FTIR and XPS investigations of a-SiOₓNy thin films structure

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Abstract. Amorphous silicon oxynitride (a-SiOₓNᵧ) thin films with large composition variation were deposited by reactive sputtering. Their structural study was carried out by mean of FTIR and XPS analysis. The IR absorption peak maximum was found to shift towards higher wavenumbers as the oxygen content increases and the absorption peaks of Si-O and Si-N bonds also appear. The Si 2p photoelectron peak was decomposed considering five tetrahedra of SiOₙNₜ (where n = 0, 1, 2, 3 and 4) following the Random Bonding Model (RBM). But the comparison between RBM theoretical and experimental predictions and the non-linear behaviour of the modified Auger parameter (α') showed that the a-SiOₓNy structure can be well described only considering a mixture of SiO₂, SiₓNᵧ and SiOₓNy phases.

1. Introduction

It is well known that the disorder degree in amorphous materials have a great influence on their properties and the determination of the structure is necessary to understand the physical mechanisms governing these properties. There are two extreme models for modelling the structure of tetrahedral amorphous alloys, such as silicon oxynitride: the Random Bonding Mode (RBM) [1] and the Random Mixture Model (RMM) [2]. These models have been widely used to describe the structure of amorphous silicon oxide (a-SiOₓ), silicon nitride (a-SiNᵧ) and silicon oxynitride (a-SiOₓNᵧ) [1, 3-5].

According to the RMM, the SiOₓNᵧ layers contain SiO₂ and SiₓNᵧ phases and Si phase if Si is an excess and only SiOₓ, SiNᵧ and SiSi₄ tetrahedra are considered. In the RBM, it is assumed that all tetrahedra are centred on Si atoms bonded to four other atoms. For SiOₓNᵧ films without Si-Si bonding, five tetrahedra of SiOₓNᵧₐ (where v = 0, 1, 2, 3 and 4) are considered.

In order to determine the structure of a-SiOₓNᵧ thin films deposited by reactive sputtering, we studied the variation of the shape and the position of FTIR absorption peak as function of the layer composition. Also, we modelled the Si 2p photoelectron peak using RMM and RBM and the behaviour of Auger parameter (α') was considered.
2. Experimental procedure

To obtain a-SiO\textsubscript{x}N\textsubscript{y} with composition varying between those of Si\textsubscript{3}N\textsubscript{4} and SiO\textsubscript{2}, a pure silicon target (99.999% purity, 100 mm diameter) was sputtered at 13.56 MHz frequency in an Alcatel SCM 450 equipment under different argon-oxygen-nitrogen gas mixtures. The total gas flow rate ($F_t$) was fixed at 5 sccm and the argon flow rate was fixed at 70% of $F_t$. The reactive gas flows were characterized using the ratio $R_f = F_{O_2}/(F_{O_2} + F_{N_2})$ where $F_{O_2}$ and $F_{N_2}$ are the oxygen and nitrogen flows respectively. A sputtering power density ($P$) of 3.18 W cm\textsuperscript{-2} was used. In order to remove surface contamination, Si target was etched under pure argon before each deposition. The layer composition was investigated by Rutherford Backscattering Spectroscopy (RBS) using 2 MeV alpha particles and an 15 nA current intensity. The Si-O and Si-N bonds were analyzed using a Perkin Elmer A6 FTIR spectrometer in the range 400-4000 cm\textsuperscript{-1} with 4 cm\textsuperscript{-1} resolution. XPS investigations were performed using SIA 200 Riber Cameca UHV two-stage spectrometer equipped with an Al-K\alpha ($\nu = 1486.6$ eV) non-monochromatized source. The photoelectron emission was obtained using Riber Cameca MAC 2 spectrometer.

3. Results and discussion

Whatever the plasma composition, RBS analysis showed that the silicon concentration remains almost constant; it only vary from 39 to 33% when $R_f$ increases from 0 to 0.5. So, it is sufficient to characterise the composition of SiO\textsubscript{x}N\textsubscript{y} deposits considering only the ratio $x/(x+y) = O/(O+N)$, where O and N are the oxygen and nitrogen atomic concentration, respectively. As shown on figure 1, the composition of our films varies quite linearly between those of silicon nitride and silicon oxide. Nevertheless, a small oxygen amount (< 3%) was detected even when no oxygen gas is introduced in the sputtering room. Residual gas and water vapour may be the source of these oxygen traces [6].

![Figure 1](image)

**Figure 1.** Variation of the atomic ratio of SiO\textsubscript{x}N thin films as function of the reactive gases ratio.

X-ray diffraction measurements showed that all deposited SiO\textsubscript{x}N\textsubscript{y} thin films were amorphous. Therefore the structural characterizations were focused on the different Si-O and Si-N bondings.

FTIR analysis showed a large absorption band located between 650 and 1350 cm\textsuperscript{-1} which is characteristic of silicon oxynitride material [7, 8]. Figure 2 shows that a shift of the absorption maximum towards higher wavenumbers when the oxygen content increases. This behaviour is explained by the progressive substitution of nitrogen atoms by oxygen ones which are more electronegative. Also, and as shown on figure 3, the absorption maximum shifts quite linearly from 840 to 1060 cm\textsuperscript{-1} for film compositions close to Si\textsubscript{3}N\textsubscript{4} and SiO\textsubscript{2} respectively. This could suggest a homogeneous SiO\textsubscript{x}N\textsubscript{y} as reported by other authors [9]. But, one can notice that the absorption peaks of Si-N and Si-O bonding, located at 890 and 1060 cm\textsuperscript{-1} respectively [6], clearly appear (dashed lines in Figure 2). This may indicate the presence of distinct Si\textsubscript{3}N\textsubscript{4} and SiO\textsubscript{2} phase.
In order to clarify the previous observations, XPS investigations were carried out. As shown in figure 4a, the maximum of the Si 2p photoelectron peak shifts towards lower binding energy (from 103.3 eV to 102.4 eV) and the full-width at half-maximum decreases from 2.9 to 2.7 eV when the ratio O/(O+N) decreases. According to the random mixture model (RMM), this peaks should have two components corresponding to the SiO2 and Si3N4 phases, located at 103.3 eV and 101.8 eV respectively, as in our reference samples (a-SiO2 and a-Si3N4 samples) [5]. The modeling of the experimental data revealed that the Si 2p peaks contains more than two components. Therefore, and regardless of composition, the RBM allows to fit all the XPS peaks very well as illustrated in figure 4b considering the five tetrahedra SiO\textsubscript{ν}N\textsubscript{4-ν} (ν = 0, 1, 2, 3 and 4). When the oxygen content increases, it was found that the contribution of SiO\textsubscript{4}, SiO\textsubscript{3}N and SiO\textsubscript{2}N\textsubscript{2} components increases to the detriment of SiON\textsubscript{3} and SiN\textsubscript{4} ones as reported for silicon oxynitride thin films deposited by low-pressure chemical vapour deposition [4, 5].

Moreover, XPS analyses showed an excess of Si-O\textsubscript{4} and Si-N\textsubscript{4} environments for O-rich and N-rich films respectively. This induces a lower contribution of mixed environments than that expected from

![Figure 2. IR absorption spectra for SiO\textsubscript{x}N\textsubscript{y} films of different composition.](image)

![Figure 3. Shift of the maximum of the SiO\textsubscript{x}N\textsubscript{y} absorption peak.](image)

![Figure 4. (a) Si 2p photoelectron peak of SiO\textsubscript{2}N\textsubscript{y} thin films; (b) RBM decomposition for sample with O/(O+N) = 0.4.](image)
theoretical RBM predictions [3] as illustrated by figure 5. So the SiO$_x$N$_y$ structure could not be described following the RBM only. As study supplement, the variation of the modified Auger parameter ($\alpha'$) as function of the film composition was followed. This parameter didn’t show a linear behaviour as expected for SiO$_x$N$_y$ whose structure is in agreement with the RBM [10]. The combination of all results leads to conclude that our material contains a mixture of SiO$_2$ and Si$_3$N$_4$ distinct phases incorporated in an amorphous SiO$_x$N$_y$ one.

![Figure 5](image_url)

**Figure 5.** (a) Theoretical and (b) experimental probabilities of the presence of polysubstituted SiO$_x$N$_{4-x}$ tetrahedra as function of the stoechiometric index following of RBM model.

## 4. Conclusion

Amorphous SiO$_x$N$_y$ thin films with quite continuous variation of their composition between those of Si$_3$N$_4$ and SiO$_2$ were obtained by sputtering a silicon target under different Ar-O$_2$-N$_2$ atmospheres. The investigation of different bonds and silicon environment by mean of FTIR and XPS analysis showed that the continuous variation in composition could not be explained by a simple substitution of nitrogen atoms by oxygen ones as suggested by the RBM. The shape of Si-O and Si-N absorption peaks, the differences between theoretical and experimental predictions of RBM and the nonlinear behaviour of the modified Auger parameter confirmed that the layer structure contains silicon nitride and silicon oxide phases incorporated in a silicon oxynitride one.

## References

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