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

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- 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:** Temperature induced phase separation and nanocrystal formation in bulk amorphous $\mathrm{Si_xGe_yO_z}$	**Experiment number**: HE-3690
Beamline: ID16	**Date of experiment**: from: 29.09.2011 to: 5.10.2011	**Date of report**: 21.02.2012 *Received at ESRF:*
Shifts: 18	**Local contact(s)**: Dr. M. Moretti	

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Report:

Since the discovery of the visible and near-infrared luminescence, oxide matrix embedded semiconductor nanocrystals (NCs) obtained great attention for a high number of industrial and scientific applications. In particular, SiO_2 matrix embedded Ge NCs are one of the most promising materials for a production of light emitting devices or fast and stable non-volatile memory devices [1-2] due to a high difference of the dielectric constant between Ge ($\kappa = 16$) and SiO_2 ($\kappa = 3.9$) compared to other matrix embedded NCs [3-4]. While a high number of studies about the NC formation is available, spectroscopic studies on the processes leading to the NC formation, e.g. phase separation and GeO_2 reduction as well as SiO_2 matrix formation are rare. This knowledge is also important to tune the electronic properties of the material. Bulk amorphous $Si_xGe_yO_z$ can serve as starting material to produce nanometer sized Ge crystals in an SiO_2 matrix. Annealing of $Si_xGe_yO_z$ in an ambient atmosphere can initiate processes like phase separation and GeO_2 reduction and lead to a NC growth. The temperature range where these processes occur strongly depends on the stoichiometry of the sample as well as annealing time.

Two bulk amorphous $Si_xGe_yO_z$ samples were prepared with high ($Si_{0.25}Ge_{0.25}O_{0.50}$) and low ($Si_{0.45}Ge_{0.02}O_{0.53}$) Ge content by simultanious evaporation of GeO_2/Ge and SiO_2/Si mixtures and by evaporations of GeO_2/Si mixture, respetively, and subsequent condensation on a molybdenum substrate. The samples were cut in pieces and subsequently annealed for 30 minutes in an ambient nitrogen ($Si_{0.45}Ge_{0.02}O_{0.53}$) and argon ($Si_{0.25}Ge_{0.25}O_{0.50}$) atmosphere between 300 °C and 1000 °C.

The samples were pre-characterized by x-ray diffraction and x-ray absorption near-edge spectroscopy at the Ge K-edge. The Ge NC formation in the sample with a high Ge amount ($Si_{0.25}Ge_{0.25}O_{0.50}$) takes place between 700 °C and 1000 °C resulting in Ge NCs with an average size of (6.9 ± 0.4) nm at 850 °C. This process is supressed in the sample with low Ge amount due to the stoichiometry. Here, Si NC formation can be observed above 1000 °C. The GeO_2 reduction by pure Si starts at about 650 °C in both samples. In high Ge amount sample, phase separation of Ge suboxides in Ge and GeO_2 takes place between 500 °C and 750 °C additionally to the GeO_2 reduction.

X-ray Raman scattering (XRS) is a well suited technique to observe the GeO_2 reduction by Si and the SiO_2 matrix formation at the Si $L_{2/3}$-edge. It is very sensitive to changes of the local electronic structure and thus to changes of the oxidation state of an absorbing atom, similar to 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 [5-6].

The measurements were carried out at beamline ID16 [7]. 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 spectra were measured between 90 eV and 120 eV energy loss in the vicinity of the Si $L_{2/3}$-edge.

To determine the fractions of different oxidation states of Si from the experimental Si L-edges of $Si_xGe_yO_z$, Si^0 and Si^{4+} spectra were measured on pure Si and SiO_2. Suboxide samples (Si^{1+}, Si^{2+} and Si^{3+}) are not availible for experimental investigations because of the high thermodynamic instability of the suboxide phases. To estimate the suboxide contribution, calculated Si L-edge spectra of suboxide clusters based on molecolar dynamic (MD) simulations as described in [6] were used (see figure 1).

Figure 2 shows Si $L_{2/3}$-edges of native and differently annealed $Si_{0.25}Ge_{0.25}O_{0.50}$ samples. A negligible contribution of pure Si can be found in the spectra but a high amount of SiO_2 can be observed according to the global stoichiometry.

To obtain the suboxide contribution reference spectra were fitted to the experimental spectra according to the equation $I_{\mathrm{observed}} = a_1 \cdot Si^0 + a_2 \cdot SiO + a_3 \cdot Si^{4+}$ where a_1, a_2 and a_3 are fitting parameters and $SiO = 0.36 \cdot Si^{1+} + 0.13 \cdot Si^{2+} + 0.51 \cdot Si^{3+}$ according to the results of the MD simulation. The fitted contribution of different oxidation states in the native $Si_{0.25}Ge_{0.25}O_{0.50}$ sample is 22% for SiO, 76% for SiO_2 and the content of pure Si is negligible with respect to the accuracy of the fit. Due to a deviation between the fitted and experimental spectra, the value for the SiO seems to be overestimated by 3-5% on costs of the SiO_2 contribution. With increasing temperature, the suboxide contribution becomes negligible above 600 °C leading to SiO_2 matrix embedded Ge NCs without significant suboxide impurities of the SiO_2 matrix.

In contrast to the sample with a high Ge amount, the shape of the Si L-edge of the native $Si_{0.45}Ge_{0.02}O_{0.53}$ sample does not show any sharp features as a result of a high overlapping of the five oxidation states (figure 3). With increasing temperature, the spectral weight in the energy loss region between 102 eV and 107 eV decreases and the contribution of the Si^{0+} and Si^{4+} phases becomes more pronounced. As known from the pre-characterization studies, almost all oxygen atoms are connected to silicon and the Ge amount is found to consist of almost pure Ge. Thus, the Si atoms containing part of the $Si_{0.45}Ge_{0.02}O_{0.53}$ sample is assumed to be SiO_x with $x = 1.1$. The chemical structure of such compunds is known to consist of some amount of pure Si and SiO_2 and a significant contribution of Si suboxides [5-6]. At high temperatures a phase separation occurs leading to a Si and SiO_2 formation on costs of the suboxides. This process leads formation of Si NCs which are surrounded by an amorphous SiO_2 matrix. The Si NC size as well as the temperature range where the phase separation takes places strongly depend on the stoichiometry parameter x which describes the ratio of silicon and oxygen atoms.

To determine the fractions of pure Si, suboxides and SiO_2, the same fitting precedure was used as for the sample with high Ge amount. Additionally, the side condition $a_2 + 2 \cdot a_3 = 1.1$ was applied to conserve the global stoichiometry of the sample. Here, the amount of the suboxides could be overestimated by 3-5 % on costs of an underestimation of the Si^{4+} contribution for the same reason as described above.

The results of the fit lead to a suboxide amount of around 92 % while the amount of pure Si and SiO_2 is below 5 % . With increasing temperature, the suboxide contribution decreases significantly down to 13 % at 1000 °C while contribution of the Si and SiO_2 increases to 42% and 45 %, respectively, similar to the behaviour found in bulk amorphous SiO [5-6] (see figure 4).

A phase separation, as described above, takes place in both samples with low and high Ge containing $Si_xGe_yO_z$ samples independent on the stoichiometry leading to a Si and SiO_2 formation on costs of the Si suboxides. At annealing temperatures above 600 °C the suboxide amount drops down to a negligible content in the $Si_{0.25}Ge_{0.25}O_{0.50}$ sample. This effect decreases the impurity grade of the oxide matrix and improves the conductivity properties of such kind of samples which makes them very interesting for industrial applications. In contrast, significant amount of pure Si could be found in the $Si_{0.45}Ge_{0.02}O_{0.53}$ sample which is not reduced due to a low Ge amount.

References:

[1] Y. Maeda: *Phys. Rev. B* **51**, 1658 (1995);
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[6] A. Sakko, C. Sternemann, Ch. J. Sahle et al.: *Phys. Rev.* B **81**, 1098 (2010);
[7] R. Verbeni, T. Pylkkänen, Simo Huotari et al.: *Journal of Synch. Rad.* **16**, 469 (2009);

Figures:

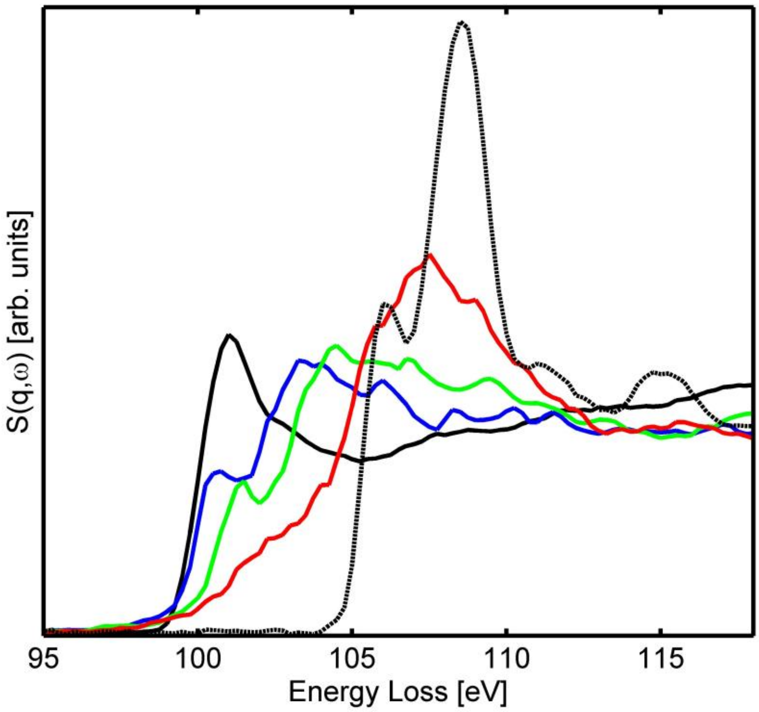

Figure 1: Experimental spectra of pure Si (Si^{0+}, black) and SiO_2 (Si^{4+}, dashed) as well as MD simulated spectra of Si^{1+} (blue), Si^{2+} (green) and Si^{3+} (red).

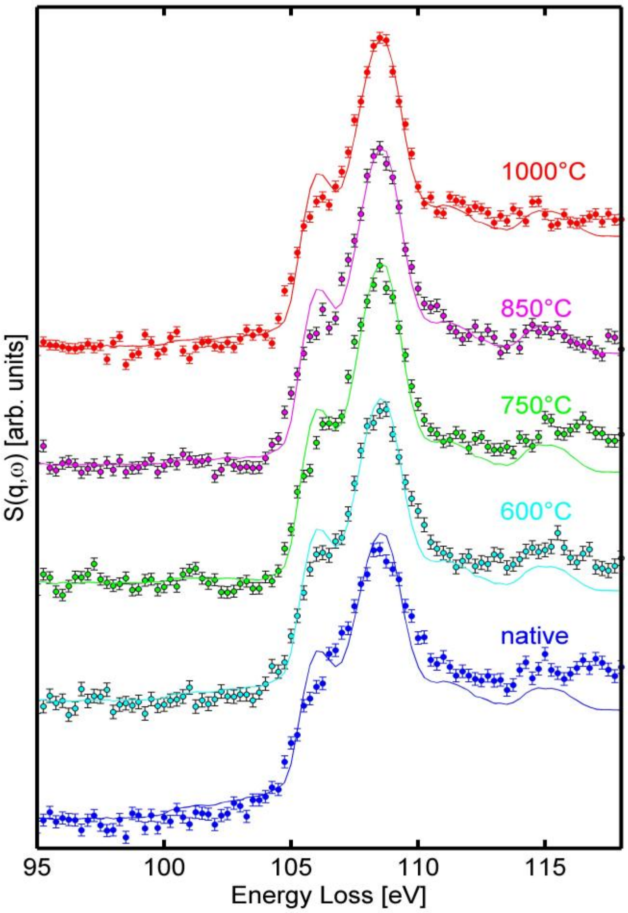

Figure 2: Experimental (points) and fitted (line) spectra of the Si $L_{2/3}$ – edge of native and differently annealed $Si_{0.25}Ge_{0.25}O_{0.50}$.

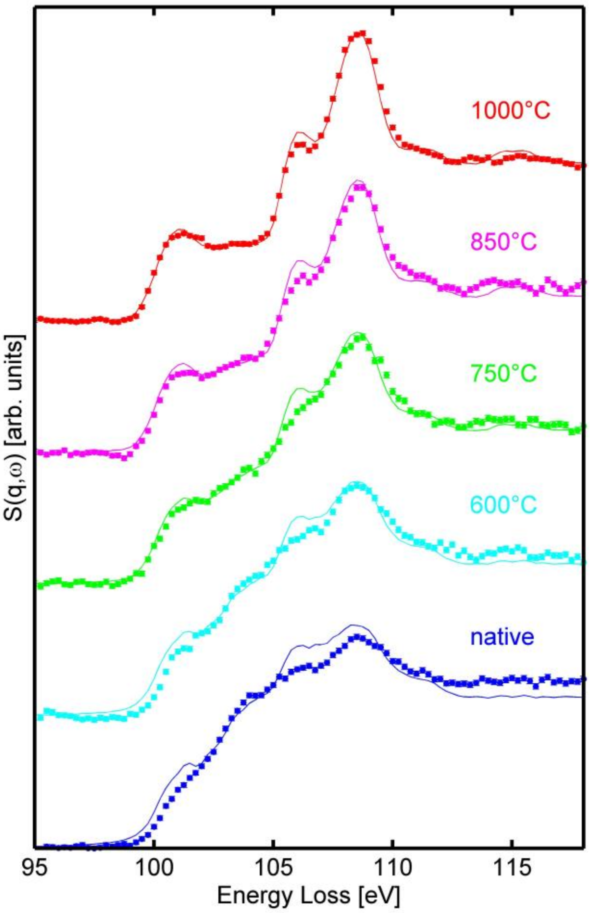

Figure 3: Experimental (points) and fitted (line) spectra of the Si $L_{2/3}$ – edge of native and differently annealed $Si_{0.45}Ge_{0.02}O_{0.53}$.

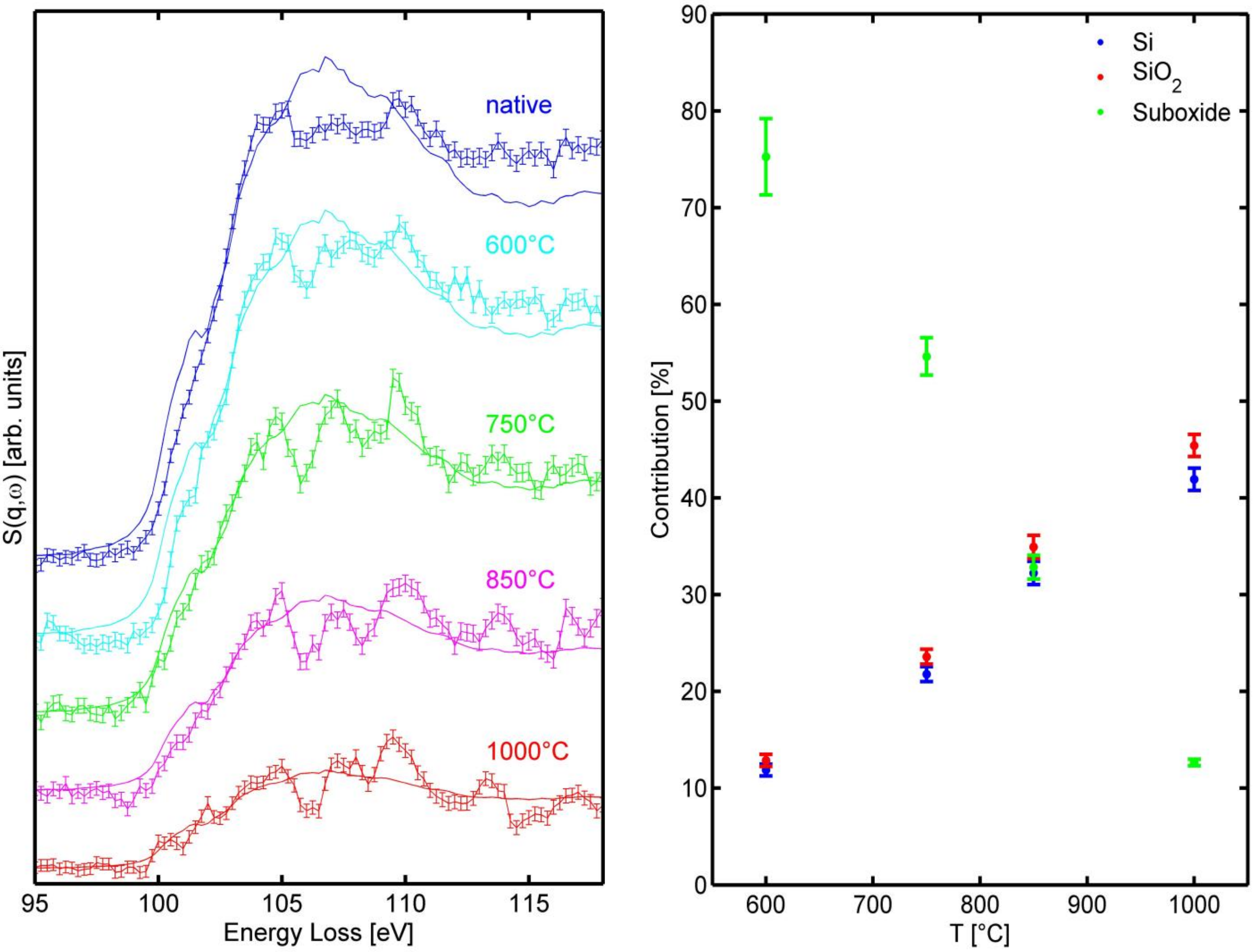

Figure 4: Extracted spectral contribution of suboxides (left) as well as Si, SiO2 and suboxide fractions of $Si_{0.45}Ge_{0.02}O_{0.53}$ at different temperatures (right).