

Effects of proton irradiation on structural and optical properties of CdS thin films used in photovoltaic applications

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The effects of irradiation with protons (3 MeV), at 10^{14} protons/cm² fluency, on structural and optical properties of polycrystalline CdS thin films used in photovoltaic applications have been investigated. Structural, surface morphology and optical properties of as deposited CdS films were investigated by XRD, SEM, VIS-UV absorption. The irradiation only produced slight changes in the XRD pattern. Also, the optical bandgap was not significantly affected by irradiation.

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1. Introduction

Cadmium sulfide (CdS) has been recognized as a very promising material for thin film solar cells. Usually the solar power generators consist of high efficiency Si and III-V cells made of single-crystalline materials. However, solar cells based on thin films have the potential for low cost production on flexible substrates, high specific power (1.5 - 3 kW/kg) and stable performance. In a preliminary study [1] the excellent stability of CdTe/CdS solar cells against high energy protons was shown.

There is a vast literature [2-7] comprising experimental and theoretical investigations of electronic band structure and related properties of this compound, but little work was done on the influence of ionizing radiations on their physical properties [1,2,8,9].

In this paper we approach the study of the effects of proton irradiation on the structural and optical properties of polycrystalline CdS layers. It is organized as follows: Experimental details about growth and proton irradiation conditions and about characterization procedures are given in the next section. The experimental results we have obtained, as well as their discussion are presented in section 3. Finally, in the last section, the main conclusions of this study are summarized.

2. Experimental procedures

The samples were prepared by thermal vacuum evaporation of CdS powder onto a glass substrate. CdS (Aldrich) powder was vacuum sublimated at a residual pressure of 10^{-5} Torr from a quartz container, heated to 770°C. To reduce the sputtering of the powder during of the source heating, the evaporator was covered with a quartz-wool plug. Finally, to improve the chemical and structural quality of the films, they were thermally treated in vacuum, for 15 minutes at 350°C. Two kind of samples were used in this study, their growth conditions being summarized in Table I. The films were 8 μm thick. The obtained CdS layers were subjected to irradiation with protons supplied by a Van de Graaff accelerator [10]. Irradiation was carried out in a vacuum chamber, at ambient temperature, with 3 MeV protons to a fluence of 10^{14} protons/cm². During irradiation the distance between the output window of the accelerator and the sample was 20 cm and the thermal effect was negligible. The beam of incident protons supplied by accelerator was directed perpendicularly to the surface of the samples.

The crystallographic structure of films was analyzed, before and after irradiation, by X-ray diffraction (XRD), with a high resolution diffractometer (D8 Discover – Bruker).

XRD spectra were recorded by using $\text{CuK}\alpha_1$ line, $\lambda = 1.5406 \text{ \AA}$, with a detector-scan method and a stationary incident beam at grazing incidence, for reducing the

diffracted intensity from the substrate. The scanning step was $\Delta(2\theta) = 0.05 \text{ \AA}$.

Table 1. Growth conditions and physical parameters of investigated CdS thin films.

Sample set	Growth conditions*	$D_{\langle 002 \rangle}$ (Å)	$D_{\langle 102 \rangle}$ (Å)	$D_{\langle 103 \rangle}$ (Å)	$D_{\langle 004 \rangle}$ (Å)	E_g (eV)
P1	$T_s=270^\circ\text{C}$; in situ thermal treatment, 350°C , 15min.	630	160	218	-	2.36
P2	$T_s=280^\circ\text{C}$; in situ thermal treatment, 540°C , 15min.	657	268	229	649	2.37

T_s – substrate temperature during deposition;

Surface morphology was examined by scanning electron microscopy (SEM), using a Tescan Vega XMU-II microscope.

Optical properties of the films were characterized by VIS-UV absorption spectra and ellipsometry.

3. Experimental results

3.1 Structure and morphology

Structural analysis of the samples by X-ray diffraction revealed that the CdS films consist of a hexagonal compact (hpc) wurtzite phase (Fig. 1). The films are polycrystalline, with most of the crystallites oriented with (002) crystalline direction perpendicular to the film surface. Crystallite sizes, summarized in Table I, were determined using Scherrer's formula:

$$D_{eff} = \frac{0.9 \lambda}{\beta_{hkl} \cos \theta} \quad (1)$$

where λ is the X-ray wavelength used ($\lambda = 1.5406 \text{ \AA}$), β_{hkl} is the integral line breadth, θ is the angle where the peak occurs. Instrumental broadening b was corrected for using a In_2O_3 standard sample with large crystallites and the formula $\beta_{hkl}^2 = (B - b)(B^2 - b^2)^{1/2}$, where B is the raw linewidth. These values, as well as the SEM micrograph shown in Fig. 3 (b), suggest that crystallites have a prismatic, columnar, form, with axial dimension greater than the base diameter.

By increasing the temperature of the in situ thermal treatment after deposition, the texture of the films and the crystallite sizes get improved (Fig. 1).

There was no change in the position of the observed peaks and in the structure of XRD patterns after irradiation. Figure 2 shows the (002) diffraction peak, recorded in the case of a P1 sample, before and after proton irradiation in the above-mentioned conditions. The peak was slightly enlarged due to radiation damage; the corresponding crystallite size was reduced to 526 \AA .

The surface morphology of the films is shown in Fig. 3. All the samples were compact, without any voids or cracks. SEM images confirmed the polycrystalline nature

of the films. No significant change in the surface morphology after irradiation was detected.

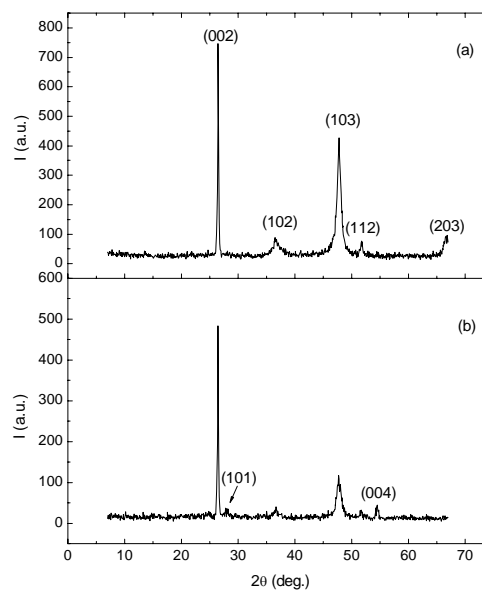


Fig. 1. Experimental X-ray diffraction pattern of CdS films; (a) sample P1 and (b) sample P2.

3.2 Optical properties

Optical absorption spectra of as-deposited and irradiated films are shown in Figs. 3 and 4. The spectra were recorded at room temperature, in VIS-UV region, by using a Perkin-Elmer Lambda 35 spectrophotometer. CdS is a direct wide bandgap semiconductor. Using the absorption spectra near fundamental threshold, the bandgap width E_g was determined with the formula:

$$\alpha = \alpha_0 \frac{(h\nu - E_g)^{1/2}}{h\nu} \quad (2)$$

where α is the absorption coefficient, $h\nu$ is the energy of incident photons, and α_0 is a quantity not depending on photon energy.

The optical band gap was found by plotting $(\alpha h\nu)^2$ versus $h\nu$ and extrapolating the linear portion of the curve to intersect the energy axis (see Fig. 4). A value of 2.36 eV was extracted for the bandgap width, both before and after irradiation. As one can easily see, proton irradiation in the above-mentioned conditions does not affect near-threshold optical absorption. Note also the featureless character of the absorption spectra in the extrinsic region, at energies below the threshold.

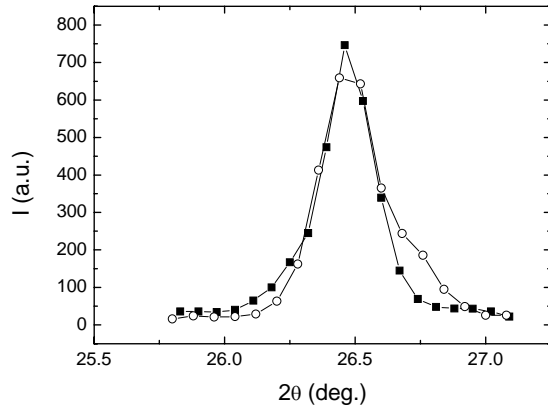


Fig. 2. (002) X-ray diffraction peak of sample P1, before (black filled squares) and after irradiation (open circles).

The wavelength dependence of the optical constants in the case of a P1 sample, as determined by ellipsometry, is shown in Fig. 5. E_0 , the optical bandgap, corresponds to transitions occurring at Γ , while E_1 and E_2 corresponds to transitions at points in [001] direction of the \vec{k} -space [11]. The presence of these peaks in the optical spectra should be correlated to the results of XRD investigations; it proves that the crystalline quality of the grains is a good one.

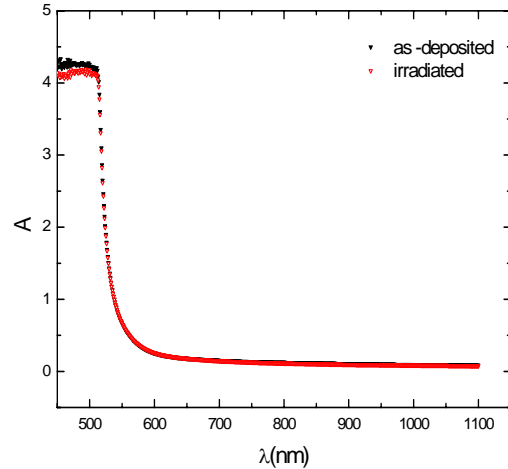
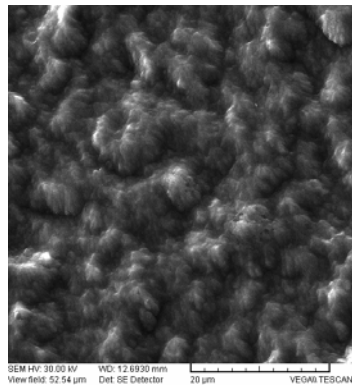
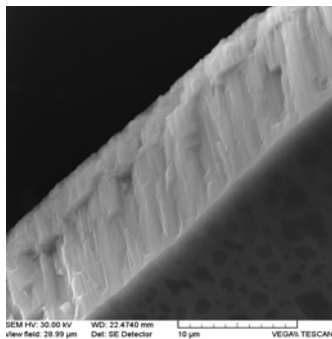


Fig. 3. Optical absorption spectra of a CdS P1 sample, before and after irradiation with 3 MeV, to a fluency of 10^{14} protons/cm².



(a)



(b)

Fig. 3. SEM micrographs of a P2 (a) and P1 (b) CdS sample. Lateral exposure of the film shows the columnar structure of the crystallites.

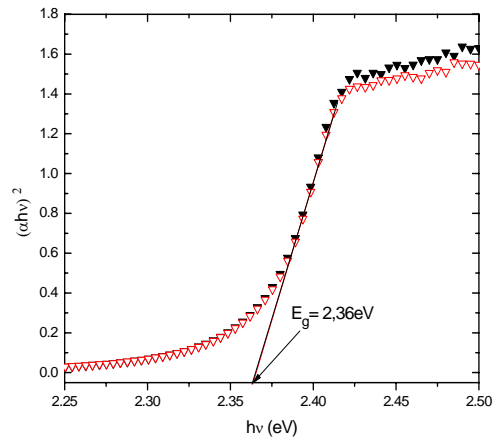


Fig. 4. Optical absorption spectra near band gap for CdS P1 thin film, before and after irradiation with 3 MeV, 10^{14} protons/cm².

4. Conclusions

An investigation on the effects of proton irradiation on structural and optical properties of CdS thin films grown by vacuum thermal deposition was performed. XRD investigation revealed that the films consist of a wurtzite phase; their crystallinity gets improved by increasing the temperature of the in situ thermal treatment, subsequent to the deposition process. The crystalline structure was not severely damaged after irradiation with 3 MeV protons (10^{14} protons/cm²), at room temperature.

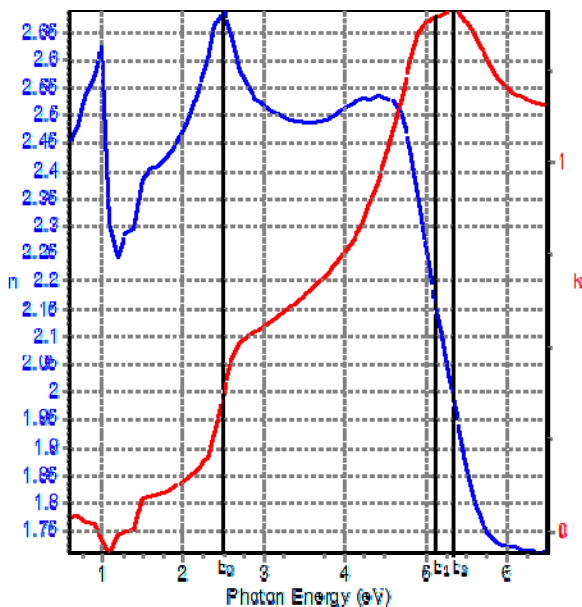


Fig. 5. *n-k* spectra of a CdS P1 film.

The effects of irradiation consisted in slightly broadening the diffraction peaks. Near threshold absorption spectra and the optical bandgap was not significantly altered after irradiation. Consequently, these films show a good stability against 3 MeV proton irradiation, at fluencies up to 10^{14} protons/cm².

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