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The evolution of the morphology of Ge nanocrystals formed by ion implantation in SiO_2

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Abstract

Grazing incidence small angle X-ray scattering was applied to study the synthesis and growth of Ge quantum dots in Ge-implanted SiO_2. Ge ion doses were up to $10^{17}/cm^2$, and subsequent annealing temperatures up to $T_a = 1000$ °C. Results suggest that ordered and correlated Ge QDs can be achieved by high-dose implantation followed by medium-T annealing.

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Keywords: Nanocrystals; Quantum dots; X-ray scattering; GISAXS; Implantation; Ge

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1. Introduction

Physical properties of Ge nanocrystals or quantum dots (QDs), like tunable absorption, intense photo- and electroluminescence and third-order optical nonlinearities, are strongly dependent on QDs size. This makes them suitable for electronic, optoelectronic and photonic applications, like in sensor technology, for integrated opto-couplers in microsystems in biotechnology, for electronic nonvolatile memories, etc. [1]. Ion implantation offers great flexibility in the QDs formation by control of the process parameters, considerable freedom from thermodynamical limitations and extreme chemical purity [2,3]. Additionally, it enables dense packing of nanocrystals, and is compatible with the conventional silicon-based integrated circuit technology.

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In this paper the formation and growth of Ge QDs in the implanted SiO_2 was investigated by means of grazing incidence small angle X-ray scattering (GISAXS), as a function of Ge ion dose and post-implantation annealing temperature.

2. Experimental details

100 keV $^{74}Ge^+$ ions were implanted into a 250 nm thick SiO_2 amorphous layer, that was grown on (100) Si substrate by wet oxidation [4]. Samples with doses of $1 \times 10^{17}\,cm^{-2}$ and $6 \times 10^{16}\,cm^{-2}$ were annealed at temperatures, T_a, ranging from $T_a = RT$ (not annealed) to 1000 °C, for 1 h in N_2 atmosphere. GISAXS experiments were carried out using X-ray photons of energy $E = 8$ keV (wavelength, $\lambda = 0.154$ nm) at the Austrian SAXS beamline of the synchrotron radiation facility ELETTRA, Trieste, Italy. The two-dimensional GISAXS patterns were recorded with a 2D CCD detector containing 1024 × 1024 pixels, placed in the y–z plane, perpendicularly to the specular x–z plane [3].

3. Results and discussion

The majority of 2D GISAXS patterns comprised of quasi-isotropic, half-rings, example of which is shown in the inset of Fig. 1. This (as well as other, not shown) GISAXS pattern showed quite a symmetric intensity distribution in all directions. These rings are interpreted as scattering from (spherical) Ge QDs; the interference maximum being related to the spatial correlation between isolated Ge QDs embedded in amorphous matrix. The formation of nanoparticles in SiO_2 substrate was confirmed by Raman spectroscopy (appearance of the frequency mode in Raman spectra), while the spherical shape of QDs was established with transmission electron microscopy (TEM) in a few analogously implanted + annealed samples (not shown). They are chemically identified as Ge QDs through the appearance of the characteristic TO mode in Raman spectra and with grazing incidence X-Ray Diffraction in some of these samples (not shown).

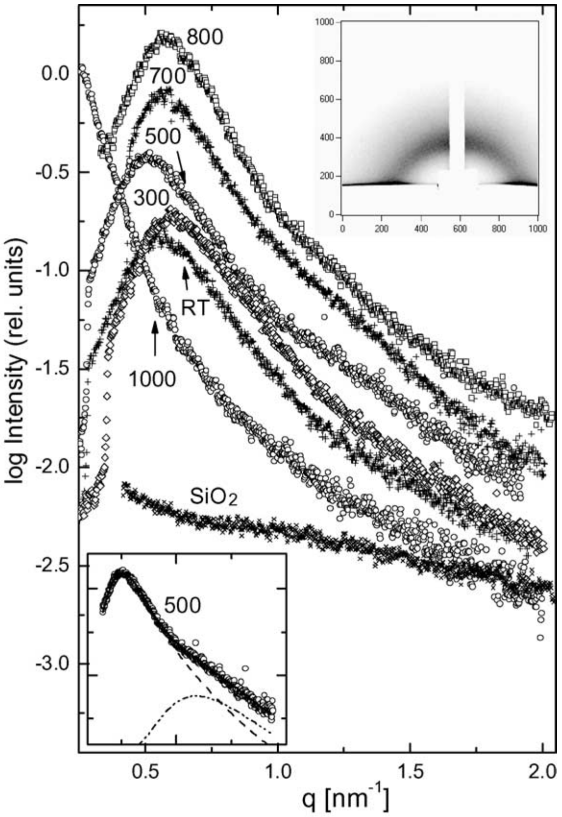

Fig. 1. Vertical scans of 2D GISAXS pattern of SiO_2 samples implanted with Ge ion dose $D_1 = 1 \times 10^{17}/cm^2$, and annealed at various annealing temperatures for 1 h in N_2. Spectrum of the unimplanted SiO_2 substrate is added for comparison. Annealing temperatures (in °C) are indicated in the figure. Inset (upper): 2D GISAXS pattern of as-implanted sample. Inset (lower): Fits of spectrum of the sample annealed at $T_a = 500$ °C using one size distribution (dashed line) and two size distributions (full line).

Fig. 1. shows one-dimensional (1D) GISAXS plots obtained by cross-sectioning 2D pattern parallel to the z-axis close to the beam-stopper, for samples implanted with the same Ge ion dose $D_1 = 10^{17}/cm^2$, but annealed at different annealing temperatures. By applying traditional analysis, the radius of gyration, R_g, of QDs was estimated from the so called Guinier plot, and the average interparticle distance, L from the curve maximum positions (Table 1). A strong half ring was present in the 2D GISAXS spectrum of as-implanted sample (inset of Fig. 1) showing that QDs were formed

Table 1
List of samples and results of Guinier analysis of 1D GISAXS spectra

Sample no.	Ion dose (cm^{-2})	T_a (°C)	R_g (nm)	L (nm)
4111	1E17	1000	5.19	
4181	1E17	800	3.15	9.7
4171	1E17	700	2.94	9.4
4151	1E17	500	2.67	9.7
4131	1E17	300	2.50	9.6
As-implanted	1E17	RT	2.65	9
4411	6E16	1000	5.69	
4481	6E16	800	2.72	9.9
4471	6E16	700	2.10	7.5
4451	6E16	500	1.78	7
4431	6E16	300	1.70	7

T_a stands for annealing temperature, R_g for the Guinier radius and L for the interparticle distance.

already during implantation ($R_g = 2.6 \pm 0.3$ nm). Both Raman and XRD indicated that these QDs are amorphous. Annealing up to 800 °C causes just moderate change in R_g and a minimal change in L. But noticeable changes in the shape of the curves indicate some reorganization of QDs, while Raman and XRD suggest that the QDs become crystallized. Annealing at $T_a =$ 1000 °C, however, resulted in a strong increase of R_g, suggesting that diffusion processes become very fast, leading to the formation of large QDs, with average diameter, D, larger than 13 nm ($D = 2 \times (5/3)^{0.5} \times R_g$). Local monodisperse approximation (LMA) [4], applied to the same set of spectra, revealed that more than one size distribution of QDs is present in these samples. It comes out that for such a high implant dose an additional distribution of small QDs, centered close to 1 nm radius range, had to be assumed in order to explain also the large-q part of the spectra (inset in Fig. 1). The co-existence of small and large nanocrystals was indeed observed by TEM in similarly processed samples [5]. Fig. 2 depicts 1D GISAXS spectra for the Ge ion dose $D_2 = 6 \times 10^{16}/\mathrm{cm}^2$. Apparently, quite similar T_a dependence occurs for this dose as well. However, in contrast to the samples implanted with D_1 dose, here just one size distribution (lognormal), with practically the same size distribution width, was present in all samples up to $T_a = 800$ °C. Only in the sample annealed at $T_a = 1000$ °C, not only the average size of QDs but also the width of the size distribution appears to increase considerably.

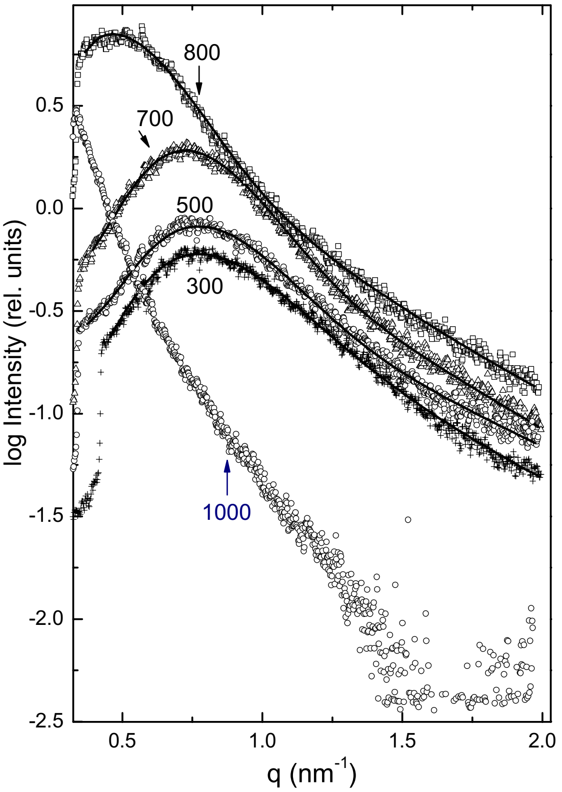

Fig. 2. Vertical scans of 2D GISAXS pattern of $\mathrm{SiO_2}$ samples implanted with Ge ion dose $D_1 = 6 \times 10^{16}/\mathrm{cm}^2$, and annealed at various annealing temperatures for 1 h in $\mathrm{N_2}$. Annealing temperatures (in °C) are indicated in the figure. The fits depict LMA results, using one lognormal size distribution, with distribution width parameter $\sigma = 0.94 \pm 0.4$ in all fits.

4. Conclusion

Grazing incidence small angle X-ray scattering was applied to study the synthesis and growth of Ge quantum dots (QDs) in $\mathrm{SiO_2}$ implanted with Ge to high doses ($0.6–1 \times 10^{17}/\mathrm{cm}^2$), and subsequently annealed at temperatures in the range $T_a = \mathrm{RT} - 1000$ °C. Ge-QDs were found to form already during implantation. Their average size changes insignificantly up to $T_a = 500$ °C, moderately in the $T_a = 700–800$ °C range and strongly after $T_a = 1000$ °C, where fast diffusion processes lead to the formation of large QDs intermixed with small QDs in the less than 2 nm size range. For dose $6 \times 10^{16}/\mathrm{cm}^2$ up to $T_\mathrm{a} = 800\ ^\circ\mathrm{C}$ all Ge QDs remain correlated in a 3D ensemble having one size distribution and similar size distribution width. High-dose implantation appears to create amorphous QDs, which can be ordered/recrystallized by annealing at medium T_a, thus avoiding processing at high T_a.

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