

Study by X-ray absorption spectroscopy of Si_3N_4 films after Cu or Fe implantation and thermal treatment

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Si_3N_4 amorphous thin layers prepared by sputtering have been implanted either with Cu or with Fe ions. X-ray absorption spectroscopy was performed at the Si K edge to characterise the electronic empty states of p character, the structural state of the initial layers and the modifications around Si induced by implantation and a post-annealing treatment. We show that the energy deposition process mainly leads to a reorganisation of the second coordination shell around Si, i.e. concerns the Si-Si bonds.

Keywords : ion implantation, clusters, Si_3N_4

1. Introduction

Si_3N_4 is a ceramic already used in many applications because of its good mechanical, chemical and thermal resistance. To improve its properties, incorporation of a second phase was suggested (Sawaguchi *et al.*, 1991). Ion implantation allows one to introduce any impurity in any matrix. It appears thus as a relevant technique to prepare in a controlled way such mixed compounds (Bolse and Peteves, 1992; Brenscheidt *et al.*, 1998; Ikeyama *et al.*, 2000).

However, ion implantation through energy deposition leads to structural defects that may alter properties. Correlation between the structural and electronic evolutions of the treated system is thus necessary to understand and even predict the new properties.

This article studies the initial state and the modification of Si_3N_4 prepared in form of thin amorphous layers submitted to Cu or Fe implantations. Recently, we showed (Zanghi *et al.*, 2000) that Co and Fe implanted in bulk polycrystalline Si_3N_4 precipitate in form of metallic clusters. The X-ray absorption coefficient measured at the Cu K edge (not shown here) shows the Cu precipitation. In the frame of this article, we did not characterise the matrix. Bolse (1999) studied the disordering and amorphisation process in polycrystalline Si_3N_4 submitted to ion irradiations at 77 K, i.e. when the incident ions go through the matrix. He mentioned that a significant amount of broken bonds is detected by X-ray absorption spectroscopy, but did not give a detailed description of the Si surrounding. Zinkle (1994) indicated that a large level of deposited energy, more than 700 eV/at., is necessary in polycrystalline Si_3N_4 to reach amorphisation, that proves the strength of the atomic bonds in such a matrix.

Under implantations performed here where Cu or Fe ions stay in the matrix in form of clusters, the initially amorphous Si_3N_4 layer is submitted to a rearrangement of the second coordination shell around Si, the first coordination shell made of N atoms being unchanged.

2. Experimental

Si_3N_4 amorphous layers, 830 Å thick, were prepared using the Dual Ion Beam Sputtering technique. Argon ions (energy = 1.2 keV, flux

= 80 mA) sputtered a Si_3N_4 target. The target and the sample holder (heated at 400°C), facing each other, were tilted 45° away from the incident beam. To get good stoichiometry, samples were irradiated during the Si deposition with a N beam (energy = 50 eV, flux = 40 mA).

Implantations were carried out at 300 K on the Irma implantor (Chaumont *et al.*, 1981) with 3×10^{16} , 6×10^{16} Cu/cm² at 150 keV and with 3×10^{16} , 6×10^{16} Fe/cm² at 130 keV. These incident energies were chosen so that Cu and Fe stop in the layers; they correspond to a deposited energy about 300 eV/at (Ziegler *et al.* 1986). Some samples implanted with Cu were annealed at 800°C for 1 hour under vacuum, a temperature that allows an increase of the cluster size (Zanghi *et al.*, 2000).

X-ray absorption spectroscopy was performed at 300 K at the Si K edge on the SA32 station of the SuperAco ring, on the as-prepared samples, on the implanted and annealed ones. XANES spectra were recorded with 0.2 eV step on the 1830-1900 eV range whereas EXAFS was recorded with 1 eV step on the 1800-2500 eV range. For comparison, Si_3N_4 bulk samples crystallised in the alpha and beta phase were also measured in the same conditions. The measurements were performed in the total electron yield detection mode since implantation concerns a depth of about 500 Å from the layer surface, corresponding to the depth probed by this detection technique.

The absorption coefficients were treated in the usual way, i.e. subtraction of the pre-edge, extraction of the EXAFS oscillations and calculation of the Fourier transform (Michalowicz, 1991). Simulation of the filtered peaks was done using phase and amplitude extracted from a calculation performed with the FEFF code (Rehr *et al.*, 1992) on the Si_3N_4 beta phase. XANES spectra were pre-edge subtracted then normalised at the energy of 1865 eV.

3. Results

In Fig. 1, are presented the XANES spectra obtained on an as-prepared Si_3N_4 layer compared to the alpha and beta phase.

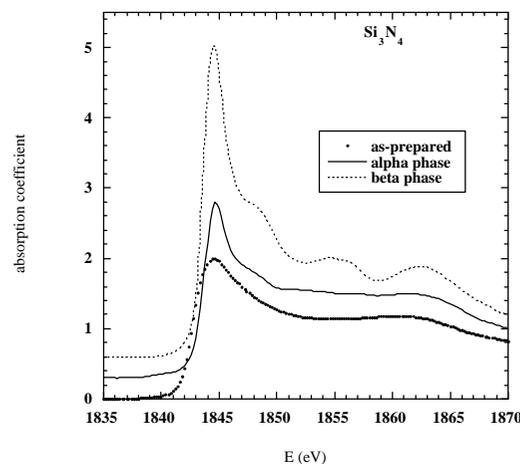


Figure 1

XANES at the K edge of Si on the as-prepared Si_3N_4 layer compared to the alpha and beta Si_3N_4 phase.

A first conclusion is that the as-prepared Si_3N_4 layer has an atomic structure closer to the one of the alpha phase. Since the first shell around Si, made of 4 N atoms is rather similar in the alpha and beta phases, the observed difference between their XANES and the one of the as-prepared layer must come from the following shells. Indeed, alpha Si_3N_4 displays a more disordered structure with two Si

sites. It has been shown that there is a compensation of their different contributions leading to the absence of structure in the XANES spectrum (Ténégal *et al.*, 1997).

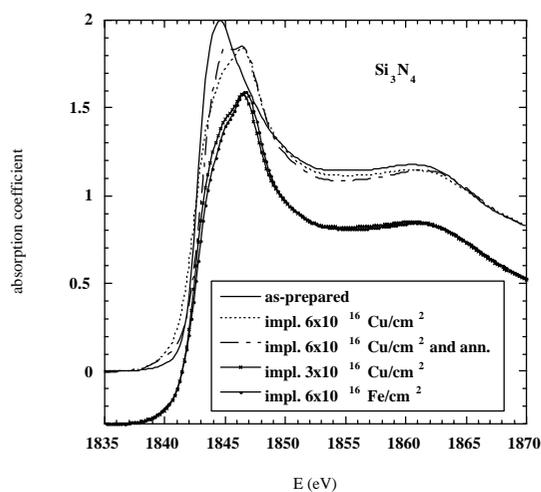


Figure 2

XANES at the Si K edge on the as-prepared Si_3N_4 layer, after implantation of 3×10^{16} Cu/cm^2 , 6×10^{16} Cu/cm^2 , 6×10^{16} Fe/cm^2 and after annealing.

A clear evolution is seen after Cu or Fe implantation and after annealing (Fig. 2). The white line located at 1844.5 eV is strongly decreased and a new structure grows at 1846.5 eV. Annealing leads to the reappearance of the structure at 1844.5 eV without modification of the new one. Note that the XANES after implantation of 3×10^{16} , 6×10^{16} Cu/cm^2 and 6×10^{16} Fe/cm^2 are nearly similar. Thus the Si K edge is sensitive to the difference neither in the nature (Fe or Cu) nor in the quantity of implanted ions. Recording that the difference in the XANES structure might come from the second shell, we guess that implantation has an effect at this level.

To look at this possibility, we calculated the Fourier transforms of the EXAFS signals for several samples that are presented in Fig. 3. Note that i) no long range order is seen in the as-prepared and implanted samples, ii) the first peak located at 1.5 Å (uncorrected from phase shift) representing the N first shell around Si is less intense in the as-prepared Si_3N_4 layer than in the Si_3N_4 alpha phase, in agreement with the amorphous character of the as-prepared samples. The main difference between the alpha phase and the samples comes from the second peak, i.e. the second coordination shell around Si. Only two small peaks are seen in the Si_3N_4 layer instead of the intense one in the alpha Si_3N_4 . Implantation leads to an intensity decrease of these two peaks and annealing induces a modification of their relative intensity. Such a small second peak intensity was already observed by Ténégal *et al.* (1996) in ultrafine amorphous $\text{Si}_x\text{C}_y\text{N}_z$ powders. The authors concluded of the absence of Si atoms in the second shell that is formed of C and N atoms only. The first peak (from 1 to 1.9 Å not corrected from phase shift) was filtered and simulated. Results of the first peak fits are presented Table 1. As the fitting procedure indicates a number of N neighbours close to 4, we fixed this value and let the Debye-Waller factors, σ , to vary.

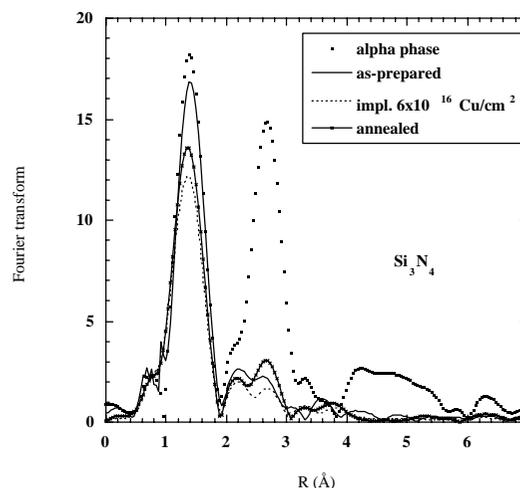


Figure 3

Fourier transform for the Si_3N_4 alpha phase, the as-prepared Si_3N_4 layer, after implantation of 6×10^{16} Cu/cm^2 at 150 keV and after annealing.

Table 1

Results of first peak simulation

Sample	N	R (Å)	σ (Å)
Alpha phase	4	1.723	0.036
As-prepared	4	1.722	0.062
As-implanted	4	1.719	0.068
Annealed	4	1.713	0.066

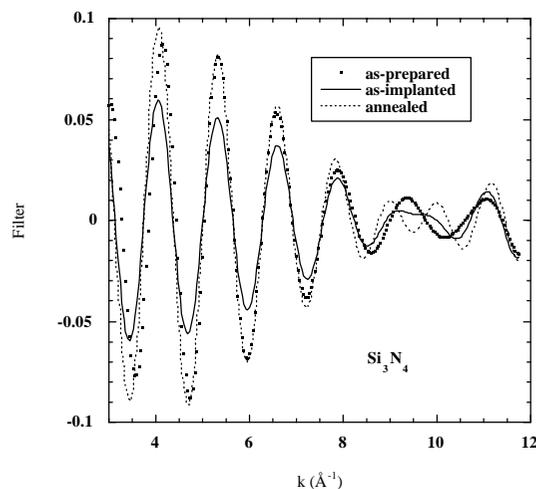


Figure 4

Filtering of the second peak of the Fourier transform of the Si_3N_4 layer as-prepared, after implantation of 6×10^{16} Cu/cm^2 at 150 keV and after annealing.

The filters of second peak (from 1.9 to 3.2 Å not corrected from phase shift) of the Fourier transforms for the as-prepared, implanted with 6×10^{16} Cu/cm^2 and annealed samples are presented in Fig. 4. To fit these filters, we started with the same assumption as Ténégal *et al.* (1996), i.e. N neighbours around Si in the as-prepared Si_3N_4 . Results of the fitting procedure for the as-prepared and implanted then annealed samples are presented Fig. 5. The second coordination

shell is mainly made of N atoms in the as-prepared state whereas, in the implanted and annealed state, it is necessary to introduce another shell made of 4 Si that is responsible of the frequency shift. The Si-Si distance that is measured is 2.99 Å, i.e. very close to the one observed in alpha Si_3N_4 equal to 3.03 Å.

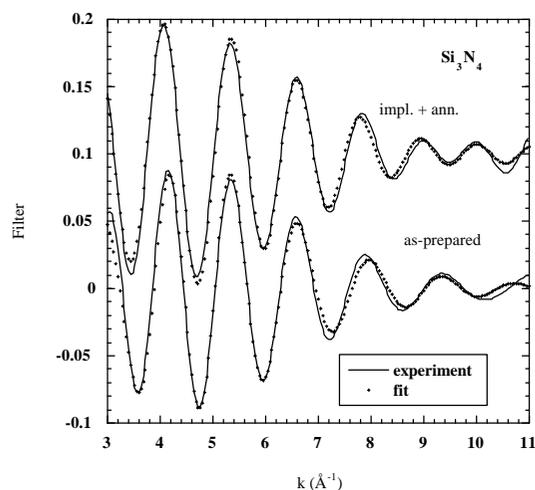


Figure 5
Fits of the second filtered peak of the Fourier transform for the as-prepared Si_3N_4 layer and for the implanted and annealed Si_3N_4 with $6 \times 10^{16} \text{ Cu/cm}^2$.

4. Discussion

Polycrystalline Si_3N_4 is a covalent system made of a network of SiN_4 tetrahedra connected by their corners. Si is coordinated by 4 N atoms and N by 3 Si atoms. No mono-atomic bonds, Si-Si or N-N are present.

In the as-prepared Si_3N_4 , the Si tetrahedra are kept, with the first N shell displaying a large disorder in agreement with the amorphous character of the layer. The disorder on this shell does not change very much as seen from the σ value evolution after implantation and after annealing. A tendency to a small R decrease is observed, although within the experimental uncertainty. The Si-N bond is so strong that, whatever the overall state of the Si_3N_4 system, crystalline, amorphous or submitted to energy deposition, the first N shell is unmodified.

On the contrary, the chemical composition of the second shell around Si appears to be strongly dependent on the structural state of the system. In the as-prepared amorphous layer, it is made mainly of N atoms. In agreement with the result found in amorphous $\text{Si}_x\text{C}_y\text{N}_z$ powders (Ténégal *et al.*, 1996), the structural picture that is suggested is that SiN_4 tetrahedra are linked mainly through monoatomic N-N bonds in such networks. After implantation and annealing, a reorganization of the system is observed. A new shell made of Si atoms located at 2.99 Å, not far from the average distance in alpha

Si_3N_4 , indicates that a network closer to the crystalline one starts to build where part of the linkage of the SiN_4 tetrahedra through Si bonds is present. The network partially crystallised at 800°C, i.e. at lower temperature than the one mentioned in Brenscheidt *et al.* (1998). However, in this work, the process is different. The starting material, beta Si_3N_4 , is first partially amorphised under Cr implantation at 1 MeV. A thermal treatment at 1000°C for 12 hours leads to the beginning of recrystallisation of the amorphised zones in the form of alpha Si_3N_4 . In our case, the initial sample is already amorphous and the energy deposited by the ion beam might participate in the recrystallisation process, so that less additional thermal energy is necessary to rebuild the alpha phase.

We suggest the following correlation between the XANES spectra and the structural state of the system, particularly the evolution of the second shell composition. The main line at 1844.5 eV in the as-prepared sample is due to the N atoms initially present in majority. The growth of the structure at 1846.5 eV after implantation corresponds to the occurrence of the Si neighbours located at 2.99 Å that are still present after annealing, whereas the disappearance of the structure at 1844.5 eV corresponds to a loss of N atoms after implantation that appears again after annealing.

5. Conclusion

We describe the evolution of the structural state and the distribution of the electronic p empty states in the case of amorphous Si_3N_4 layers submitted to Cu or Fe implantations. Neither the nature nor the amount of implanted ions plays a significant role. However, the energy that is deposited in the network via atomic collisions between the incident ions and the matrix atoms is responsible for a rearrangement of the SiN_4 tetrahedra. Part of them connected via N atoms in the initial amorphous state become connected via Si atoms, i.e. like in the crystalline phase.

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