Local Order Structure of a-SiO_xN_y:H Grown by PECVD

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Received on 23 April, 2001

In this work we study the structural properties of amorphous oxynitride films (a-SiO_xN_y), grown by plasma enhanced chemical vapour deposition (PECVD)at 320^{0}C. The films were deposited at different flow ratio of N_2O and SiH_4. The atomic composition of the samples was determined by means of Rutherford backscattering spectrometry (RBS). The local order structure was studied by X-ray absorption spectroscopy (XAS) and the chemical bondings were investigated by Fourier transform infrared (FTIR) spectroscopy. The results evidence a tetrahedric arrangement of the oxynitride network. The tetrahedrons are similiar to SiO_3N for x values between 1.43 and 1.64. For x values higher than 1.64 the tetrahedrons are similar to SiO_4.

The Plasma Enhanced Chemical Vapour Deposition (PECVD) method has been extensively applied to obtain silicon based dielectric films. In particular, the use of SiO_2 and SiO_xN_y films, grown by PECVD at low temperature, became very attractive due to the possibility of integrating optical and electrical devices in the same chip[1, 2, 3]. Moreover, PECVD is a useful technique to deposit thick films, about 4-5 (μm), a common requirement in optical device technologies. The fundamental advantage of this technique is the possibility of controlling the chemical composition, as well as the structural and optical properties of the silicon oxynitride films, by adequately adjusting the deposition parameters[4, 5, 6]. Our previous works[4, 7, 8, 9] established the experimental conditions to grow a-SiO_xN_y:H films at high deposition rates, having a continuous variation in its refractive index, with controlled thickness, selected chemical bonds and improved morphology. In particular, high quality, low temperature a-SiO_2 films were deposited.

The aim of this work was to determine the local atomic structure around the Si atoms of our good quality a-SiO_xN_y:H films as a function of their chemical composition. The atomic content was determined by Rutherford backscattering spectrometry (RBS); the chemical and structural properties were investigated by extended X-ray absorption fine structure (EXAFS), X-ray absorption near edge structure (XANES) and Fourier transform infrared spectroscopy (FTIR).

The RBS experiments, used to determine the film's composition, were performed at LAMFI/USP, São Paulo, using a He^+ beam with energy E=1.7 MeV, charge Q=30 μC, current I= 30 nA and detection angle θ=170 ^{o}. The RBS data were analyzed through the RUMP routine[10] and provided the Si, N and O atomic density (atoms.cm^{-2}).

The analysis of the chemical bonds was performed by means of the Fourier transform infrared (FTIR) spectroscopy in a BioRad FTS-40 spectrometer, on films deposited over polycrystalline silicon wafer, with high resistivity. The films were measured at room temperature in a nitrogen atmosphere, with a resolution of 4 cm^{-1}. The H content in the films was calculated using the FTIR N-H signal. It decreases from 5 at. % in the most nitrogenated film to zero in films without detectable amount of H.

The XAS (X-ray absorption spectroscopy) experiments were carried out at the SXS beamline[11] of the Synchrotron Light National Laboratory (LNLS, Campinas, Brazil). The measurements were performed in the energy range of (1800-2300) eV, using a double-crystal InSb(111) monochromator. The EXAFS spectra of the a-SiO_xN_y films, a-SiO_2 and β-Si_3N_4 reference samples were recorded at the Si K-edge, at room temperature, being collected in TEY mode, with 1 eV step. Further, more accurate measurements were done in the near absorption edge (XANES) region, in the (1840-1870) eV energy range, with 0.2 eV step.

Table I shows the RBS data, i.e, reveals the concentration ratio [O/Si], x, and [N/Si], y, of different ana-

lyzed films. It's clear from this table that the chemical composition is dependent on the deposition conditions. In fact, the [O/Si] concentration ratio varied from 1.43 to 1.85 with the increasing of the N_2O flow in the deposition chamber. On the other hand, the [N/Si] concentration ratio decreased almost 6 times (from 0.57 to 0.12) as the nitrous oxide flow increased. It's important to point out that the [(O+N)/Si] concentration ratio is always close to 2.

Table I. Sample name, flow ratio [N_2O/SiH_4] and concentration atomic ratio x=[O/Si] and y=[N/Si] determined by RBS technique.

Sample	[N_2O/SiH_4]	x	y
A	2.0	1.43	0.57
B	2.5	1.57	0.34
C	3.0	1.64	0.29
D	4.0	1.80	0.12
E	5.0	1.85	0.12

The infrared spectra of the a-SiO_xN_y films are shown in Fig. 1. It should be noted that the 2500 to 4000 cm^{-1} spectral region was magnified 5 times in order to better appreciate the N-H band. The FTIR data present a continuous shift in the peak position of the Si-O streching vibration mode to lower frequencies, as the amount of O in material matrix decreases. This shift is explained by the presence of the Si-N bonds. Also, the shoulder at around 1250 cm^{-1} [12, 13], characteristics of SiO_2, becomes less defined. The 3400 cm^{-1} band, corresponding to the stretching vibration mode of the N-H bonds, indicates the presence of N-H bonds in films A, B and C, that have higher nitrogen content. The sample with high oxygen content (sample E) presents a FTIR spectrum very similar to the thermically grown a-SiO_2.

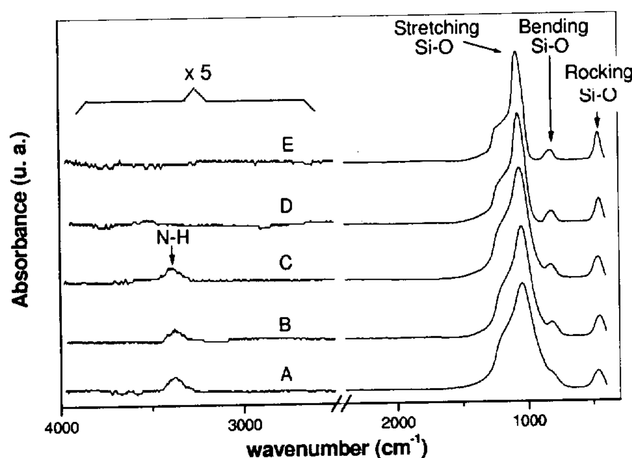

Figure 1. FTIR spectra for all studied samples, see table I.

The XANES spectra of amorphous silicon dioxide, polycrystalline silicon nitride and amorphous silicon oxynitride films have been taken at the silicon K edge, as shown in Fig. 2. The spectra of β-Si_3N_4 and a-SiO_2 show no significant difference from those previously reported[14, 15]. From Fig. 2, one can see strong threshold peaks of the a-SiO_xN_y films, located between β-Si_3N_4 and a-SiO_2, closest to a-SiO_2. There is a broad structure between 1860 and 1870 eV, for all XANES spectra, similiar to a-SiO_2.

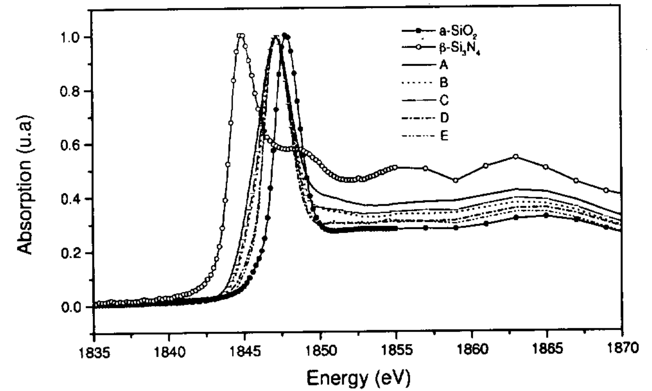

Figure 2. Comparison betweem the Si K edge XANES spectra for a-SiO_2, β-Si_3N_4 and samples (table I).

The XANES spectra of all samples and of a-SiO_2 reference are very similar and confirms the amorphous state of our samples. One can notice the existence of a chemical shift from silicon nitride to silicon dioxide. This shift indicates that the threshold position is dependent on the nature of the atoms which build the tetrahedron environment of Si and is directly related to the electronegativity of the surronding atoms. We can observe that the threshold position of all samples changes continuously but it stays between the values of the silicon nitride and silicon dioxide references (see Fig. 2). This result is consistent with the formation of a fourfold coordinate Si network such that Si is either connected to O and/or N in tetrahedra having the $SiO_\nu N_{4-\nu}$(ν=0,1,2,3 and 4) configurations.

The Fourier transform (F.T.) in the real-space (also referred to R-space) of the k^2-weighted oscillation was calculated over the same energy range (1.5 - 9.5 Å) for all samples and references. The back Fourier transform in the reciprocal-space (k-space) corresponding to a given coordination shell was fitted with electronic parameters extracted from the reference samples, whose structure are similar to those being investigated in this work.

The Fourier transform curves obtained for the samples (Fig. 3), can give us some qualitative information about the local order structure. First, one can observe the absence of long-range order (for R values higher than 3 Å). Nevertheless, the short range order is slightly dependent on the chemical composition, as evidenced by the magnitude of the first peak in the Fourier transform (Fig. 3).

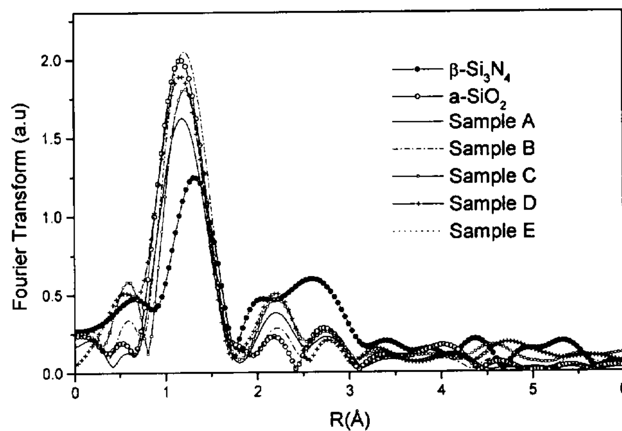

Figure 3. F.T. of the a-SiO_2 and β-Si_3N_4 references and samples (table I).

The EXAFS data analysis was done considering a two-shell model with partial coordination numbers N_{N-O} and N_{Si-O} which provides an average picture of the local arrangement of the N and O atoms in the first coordination shell surrounding the absorbing Si atoms. The EXAFS results provide the coordination number, average interatomic distance and the Debye-Waller factors, as presented in table II.

Table II. First shell structural parameters obtained with two-shell fit (Si-O + Si-N) for different samples (see table I), where N_i(10%), σ_i(15%) and R_i(1%) correspond to coordination number, Debye-Waller factor($\AA^{-1}$), and interatomic distance ($\AA$), respectively (i=1, Oxygen, i=2, nitrogen).

Sample	N_1	σ_1	R_1	N_2	σ_2	R_2
A	2.8	0.036	1.60	1.3	0.001	1.70
B	3.1	0.000	1.63	1.2	0.000	1.64
C	3.2	0.000	1.63	0.8	0.000	1.66
D	4.0	0.000	1.60	-	-	-
E	4.0	0.000	1.60	-	-	-

The results show that the disorder of the films is comparable to that of the reference compounds, being larger for the film with the highest nitrogen content.

The RBS data showed that [(O+N)/Si] concentration ratio is always close to 2. This result suggests that both oxygen and nitrogen atoms occupy the first coordination shell around the Si atoms, keeping the tetrahedral Si coordination. This structural model was confirmed by the fitting of the EXAFS signal, considering that the first Si coordination shell is partially filled with O and N atoms, whose concentration was taken from the RBS data. These results, together with the FTIR data, suggest that the better description of the material is a homogeneous network formed by $SiO_\nu N_{4-\nu}$ tethahedrons.

Acknowledgments

This work was supported by FAPESP/Brazil (process number: 98/09806-6). We acknowlegde Dr. F.C. Vicentin for the XAS measurements at LNLS/Brazil and Dr. M.H. Tabacniks for the RBS measurements.

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