

# CdS nanocrystals formed in SiO<sub>2</sub> substrates by ion implantation

U.V. Desnica<sup>a,\*</sup>, O. Gamulin<sup>b</sup>, A. Tonejc<sup>c</sup>, M. Ivanda<sup>a</sup>, C.W. White<sup>d</sup>,  
E. Sonder<sup>d</sup>, R.A. Zuhr<sup>d</sup>

<sup>a</sup> Semiconductors Laboratory, Division of Materials Physics, Physics Department, R. Boskovic Institute, Bijenicka 54, HR-10000 Zagreb, Croatia

<sup>b</sup> School of Medicine, Zagreb University, Salata 3, HR-10000 Zagreb, Croatia

<sup>c</sup> Department of Physics, Zagreb University, HR-10000 Zagreb, Croatia

<sup>d</sup> Oak Ridge National Laboratory, PO Box 2008, Oak Ridge, TN 37831, USA

## Abstract

In this work, CdS nanocrystals were formed in SiO<sub>2</sub> substrates by implantation of Cd and S atoms (up to 10<sup>17</sup>/cm<sup>2</sup>) 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. © 2001 Elsevier Science B.V. All rights reserved.

**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  $\gamma$ -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 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 [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

SiO<sub>2</sub> substrates (fused silica; amorphous, Corning 7940) were implanted with three different doses: 2.5 × 10<sup>16</sup>/cm<sup>2</sup>, 5 × 10<sup>16</sup>/cm<sup>2</sup> and 10<sup>17</sup>/cm<sup>2</sup> of Cd and S atoms, that resulted in volume peak concentrations up to about 6.3 × 10<sup>21</sup>/cm<sup>3</sup>, at depths of 130 nm. Implantation energies (320 keV for Cd and 115 keV for S) were selected to create similar concentration profiles for Cd and S atoms, which were proven by Rutherford back scattering (RBS).

Annealing temperatures,  $T_a$ , were in the 300–900°C range (1 h at each  $T_a$  in vacuum). Non-implanted substrates, as well as implanted but unannealed samples were used as references. Other references were unimplanted pieces of the same substrate (SiO<sub>2</sub>), 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 transmit-

\* Corresponding author. Tel.: +385-1-4561-173; fax: +385-1-4680-114.

E-mail address: desnica@rudjer.irb.hr (U.V. Desnica).

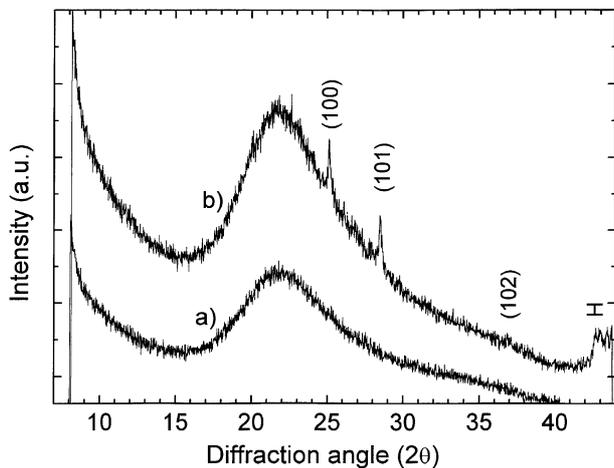


Fig. 1. X-ray diffraction pattern of  $\text{SiO}_2$  substrate (a), and of a sample implanted with  $10^{17}/\text{cm}^2$  of Cd and S atoms and subsequently annealed at  $900^\circ\text{C}$ . (b) CdS-related lines are indicated, while the band H originates from the steel sample holder.

tance and reflectance measurements (energy range 1.4–6.5 eV).

### 3. Results and discussion

#### 3.1. X-ray diffraction

Fig. 1 depicts the X-ray diffraction (XRD) pattern of the  $\text{SiO}_2$  substrate (a), and that of  $\text{SiO}_2$  after implantation with Cd and S ions and annealing at  $900^\circ\text{C}$  (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 character-

istic CdS peaks are quite weak, indicating that the content of CdS embedded in  $\text{SiO}_2$  is rather small in the volume region probed by X-rays.

#### 3.2. Optical characterization

Representative spectra in Fig. 2 illustrate changes in optical absorption due to the formation of a CdS phase in the  $\text{SiO}_2$  matrix after annealing of samples implanted with different doses of Cd and S. The absorbance of the CdS bulk monocrystal and that of the  $\text{SiO}_2$  substrate are shown for comparison. Fig. 2(a) demonstrates the increase of optical density (absorbance) due to the formation of the CdS phase. The onset of 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  $T_a$ .

To study the effects more quantitatively, the numerical first derivative of the absorbance (Fig. 2(b)) 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 20 nm, depending on the ion dose and  $T_a$ .

The reflectivity ( $R$ ) in the 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.

Several representative spectra of  $R$  in the 1.4–6.2 eV range, for samples implanted with  $5 \times 10^{16}/\text{cm}^2$  of Cd and S atoms, are presented in Fig. 3. The mere incorpora-

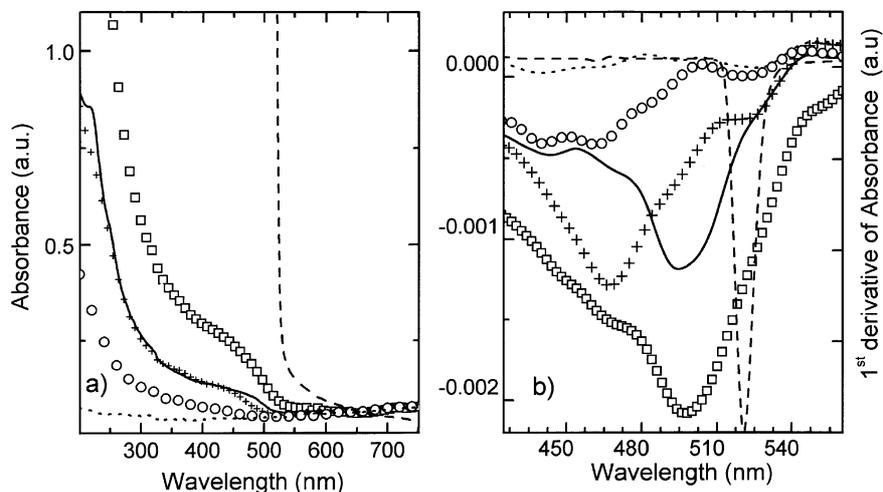


Fig. 2. Representative optical absorption spectra of CdS formed in  $\text{SiO}_2$  (a), and the first derivatives of the same spectra. (b) Dose effects for  $T_a = 700^\circ\text{C}$ : ( $\square$ )  $10^{17}/\text{cm}^2$ , ( $+$ )  $5 \times 10^{16}/\text{cm}^2$ , ( $\circ$ )  $2.5 \times 10^{16}/\text{cm}^2$ . Solid line refers to  $5 \times 10^{16}/\text{cm}^2$  but for  $T_a = 900^\circ\text{C}$ . Also shown: bulk CdS (dash), and  $\text{SiO}_2$  (dots).

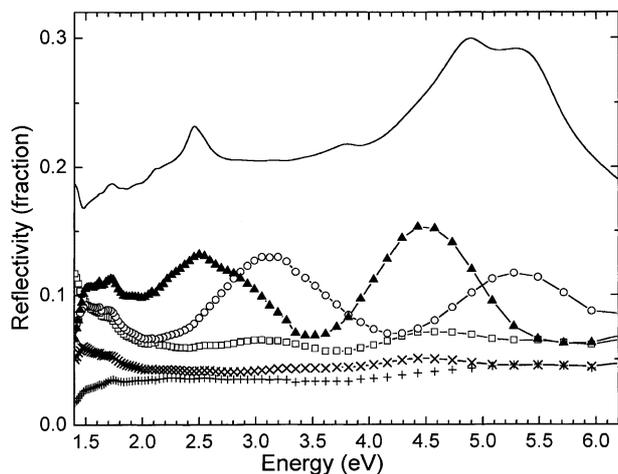


Fig. 3. Representative reflectivity spectra after implantation with  $5 \times 10^{16} / \text{cm}^2$  of Cd and S ions and annealing at:  $T_a = \text{RT}$  ( $-\times-$ );  $T_a = 300^\circ\text{C}$  ( $-\square-$ );  $T_a = 500^\circ\text{C}$  ( $-\circ-$ ) and  $T_a = 900^\circ\text{C}$  ( $-\triangle-$ ). Also shown: spectra of  $\text{SiO}_2$  substrate ( $-+-$ ) and bulk CdS (solid line).

tion of Cd and S atoms into the substrate does not alter the reflectivity of  $\text{SiO}_2$  significantly (curve for  $T_a = \text{RT}$ ). This means that the refractive index of the Cd + S implanted layer,  $n_1$ , has not deviated substantially from the  $\text{SiO}_2$  value, ( $n_{\text{SiO}_2} = 1.44\text{--}1.46$  in the above range). However, as  $T_a$  increases, the formation of CdS crystallites in  $\text{SiO}_2$  becomes nicely observable through the appearance of strong interference fringes, resulting from the increase of the average  $n_1$ , since the refractive index of CdS is substantially higher ( $n_{\text{CdS}} = 2.4\text{--}2.7$ ). Annealing temperatures above  $500^\circ\text{C}$  are sufficient to create CdS material and the resulting strong fringes. However, only for  $T_a$  in  $800\text{--}900^\circ\text{C}$  range do the CdS crystals become large enough to show a distinct structure at about  $2.5\text{ eV}$ , characteristic of bulk CdS, which is superimposed on fringes. This structure in bulk CdS 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  $T_a$ . The change of spacing between the extrema of interference fringes reflects changes of the effective thickness 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  $300\text{ cm}^{-1}$ , 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  $\text{SiO}_2$  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  $\text{SiO}_2$ -related broad background. In the transmittance measurements, absorption above  $2.5\text{ eV}$  was observed, exhibiting a blue shift in  $E_0$ , and indicating the confinement of charge carriers. Consistent results were obtained in the reflectance measurements—the appearance of interference fringes reflecting the formation of nano-CdS and structures related to bulk-CdS for higher  $T_a$ , as well as 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.

#### Acknowledgements

This research was supported by the Ministry of Science and Technology of Croatia. A portion of this research was performed at Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the US Department of Energy under contract DE-AC05-00OR22725.

#### References

- [1] U.V. Desnica, Prog. Cryst. Growth Charact. Mater. 36 (1998) 291–357.
- [2] R.F. Service, Science 271 (1996) 920–922.
- [3] L.E. Brus, Appl. Phys. A53 (1991) 465–474.
- [4] C.B. Murray, M. Nirmal, D.J. Norris, M.G. Bawendi, Z. Phys. D 26 (1993) 231–233.
- [5] A. Meldrum, C.W. White, L.A. Boatner, I.M. Anderson, R.A. Zuhr, E. Sonder, J.D. Budai, D.O. Henderson, Nucl. Instrum. Methods Phys. Res., Sect. B 148 (1999) 957–963.
- [6] B.G. Potter Jr., J.H. Simmons, J. Appl. Phys. 68 (1990) 1218–1224.
- [7] L.E. Brus, J. Chem. Phys. 80 (1984) 4403–4409.
- [8] S. Ninomiya, S. Adachi, J. Appl. Phys. 78 (1995) 1183–1190.