# Grazing incidence small-angle X-ray scattering studies of the synthesis and growth of CdS quantum dots from constituent atoms in SiO<sub>2</sub> matrix

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Grazing incidence small angle X-ray scattering was applied to study the synthesis and growth of CdS quantum dots (QDs) from Cd and S atoms implanted in SiO<sub>2</sub>. For a dose of  $10^{17}$ /cm<sup>2</sup>, the partial synthesis of CdS QDs occurred already during implantation, with only moderate size increase upon subsequent annealing up to  $T_a$ =1073 K. The dynamics of QD synthesis and growth were considerably different for just two times lower dose, where synthesis started only if the implanted samples were annealed at  $T_a = 773$  K or higher, with a strong increase of the size of QDs upon annealing at higher  $T_a$ . The results suggest that high-dose implantation followed by low-temperature annealing could lead to better defined sizes and narrower size distributions of QDs.

### Keywords: nanocrystals, quantum dots, X-ray scattering, SAXS, GISAXS, implantation, CdS

#### 1. Introduction

Nanosized semiconductor particles or quantum dots (QDs) have been investigated extensively during the last decade, due to considerable change of electronic, optical and other properties of nanoparticles with respect to corresponding bulk materials. The main interest in wide-band-gap semiconductors QDs stem from pronounced effects of quantum confinement and from powerful visible photoluminescence, which are strongly dependent on the particle size. By controlling the particle size the tunability of the bandgap becomes possible. Wide band-gap II-VI semiconductorglass composites, in particular, have been rising considerable interest, since it was reported, first by Jain and Lind (1983), that they posses a substantial third-order optical nonlinear coefficient at room temperature. Thanks to that property as well as to the fast response time, such systems have a potential for interesting applications in optical devices such as wave-guides, high-speed optical switches, or bistable resonators (Meldrum et al., 2001).

Synthesis of QDs by ion implantation has a number of advantages: more freedom from limitations of thermodynamics, extreme chemical purity, exceptional versatility in the choice of active components and underlying matrix, and compatibility with planar technology. In contrast to equilibrium processes, here the low solubility of implanted species in the matrix is an advantage, since implantation and subsequent annealing leads to precipitation, i.e. the formation of nanocrystals.

Sequential implantation of equal doses of constituent atoms offers a unique way to produce compound-semiconductor QDs (Budai *et al.*, 1997; White *et al.*, 1998, 1999; Meldrum *et al.*, 1999; Bonafos *et al.*, 1999; Desnica *et al.*, 2000; Meldrum *et al.*, 2001; Karl *et al.*, 2001). However, optimization of implantation parameters and post-implant procedure, in order to achieve a proper size and

size distribution of implantation-produced QDs appears to be the most challenging task for this otherwise unparalleled method (Meldrum *et al.*, 2001). In this paper the formation and growth of CdS QDs in the implanted layer, as a function of annealing temperature and ion dose was investigated by means of grazing incidence small angle X-ray scattering (GISAXS).

#### 2. Experimental details

Amorphous SiO<sub>2</sub> substrates (fused silica; Corning 7940) were implanted with 3 different doses:  $D1=10^{17}/\text{cm}^2$ ,  $D2=5x10^{16}/\text{cm}^2$  and  $D3=2.5x10^{16}/\text{cm}^2$  of Cd and S atoms (each), that resulted in volume peak concentrations up to about  $6.3x10^{21}/\text{cm}^3$ . That corresponds to ~20% atomic fraction of Cd+S atoms, or ~40% of the weight fraction in SiO<sub>2</sub>. Implantation energies (320 keV for Cd and 115 keV for S) were selected to create similar concentration profiles of Cd and S atoms. After the implantation, in order to incite diffusion of Cd and S atoms and stimulate the formation and growth of CdS nanocrystals, each sample was annealed at a selected annealing temperature,  $T_a$ , in the 573 to 1173 K range (for 1h, in vacuum). Implanted but unannealed samples and non-implanted but equally annealed substrates were used as references.

GISAXS experiments were carried out by using X-ray photons of energy E = 8 keV (wavelength,  $\lambda = 0.154$  nm) at the Austrian SAXS beamline (Amenitsch *et al.*, 1997) of the synchrotron radiation facility ELETTRA, Trieste, Italy. The GISAXS patterns were recorded with a 2D CCD detector containing 1024x1024 pixels, placed in the *y*-*z* plane, perpendicularly to the specular *x*-*z* plane. Spectra were first corrected for background intensity and detector response, and then for refraction and absorption effects (Buljan *et al.*, 2002; Kutsch *et al.*, 1997).

#### 3. Results and discussion

Fig. 1 depicts the volume concentration of implanted ions as a function of depth, as deduced from Rutherford back scattering (RBS) measurements. For all three doses the volume peak concentration was at a depth of  $\sim$ 130 nm, and the maximum depth was around 260 nm. The concentrations of Cd and S atoms are overlapping for all three doses within a few percent showing that the implantation parameters were well selected.



#### Figure 1

Depth distributions of concentration of Cd ions (full symbols) and S ions (empty symbols) after implantation into SiO<sub>2</sub>, with doses  $D1=10^{17}/\text{cm}^2$ ,  $D2=5\times10^{16}/\text{cm}^2$  and  $D3=2.5\times10^{16}/\text{cm}^2$  of Cd and S atoms, each, as determined from RBS.

Fig. 2 shows two-dimensional (2D) GISAXS patterns of CdS nanoparticles in  $SiO_2$  for unannealed and annealed samples

implanted with the dose  $D1 = 10^{17}$ /cm<sup>2</sup> of Cd and S atoms each. The incidence angle of the X-ray beam,  $\alpha$ , was  $\alpha = \alpha_{c} + 0.05^{\circ}$  (which corresponds to the penetration depth of 170 nm), where  $\alpha_{\rm c}$  denotes the critical angle for the total external reflection (0.23°). The 2D patterns exemplify maps of scattering intensities in reciprocal space  $(S = q/2\pi)$ , where  $q = (4\pi/\lambda)\sin\beta$  is the modulus of the scattering vector, and  $2\beta$  is the scattering angle). In order to block strong surface signals (reflected beam, Yoneda peak, etc.) in/close to the specular plane, a beam stopper was inserted, allowing better sensitivity for the weak diffuse scattering at larger S. Both GISAXS patterns comprise a highly intense region close to the center (remaining part of surface and possibly other signals, which are not of particular interest in this paper) and half rings, which are considered as due to scattering from CdS nanocrystals formed in the substrate. Hence, we can conclude that even in the as-implanted sample isolated CdS nanoparticles are already being formed. After the appropriate corrections were applied, both rings proved to be circular and similar in shape in all directions [Buljan et al., 2002]. The distance of the ring from the origin is related to the average separation of the nanocrystals in a particular direction, hence the average interparticle distance, L, is very similar in all directions. Analogously, shape of the scattering pattern being very similar in all directions indicates that particles are nearly spherical. Annealing causes the increase of the total scattering intensity, the moderate shift of the maximum intensity toward smaller S and localization of the intensity around the ring. However, annealing did not change considerably the basic morphology and distribution of CdS nanoparticles, formed already during implantation.



#### Figure 2

Two-dimensional GISAXS patterns of CdS in SiO<sub>2</sub>, obtained by implantation of constituent atoms with dose  $D1=1\times 10^{17}$  /cm<sup>2</sup>. (a): as-implanted sample; (b) sample annealed for 1h in vacuum at 1073 K.

Comparative scans of 2D GISAXS patterns along the z-axis, offset for the beam-stopper width, are depicted in Fig. 3 for the series of samples implanted with the same dose,  $D1=10^{17}$ /cm<sup>2</sup>, but annealed at different annealing temperatures,  $T_a$ , from room temperature (not annealed sample) till the  $T_a = 1073$  K. Spectra depict the dependence of scattering intensity, I(S), on S along the z axis. Specifically, each annealing step causes a certain shift of the

intensity maximum toward lower *S* as well as a somewhat steeper decrease of I(S) on the right side of the maximum. However, neither the peak position nor the shape of the spectra change significantly for the whole range of applied  $T_{a}$ .

When a simple particle scattering model (Guinier approximation) is applied in the analysis of such GISAXS profiles, the average cluster diameter D is obtained from the radius of gyration,  $R_{g}$ , computed from the slope of the linear region of the  $\ln I(q)$  versus  $q^2$  dependence. The average distance among nanocrystals is determined from the position of the interference peak,  $S_{\rm m}$ , as  $L=1/S_{\rm m}$ . Numerical results for  $R_{\rm g}$  and L for both samples are given in the inset of Fig 3. The error in determination of absolute values of  $R_g$  and L was less than  $\pm 10\%$ , and comes primarily from the narrow angular range where the approximation is applicable, limited by a strong structural factor influence from the low angle side, and by the large qR product from the wide angle side. However, keeping in mind the very good measurement statistics, the relative error is much smaller. The finding that for  $D1=10^{17}$ /cm<sup>2</sup> (and only for such very high dose) a fraction of Cd and S atoms synthesize already during implantation agrees well with the qualitative evidences obtained by other methods on the same series of samples. In UV-visible light transmittance measurements new absorption features were observed: an absorption peak just above 2.5 eV was interpreted as the (blue-shifted) Eo transition, while two absorption peaks around 5 eV were perceived as the  $E_{1A}$  and  $E_{1B}$ transitions in CdS (Desnica et al., 2001a). In reflectance measurements performed in the same spectral range the interference fringes appeared, revealing the change of index of refraction, apparently due to the formation of the CdS phase in the implanted layer (Desnica et al., 2001b). In Raman spectrum the CdScharacteristic LO peak appeared around 300 cm<sup>-1</sup>, as well as a low frequency Raman band, which was assigned to the presence of nanocrystals (Desnica et al., 2000).



#### Figure 3

Specular scans along z axis, offset for the beam-stopper width, of 2D GISAXS pattern of samples implanted with dose  $D1=1\times 10^{17}$  /cm<sup>2</sup> of Cd and S ions, each, and annealed at various annealing temperatures,  $T_a$ : room temperature (not annealed), 573 K, 773 K, 973 K and 1073 K, for 1h in vacuum. The inset shows numerical data for Guinier radius  $R_g$ , and average inter-cluster distance, *L*.

The implantation at just half the dose,  $D2=5\times10^{16}/\text{cm}^2$ , did not cause any detectable synthesis of Cd+S atoms during implantation. This GISAXS finding again agrees well with results of the other methods mentioned above, where no CdS-related signal could be observed in as-implanted samples. Furthermore, for samples annealed with dose D2 the dynamics of nanocrystals synthesis and growth appears to be considerably different. The first QD-related GISAXS signal was observable only after annealing at  $T_a$  = 773 K, while annealing at higher  $T_a$  resulted in considerably larger average size of the QDs. The comparative signals for doses D1 and D2 again scans of 2D GISAXS patterns along the z-axis - are shown in Fig. 4 for samples annealed at  $T_a$ = 773 K and  $T_a$ = 1073 K. While for dose D1 the increase in the average size of QDs was less than 10%, for D2 the average size almost doubled going from  $T_a = 773$  K to  $T_a =$ 1073 K (for dose D1 the whole increase in size was just 20%, going from  $T_a = RT$  to 1073 K). Samples implanted with even lower dose, D3 (not shown), revealed analogous dynamics of nanocrystal growth: The first QDs-related GISAXS signal appeared only after annealing at  $T_a = 973$  K (with  $R_g = 1.15$  nm, and L = 5.2 nm), again showing strong increase of  $R_g$  and L with the increase of  $T_a$ .

For dose *D*1, the average size of QDs in as-implanted sample was D = 5.4 (assuming diameter  $D = 2R_g(5/3)^{1/2}$ ). It appears that these QDs, formed already during the implantation, act as nucleation centers, growing very slowly (at least up to  $T_a = 1073$  K). In contrast, at lower doses, it seems that energy brought in by implantation cannot be used effectively for the synthesis of QDs.





Comparative specular scans along *z*-axis of samples implanted with doses  $D1=1\times 10^{17}$  /cm<sup>2</sup> (thin lines) and  $D2=5\times 10^{16}$  /cm<sup>2</sup> (thick lines) after annealing at 1073 K and 773 K. The inset shows numerical data for Guinier radius  $R_{\rm g}$ , and average inter-cluster distance, *L*.

Therefore post-implantation annealing at relatively high  $T_a$  is necessary to accomplish Cd+S synthesis by the diffusion processes only. For example, for dose D2 the one-hour annealing at 1073 K was needed to obtain approximately the same quantity of CdS QDs as in un-annealed sample, implanted with just twice higher dose. High annealing temperatures are generally undesired in material processing due to potential contamination and in synthesis of QDs have additional disadvantages. Treatments at high temperatures are diffusion-controlled processes, which allow less outer control over the QDs synthesis and growth. Furthermore, equilibrium, thermodynamical requirements tend to broaden the size distribution, since the size increase of larger QDs is energetically more favorable (larger decrease of free energy) than the size increase of smaller QDs (Reiss & Heinig, 1996). Hence, the combination of very high-dose implantation and low-*T* post-implantation annealing should give a better chance to obtain a narrower size distribution at a desired average size, particularly if combined with multi-energy implantation, which gives initial quasi-uniform distribution of implanted atoms.

Spectra for implantation doses D1 and D2 after  $T_a = 1073$  K, taken at different incident angles, are shown in Fig 5. Incidence angles  $\alpha$  were selected as  $\alpha_c$ ,  $\alpha_c + 0.05^\circ$ ,  $\alpha_c + 0.1^\circ$ , and  $\alpha_c + 0.2^\circ$ , corresponding to the penetration depths 35 nm, 170 nm, 250 nm and 390 nm, respectively. This series of measurements was used for depth profiling of average sizes and distances. At  $\alpha = \alpha_c$ , the incident beam propagates quasi-parallel along and underneath the sample surface. Even a very small increase of  $\alpha$  results in a considerable increase of penetration depth, so that in depth-profiling the first step above  $\alpha_c$  cannot be made very small. At the first step selected in this study ( $\alpha = \alpha_c + 0.05^\circ$ ) X-rays penetrate already up to the depth somewhat deeper than the maximum of the concentration of implanted atoms. The average size of QDs for this incidence angle was found to be considerably larger than for  $\alpha_{\rm c}$ . This expected increase is in qualitative agreement with the RBS results (Fig. 1). Further increase of incident angle did not bring practically any change, which is understandable, taking into account that a relatively small fraction of additional QDs contributes to the GISAXS signal, and that their influence to the signal is further diminished due to attenuation of both incident and exit beams from deeper parts of the implanted layer.



#### Figure 5

Specular scans along *z*-axis taken for different angles of incidence,  $\alpha$ , from samples implanted with doses dose  $D1 = 1 \times 10^{17}$ /cm<sup>2</sup> and dose  $D2 = 5 \times 10^{16}$ /cm<sup>2</sup> after annealing at 1073 K. 1:  $\alpha = \alpha_c$ ; 2:  $\alpha = \alpha_c + 0.05^\circ$ ; 3:  $\alpha = \alpha_c + 0.1^\circ$ ; and 4:  $\alpha = \alpha_c + 0.2^\circ$ . The inset shows numerical data for Guinier radius  $R_g$ , and average inter-cluster distance, *L*, for the first two angles.

Spectra were also analyzed with LMA approximation (Pedersen, 1994; Babonneau et al., 2001). No reasonable fit could be obtained with a single Gaussian size distribution function. This is in contrast to spectra of CdS QDs obtained by multi-energy implantation of Cd and S atoms (in which the concentration of implanted ions was, therefore, quasi-constant along most of the implanted layer), where excellent LMA fits were obtained assuming single Gaussian distribution (Buljan et al. 2002; Desnica et al., 2002b). An unsatisfactory fit might not be surprising, since for samples implanted with single energy there is a considerable initial depth distribution of atoms (Fig. 1). Hence, it is very likely that the size of synthesized QDs has a strong depth distribution as well, which may easily deviates from the (single) Gaussian distribution, as discussed below. When two size distributions of QDs were assumed, one centered around a relatively large and the other around a considerably smaller average size, very good fits were obtained. However, in such analysis there is twice the number of fitting parameters, so conclusions drawn from it have to be treated with great caution. For samples implanted with dose D1, the LMA analysis suggested that the increase of  $T_a$  primarily increased the total fraction of synthesized CdS material, and the fraction of 'large' QDs (diameter D<sub>1</sub> being around 6.3 nm, with standard deviation,  $\sigma$ = 1.4) toward 'small' QDs (diameter  $D_s$  being around 3.6 nm,  $\sigma = 0.4$ ). The diameter and  $\sigma$  of neither larger nor of smaller nanoparticles increased significantly with  $T_{\rm a}$ . Hence, LMA results suggest that  $R_{\rm g}$ radii obtained from Guinier approximation are, in fact, averaged values of two size distributions.

The possibility of bimodal distribution of CdS QDs, obtained after annealing of samples having initial simple quasi-Gaussian distribution of implanted Cd and S atoms (Fig. 1) is intriguing. However, bimodal distributions have been already observed for several other II-VI semiconductors, also in cases when QDs were obtained by ion implantation of constituent atoms and subsequent annealing. For instance, Bonafos et al. (1999) have observed bimodal distribution of ion-beam synthesized ZnS nanoparticles in SiO<sub>2</sub>, Meldrum et al. (2001) of PbS nanoparticles in SiO<sub>2</sub>, and Karl et al. (2002) of ZnTe in SiO<sub>2</sub>; all evidenced by cross-sectional TEM. We tentatively interpreted possible bimodal size distribution in our samples as being a result of strong concentration-enhanced diffusion of smaller CdS QDs and their further clustering into large QDs (Oswald ripening) in the central part of the implanted layer, where the concentration of implanted atoms is much higher. Hence, we assume that small QDs in regions of diluted concentrations of Cd and S atoms (regions near the surface and close to the end of the implant range) grow slowly (at least in  $T_a$  range applied in this study) since they are relatively far apart. In contrast, small QDs formed close to the maximal concentration of Cd and S atoms still remain close to each other due to very high initial concentrations of Cd and S atoms. Therefore they continue to grow quickly into large CdS nanocrystals. Stronger lattice strain in this region, present due to huge concentration of large foreign atoms in a small-atom host (Meldrum et al., 2001), possibly also promotes the additional clustering. Cross-sectional TEM analysis has to be done in order to check the above hypothesis. The results exemplify additional problems of single-energy implants, which brings strongly uneven concentration of initial atoms, and then even more varying sizes of synthesized QDs throughout the implanted layer.

#### 4. Conclusions

Grazing incidence small angle X-ray scattering (GISAXS) was applied to study the synthesis and growth of CdS quantum dots (QDs) in SiO<sub>2</sub>, after ion implantation of high and equal doses of Cd and S atoms, and subsequent annealing. The analysis of GISAXS patterns gave an estimate of the nanocrystallite average size, shape and intercluster distance, as well as the size and distance depth distributions, and revealed changes of these parameters as a function of thermal treatment. The GISAXS study proved the success of formation of CdS quantum dots from constituent atoms as well as the establishment of isotropically distributed 3D ensemble of these QDs in the amorphous SiO<sub>2</sub> substrate. Only for the highest dose,  $10^{17}$ /cm<sup>2</sup>, the synthesis of CdS quantum dots occurred already during implantation. For those samples the increase of average size of QDs and intercluster distances was very moderate from room temperature up to  $T_a = 1073$  K annealing step, with annealings primarily changing the fraction of synthesized Cd and S atoms. In contrast, for lower doses, where synthesis occurred only by thermal treatmentinduced diffusion of constituent atoms, the dynamics of QDs synthesis and growth is very different, resulting in a strong increase of size with  $T_{\rm a}$ . The results suggest that the combination of very high-dose multi-implantation and low-T post-implantation annealing could give a better chance to obtain a narrower size distribution at a desired average QD size, particularly if combined with multi-energy implantation.

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