

ATOMIC FORCE MICROSCOPY OF CADMIUM SULPHIDE THIN FILMS

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ABSTRACT

The morphology and microstructure of cadmium sulphide (CdS) thin films are a major concern in the fabrication of CdTe solar cells. In this work we investigate the morphology and microstructure of chemical-bath-deposited (CBD) and electro-chemical-deposited (ECD) CdS in order to better understand the growth conditions that give rise to films for optimum device performance. Advantages of atomic force microscopy methods are discussed.

INTRODUCTION

Metal chalcogenide films are of large interest for various electronic applications. Cadmium sulphide is commonly used as n-type semiconducting layer in different kind of "sandwich" structures for solar cells, such as CdTe/CdS/ITO/glass. Multilayered CdS films can be also employed in the manufacture of the optoelectronic devices. The film deposition could proceed by different techniques such as: evaporation, sputtering, chemical vapour deposition, chemical bath deposition or electrodeposition. The obtained films may differ by topography, luminescent, mechanical and optical properties. For investigation of the physical properties and to give recommendations in technology process, advanced physical methods such as electron microscopy (EM), atomic force microscopy (AFM) and cathodoluminescent spectroscopy (CLS) were applied. Atomic Force Microscopy allows imaging not only semiconductor samples, but also and insulating materials and in non-vacuum environments. It is perhaps not surprising that AFM has become a primary tool in the study of nanoscale materials and devices in both physical and materials sciences.

MATERIAL PREPARATION

CdS/glass/CdS (*series A*) and CdS/ITO/glass (*series B*) structures were prepared by different techniques.

Sample series A was prepared by chemical bath deposition (CBD) method, from cadmium acetate and thiourea solutions. CBD method was adapted for multilayered CdS films formation onto optical glass platelets. The experiments were conducted in a stable thermal regime at $70 \pm 72^\circ \text{C}$, under continuous stirring, with a strict pH control.

Cadmium sulphide films were formed in many successively deposition steps that always were performed in renewed chemical bath prepared of 0,1 M cadmium acetate, 2M NH_3 aqueous solution, 1M sodium citrate and distilled water. The deposition bath was continuously stirred and heated to the required temperature. The glass platelets were acid etched, water cleaned and immersed into the deposition bath, by vertically suspending them around the stirrer. After the thermal equilibrium was reached, 1M thiourea solution was added under stirring. Deposition parameters were: $[\text{Cd-acetate}] = 3 \times 10^{-3}$ mole/L; $[\text{Na-citrate}] = 1.2 \times 10^{-1}$ mole /L; $[\text{ammonia}] = 3 \times 10^{-1}$ mole / L; $[\text{thiourea}] = 3 \cdot 10^{-2}$ mole / L; $[\text{Cd}^{2+}]:[\text{CS}(\text{NH}_2)_2]:[\text{NH}_3]:[\text{Na-citrate}] = 1:10:100:4$; deposition pH = 9.0 ± 10.5 .

The multi-layer deposition procedure was as follows: glass supports were immersed into the hot chemical bath; after 1.0 hr. they were taken out, washed and reintroduced into a renewed hot CB; after another hour, the platelets were taken out, washed and reintroduced into a renewed hot CB for

one more hour and so on. Samples A11.1, A11.2 and A11.4 were prepared of 2; 4 and 6 consecutively deposited CdS layers. All samples were washed, dried and annealed for 1 hr at 350°C.

Sample series B was prepared by electrochemical deposition technique performed onto ITO coated glass platelets (OPTICAL FILTERS Ltd.). The glass that serves as electrode must be electroconductive, so it was coated with a layer of indium tin oxide (ITO). CdS/ITO/glass structures were prepared by using a three electrodes system formed from one working electrode (ITO / glass), one reference electrode (Ag/AgCl) and one counter electrode (Pt wire). Electrodeposition was carried out with a POTENTIOSTAT MODEL 263 (EGG Instruments) coupled to a computer.

ITO coated glass platelets were ultra sound cleaned in acetone and alcohol mixture and immersed into the electrochemical bath containing 0.1 mole/L natrium thiosulphate and 0.2 mole /l cadmium chloride. Deposition conditions were: inert atmosphere, pH = 1.5; T = 50°C and t = 1hr and stabilised electrical parameters (I = 10 mA; U = - 600 mV).

The as prepared B samples were washed and dried. Supplementary, B2.7 was annealed for 1 hr at 350 °C.

RESULTS AND DISCUSSION

1. Scanning electron microscopy (SEM)

First of all to study the homogeneity and heterogeneity of the films and to compare one with another, the surface investigations in the SEM VEGA TS-5130 were performed. We used secondary electron mode at accelerating voltage 7-15 keV and absorbed current 4-50 pA. The results are presented in Fig.1.

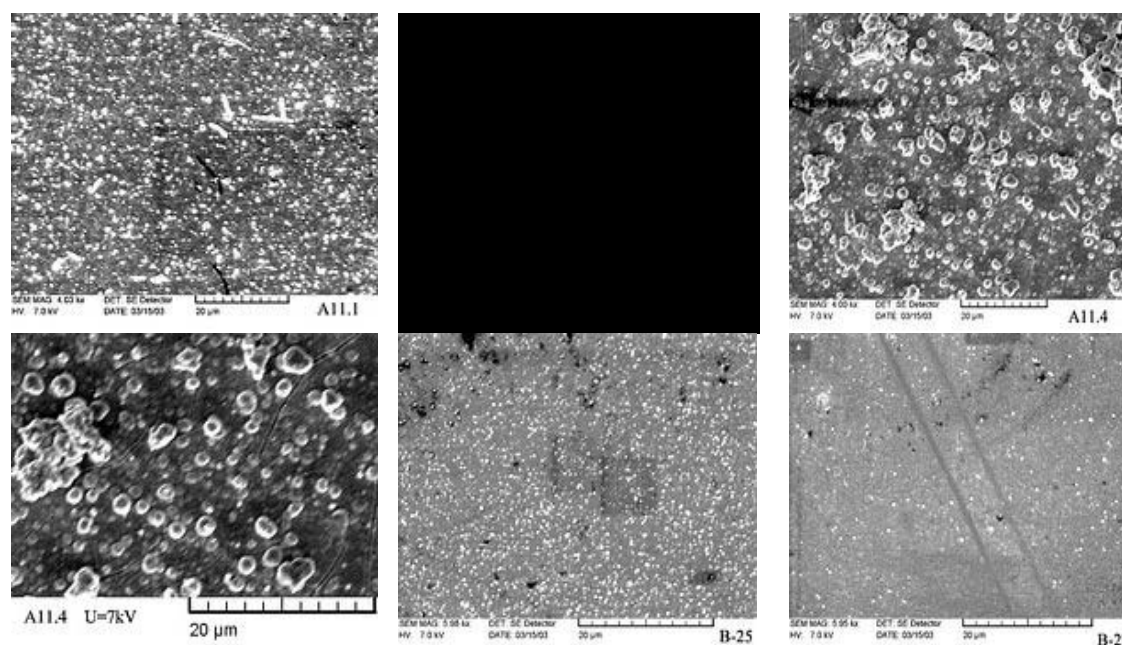


Fig.1. SEM images of CdS films obtained by different technologies.

The most homogeneous films (series B: B-25 and B-27), as it is seen from fig.1, were obtained by electrochemical deposition technique performed onto ITO coated glass platelets. On the films of series A, obtained in the hot chemical bath, one can see many separated particles. The heterogeneity increases with the number of layers. If the first layer (A11.1) is more uniform, the last one (A11.4) contains many scattered particles about 1-2 microns in diameter and their conglomerates up to 10 µm.

The SEM method allows us to reveal also some cracks in the films A11.1, A11.2 and A11.4, prepared by CBD. This could have a significant impact on cell performance as these cracks may provide shunting paths between the CdTe and SnO₂. No cracks were revealed in the samples B-25 and B-27, prepared by electrochemical deposition technique.

An image analysis of the SEM maps taken from the powders or from the samples with many separated particles (fig.1 A11.4) must account the peculiarities of SE-contrast, which have not been observed in the maps for solid uniform specimens. Besides, the traditional method of the image formation in the SEM results in some cases in the formation of artefacts. In the case of powders [1,2] the main artefacts are topographic contrast (aureoles). The aureoles correspond to a light at the particle perimeter seen in Fig 1. As it will be shown later, these artefacts (aureoles) don't exist in atomic force microscopy.

2. Optical Microscopy (OM)

Before atomic force measurements a high quality optical microscope was used to choose the investigated area.

The NANO-Station II is a new concept in Scanning Probe Microscopy (SPM) that combines precision and productivity in a single instrument. The combination of a high quality optical microscope with a SPM of the ULTRA-Objective series on a most rigid granite stand allows to select sample areas with an unmatched speed and to perform high resolution SPM measurements.

The system is modular and multifunctional. The basic version comes with a SPM that provides scanning ranges of up to 40µm and is upgradable with numerous SPM modes. In addition, the optical microscope is equipped with bright- and darkfield observation, and is also extendable with the most common optical methods and supplementary instrumentation, e.g. CCD-camera, etc

Moreover, some additional information about the surface can be derived. Films with the different thickness are coloured differently in OM. From Fig.2 we can confirm our conclusion about the films heterogeneity and we can previously see the specially prepared places for measure of the thickness of the films in AFM (bottom row in Fig.2).

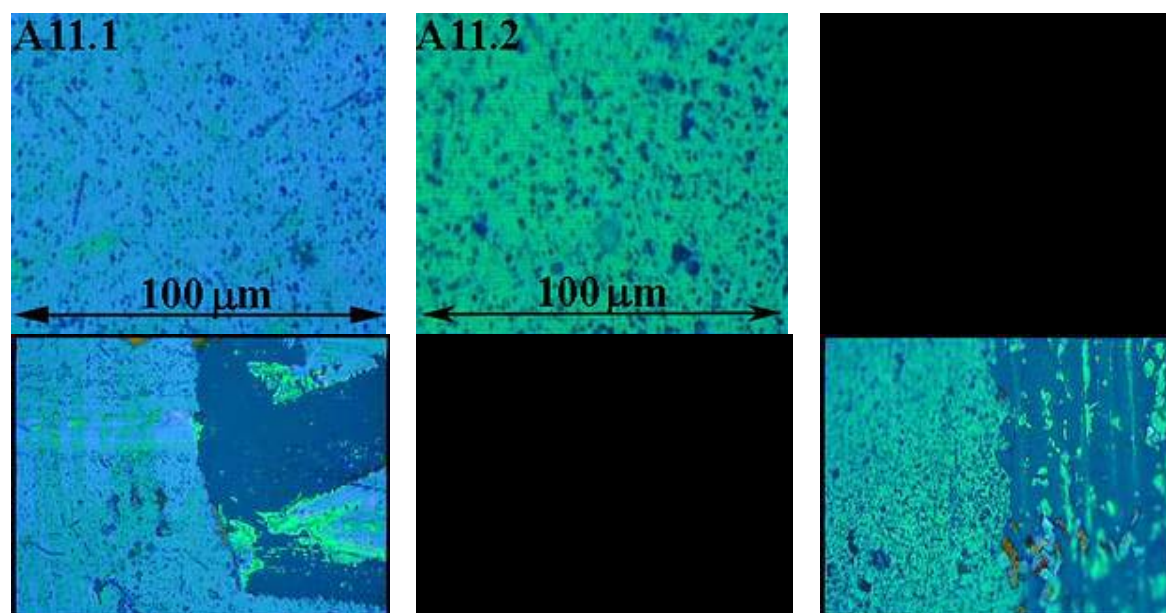


Fig.2. Optical images of CdS/glass surface and special prepared steps for thickness measurements.

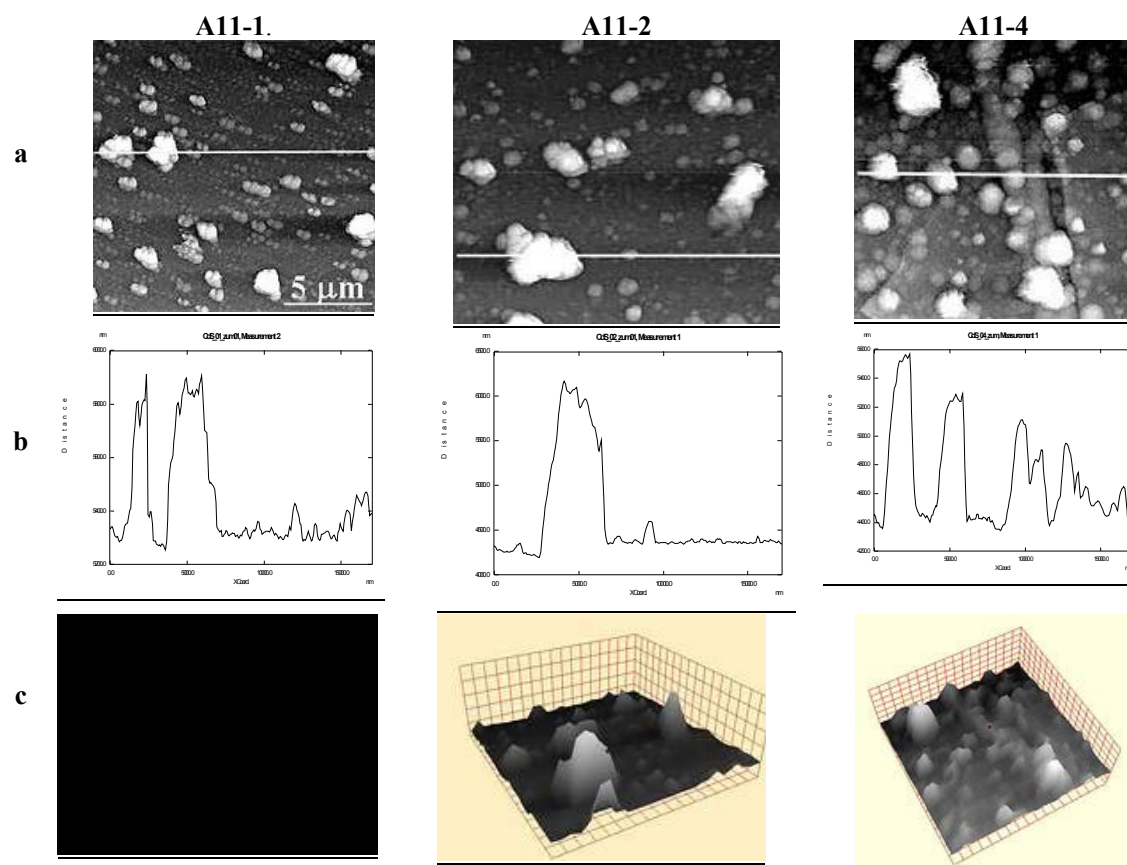
3. Atomic Force Microscopy (AFM)

The surface inspection system with high resolution ≈ 1 nm was applied in AFM to control the technology process in preparing cadmium sulphide films by different techniques. 2D and 3D surface images are shown in Fig.3 (for A-series) and in Fig.4 (for B-series), correspondingly. The detailed profiles of impurities and thickness steps are also presented. The scanning lines in figures 3a correspond to the measured profiles.

The atomic force microscopy method allows seeing some pinholes and discontinuities varying in size and density that could not be found out by other methods. These revealed pinholes could have a significant impact on cell performance as these pinholes may provide shunting paths between the CdTe and SnO₂.

Overwhelming majority of particles in A11.1 film have dimensions about 100 nm. Sometimes the particles 0.5-1 μm occur. And the most of such particles one can find in the last layer in A11.4 film. The thickness of films is 280 nm, 600 nm and 1100 nm for A11.1, A11.2 and A11.4, correspondingly, that is in a good agreement with other methods. For the films obtained by electrochemical deposition technique performed onto ITO coated glass platelets B-25 and B-27, the thickness is significantly less and is about 80 nm. The thickness of the films was shown to be strongly influenced by the deposition time. The controlling of thickness in dependence of time deposition is very important in production of thin films. Any principal new morphological defects have been found with increasing the thickness.

The luminescent properties and their correlation with films thickness were carried out with cathodoluminescence methods.



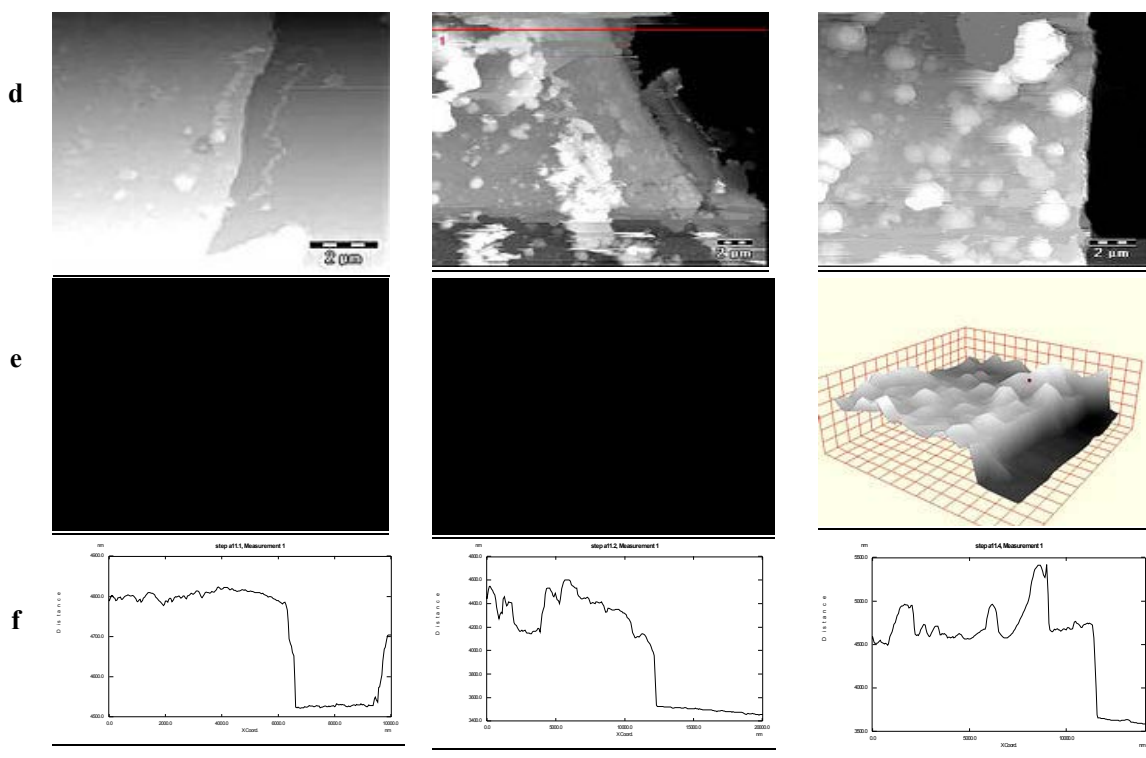


Fig.3. 2D and 3D CdS surface images and topography profiles in AFM

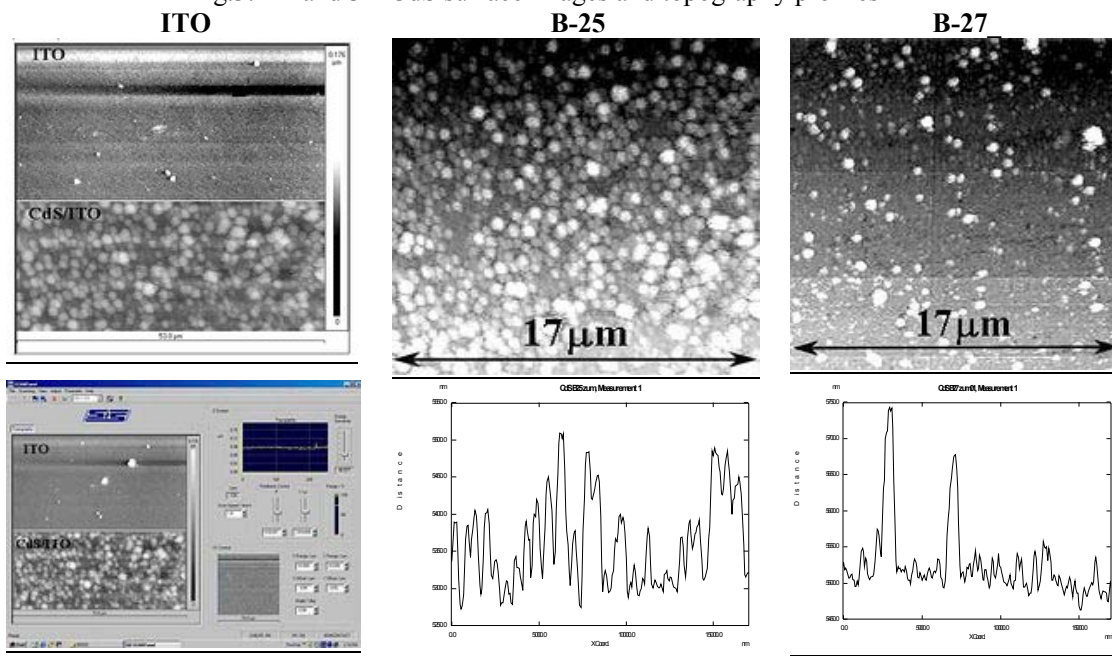


Fig.4. AFM images and profiles of CdS/ITO/glass films obtained by electrochemical deposition

4. Cathodoluminescence spectroscopy (CLS)

Spectral investigations were performed on CL spectrometer combined with an electron probe microanalyzer “Camebax” [3]. Optical emission was excited by electron beam 1-3 μm in diameter at

accelerating voltage $U=5$ keV and with an absorbed current $I=10$ nA. Obtained spectra are presented in fig. 5 and 6.

The main band at 521 nm is associated with CdS emission. The band at 624 nm (1.9 eV in fig.5 for A11.1) may be attributed to nonbridging oxygen state [4] in SiO_2 because the electron energy at accelerating voltage 5 keV is enough to penetrate in substrate in the case of thin A11.1 film.

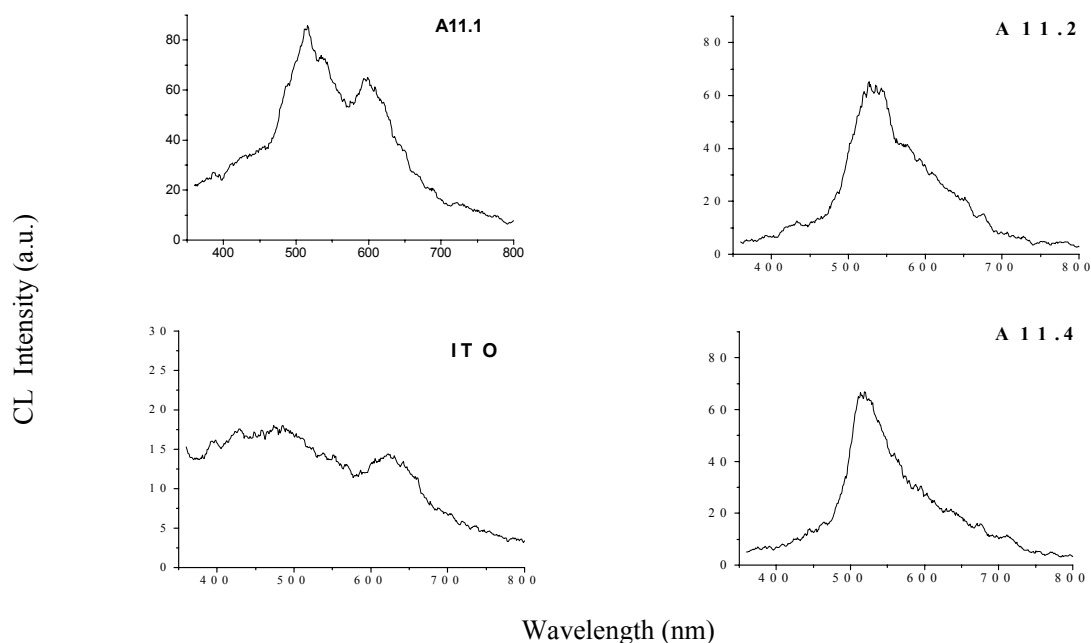


Fig. 5. CL spectra from CdS films series A and substrate (ITO)

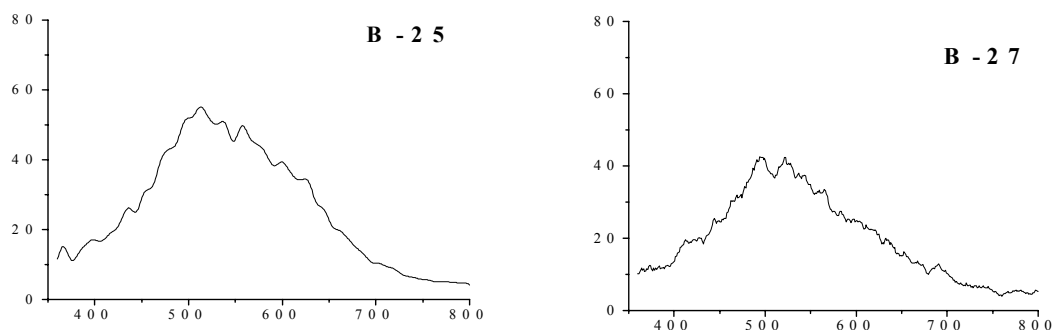


Fig. 6. CL spectra from CdS films series B

The calculation of maxima electron penetration depth R (micron) in a solid with density ρ (g/cm^3) and atomic weight A (g/mol) was done by Kanaya et al. [5], taking into account the elastic and inelastic scattering:

$$R = \frac{2.76 \cdot 10^{-2} AU^{5/3}}{\rho \cdot Z^{8/9}} \quad (1)$$

where Z is the atomic number and U denotes the accelerating voltage in keV.

The dependence of electron penetration depth R versus an accelerating voltage is presented in fig.7.

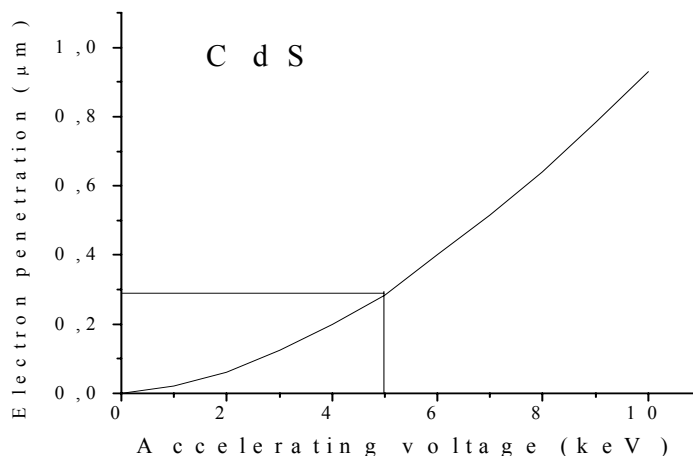


Fig.7. The dependence of electron penetration depth R versus an accelerating voltage

The thickness R_0 of the surface layer from which 95% of the CL intensity originate is considered to be the information depth of the CL signal. In this model it can be expressed as:

$$R_0 = R/2 \left[1 - \frac{C^2 \gamma^2}{(1 + \gamma)^2} \right] \quad (2)$$

where $\gamma = 0.187 Z^{2/3}$; $C = 1.1$. In this way, for investigated cadmium sulphide films ($A = 144.6$ g/mol; $\rho = 5.6$ g/cm³; $Z = 64$)

$$R_0 \approx 0.2 R.$$

A useful analytical expression of the information depth (nm) as a function of electron beam accelerating voltage (keV) can be given:

$$R_0 = 4 U^{5/3} \text{ (nm)} \quad (3)$$

This formula was applied to determine the depth of CL intensity maxima for cadmium sulphide thin films. The data obtained through these calculations are in a good agreement with experiments.

CONCLUSIONS

In summary, all the CdS films examined in this study exhibited cracks, pinholes and discontinuities varying in size and density. This could have a significant impact on cell performance as these cracks and pinholes may provide shunting paths between the CdTe and SnO₂. Additionally, the CdS grains are heavily faulted, with a high density of stacking faults. This will have a deleterious effect on CdS/CdTe interface region because those planar defects in CdS tend to propagate into the CdTe films.

ACKNOWLEDGEMENTS

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