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Introduction

The objective of this experiment was to study the formation of Sn and Sb nanoclusters in thin SiO_2 films by ion implantation followed by thermal treatments. In particular the evolution of the local environment of the implanted ions as a function of annealing treatments was investigated by using K-edge fluorescence XAS [1].

The study of metallic and semiconducting nanocrystals embedded in dielectric materials is of considerable current interest due to their novel electrical (such as single electron effect) and optical properties. Moreover, memory devices using nanocrystals as charge storage elements and single electron transistors based on metal nanoparticles have been demonstrated. However, a better understanding of formation and properties of nanocrystals is required for their technological applications.

This experiment was ESRF-specific. The use of a high brilliance beam at high energy is mandatory due to the use of the K edge and to the low dose of the absorbing atom (5×10^{15} - 1×10^{16} atoms/cm^2). Despite of the requested 18 beam shift, only 9 of them was allocated for this experiment and therefore in the three days of beam-time we concentrated on Sn implanted samples. XAS analyses on the Sb implanted SiO_2 films were performed in the following experiment 08-01-307.

The measurements were technically very challenging because of the low concentration of implanted ions, the small absorption cross section at the K-edge and because of the presence in the radiation scattered from the sample of a strong Compton component due to the Si substrate. Notwithstanding the experimental difficulties, good signal-to-noise ratio spectra were obtained on four samples and three reference compounds (Sn, SnO and SnO_2).

Experimental details and results

85 nm thick SiO_2 films were thermally grown on (001) silicon substrates by dry oxidation at 1000 °C and subsequently implanted at room temperature with 80 KeV/1x10^{16} cm^{-2} Sn ions. Post-implantation thermal treatments were performed at 800-900 °C for 30-120 s by rapid thermal processing (RTP) in N_2 atmosphere.

Sn absorption coefficient was monitored in the fluorescence mode at the K-absorption edge by using a thirteen-element Ge detector and a sagitally focusing Si (311) monochromator. In order to reduce spectral distortion due to the excitation of Bragg peaks in the substrate and to reduce the thermal damping of the signal, the samples were mounted on a vibrating and liquid nitrogen cooled holder.

The near edge (XANES) and the extended region (EXAFS) of the absorption coefficient were analyzed for all samples and reference compounds. Raw absorption data were background-subtracted using the AUTOBK routine and EXAFS data were quantitatively analyzed with FEFFIT programs using theoretical phase signals generated by FEFF 8.0.

All the absorption spectra (not reported here) showed a clear "white line" feature typical of an oxide compound. The position of absorption edge of the Sn samples is close to that of β-Sn (29200 eV) and SnO (29201 eV) reference compounds. The reference compound SnO_2 exhibits an absorption edge shifted by about 3 eV to higher energies compared to other samples.

Figure 1 shows the magnitude of the Fourier Transform (FT) of the EXAFS data (k^2 weighted, k: 2.5-9.2 $Å^{-1}$) for the Sn as-implanted and annealed samples and for the β-Sn reference compound. The dashed lines represent the fit of the experimental data (continuos lines) performed in the range R: 0.25-3.6 Å. The spectrum of as-implanted sample was fitted with a single Sn-O coordination shell, while the spectra of annealed samples were fitted with a combination of a Sn-O signal at a single interatomic distance and of a Sn-Sn signal with a split coordination shell, as in metallic β-Sn. The local structural parameters determined by the fit are reported in Table 1.

Conclusions

In summary, XAS analyses provided otherwise unavailable information on the local environment of Sn atoms implanted in thin SiO_2 films both after ion implantation and after different thermal treatments. Sn atoms are fully oxidized in the as-implanted, while after annealing also the ß-Sn phase is found. By comparing XAS data with ^{119}Sn CEMS and TEM results [2] we concluded that the metallic β-Sn phase is related to Sn crystalline clusters formed after annealing, while the oxidized Sn is due to atoms dissolved in the matrix or in small precipitates of SnO_2 or SnO_x.

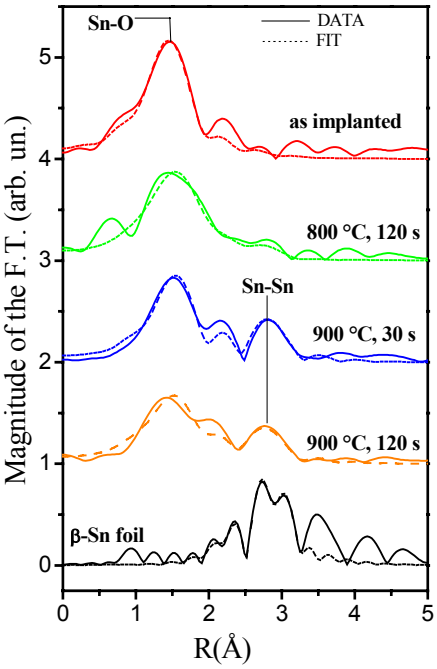

Figure 1. Magnitude of the Fourier Transform (F.T.) of the EXAFS experimental data.

Sample	Sn neighbors	N	R(Å)	σ^2 (10^{-3} Å)
As-implant.	O	2.4±0.3	2.00±0.01	0.008±0.002
800 °C, 120 s	O	2.9±0.6	2.10±0.03	0.020± 0.005
	Sn1	0.3±0.5	3.0±0.1	0.01±0.03
	Sn2	0.1±0.2	3.1±0.1	0.01±0.03
900 °C, 30 s	O	1.7±0.4	2.08±0.02	0.004±0.004
	Sn1	0.8±0.4	2.96±0.03	0.001±0.006
	Sn2	0.4±0.2	3.12±0.03	0.001±0.006
900 °C, 120 s	O	2.1±0.7	2.09±0.04	0.0180±0.008
	Sn1	0.8±0.7	2.94±0.05	0.00±0.01
	Sn2	0.4±0.2	3.09±0.05	0.00±0.01
reference compounds				
β-Sn ref	Sn1	4	3.047±0.003	0.0060±0.0003
	Sn2	2	3.196±0.004	0.0037±0.0003
SnO ref	O	4	2.23±0.001	0.001±0.002
SnO_2 ref	O1	2	1.98±0.02	0.001±0.002
	O2	4	2.05±0.02	0.001±0.002

Table 1. Local structural parameters for the Sn implanted samples and reference compounds.

[1] S. Spiga, M. Fanciulli, N. Ferretti, F. Boscherini, F. D'Acapito, G. Ciatto, B. Schmidt, *Formation and structure of Sn and Sb nanoclusters in thin SiO_2 films,* Nucl. Instr. and Meth. B 200 (2003) 171-177.

[2] S. Spiga, R. Mantovan, M. Fanciulli, N. Ferretti, F. Boscherini, F. D'Acapito, B. Schmidt, R. Grötzschel, A. Mücklich, *Local structure of Sn implanted in SiO_2*, in preparation.