(N):H films obtained by PECVD in $C_4H_6-N_2$ and $C_4H_6-NH_3$ atmospheres. Despite not observing a significant change on the hybridization state of carbon atoms upon nitrogen incorporation using N_2, those authors reported an increase in the carbon sp^3/sp^2 bond ratio by a factor of about 50% with the use of NH_3. Our results show a strong increase in the sp^2 fraction of the carbon atoms, for both nitrogen precursor gases. The increase in the sp^2 character agrees with previously reported work on nitrogen incorporation within carbon films by using either plasma or ion beam deposition methods; as evidenced by Raman spectroscopy,[9] by electrical and optical properties in a-C(N):H films,[16,17] and by EELS in highly tetrahedral C:N films at high atomic N contents.[10,11,18] The observed strong initial increase in $f_C(sp^2)$ indicates a strong inductive effect, which is similar to that observed by others in *ta*-C:N films.[10,11] The increase in the sp^2 fraction of

TABLE I. Chemical composition, atom number density, and compressive internal stress of deposited films as a function of the partial pressure of the nitrogen precursor.

Nitrogen precursor	Partial pressure (%)	C (at. %)	N (at. %)	H (at. %)	Density (10^{23} atom/cm^3)	Internal stress (GPa)
⋯	⋯	83.0	0	17.0	1.3	2.75
N_2	12.5	80.0	4.1	16.0	1.2	2.55
N_2	25.0	79.0	7.4	13.6	1.2	1.95
N_2	37.5	79.5	8.4	12.0	1.3	1.73
N_2	50.0	72.3	11.1	16.6	1.2	⋯
NH_3	3.75	73.0	5.5	21.5	0.9	1.43
NH_3	7.50	73.0	8.0	19.0	0.9	1.30
NH_3	12.5	73.0	11.0	16.0	1.0	1.39

Downloaded¬20¬Sep¬2010¬to¬131.227.178.118.¬Redistribution¬subject¬to¬AIP¬license¬or¬copyright;¬see¬http://apl.aip.org/about/rights_and_permissions

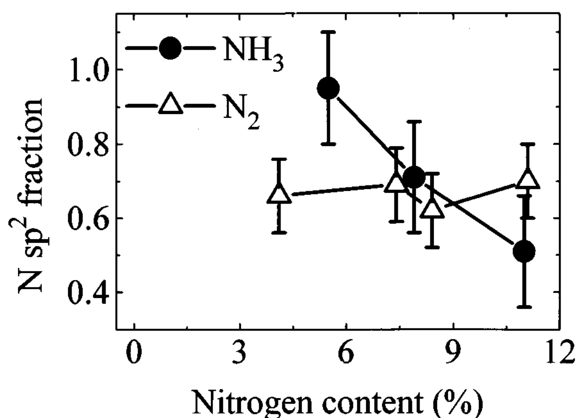

FIG. 3. Nitrogen atoms sp^2 fraction $f_N(sp^2)$ as a function of nitrogen content in the film, for N_2 and NH_3-derived films.

carbon atoms was ascribed to a reduction in the energy barrier for the transition between a metastable sp^3 state to a sp^2 state.[10] The increased sp^2 character of the amorphous C network upon nitrogen incorporation is an obstacle in obtaining the β phase of C_3N_4, as reported by Gilkes *et al.*[18]

The compressive internal stress values measured in our films are also listed in Table I, for films obtained from CH_4-N_2 and CH_4-NH_3 mixtures. The films are highly stressed, with stress values consistent with that normally observed in hard *a*-C:H films.[8] For both nitrogen precursor gases, data show a decrease in stress upon nitrogen incorporation, with distinct dependencies. For the NH_3-derived samples, a more subtle decrease is observed, which is followed by an almost constant behavior. For N_2-derived films a continuous decrease is observed in the range of films measured. The observed stress reduction was obtained with minor changes in the measured Vickers microhardness values, which are about 20 GPa, for films obtained with both N_2[5] and NH_3 precursors. The relatively small dependence of the hardness upon nitrogen incorporation was also observed by others,[7,17] for films obtained with similar conditions of total pressure and substrate bias.

It is well known that the high internal compressive stresses observed in hard *a*-C:H films may be viewed as a result of the material being overconstrained. This means that the relatively high sp^3 fraction observed in hard *a*-C:H films, causes the mean atomic coordination number to be higher than the ideal value predicted for a fully constrained network.[19] Even when the structure of such films are considered to be graphitic (sp^2) carbon clusters dispersed in a network of sp^3 and sp^2 carbon atoms and monovalent hydrogen atoms, arguments as to an overconstrained network is still valid, as has been discussed.[8,20] In this scheme, any stress relief process may be strongly coupled to the mean-atomic coordination number. In the case of *a*-C(N):H films the observed reduction in stress is conceived to be a consequence of changes in both chemical composition and hybridization states.

Nitrogen incorporation itself is a source of reduction in the mean-coordination number since nitrogen atoms prefer to bond with three atoms, instead of the four bonds admitted by the carbon. Besides the nitrogen incorporation, the increase in $f_C(sp^2)$ is also a source of decrease on the mean-atomic coordination number, in agreement with the observed reduction in the internal stress. However, the distinct behavior determined for the two series of films does not seem to be only related to the hybridization state of carbon and nitrogen atoms. The observed variation in stress for the NH_3-derived series of film does not correspond to the lower $f_C(sp^2)$ values obtained for this series, as compared to that obtained for the N_2-derived films. The increased coordination number for the NH_3 series that should arise due to the lower $f_C(sp^2)$ values should show up as an increase in the internal stress. A possible reason for such conflicting behavior may be related to the higher hydrogen content observed for films deposited with the CH_4-NH_3 mixture. The hydrogen content may also be related to the decrease observed in the atom number density, when compared to N_2-derived films.

In conclusion, the influence of the nitrogen precursor gas N_2 or NH_3, on the chemical composition, hybridization state of carbon and nitrogen atoms and compressive internal stress of *a*-C(N):H films deposited by PECVD is examined. It is found that nitrogen incorporation strongly affects the hybridization state of carbon atoms by increasing the sp^2 fraction for both nitrogen precursors, which is consistent with the observed internal stress reduction. The minor differences observed in the stress variation of the two series of films is ascribed to the enhanced hydrogen content in the NH_3-derived films, which may also explain the lower atom number density measured in these films when compared with N_2 deposited films.

[1] A. Y. Liu and M. L. Cohen, Science **245**, 841 (1989).
[2] J. H. Kaufman and S. Metin, Phys. Rev. B **39**, 13053 (1989).
[3] O. Amir and R. Kalish, J. Appl. Phys. **70**, 4958 (1991).
[4] S. R. P. Silva and G. A. J. Amaratunga, Thin Solid Films **270**, 194 (1995).
[5] D. F. Franceschini, C. A. Achete, and F. L. Freire, Jr., Appl. Phys. Lett. **60**, 3229 (1992).
[6] A. Grill and V. Patel, Diam. Relat. Mater. **2**, 1519 (1993).
[7] S. Mettin, J. H. Kaufman, D. D. Saperstein, J. C. Scott, J. Heyman, and E. E. Haller, J. Mater. Res. **9**, 396 (1994).
[8] M. A. Tamor, W. C. Vassel, and K. R. Carduner, Appl. Phys. Lett. **58**, 592 (1991).
[9] G. Mariotto, F. L. Freire, Jr., and C. A. Achete, Thin Solid Films **241**, 255 (1994).
[10] V. S. Veerasamy, J. Yuan, G. A. J. Amaratunga, W. I. Milne, K. W. R. Gilkes, M. Weiler, and L. M. Brown, Phys. Rev. B **48**, 17954 (1993).
[11] J. Robertson and C. A. Davis, Diam. Relat. Mater. **4**, 441 (1995).
[12] J. Seth, A. J. I. Ward, and S. V. Babu, Appl. Phys. Lett. **60**, 1597 (1992).
[13] J. Seth, R. Padiyath, and S. Babu, Diam. Relat. Mater. **3**, 210 (1994).
[14] F. L. Freire, Jr., D. F. Franceschini, and C. A. Achete, Nucl. Instrum. Methods B **85**, 268 (1994).
[15] S. D. Berger, D. R. M. Mackenzie, and J. P. Martin, Philos. Mag. Lett. **57**, 285 (1988).
[16] P. Wood, T. Wydeven, and O. Tsugi, Thin Solid Films **258**, 151 (1995).
[17] J. Shwan, W. Dworschak, K. Young, and H. Erhardt, Diam. Relat. Mater. **3**, 1034 (1993).
[18] K. W. R. Gilkes, J. Yuan, and G. A. J. Amaratunga, Diam. Relat. Mater. (to be published).
[19] J. C. Angus and F. Jansen, J. Vac. Sci. Technol. A **6**, 1778 (1988).
[20] J. Robertson, Phys. Rev. Lett. **68**, 220 (1992).

Downloaded¬20¬Sep¬2010¬to¬131.227.178.118.¬Redistribution¬subject¬to¬AIP¬license¬or¬copyright;¬see¬http://apl.aip.org/about/rights_and_permissions