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Ion beam synthesis and characterization of Ge nanoparticles in SiO_2

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Abstract

Ge quantum dots embedded in SiO_2 have been obtained by implantation of Ge ions in the 10^{16}–10^{17} cm^{-2} dose range, followed by post-implantation annealing in the temperature range $T_a = 300-1000$ °C. Using Rutherford back-scattering, grazing incidence X-ray diffraction and grazing incidence small angle X-ray scattering it was found that Ge-QDs are synthesized as discrete, spherical QDs, with radius ranging from 1.7 to 10 nm, depending on dose and T_a. For T_a above 800 °C the Ge atom diffusion becomes considerable, leading to a strong increase of both size and size distribution of Ge QDs, but still without sizeable loss of Ge atoms from the implanted layer.

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1. Introduction

There is an intense research activity going on to develop technology for the efficient and controllable synthesis of nanocrystals or quantum dots (QDs) [1–5]. Semiconductor materials in the form of QDs display significant dependence of many properties on the size of nanoparticles, which are generally ascribed to quantum confinement effects. Specifically, Ge quantum dots embedded in a transparent matrix exhibit particularly strong size dependence of optical properties [6]. This enables the tunability of the nano-Ge band gap over a considerable part of the range of visible light wavelengths, which opens a large number of potential applications in semiconductor and other industries.

Ion implantation offers great flexibility in the QDs formation through the control of the process parameters. It enables dense packing of nanocrystals, offers considerable freedom from thermodynamical limitations, extreme chemical purity and compatibility with the conventional integrated circuit technology.

2. Experimental details

100 keV $^{74}Ge^+$ ions were implanted into a 250 nm thick SiO_2 amorphous layer, which was grown on (1 0 0) Si substrate by wet oxidation [4]. Samples implanted with a dose of 1×10^{17}, 6×10^{16} or 1×10^{16} cm^{-2} were annealed at temperatures, T_a, ranging from $T_a = RT$ (not annealed) to $T_a = 1000$ °C, for 1 h in N_2 atmosphere. Rutherford back scattering (RBS) measurements were done by 6 MV EN Tandem Van de Graaff accelerator in Zagreb, using 1.5 MeV ^4He ions, which were extracted from the Alphatross ion source. The accelerated alphas were directed normally to the target surface. Spectra were collected using the surface barrier detector positioned at 165° relative to the beam direction. GISAXS (grazing incidence small angle

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X-ray scattering) experiments were carried out using X-ray photons of wavelength, $\lambda = 0.154$ nm, at the Austrian SAXS beamline of the synchrotron radiation facility ELETTRA, Trieste, Italy [7]. Two-dimensional GISAXS patterns were recorded with a 2D CCD detector having 1024×1024 pixels, placed in the y–z plane, perpendicularly to the specular x–z plane [5]. Grazing incidence X-ray diffraction (GIXRD) images of the samples with and without implanted Ge were taken at a rotating anode X-ray generator (from Enraf–Nonius), and were recorded with an image plate detector (Marresearch).

3. Results and discussion

3.1. RBS results

To determine the success of incorporation of Ge atoms implanted into SiO_2 substrate, as well as the possible instability of their position or even loss from the implanted layer due to the post-annealing thermal treatment the RBS method is applied. Examples of the results, for the highest Ge ion dose of 1×10^{17} cm^{-2} are shown in Fig. 1. Fig. 1(A) depicts the whole spectra for the as-implanted sample and for a few annealed samples. Particle-solid angle product was determined by adjusting the height of the simulated spectra to the substrate signal of the experimental spectra using program SIMNRA [8] and taking into account that the cross sections for all elements are of Rutherford type. Distribution of implanted Ge was simulated with eight thin layers with Ge concentrations in each according to SRIM calculation. The depth distribution of Ge in the implanted layer is shown in Fig. 1(B). The error in Ge-concentration determined in such a way was estimated to be ±5%. The depth distribution of Ge in the implanted layer is shown in Fig. 1(B).

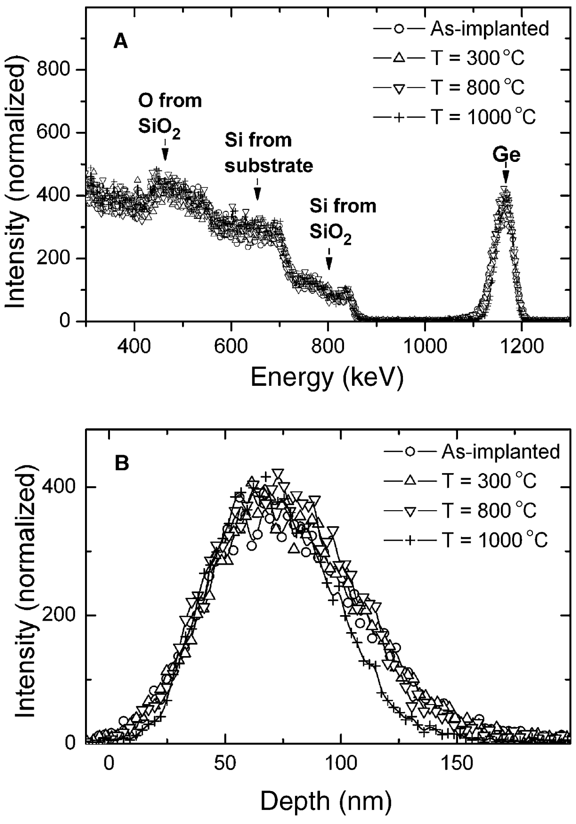

Fig. 1. (A) RBS spectra of SiO_2 samples on Si substrate implanted with 100 keV $^{74}Ge^{+}$ ions obtained with 1.5 MeV He projectiles, (B) Ge depth profile in SiO_2 obtained for different annealing temperatures, indicated on the figure. The Ge ion dose was 1×10^{17} cm^{-2}.

The main findings from RBS measurements are the following:

(a) Practically all implanted atoms were indeed incorporated into the SiO_2 substrate, even for the highest dose (1×10^{17} cm^{-2}).
(b) After thermal processing, up to $T_a = 800$ °C there is no loss of Ge atoms from the sample (i.e. there is no perceivable loss of Ge, which would exceed the inaccuracy of the measurement).
(c) For $T_a = 1000$ °C, a very small fraction of Ge atoms in-diffuses deeper into the substrate (this could be better seen when Li ions instead of alphas were used for the RBS experiment; not shown). More importantly, some loss of Ge atoms (cca 13%) was also observed. Both effects indicate that at $T_a = 1000$ °C the diffusion of Ge atoms in SiO_2 becomes significant.

3.2. GISAXS results

The majority of 2D GISAXS patterns comprised of quasi-isotropic half-rings. An example, for the dose of 1×10^{17} cm^{-2}, is presented in [9]. Such rings indicate the formation of discrete, spherical, uniformly distributed, spatially correlated QDs embedded in the matrix [2,3,9]. For the two larger doses, 6×10^{16} and 1×10^{17} cm^{-2}, the synthesis of QDs occurs already during implantation, while for the smallest dose of 1×10^{16} cm^{-2} the ring appeared only after $T_a = 800$ °C. Fig. 2 depicts one-dimensional (1D) GISAXS spectra showing scattering intensities as a function of the wavevector q, where $q = (4\pi/\lambda)\sin\beta$; 2β being the scattering angle. Plots were obtained by cross-sectioning 2D GISAXS pattern for samples implanted with all 3 doses and annealed at several annealing temperatures. GISAXS spectra were analyzed using the local monodisperse approximation (LMA) [10], assuming a lognormal size distribution. Results of the LMA analysis for the samples shown in Fig. 2. are given in Table 1. Annealing generally causes an increase of particle size and of size distribution, but both appear to be also considerably dose-dependent. The annealing at $T_a = 1000$ °C causes a substantial increase in QDs average size and a drastic increase of the width distribution parameter, for all doses. These results are consistent with the RBS findings of considerable increased diffusion of Ge atoms for $T_a = 1000$ °C.

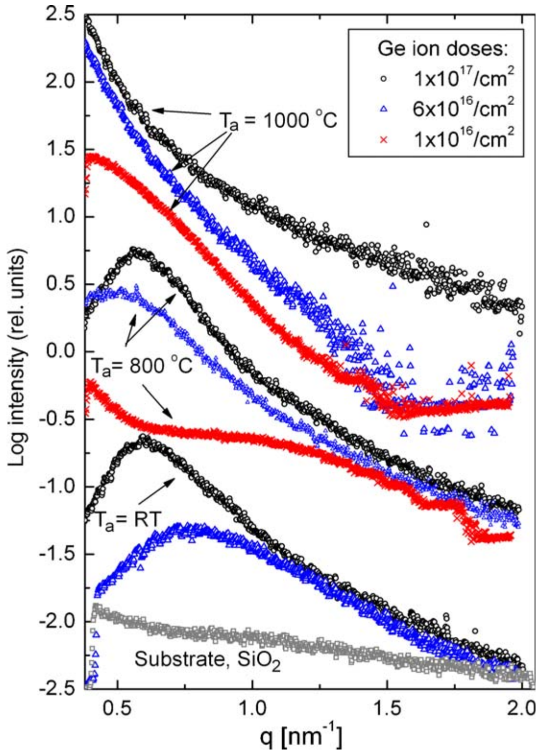

Fig. 2. 1D cross-sections of 2D GISAXS patterns of Ge-implanted SiO_2 after annealing at various annealing temperatures for $T_a = 1$ h in N_2. Doses of Ge ions and values for T_a (in °C) are indicated in the figure.

Table 1
Results of LMA analysis of 1D GISAXS spectra for samples shown in Fig. 2[a]

	Ion dose (cm^{-2})	Annealing temperatures T_a (°C)		
		RT	800	1000
R (nm)	1E17	4.42	4.56	9.15
W (nm)		0.94	1.12	7.06
R (nm)	6E16	2.92	4.37	5.91
W (nm)		0.64	1.41	6.89
R (nm)	1E16	–	1.68	3.29
W (nm)		–	0.1	1.36

[a] R stands for the radius of Ge QDs and W is the distribution width parameter in lognormal distribution.

3.3. Grazing-Incidence XRD results

Normal XRD (not shown) proved not to be an adequate method for analyzing this type of samples. However, grazing incidence XRD gave useful spectra, as illustrated in Fig. 3 for the sample implanted with a Ge ion dose $D1 = 10^{17}$ cm^{-2}, and annealed at 1000 °C, a sharp peak in the spectrum appears at $\theta = 13.6°$, belonging to the $\langle 111 \rangle$ Ge reflection. The sample annealed at $T_a = 800$ °C has a broader line. When Sherrer's formula was used to asses the radius R of Ge QDs, the values of 9.1 nm and 5.3 were obtained for $T_a = 1000$ °C and $T_a = 800$ °C, respectively; in reasonable agreement with the GISAXS results (Table 1). In the as-implanted sample, the peak at approximately the same position is drastically broadened, indicating that Ge QDs are already synthesized (again in accordance with GISAXS) but that they are highly disordered and probably amorphous.

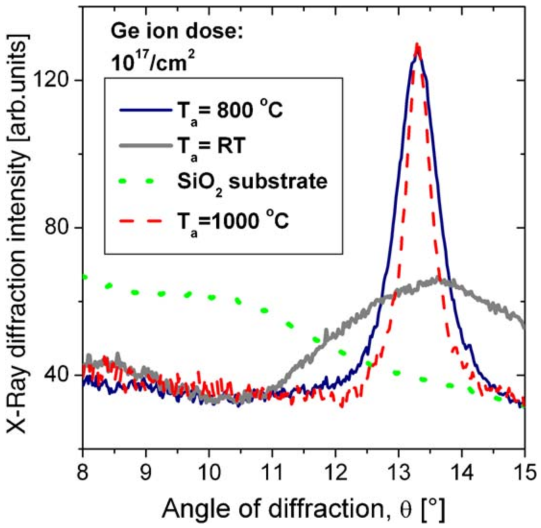

Fig. 3. Grazing incidence X-ray diffraction (GIXRD) of the samples implanted with the ion dose 1×10^{17} cm^{-2}. Annealing temperatures are indicated on the picture. Signal from the non-implanted substrate is also shown for the comparison.

4. Conclusion

Ge quantum dots (QD) have been obtained by implanting Ge ions into SiO_2 substrate with ion doses of 10^{16}–10^{17} cm^{-2}, followed by post-implantation annealing in the temperature range $T_a = RT - 1000$ °C. The samples were analyzed by RBS, GIXRD and GISAXS. The Ge nanoparticles were found to be synthesized as discrete, spherical QDs, embedded in the SiO_2 matrix, which remain uniformly distributed and spatially correlated up to $T_a \leqslant$ cca 800 °C. Depending on the ion dose and annealing temperature an average size for the radius of the Ge QDs was obtained in the range from 1.7 to over 9 nm. No sizable loss of Ge atoms occurred up to $T_a = 800$ °C. At $T_a = 1000$ °C the diffusion of Ge atoms becomes considerable, leading to the strong increase of the average size of QDs, to the substantial widening of their size distribution, and some small but perceivable loss of Ge from the implanted layer.

Acknowledgments

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