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GISAXS study of shape and size of CDS nanocrystals formed in monocrystalline silicon by ion implantation

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Abstract

Grazing incidence small angle X-ray scattering (GISAXS) was applied to study size and shape as well as distribution of CdS nanocrystals formed in monocrystalline silicon substrate by separate implantation of constituent elements with a dose of $4.5 \times 10^{16}/cm^2$ each, and subsequent annealing at 1000 °C. Apart from surface scattering, the 2D GISAXS patterns also show a particle contribution, which is twofold: diffuse scattering centered at the direct beam position, and two streaks at both sides, crossed at the direct beam position, coming from the surface scattering from the facets of the particles.

The streak inclination to the sample surface corresponds to the silicon (1 1 1)-plane angle, where there is a minimum in nanocrystal growth energy. From the intensity distribution along the streak, the sizes of the facets are determined and compared to the overall particle sizes determined from the diffuse part of the scattering in order to gain information about the nanocrystal shape.

Keywords: Nanocrystals; Quantum dots; SAXS; GISAXS; Implantation; CdS

1. Introduction

Direct wide-band-gap II–VI semiconductors, like CdS, have a huge potential for a variety of applications, especially in the areas of light-emitting and light-detecting devices, photovoltaic conversion (solar cells), X-ray and γ-ray detection, etc. Systems of small dimensions (nanocrystals or quantum dots) exhibit considerably different optical and electronic properties than bulk semiconductors due to quantum confinement. Due to their large optical nonlinearity as well as fast response times, systems of CdS crystallites buried in glass show promise for very interesting applications in optical devices such as wave-guides, high-speed optical switches or bistable resonators.

The traditional method of preparing quantum dots in optical semiconductor devices is adding semiconductor components into glass melt. During the solidification process however, one has not sufficient control over the growth process, which

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results in nonideal sample properties (defects, semiconductor surface states, fluctuations in dopant size and distribution). Most of these drawbacks are overcome by the novel technique of ion implantation [1–3]. In order to investigate the structure of films prepared by this new method, the grazing incidence small angle X-ray scattering (GISAXS) technique was applied on monocrystalline silicon films, in which CdS nanocrystals had been synthesized by separate implantion of Cd and S ions, and which had been annealed subsequently. Implantation into an amorphous substrate, where the growth of particles is suppressed by isotropical forces of the amorphous matrix usually results in spherical shape. However, in a monocrystalline surrounding, one can expect the growth of faceted particles because the diffusion of constituent atoms is directed by the crystal field and the pressure of the crystalline matrix limiting the particle growth is defined by the crystal symmetry.

2. Experiment

In this work, a standard monocrystalline silicon substrate, about 0.5 mm thick, was implanted with a dose of $4.5 \times 10^{16}/\mathrm{cm}^2$ Cd and S atoms each. The ion energy was chosen to give the same (Gaussian) depth density distribution of the dopants. The resulting peak volume concentration was about 3×10^{21} cm^{-3} for each of the Cd and S atoms at $\sim$130 nm depth, as determined by Rutherford backscattering. This corresponds to a 10% atomic fraction of Cd + S atoms (compared to the number of host atoms), or $\sim$20% weight fraction. The sample was subsequently annealed at 1000 °C, to provoke diffusion and synthesis of CdS crystallites. In this way a CdS nanocrystallite rich "film" was formed inside the monocrystalline silicon substrate.

The structure of the film was investigated by means of small angle X-ray scattering (SAXS). To avoid the problem of high absorption in the silicon substrate, grazing incidence was applied (GISAXS).

For X-rays, the index of refraction at an air/solid interface is less than 1, i.e. $n = 1 - h' - \mathrm{i}h''$, where h' and h'' are dispersion and absorption coefficient, respectively. Therefore, total reflection happens for angles smaller than $\alpha_\mathrm{C} = (2h')^{1/2}$ (the critical angle). For larger angles, reflectivity decreases steeper than the value given by Fresnel theory due to deviations from ideal flatness [4]. Together with the reflected beam a diffuse scattering is present, although of much lower intensity. This diffuse scattering from a surface, measured under nonspecular condition, i.e. when the scattering angle is different from the incidence angle, yields information about structural features along the surface. With the change of incidence angle, the penetration depth is changing, and this can be used to probe different parts of the sample versus the distance from the top surface. When randomly distributed, well defined particles are present within the film, they cause additional scattering, which is easily separated from the surface scattering, since the former is not incident angle dependant [5].

GISAXS measurements were performed at the ELETTRA synchrotron radiation source at Trieste (Italy), at the SAXS beamline, using a X-ray photon energy of 8 keV ($\lambda = 0.154$ nm) [6]. The shape and size of the incident beam was adjusted by slits ($h = 0.1$ mm, $w = 5$ mm). The sample was mounted on a stepper-motor controlled tilting stage with a step resolution of 0.001°. The stage (and the sample surface) was aligned horizontally and parallel to the beam within 0.1°. Measurements were taken at different, fixed grazing angles on the sample, using a 2D CCD detector at a fixed position. The specular part of the scattered intensity had been blocked by a beamstop in order to increase the sensitivity for the diffuse part of the scattering off the specular plane (particle contribution).

3. Results and discussion

In Fig. 1 the 2D GISAXS pattern from the annealed, cadmium and sulfur implanted monocrystalline sample is shown, where $S = (2\sin\theta)/\lambda$, 2θ is the scattering angle and λ is the X-ray wavelength. The central part (white vertical strip in the figure),

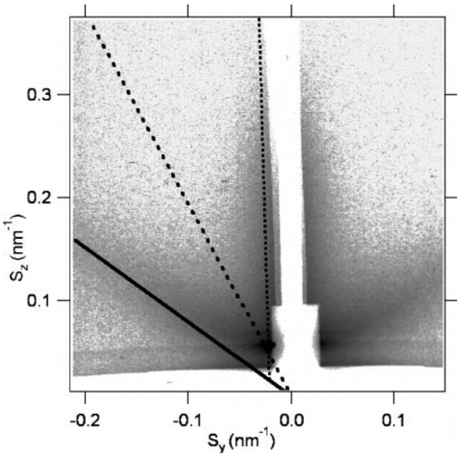

Fig. 1. 2D GISAXS pattern (S_z and S_y are in direction perpendicular and parallel to the sample surface, respectively) from annealed, Cd and S separately implanted monocrystalline silicon. The white, vertical strip is the covered specular plane intensity.

where the intense surface scattering would be, has been covered by a beamstop in order to resolve the much weaker diffuse scattering from the particles. Still, the wide (horizontally) Yoneda peak can be seen at the angle which equals the grazing plus critical angle (the minimum angle at which the scattering from within the sample can be detected). The rest of the scattering pattern is attributed to the particle scattering and it is not changing it's position with the change of grazing angle. Besides of spherical or isotropicaly oriented particles contribution (which is also present, but depends only on the total scattering angle), some kind of preferred orientation of nonspherical particles is evident. The direction of the inclined streaks makes about 30° with the sample surface, i.e. to the crystal (0 0 1)-plane, which corresponds to silicon (1 1 1)-plane orientation.

Evidently, the nanoparticles do not have spherical, but faceted shape. When grown without confinement from outside (like in free space, or in isotropic external force field, like in amorphous substrate), spherical particles are grown typically, and only under certain conditions faceted shape would be formed. These facets would follow the directions defined by crystal planes in the particle, but there would be no reason for them to have preferred orientation to some external plane. Also the found inclination angle does not match the d-spacing/plane orientations in an CdS crystal.

Since the particles have been grown in a silicon crystal, the resistance that the crystal poses for their growth is defined by the silicon crystal planes orientation, and therefore the shape of the particles is defined by these planes. Furthermore, as the substrate is a single crystal the facets would have the same orientation to the sample surface, i.e. (0 0 1) crystal plane. Not accidentally, the inclination of the streaks is very close to the silicon (1 1 1) diffraction angle (30°) and it has already been found that implant nanoparticles in silicon have facets in this plane [7]. Depending on the implant and implantation parameters, these faceted particles are found in truncated (''hexagonal'') or nontruncated (octahedral) shape [1].

In principle, a scattering pattern similar to that in Fig. 1 could be generated by vacancies and/or alien atom agglomerated to the low surface energy (1 1 1) Si crystal plane in form of plates or needles. However, TEM investigation of this sample has detected only the CdS nanocrystals with the facets aligned with the (1 1 1) Si crystal plains.

Given the single energy implantation, the density of Cd and S close to the sample surface is quite low, therefore the presence of CdS on the sample surface (e.g. in form of pyramid-like islands) is not probable. Therefore, we conclude that the observed scattering comes from the inside of the silicon.

CdS has about four times the electron density of Si, and because of this difference in dielectric constant, the facets act like small fragments of a mirror. Since the angle to the incoming beam is very small (roughly equal to the grazing angle) the reflectivity is rather high, and although distributed randomly within the substrate, they reflect coherently into same direction. Therefore the intensity along the streaks is much higher than the isotropic particle scattering (standard SAXS) which is also present as a consequence of the difference of the electron density, and because there is a certain concentration of nonfaceted particles in a rather broad size distribution, as can be seen from Fig. 2

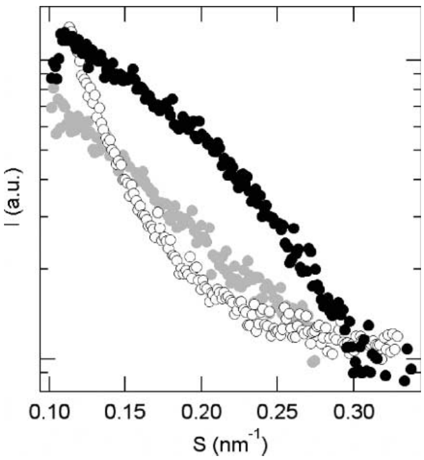

Fig. 2. Scans of GISAXS taken from Fig. 1 versus S. Black and gray dots (facets scattering) and open circles (diffuse particle scattering), are taken along dotted, full and dashed line, respectively.

(open circles). The concentration of the later can be estimated to be less than 10%, according to the diffuse scattering intensity.

In Fig. 2 scans of the scattering intensity are shown as black and gray dots and open circles, obtained along dotted, full and dashed line, respectively, in Fig. 1. The open circles represent the diffuse scattering from particles (distributed evenly around the direct beam), while the scattering caused by the facets, corrected for the particle and surface scattering, is represented by full dots. The similarity of scattering along vertical and inclined streaks is the confirmation of the truncated shape of the particles. Due to the Silicon crystal symmetry, the particles are expected to be similar to truncated tetrahedra, i.e. roundshaped sufficiently for applying Guinier analysis in order to estimate their size. From a simple Guinier fit, a Guinier radius $R_G = 1.5$ nm is found. If the particles are approximated with spheres ($R_{SPH} = \sqrt{(5/3)}R_G$), an average nanoparticle size of 3.8 nm is obtained.

4. Conclusion

GISAXS was successfully applied to the study of shape and size of CdS nanoparticles formed in monocrystalline silicon by annealing after separate implantation of Cd and S. The scattering arises from CdS nanocrystals, which are mainly faceted particles with (1 1 1) silicon plane oriented facets, together with (1 0 0) oriented truncation planes.

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