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UV–visible reflectivity study of the synthesis and growth of nanocrystals obtained by ion implantation

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Abstract

The reflectivity (R) in the UV–visible range was used to study CdS nanocrystals obtained by implantation of Cd and S ions into SiO_2 and subsequent annealing ($T_a = 300\text{--}900^\circ\text{C}$). We demonstrate that such an analysis can give very useful information about the process of nanocrystal formation and growth. The synthesis of even a small fraction of CdS is readily observable through the appearance of interference fringes since the refractive index of CdS, n_{CdS} , is substantially higher than that of SiO_2 , n_{SiO_2} . Extensive CdS synthesis, resulting in strong fringes, occurs for $T_a \geq 500^\circ\text{C}$. In addition, for higher T_a , a peak in R with a maximum at 2.45 eV ($R_{2.45}$) becomes discernable indicating the formation of larger nanocrystals. It is shown that the blue shift of $R_{2.45}$ relative to its energy in the bulk CdS closely corresponds to the shift of bandgap, E_g , with crystallite size and may, therefore, be used to estimate the size of the nanocrystals. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Due to the large optical non-linearity and fast response times, CdS crystallites buried in glass are promising for very interesting applications in optical devices. Ion implantation has been established as a practical technique for fabricating sulfide nanocrystals [1–3]. The elements (ions of transitional metals and S) are implanted sequentially into the selected substrate, forming a super-saturated solid solution in the implanted region. A

subsequent thermal processing causes the implanted ions to nucleate as discrete precipitates in a thin implanted layer. Progress in the fabrication of various nanocomposites by this method, including important technological advantages as well as some of the problems, was recently reviewed [2].

In this work, CdS nanocrystals of various sizes and densities were formed in amorphous SiO_2 by synthesis of implanted Cd and S atoms. The influence of ion dose and post-implantation annealing on the formation and size-growth of CdS nanocrystals in an SiO_2 matrix were followed by analyzing changes in the reflectivity spectra. The reflectivity (R) in the IR region has been often

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used to analyze nanocrystal-size structures. We are demonstrating here that data in the visible–UV range can also give very useful information.

2. Experimental details

Amorphous SiO_2 substrates were implanted with three different doses: $D1 = 2.5 \times 10^{16} \text{ cm}^{-2}$, $D2 = 5 \times 10^{16} \text{ cm}^{-2}$ and $D3 = 10^{17} \text{ cm}^{-2}$ of Cd and S atoms, and subsequently annealed in the 300–900°C range, as described elsewhere [3]. Implantation energies were selected using the TRIM code to give overlapping concentration profiles, while equal doses of Cd and S ions were used to achieve the proper stoichiometry. For the dose $D3$ the peak volume concentration reached $\sim 6.3 \times 10^{21} \text{ cm}^{-3}$, which corresponds to $\sim 20\%$ atomic fraction of Cd+S atoms, or $\sim 40\%$ of the weight fraction. For all three doses the peak volume concentration was at a depth of $\sim 130 \text{ nm}$, while the total depth was $\sim 260 \text{ nm}$, as checked by Rutherford back scattering (RBS). Implanted but unannealed samples and non-implanted but equally annealed substrates were used as references. The reflectivity measurements were performed using a UNICAM UV/VIS 4 spectrometer in the 1.4–6.0 eV range at room temperature (RT).

3. Results and discussion

Typical reflectivity spectra of samples implanted with doses $D1$ (dashed) and $D2$ (solid), are presented in Fig. 1a. For $D1$, only the RT and 900°C reflectivity curves are shown. Before annealing, no changes in $R_{D1, \text{RT}}$, and just slight change in $R_{D2, \text{RT}}$, in comparison with R_{SiO_2} , can be noticed. It means that mere incorporation of foreign atoms at these doses does not change perceivably the refractive index of the SiO_2 substrate ($n_{\text{SiO}_2} = 1.44\text{--}1.46$ in the above range). However, as T_a is raised above 500°C the interference fringes appear with an increasing amplitude. Since, for a given dose, the content of foreign atoms in the layer is fixed, and $n_{\text{CdS}} (= 2.4\text{--}2.7)$ is considerably higher than n_{SiO_2} , the appearance of fringes and

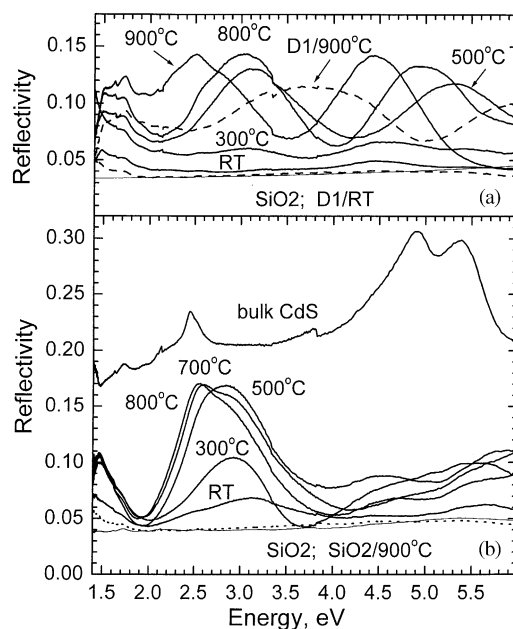


Fig. 1. Reflectivity spectra after implantation and annealing at indicated temperatures. (1a) Samples implanted with doses $D1 = 2.5 \times 10^{16} \text{ cm}^{-2}$ (dashed) and $D2 = 5 \times 10^{16} \text{ cm}^{-2}$ (solid). R of the SiO_2 substrate is shown for a comparison. (1b) Samples implanted with $D3 = 1 \times 10^{17} \text{ cm}^{-2}$, reflectivity of bulk-CdS, SiO_2 substrate unannealed (solid) and annealed at $T_a = 900^\circ\text{C}$ (dashed).

the increase of their amplitude undoubtedly reflects the synthesis and increase in content of the CdS phase in SiO_2 . Furthermore, for $T_a \geq 800^\circ\text{C}$, a peak-like structure close to 2.5 eV appears superimposed on the fringes. Analogous results are obtained for the dose $D1$, but the fringes appear at higher T_a and have smaller amplitudes. Moreover, even for $T_a = 900^\circ\text{C}$, no distinct peak superimposed on the fringes could be resolved. The superimposed structure was identified as originating from the bulk CdS, since R spectra of monocrystalline CdS display a peak at the same position, as shown in Fig. 1b. This peak with a maximum at 2.45 eV—hereafter referred as $R_{2.45}$ peak—was found to be associated with the three-dimensional M_0 critical points in the Brillouin zone of bulk, hexagonal, CdS [4]. In a spectroscopic ellipsometry study of CdS it was discovered that the $R_{2.45}$ peak reflects significant

changes, occurring both in n_{CdS} and in absorption coefficient, α_{CdS} , in this energy region [5].

For the dose $D3$ (Fig. 1b) $R_{D3,RT}$ differs considerably from R_{SiO_2} even prior to annealing. The fringes are substantial already at $T_a = 300^\circ\text{C}$, and the superimposed $R_{2.45}$ peak is resolved for $T_a \geq 500^\circ\text{C}$. In addition, a strong damping of fringes occurs in the high-energy region, where α_{CdS} is very high ($1.5 \times 10^5 \text{ cm}^{-1}$ at 3 eV to almost $1 \times 10^6 \text{ cm}^{-1}$ at 6 eV). As expected, Fig. 1b also shows that thermal treatment of the unimplanted substrate does not induce fringes (no change in n_{SiO_2}). The changes in spacing between extrema reflect the changes of effective thickness, d , of the layer containing CdS nanocrystallites. The wavelength positions of the maxima and minima, λ_{extr} , are fixed by the condition [6]

$$m\lambda_{\text{extr}} = 2nd, \quad (1)$$

where n is the refractive index of the layer and m is the interference order. The approximate value of the refractive index of the CdS/SiO₂ mixture was estimated from the weighted linear extrapolation of n_{CdS} and n_{SiO_2} . Interference order m is not known, but it can be derived from a plot of $n(\lambda_{\text{extr}})/\lambda_{\text{extr}}$ against an arbitrary chosen interference order m^* as shown in Fig. 2. The difference of m^* from the true interference order m is then given by the abscissa intersection of the resulting straight line. The slope of the curve yields the value of d as 150, 190 and 200 nm, for $D1$, $D2$ and $D3$, respectively. The difference in ‘optical path length’ and the maximum ion range determined by RBS is

understandable. Due to a single-energy implantation, the depth distribution of Cd and S (and of CdS) is near Gaussian, making the edges of the implanted layer optically indistinguishable from the substrate. This effect is more pronounced for smaller ion doses. For the dose $D3$ and higher T_a , the last three points in Fig. 2b—for energies above 4.5 eV—depart from the linear dependence of Eq. (1). Comparing with the spectrum of bulk CdS, one can conclude that, these last two ‘fringes’, are, in fact, genuine peaks in R spectra, whereas fringes are completely damped for $T_a > 300^\circ\text{C}$. These peaks were identified as E_{1A} and E_{1B} transitions, higher gaps of CdS associated with 3D M1 critical points of hexagonal CdS [4].

To further analyze the $R_{2.45}$ peak and its dependence on the implantation/annealing parameters, the interference fringes were subtracted, as demonstrated in the inset of Fig. 3. In Fig. 3 the results are shown for all samples where $R_{2.45}$ peaks could be distinguished. Full lines refer to samples implanted with dose $D3$, and symbols to dose $D2$. There is a distinct shift of the maxima of $R_{2.45}$ in CdS/SiO₂ composites from the bulk-CdS value. The dependence of the $R_{2.45}$ maximum on ion dose and annealing temperature is summarized in Fig. 4.

It is well known that the shift of the bandgap E_g , observable in absorption measurements, can be related to the average size (diameter) of nanocrystals, d [1,2], namely, the reduction of size leads to a quantum confinement of free carriers resulting in an increase (‘blue shift’) of E_g . The results of absorption measurements and blue shifts in E_g obtained for this same set of samples are also shown in Fig. 4 (open symbols). There is an obvious correspondence between the blue-shifts of $R_{2.45}$ and of E_g in all cases where $R_{2.45}$ could be determined. Although both the $R_{2.45}$ and E_g peaks are associated with optical transitions from the same critical points, their similar dependence on nanocrystal size is not a priori inevitable/certain, since $R_{2.45}$, as well as the whole R spectrum, depends not only on changes in α but also in n . The same energy shifts of both $R_{2.45}$ and E_g in the same samples mean that these two features have the same size-dependence. Hence, the presented results demonstrate that the size of the nanocrystals can

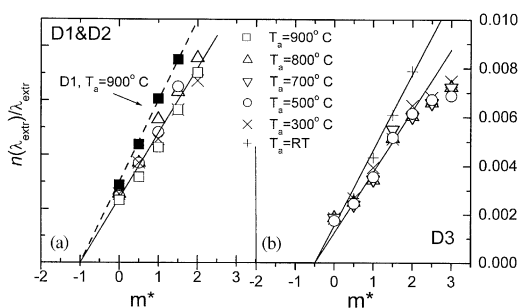


Fig. 2. The quantity $n(\lambda_{\text{extr}})/\lambda_{\text{extr}}$ calculated from Fig. 1 plotted against an arbitrarily chosen interference order m^* . Various symbols designate different annealing temperatures.

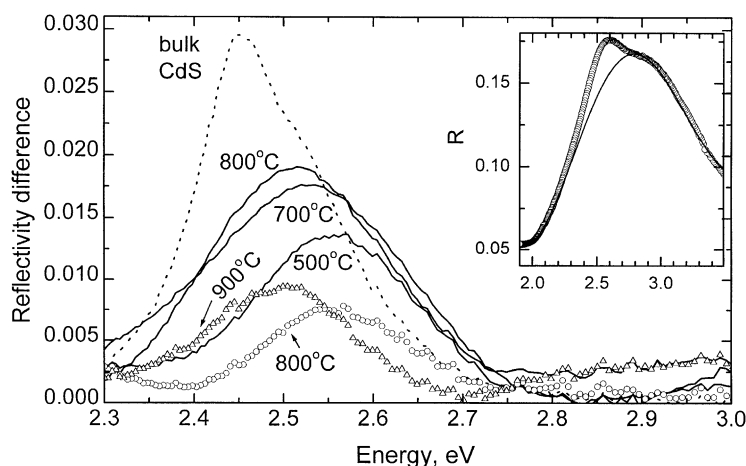


Fig. 3. Energy dependence of the $R_{2,45}$ peak, for indicated T_a and ion doses; D3 (solid) and D2 (symbols). Values are obtained after subtracting interference fringes, as shown in the inset (D3, $T_a = 700^\circ\text{C}$).

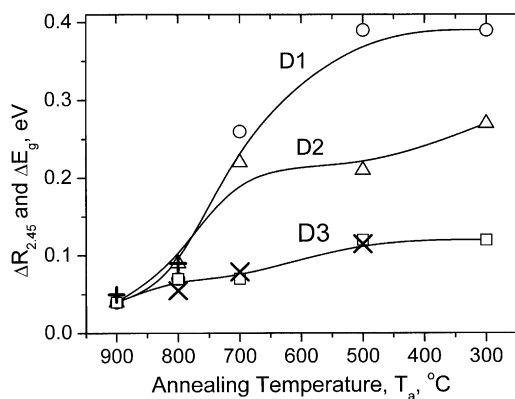


Fig. 4. Energy shift of the $R_{2,45}$ peak in reflectivity and bandgap shift, E_g , obtained from absorption measurements, as functions of ion dose and annealing temperature. Symbols (\times and $+$) refer to shifts of $R_{2,45}$ peak whereas open symbols (\square , \triangle , \circ) correspond to shifts in E_g .

be estimated by reflectivity measurements, using the same formalism developed to connect the E_g shift with nanocrystal size [1,2]. However, the sensitivity of the method is somewhat reduced (mostly due to large ‘noise’, i.e. interference fringes, which have to be subtracted to obtain the ‘signal’). On the other hand, appearance of fringes is by-itself a very sensitive indication of the synthesis of a new material with higher n within a matrix of low n .

4. Conclusion

We have demonstrated that reflectivity measurements in the UV–visible range can give useful information about the formation and growth of CdS nanocrystals in SiO_2 substrates. The mere incorporation of Cd and S atoms did not alter the reflectivity of SiO_2 significantly. However, synthesis of the CdS phase is nicely observable in reflectivity, since n_{CdS} is substantially higher than n_{SiO_2} , causing the appearance of interference fringes. Annealing temperatures $T_a \geq 500^\circ\text{C}$ are sufficient to produce strong fringes, indicating extensive formation of CdS. In addition, for higher T_a , a distinct peak appears in reflectivity with a maximum at about 2.5 eV. The energy shift of the maximum of this peak can be used to estimate the nanocrystal size in the same way as the shift of the bandgap E_g , derived from absorption measurements. For the highest dose, the structures related to the E_{1A} and E_{1B} transitions of higher gaps of hexagonal CdS were discerned as well.

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