ESRF	**Experiment title:** Ion beam synthesis of Sb nanoclusters in thin SiO_2 for electronic applications: a Refle-XAFS study.	**Experiment number**: 08-01-307
Beamline: BM08	**Date of experiment**: from: 31/1/2002 to: 5/2/2002	**Date of report**: 24/2/2003
Shifts: 12	**Local contact(s)**: Dr. Francesco D'Acapito	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

S. Spiga*, M. Fanciulli, Laboratorio MDM-INFM, via C. Olivetti 2, I-20041 Agrate Brianza (Italy)

F. Boscherini, N. Ferretti*,* INFM andDepartment of Physics, University of Bologna, I-40127 Italy

F. D'Acapito*, INFM-OGG c/o ESRF, GILDA CRG, Grenoble, F-38043 France

G. Ciatto*, CNR c/o ESRF, GILDA CRG, Grenoble, F-38043 France

Introduction

The ion beam synthesis of nanoparticles in amorphous matrix has received great attention in the last years as a promising technique for nanocrystal formation in insulating layers. Metallic and semiconducting nanoclusters embedded in SiO_2 have been recognized as potential materials for the production of memory devices and optoelectronic components. However, a better understanding of formation and properties of nanocrystals is required for their technological applications.

The aim of the proposed experiment was to study the formation mechanism of Sb nanoclusters in thin SiO_2 films by ion implantation followed by different annealing treatments. In particular, the local atomic environment of Sb ions in SiO_2 under different annealing conditions was investigated by X-ray Absorption Spectroscopy (XAS) with synchrotron radiation [1].

Due to the low concentration of implanted atoms (5×10^{15} atoms/cm^2), and to the limited thickness of this system, we used K-edge fluorescence XAS in the grazing incidence geometry (Refl-EXAFS). The Refl-EXAFS technique, useful in the study of thin films, permits to minimize the scattering signal (Bragg peaks, Compton scattering...) from the substrate by limiting the penetration of the beam to a few nm.

Experimental details and results

22 nm thick SiO_2 films were thermally grown on (001) silicon substrates and were implanted at room temperature with 10 keV/5x10^{15} cm^{-2} Sb ions. Post-implantation thermal treatments were performed at 1000-1100 °C for 30 s by rapid thermal processing (RTP) in N_2 atmosphere. The films were also annealed at 900 °C for 600 s in a standard furnace either in N_2 and Ar+7%H_2 ambient.

Sb absorption coefficients were monitored in the fluorescence mode at the K-absorption edge in the grazing incidence geometry by using a thirteen-element Ge detector. The monochromator was equipped with a pair of Si(511) crystals running in dynamical sagittal focusing mode. The beam on the sample was sized to 40 μm by a pair of slits placed at a distance of 2 m. The incidence angle on the sample was chosen to be at the critical value for total reflection (1 mrad at 30500 eV) on SiO_2. Reference compounds, i.e. powder of Sb, Sb_2O_3, Sb_2O_5, were measured in the transmission mode.

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

Figure 1(a) shows the XANES spectra of Sb implanted SiO_2 films and of the reference compounds Sb_2O_3, Sb_2O_5 and metallic Sb. The zero of energy scale is set to the absorption edge of metallic Sb. The position of absorption edges of the samples is intermediate between that of Sb and Sb_2O_3, and always about 4 eV lower than Sb_2O_5 The XANES line shape of Sb implanted samples is similar to that of the oxides, except for the sample annealed in Ar+7%H_2 which bears a closer resemblance to metallic Sb.

Figure 1(b) shows the magnitude of the Fourier Transform of the EXAFS data (k^2 weighted, k: 2.5-10 $Å^{-1}$) for the Sb as-implanted and annealed samples in different conditions, and for metallic Sb . The dashed lines represent the fit of the data performed in the range R: 0.7-3.2 Å. The spectrum of the as-implanted sample was fitted with a combination of Sb-O and Sb-Sb signals. The thermal treatments lead to either an increase of metallic correlation indicating the formation of metallic Sb nanoclusters or to an oxidation of all the atoms in the matrix, depending on annealing temperature or atmosphere.

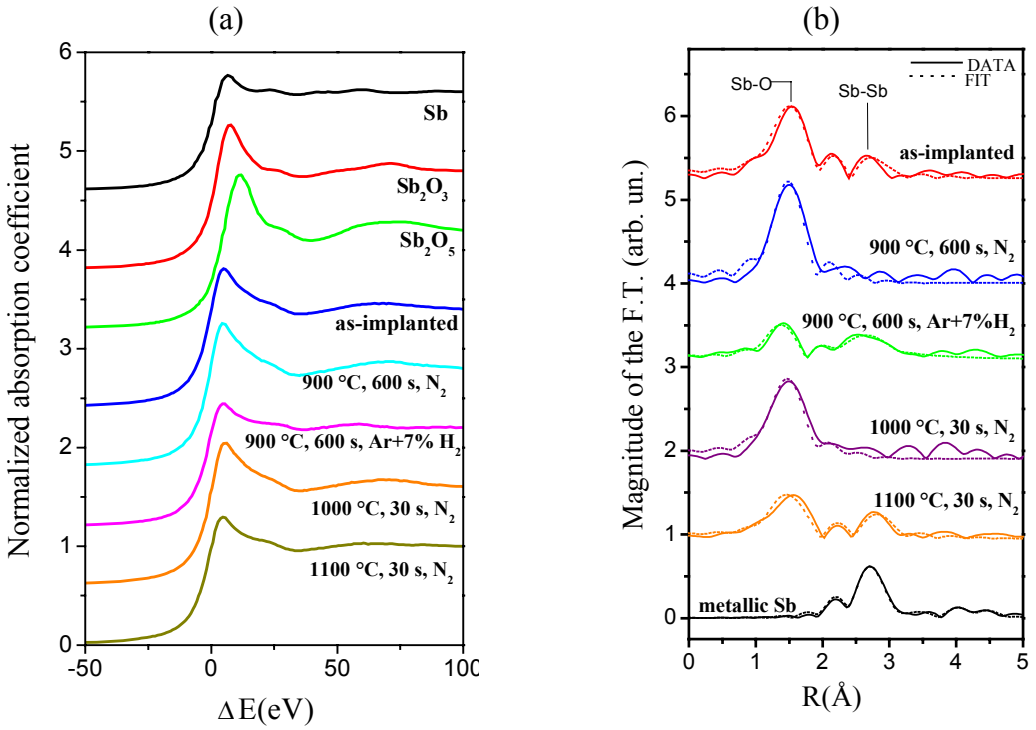

Figure 1. (a) XANES spectra of Sb implanted SiO_2 films and reference compounds (b) Magnitude of the Fourier Transform (F.T.) of the EXAFS experimental data (k^2 weighted, k: 2.5-10 $Å^{-1}$).

Conclusions

In summary, XAS analyses provided otherwise unavailable information on the local environment of Sb atoms implanted in thin SiO_2 films both after ion implantation and after different thermal treatments. Sb atoms are mainly coordinated with oxygen after ion implantation even if Sb-Sb correlations are present. Annealing at higher temperature (1100 °C) in a N_2 atmosphere or at lower temperature (900 °C) in a reducing atmosphere Ar + 7%H_2 leads to the formation of metallic Sb clusters, as confirmed by HREM.

[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.