ROBL-CRG	**Experiment title:** Growth of Ge NC´s out of a GeO_x/SiO_2 multilayer monitored *in-situ* by X-ray scattering techniques	**Experiment number**: 20-02-674
Beamline: BM 20	**Date of experiment**: from: 27.11.2008 to: 2.12.2008	**Date of report**: 12.10.2009
Shifts: 15	**Local contact(s)**: N.M. Jeutter	*Received at ROBL:*

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Report:

The confinement properties of semiconductor nanocrystals (NC's) offer an interesting approach for new light emitter or solar cell devices. One possibility to get a controlled size of NC's is the use of superlattice structures [1-3]. For this experiment various samples of $(GeO_x / SiO_2)^{19x}$ superlattices, characterized by different GeO_x thicknesses and stoichiometries, have been prepared by reactive magnetron sputtering. At ROBL the samples were mounted in a furnace chamber equipped with a semi-spherical Be dome and subsequently annealed at different temperatures under UHV conditions ($< 10^{-7}$ mbar) while continuously monitoring the superlattice properties and the Ge NC's formation with x-ray reflectivity (XRR) and grazing incidence x-ray diffraction (GIXRD), respectively.

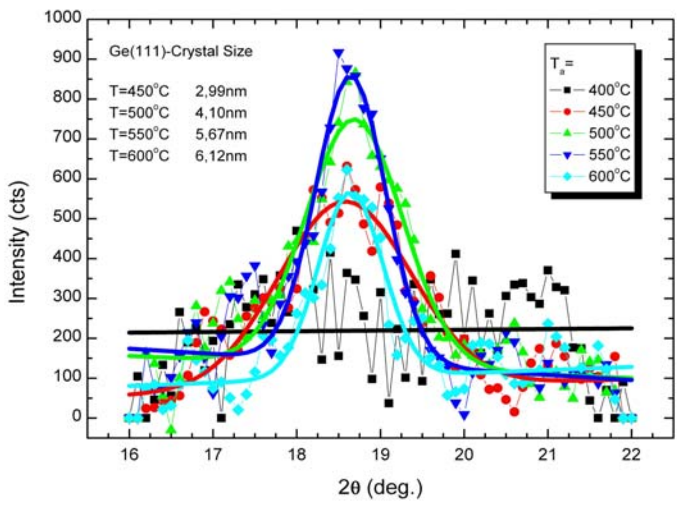


Fig. 1: *GIXRD of # 169 showing the formation of Ge NC's at low annealing temperature and the Ge-loss during annealing above 550°C.*

The onset of GeO_x/SiO_2 superlattice degradation as a result of GeO_x phase separation strongly depends on the GeO_x stoichiometry with a clear tendency towards an enhanced stability of Ge rich GeO_x films ($x < 1$), in agreement to previous experiments (20-02-658 / 667) [4].

The following details are discussed for #169 characterized by a superlattice of $(5.2\ nm\ GeO/2.4\ nm\ SiO_2)^{19x}$ (i.e. $x = 1$). Ge NC's are formed at annealing at $T_A = 450°C$ (see Fig.1), whereas at $T_A = 550°C$ the superlattice starts to degrate which is correlated with a significant Ge loss due to the emanation of volatile GeO. As prooved by RBS, after an annealing at 600°C more than half of the Ge gets lost. Consequently, in GIXRD a clear decrease in the peak area of Ge (111) is obtained (Fig. 1). As shown by ex-situ TEM investigations (Fig. 2) the multilayer structure is completely dissolved. The nanocluster distribution are characterized by the formation of large clusters up to 20 nm size and does not show vertical or lateral ordering anymore.

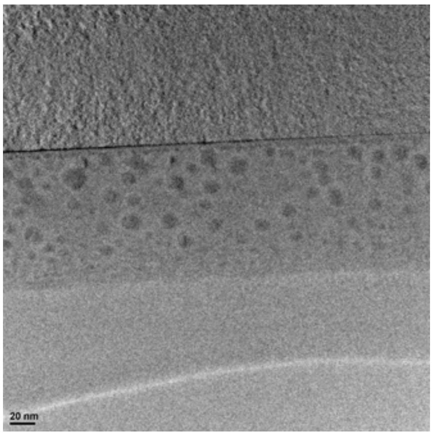
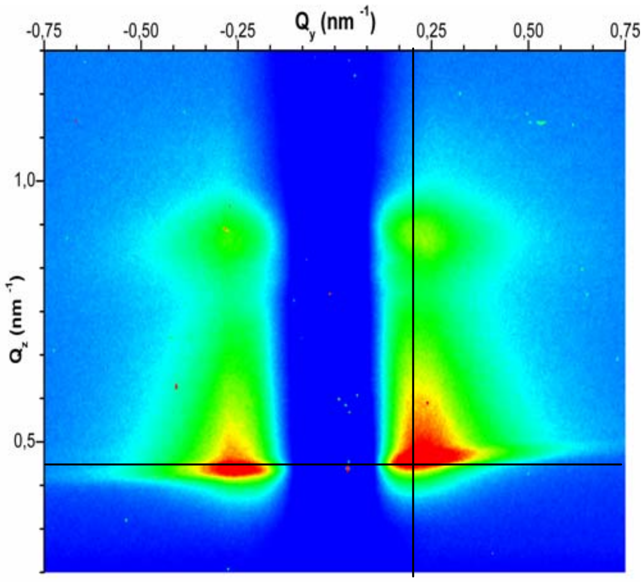


Fig. 2: TEM micrograph of the sample 169, annealed to T=600^{O}C, the particles have an average distance of more then the observed distance of 25nm.

GISAXS investigations of the sample 169 annealed to T=500^{o}C (Fig.3a) showed a clear peak at Q_z=0.895 nm^{-1} confirming the size of the double layer (GeOx/SiO2) to be 7.02 nm (similar to the XRR results of 7.4 nm). Also the denisty variation lateraly (e.g. the fomation of Ge NC's in the matrix) could be determined to be in the length of Q= 0.25 nm^{-1} or less. This leads to average particle – particle distance of 25nm or more at T_A= 500^{o}C (Fig.3b). At 600 ^{o}C the GISAXS signal gets very weak due to the loss of the volatile GeO. A strong drop in intensity of the peak at Q_z indicates the destroying of the SL structure (Fig.3b). But also in the signal of the Yonada wing showed a strong decrease in intensity, confirming the GIXRD and the RBS results of the loss of GeO during the annealing to 550-600 ^{o}C.



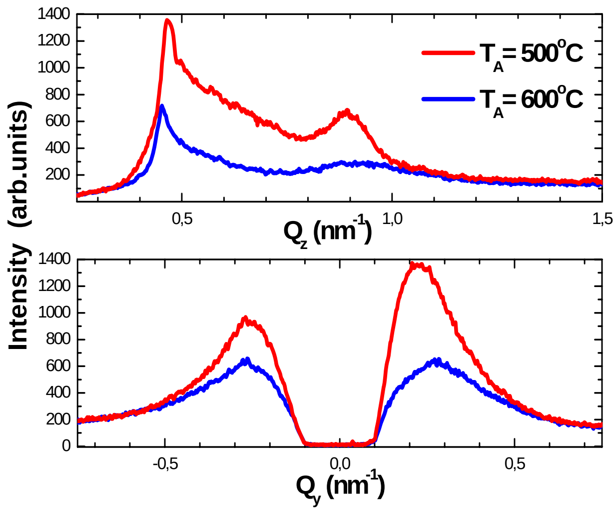


***Fig. 3a:** GISAXS pattern of the superlattice at T=500^{o}C, the black lines indicate the position of the red lincut, shown in in Fig. 3b. The two upper maxima indicate the average size of the SL double layer, in this case 7.02nm.*

***Fig. 3b:** Line cuts obtained from the GISAXS pattern at T_A=500^{o}C(red line, out of Fig.3a) and T_A=600^{o}C(blue line, image not shown here). The upper graph (Q_z Linecuts) clearly shows the drop of Intensity at Q_z=0.895nm^{-1} due to the degradation of the superlattice. The loss of scatters (Ge-Atoms) can be also seen in the lower graph (Q_y profiles).*

References:

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[3] M. Buljan et al., Nanotechnology **20**, 085612 (2009)

[4] M. Zschintsch et al., Journal of Applied Physics, in print, (2010)