Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Phase separation and Si/Ge nanocrystal formation in $Si_xGe_yO_z$	**Experiment number**: HE-3467
Beamline: ID16	**Date of experiment**: from: 10/02/2011 to: 14/02/2011	**Date of report**: 14/09/2011
Shifts: 12	**Local contact(s)**: Dr. Laura Simonelli	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

Due to the unique electronic and optical properties of semiconductor nanocrystals (NCs), Ge and Si NCs are promising candidates for, e.g., light emitting diodes [1-2], fast and stable non-volatile flash memory devices [3] and fluorescent biological labels [4]. Despite the intensive research regarding the electrical and optical properties of nanoparticles embedded in oxide matrices, spectroscopic studies of the formation process of nanoparticles and the corresponding changes of the local structure are rare. This information though is important for understanding the formation of embedded NCs in general. In recent years special attention is given to $Si_xGe_yO_z$ three component systems since (i) oxide embedded Ge NCs have a smaller band gap and a higher dielectric constant compared to Si NCs which results in higher charge retention times and (ii) Si is preferentially oxidized so that Ge NC formation can be tuned [5].

X-ray Raman scattering (XRS) is a powerful technique to probe the local atomic and electronic structure of a system, similar to the conventional x-ray absorption spectroscopy. Using hard x-rays, bulk sensitive studies of Si absorption edges yield unique information about the local chemical environment of Si contained in $Si_xGe_yO_z$. This has been shown in earlier studies of the phase separation in SiO [6-7]

The measurements were carried out at beamline ID16 [8]. The multi-analyzer spectrometer in Rowland geometry was used at an analyzer energy of 9.68 keV and scattering angles between 127° and 153° resulting in momentum transfers between 8.89 $Å^{-1}$ and 9.66 $Å^{-1}$. The $Si_xGe_yO_z$ samples were annealed ex situ at different temperatures to cover the regime of interest between 300 °C and 1200 °C in an argon atmosphere for 30 minutes. XRS spectra were measured between 90 eV and 120 eV energy loss in the vicinity of the Si L-edge.

The samples had been pre-characterized by x-ray diffraction and x-ray absorption near-edge structure at the Ge K-edge. The nanocrystal formation in the sample with a low Ge-amount ($Si_{0.45}Ge_{0.02}O_{0.53}$) takes place above 950 °C resulting in Si nanocrystals with an average diameter of (4.6±0.2) nm at 1000 °C. Due to the stoichiometry of the sample, the structure of the native sample is very similar to the structure of bulk amorphous SiO [7]. Thus temperature induced structural changes of the shape of the Si $L_{2/3}$-edge are similar compared to SiO indicating a phase separation in the SiO_x content. In the sample with a high Ge amount ($Si_{0.25}Ge_{0.25}O_{0.50}$) a Ge nanocrystal formation between 700 °C and 1000 °C takes place. Here, no phase separation of the SiO_x content was observed due to a high Ge amount. Above 500 °C GeO_2 reduction takes place resulting in a Ge cluster formation embedded in a SiO_2 matrix.

XRS spectra of differently annealed samples with low and high Ge content are presented in figure 1. In the spectrum of $Si_{0.45}Ge_{0.02}O_{0.53}$ an increase of the spectral intensity in the regions A and C can be observed for the sample annealed at 1000 °C while the intensity in the region B decreases. This changes indicate a temperature induced phase separation when Si and SiO_2 regions grow on cost of the sub-oxide-interfaces [7]. In general, only changes in the regions B and C can be observed in the spectra of the $Si_{0.25}Ge_{0.25}O_{0.50}$ sample which shows a similar trend compared to $Si_{0.45}Ge_{0.02}O_{0.53}$. Here, only SiO_2 formation can be extracted from the spectra on cost of a reduction of Si sub-oxides. Small amounts of pure Si may exist but changes in the region A are below the statistical limits. Here, the pure Si which occurs due to the temperature induced phase separation in the Si sub-oxide directly initiates a GeO_2 reduction leading to SiO_2 embedded Ge clusters. The analysis of the data is in progress and further measurements are planned to increase statistical accuracy and to measure more temperature points.

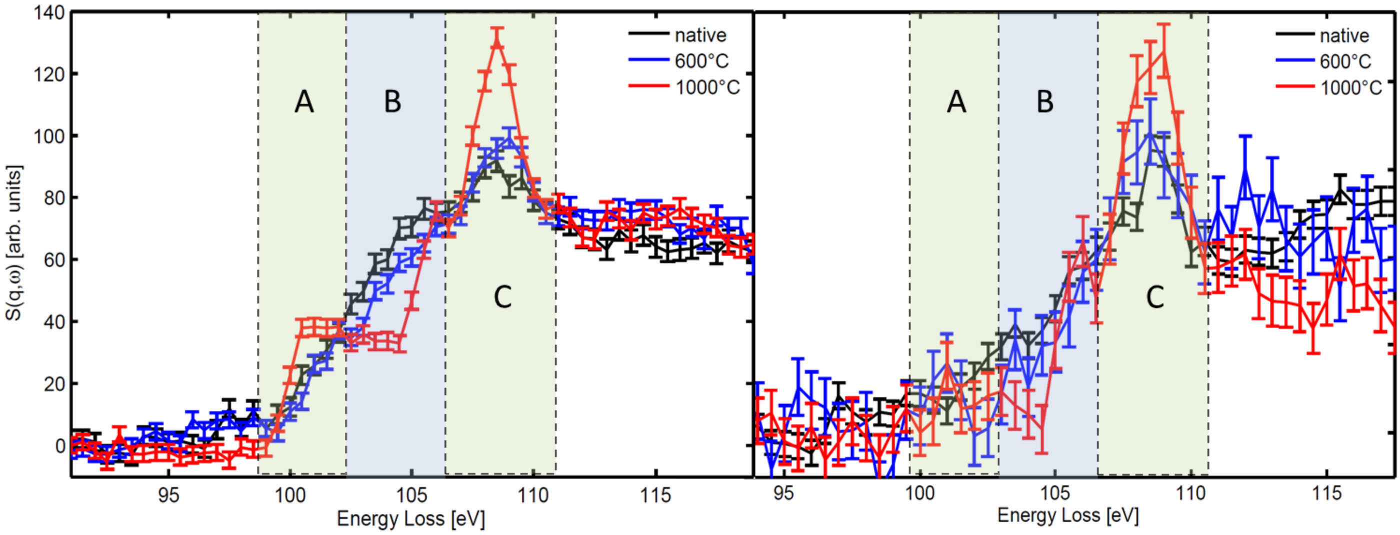

Figure 1: Si $L_{2/3}$-edge of the native and differently annealed $Si_{0.45}Ge_{0.02}O_{0.53}$ (left) and $Si_{0.25}Ge_{0.25}O_{0.50}$ (right) samples.

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