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CdS Nanocrystals Formed in SiO₂ Substrates by Ion Implantation

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Abstract

In this work CdS nanocrystals were formed in SiO₂ substrates by implantation of Cd and S atoms (up to 10¹⁷/cm²) and subsequent annealing (up to 900°C). The implanted and annealed layer was studied by X-ray Diffraction (XRD), UV transmittance and reflectance measurements (energy range 1.4 - 6.5 eV), and Raman spectroscopy. Upon annealing all methods proved the synthesis of CdS crystallites from the starting components, and the features characteristic of the CdS-phase were strongly and consistently dependent on ion dose and annealing temperature. The analysis of the results shows that by implantation and post-implantation treatment the average size of CdS crystallites can be controlled, and that smaller CdS nanocrystals are obtained for lower doses and lower annealing temperatures.

Keywords: nanocrystals, Cadmium Sulfide, CdS, II-VI, implantation

1. Introduction

Direct wide-band-gap II-VI semiconductors, including CdS, have a huge, still insufficiently tapped, 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.* [1]. Systems of small dimensions (nanocrystals or quantum dots), exhibit considerably different optical and electronic properties than the bulk semiconductors due to quantum confinement [2]. Due to the large optical non-linearity as well as a fast response time, 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[3,4]. In this work ion beams were used for the synthesis of CdS nanocrystals. In contrast to conventional methods, implantation offers exceptional flexibility in the choice of active components and underlying matrix [5], good control and reproducibility, and materials engineering on a sub-micron scale providing and enabling exceptionally small technological devices.

2. Experimental details

SiO₂ (fused silica; amorphous) substrates (Corning 7940) were implanted with 3 different doses: 2.5·10¹⁶/cm², 5·10¹⁶/cm² and 10¹⁷/cm² of Cd and S atoms, that resulted in volume peak concentrations up to about 6.3·10²¹/cm³, at depths of 130 nm. Implantation energies (320 keV for Cd and 115 keV for S) were selected to create similar concentration profiles of Cd and S atoms, which was proven by Rutherford Back Scattering (RBS).

Annealing temperatures, T_a, were in the 300° to 900° C range (1 hour at each T_a in what environment??). Non-implanted substrates as well as implanted but unannealed samples were used as references. Other references were unimplanted pieces of the same substrate (SiO₂), which went through the same annealing procedure at the same annealing temperatures as the implanted and annealed samples.

The implanted and annealed layer was studied by X-ray Diffraction (XRD), Raman spectroscopy, and UV transmittance and reflectance measurements (energy range 1.4 - 6.5 eV).

3. Results and Discussion

3.1. X-ray diffraction

Figure 1 depicts the X-ray diffraction (XRD) pattern of the SiO₂ substrate (a), and that of SiO₂ after implantation with Cd and S ions and annealing at 900°C (b). Sharp peaks in curve b), superimposed on the broad amorphous substrate signal, were identified as CdS (hexagonal) by matching with the JCPD database (Joint Committee on Powder Diffraction Standards). In comparison to the background signal from the amorphous substrate, the characteristic CdS peaks are quite weak, indicating that the content of CdS embedded in SiO₂ is rather small in the volume region probed by X-rays.

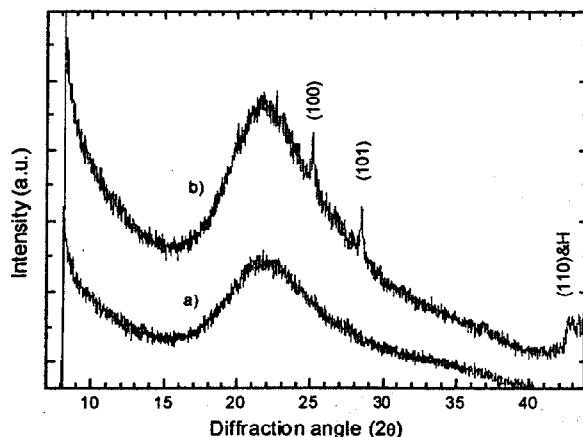


Fig. 1. X-ray diffraction pattern of SiO₂ substrate (a), and of a sample implanted with 10¹⁷/cm² of Cd and S atoms and subsequently annealed at 900°C (b). CdS-related lines are indicated, while the band H originates from the steel sample holder.

3.1. Optical Characterization

Representative spectra in Fig. 2 illustrate changes in optical absorption due to the formation of a CdS phase in the SiO₂ matrix after annealing of samples implanted with different doses of Cd and S. The absorbance of the CdS bulk monocystal and that of the SiO₂ substrate are shown for

comparison. Figure 2a demonstrates the increase of optical density (absorbance) due the formation of the CdS phase. The onset of the absorption depends on the ion dose and post-implantation thermal treatment, and shifts toward larger wavelengths (approaching the position of the bulk CdS; dashed curve) for larger doses and higher T_a s.

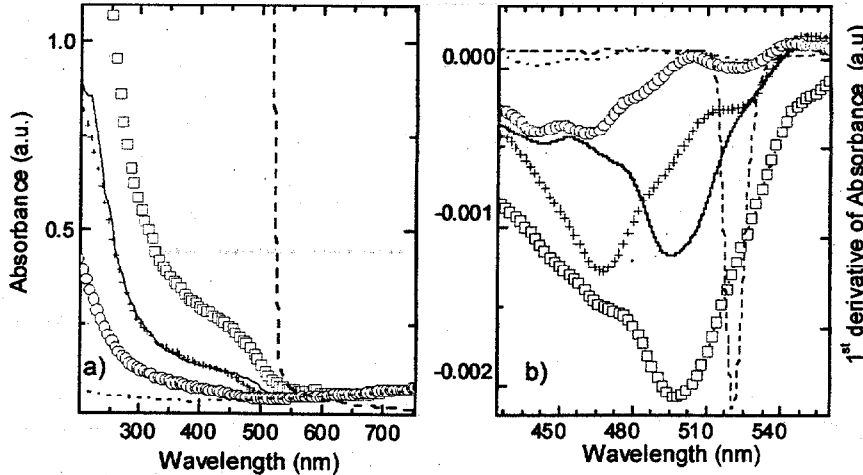


Fig.2. Representative optical absorption spectra of CdS formed in SiO₂ (a), and the first derivatives of the same spectra (b). Dose effects for $T_a = 700^\circ\text{C}$: \square - $10^{17}/\text{cm}^2$, $+$ - $5 \cdot 10^{16}/\text{cm}^2$, \circ - $2.5 \cdot 10^{16}/\text{cm}^2$. solid line refers to $5 \cdot 10^{16}/\text{cm}^2$ but for $T_a = 900^\circ\text{C}$. Also shown: bulk CdS (dash), and SiO₂ (dots).

To study the effects more quantitatively the numerical 1st derivative of the absorbance (Fig. 2b) was used. The position of the minimum provides an estimate of the energy bandgap of the CdS nanocrystals in a particular sample [6]. The blueshift in the optical absorption spectra reflects the confinement of the charge carriers. By using the relation connecting the blueshift and the average size of the nanocrystals in an effective mass model [7], the average size of the nanocrystals is estimated to be in the range from 3 to above 30 nm, depending on ion dose and T_a .

Reflectivity (R) in IR region has often been used to analyze nanometer-size structures. Here we demonstrate that data in the visible-UV range can also give useful additional information.

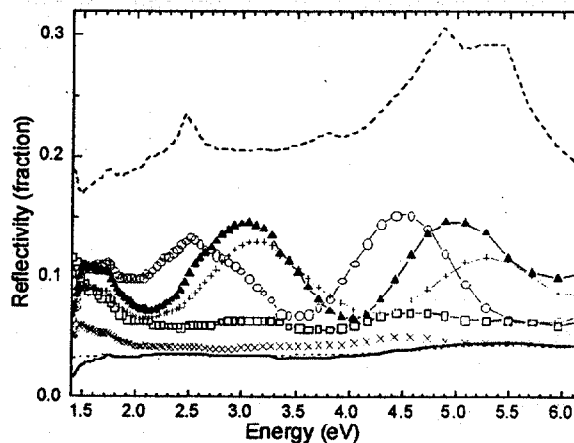


Fig. 3. Representative reflectivity spectra after implantation with $5 \cdot 10^{16}/\text{cm}^2$ of Cd and S ions and annealing: $T_a = \text{RT}$ (-x-); $T_a = 300^\circ\text{C}$ (-□-); $T_a = 500^\circ\text{C}$ (-+-); $T_a = 800^\circ\text{C}$ (-▲-); and $T_a = 900^\circ\text{C}$ (-○-). Also shown: spectra of SiO₂ substrate (solid line) and after $T_a = 900^\circ\text{C}$ anneal (dots); bulk CdS (dash).

Several representative spectra of R in the 1.4-6.2 eV range, for samples implanted with $5 \cdot 10^{16}/\text{cm}^2$ of Cd and S atoms, are presented in Fig. 3. The mere incorporation of Cd and S atoms into the substrate does not alter the reflectivity of SiO_2 significantly (curve for $T_a = \text{RT}$). This means that the refractive index of the Cd+S implanted layer, n_i , has not deviated substantially from the SiO_2 value, ($n_{\text{SiO}_2} = 1.44-1.46$ in the above range). However, as T_a increases, the formation of CdS crystallites in SiO_2 becomes nicely observable through the increase of the average n_i and the resulting appearance of strong interference fringes, since the refractive index of CdS is substantially higher ($n_{\text{CdS}} = 2.4-2.7$). (Thermal treatment of the substrate (dotted curve), also does not produce fringes, as expected). $T_a \geq 500^\circ$ is sufficient to create CdS and the resulting strong fringes. However, only for T_a above 800°C do the CdS crystals become large enough to show a distinct structure at about 2.5 eV, characteristic of bulk CdS, which is related to the E_0 transitions from the three-dimensional M_0 critical points in the Brillouin zone [8]. For higher ion doses (not shown) structures related to higher gaps of the E_{1A} and E_{1B} transitions become discernable, again only at high T_a s. The change of spacing between the extrema of interference fringes reflects changes of the effective thickness and n_i of the layer containing CdS nanocrystals.

In Raman spectra (not shown) the formation of CdS nanocrystals resulted in the appearance of a crystalline zone-center LO peak close to 300 cm^{-1} , and a 2LO peak, as well as in the emergence of low frequency Raman band. The width of the LO peak as well as the peak position of low frequency band were dependent on the size of the CdS nanocrystals.

4. Conclusions

CdS crystallites were formed in SiO_2 substrates by implantation of Cd and S ions. Upon annealing, all the characterization methods proved the synthesis of a CdS phase. In XRD the sharp lines, characteristic of hexagonal CdS, emerged superimposed on the amorphous SiO_2 -related broad background. In the transmittance measurements, absorption above 2.5 eV was observed, exhibiting a blue shift in E_0 , and indicating confinement of charge carriers. Consistent results were obtained in the reflectance measurements (appearance of interference fringes reflecting the formation of nano-CdS and structures related to bulk-CdS for higher T_a), as well in Raman spectroscopy (the appearance of the CdS LO peak and low frequency Raman band). All of these features were strongly and consistently dependent on ion dose and annealing temperature, while none of them appeared in control samples. Smaller CdS nanocrystals were obtained for lower doses and lower annealing temperatures.

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