ROBL-CRG	**Experiment title:** **Temperature dependent crystallization and ordering of Ge NCs in a SiO_2 matrix**	**Experiment number**: **20-02-695**
Beamline: BM 20	**Date of experiment**: from: 6.05.2010 to: 11.05.2010	**Date of report**: 14.02.2011
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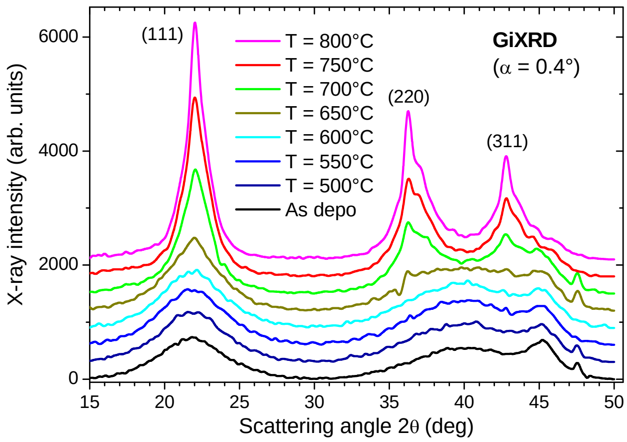
Report:

Promising materials for new generations of light emitters or solar cells are based on semiconductor nanocrystals (NCs). The optical properties are highly linked to their size, crystallinity and location within a matrix. A successful method to get uniformly sized NCs is the use of multilayer (ML) structures [1,2]. In a series of ongoing studies (20-02-658, -667, -674), during this ROBL experiment $(Ge\text{-}SiO_2 / SiO_2)^{50x}$ ML are investigated. The simultaneous deposition of Ge+SiO_2 by reactive magnetron sputtering from Ge and Si targets in the dc mode uses a certain process window for the oxygen partial pressure [4]. Samples, prepared at FZD beforehand, differ with respect to deposition temperatures, ML period thicknesses and the Ge/SiO_2 ratios. The variation of the stoichiometry was quantified by Rutherford Backscattering Spectrometry (RBS) prior to the beam time.

At the ROBL beamline the samples were *ex-situ* stepwise annealed in a separate UHV oven (base pressure low 10^{-8} mbar range) between 500 – 800°C (ΔT = 50K), in between characterized with x-ray (λ = 1.24 Å) scattering and diffraction. In the following the results of one representative sample are presented: substrate Si(001), deposition temperature T = 425°C, ML period thickness 5.8 nm, and Ge to SiO_2 ratio 1:2. The SiO_2 separation layers thickness amounts to 1.0 nm.

As shown in fig. 1, after deposition and annelings up to 600°C, only the broad Ge near-order peak at about 2θ = 22° appears in the GiXRD pattern (Scherrer size ~ 1.5 nm). The crystallisation of Ge starts at 650°C indicated by Ge(111) peak narrowing and the appearance of the Ge(220) and Ge(311) reflections. For annealing temperatures > 650°C, the peaks are characterized by the superposition of two contributions from Ge NCs of different sizes. Subsequent electron microscopy investigations reveal the existance of small Ge NCs in the ML (4 nm as visible in TEM fig. 3) and bigger NCs with sizes between 30 - 150 nm at the surface (SEM in fig. 4). After annealing at 800°C the crystallisation of Ge is completed as proofed by Raman spectroscopy.

In the XRR pattern (fig. 2), the partial coverage of surface with Ge NCs leads to a dip in the spectra at very low angles (grey rectangle). This can be interpreted as a second critical angle for SiO_2 which originates from the part of the surface not covered by Ge NCs. Furthermore, with increasing temperatures the 1st order ML peak is shifted to a larger angel which indicates a slight decrease of the ML period thickness due to ongoing Ge redistribution from the ML towards the surface.



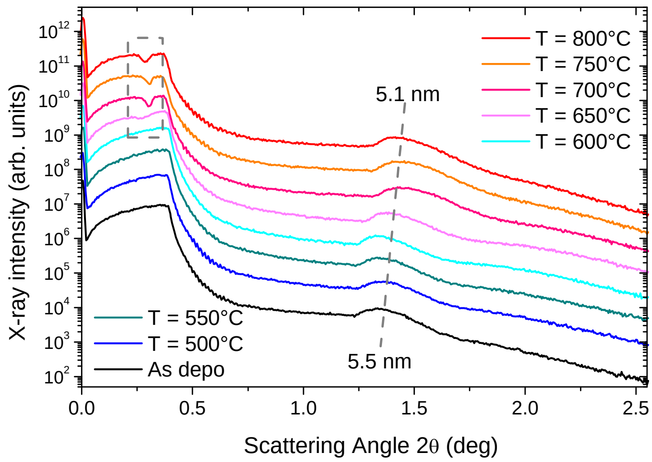
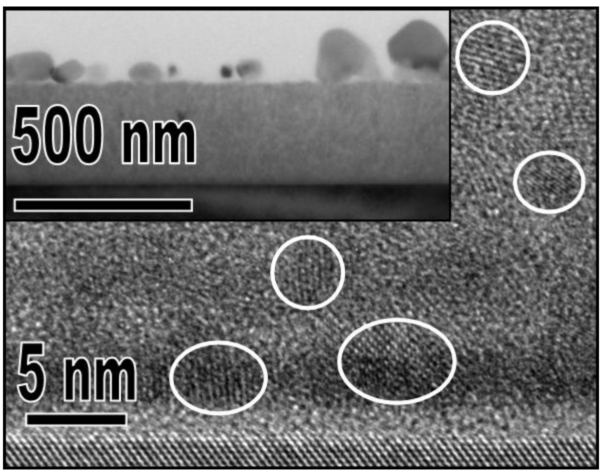


Fig. 1: *Ge NCs formation confirmed by grazing incidence X-ray diffraction (GiXRD, α = 0.4°)*

Fig. 2: *XRR reveals growth of Ge NC on surface and decrease of Ge-SiO₂-multilayer period.*

The TEM picture in fig. 3 reveals that the ML structure is still visible for the first layers, but with increasing distance to the Si substrate it seems to be washed out. In contrast XRR shows still a multilayer peak for the annealed samples so that there must be a density variation with a fixed length, which maybe ca nnot resolved in TEM. In the inset in fig. 3 and in fig. 4 the size, crystallinity and even the facetts of the Ge NCs on top of the multilayer are visible.



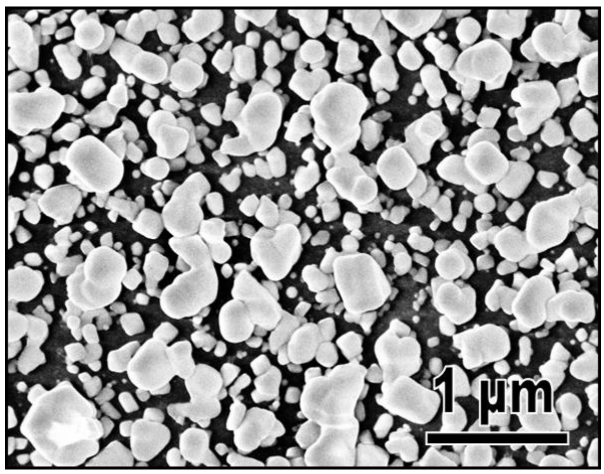


Fig. 3: *Ex-situ TEM pictures show Ge NCs in and on top (inset) of the multilayer*

Fig. 4: *Ex-situ SEM show Ge NCs on top of the surface.*

From the data evaluation of the complete sample set the following conclusions can be derived:

(1) the Ge crystallization temperature in (Ge+SiO_2)/SiO_2 ML is considerably (~ 150°C) higher than in GeOx/SiO_2 ML, where Ge NCs are formed already at 550°C,

(2) the Ge NC size (2-10 nm) can be well tailored by the Ge containing ML sub-layer thickness and temperature,

(3) the formation of a high density of larger Ge NCs (30 – 100 nm) at the surface becomes more pronounced with increasing Ge to SiO_2 ratio and decreasing deposition temperature.

References:

[1] S. Foss et al., Thin Solid Films **515**, 6381 (2007)

[2] M.Buljan et al. Phys.Rev.B **79**, 035310, (2009), and Nanotechnology **20**, 085612 (2009).

[3] M.Zschintsch et al., Journal of Applied Physics **107**, 034306 (2010)