

GROWTH AND CHARACTERIZATION OF NANOCRYSTALLINE CdS THIN FILMS

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Nanocrystalline cadmium sulfide (CdS) thin films were deposited by thermal vacuum evaporation (TVE) from single source onto ITO covered optical glass substrates. These films were analyzed by atomic force microscopy (AFM), scanning electron microscopy (SEM) and spectroscopic ellipsometry (SE) in the range of 250 – 1700 nm. The optical constants as well as the films thicknesses and the optical band gaps were obtained by fitting the experimental ψ and Δ spectra from ellipsometric measurements. The recorded data were analyzed using a dedicated software package specially designed for optical modeling. The ellipsometrical parameters ψ and Δ were acquired at three incidence angles (65°, 70°, 75°) for a high number of wavelengths in the mentioned wavelength range. In order to determine the refractive index, the thickness and the surface roughness of CdS thin films, as well as for obtaining a smooth control for the experimental data fitting processes, the identification of the spectral regions in which the films showed good transparency is required. This working procedure generates a significantly increased number of optical models with a slightly reduced number of fitting parameters.

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1. Introduction

As it is known, cadmium sulfide (CdS) is one of the most suitable II – VI semiconductor materials for applications in solar cells technology. Also, there is a vast literature comprising the use of CdS in many other applications, like thin film transistors for flat panel displays, light emitting diodes, optical filters, photo detectors, nonlinear optics, gas sensors, etc. [1 – 10]. Because of such an extended area of applications for this material, CdS thin films were deposited by various techniques, such as physical vapour deposition [11], sputtering [12 – 13], electro-deposition [14 – 15], spray pyrolysis [16 – 17], molecular beam epitaxy (MBE) [18], metal organic chemical vapour deposition (MOCVD) [19], chemical bath deposition (CBD) [20 – 21], pulse laser evaporation [22], successive ionic layer adsorption reaction (SILAR) [23] and screen printing [24].

In applications regarding thin films photovoltaics, numerous theoretical and experimental investigations have been made on CdS [25 – 28] and related to some of its properties, such as its energy bands structure, electrical transport mechanisms, growing conditions and substrate influences on these mechanisms, post-deposition thermal treatments, etc. Despite that, the physical

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properties of CdS (such as its direct wide optical bandgap of 2.35 eV in the thermodynamically stable würtzite phase), as well as its good chemical and mechanical stability, recommend CdS as an ideal semiconductor material for electronic and optoelectronic applications, in particular, for manufacturing of thin films based solar cells.

Such type of solar cells is particularly important in the space technology, where the study of the ionizing radiations (for example, proton irradiation) on CdS physical properties (structural, electrical and optical properties) is critical [29 – 30]. In all these applications, CdS is a low-cost material who exhibits good energy conversion efficiency (around 15 %) when employed in association with CdTe, making a CdS / CdTe heterojunction solar cell (also CdS can be associated with CIS or CuInSe₂). One of the first proposed CdS (n-type) / CdTe (p-type) heterojunction solar cell had a rather small energy conversion efficiency of about 5 % [31], making it less competitive.

In this kind of solar cell, CdS thin film acts like an n – type semiconductor for the window layer, so in order to ensure a sensitive control of CdS thickness and transmittance, a characterization method with high thickness sensitivity must be used after the films preparation, this method being the spectroscopic ellipsometry. So we need to deposit transparent and high resistive polycrystalline thin films of cadmium sulfide, but the control of CdS thicknesses is very important, due to the fact that if CdS layers are too thin, the probability to have a short circuit between the CdTe absorber layer deposited on top of CdS and the front contact (which usually is represented by a TCO layer) is significantly increased.

So far, the most used method to deposit CdS thin films as n – type window layers for CdTe heterojunction solar cells with good efficiencies, was the chemical bath deposition (CBD) method, mostly because the CdS thin films deposited by this method were very compact and therefore they covered perfectly the entire TCO layer [32]. However, it must be taking into account the fact that the CBD method is not suitable for large – scale production since it is not fast and gives a waste that needs to be recycled. This is the particular reason why we choose to prepare our films using other deposition technique, namely the thermal vacuum evaporation (TVE) method.

So the goal of this paper is to study some of the most important properties of CdS polycrystalline thin films deposited by TVE, such as the optical constants and thicknesses, the surface morphological properties, including the surface roughnesses, in order to make these films compatible with the manufacturing of high performance thin film CdS / CdTe photovoltaic cells.

2. Experimental details

The polycrystalline CdS thin films were obtained by thermal vacuum evaporation (or sublimation) TVE method. As substrates we have used ITO (indium tin oxide, or tin-doped In₂O₃) coated optical glasses. We used ITO because is one of the classical TCO's (transparent conductive oxides) used as front contact in a CdS / CdTe heterojunction solar cell in superstrate configuration, due to its high transparency (more than 85 % in the visible range), low resistivity (about $2.5 \times 10^{-2} \Omega \cdot m$) and a good stability at the temperature which CdS thin films will be prepared. Several types of ITO coated glass substrates have been used, depending on the ITO's sheet electrical resistance (between $8 - 25 \Omega_{\text{square}}$).

The CdS thin films were deposited by thermal vacuum evaporation of CdS powder from a single crucible. The CdS powder sublimated at a pressure inside the deposition chamber of 3×10^{-4} mbar from a quartz container heated at 750° C, the substrate temperature being maintained at 250° C. In order to avoid the sputtering of the CdS powder during the evaporation (sublimation), the crucible was covered with a special designed quartz-wool plug. After finishing the deposition of all the samples, the CdS thin films were subjected to a thermal treatment consisting in heating the films at 350° C, in vacuum, for almost 15 minutes. The aim of this post-deposition procedure is to improve the structural and chemical quality of the films.

The characterization of CdS thin films were made using spectroscopic ellipsometry (SE), atomic force microscopy (AFM) and scanning electron microscopy (SEM).

In order to measure the films thicknesses and the optical constants, we have used a WVASE 32 spectro-ellipsometer from Woollam, which enable us to perform ellipsometric

investigations by light reflection from samples, as well as by light transmission through samples (such that both reflectance R and transmittance T can be measured). The wavelength setting for the incident light is automatically made using a HS – 190 scanning monochromator, capable to optimize the scanning speed, the wavelength selection accuracy and the spectral resolution. The spectral range available is between 193 nm (6.4 eV) up to 2200 nm (0.56 eV). The maximum number of wavelengths is 500, so we can record ellipsometric spectra containing a maximum number of 500 values for the ellipsometric angles. The incidence angle of light on the film surfaces can be set between 15° and 90° (depending on each type of material) with an accuracy of 0.01°. The data acquisition time is between 0.1 s to 3 s for each wavelength, depending on the sample reflectivity (for high accuracy measurements using the auto-retardation function, 20 s per wavelength are necessary).

The investigations regarding the surface morphology for the CdS thin films have been made using both techniques, AFM (atomic force microscopy) and SEM (scanning electron microscopy). The equipment used for SEM characterization is a Tescan Vega XMU-II microscope using secondary electrons as signal (with the acceleration voltage between 200 V to 30 kV, in 10 V steps, the magnification between 3x and 500.000x and adjustable scanning speed between 160 ns / pixel to 10 ms / pixel). For AFM characterization we have used an AFM microscope from Ape Research (AFM A 100 – SGS).

3. Results and discussion

We started first with the ellipsometric investigations of CdS deposited thin films. As it is known, ellipsometry measures the change in the light state of polarization upon light reflection on a sample (or light transmission by a sample) [33]. The results of the ellipsometric measurements are the two values (angles) Ψ (psi) and Δ (del), defined as the amplitude ratio (psi) and phase difference (del) between light waves known as “p-” and “s-” polarized light waves, one parallel (p) to the plane of incidence and the other (s) perpendicular to that plane. In spectroscopic ellipsometry (SE) [34], psi and del spectra are measured by constantly changing the light wavelength using the scanning monochromator. The measurements were carried out using a variable angle, rotating-analyzer spectroscopic ellipsometer VASE from Woollam Co, operated in the wavelength range 250 - 1700 nm. The angles of incidence were 65, 70 and 75 degrees. These angles were selected after a simulation process necessary to generate a more sensitive data to the parameters of interest (Ψ and Δ).

To extract accurate material properties from VASE analysis, it is necessary to build an appropriate optical model to fit the experimental data. The optical constants (refractive index n, extinction coefficient k) and layer thickness are obtained by mathematical modeling of the layer including the substrate material (optical glass). The mathematical model can be extended by additional parameter such as surface roughness. The optical constants of the samples, respectively the refractive index $n(\lambda)$ and the extinction coefficient $k(\lambda)$, were measured after obtaining the experimental (Ψ , Δ) spectra and then fitting these spectra using the Cauchy model [34].

For CdS polycrystalline thin films with good transparency, the refractive index $n(\lambda)$ was approximated by a simple Cauchy function:

$$n(\lambda) = A_n + \frac{B_n}{\lambda^2} \quad (1)$$

The fitting of the ellipsometric spectra was made in such manner that a minimum value for MSE (mean squared error) were reached. We have used the MSE as a risk function in order to quantify the experimental spectra fitting procedure. Because we have reached a value for MSE = 3.76, this assured a good fitting for all parameters, including Cauchy parameters A_n and B_n . The range of measured thicknesses for CdS samples was between 125 nm and 245 nm.

The dependencies of the refractive indices and extinction coefficients on the incident wavelengths are shown in Fig.1, for two samples with different thicknesses.

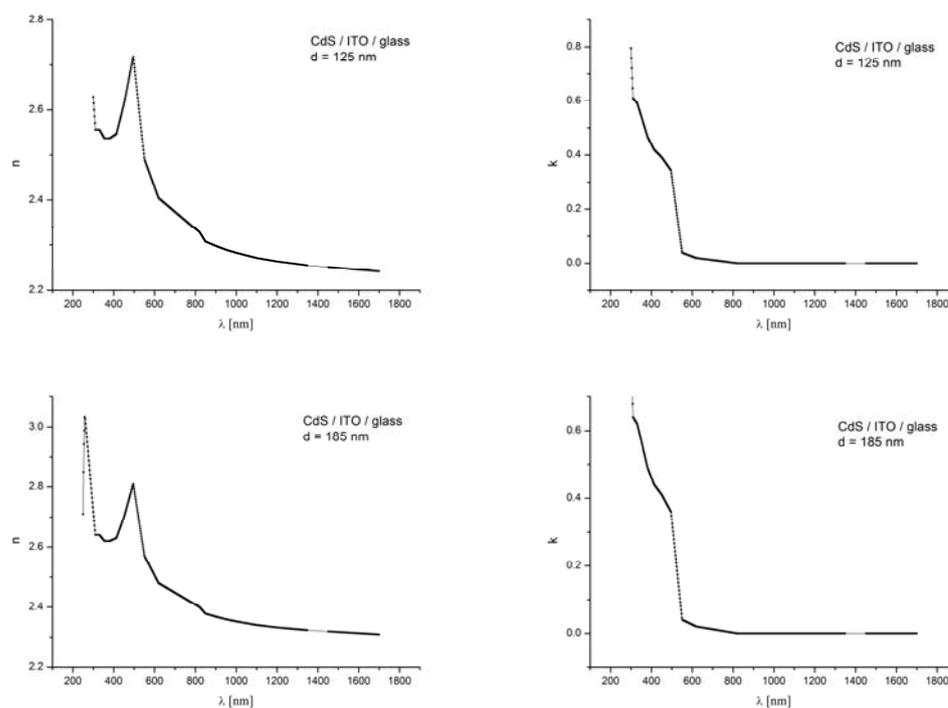


Fig. 1 – Variation of the refractive index and the extinction coefficient with the incident light wavelength for CdS thin films of two measured thicknesses: 125 nm (upper row) and 185 nm (lower row).

From the Fig. 1 we can see a slight increase of the refractive index with the increase of the CdS films thicknesses and, as AFM studies will show, with the increase of the particle size. From the variations of the extinction coefficients with the incident wavelength, it is observed that the extinction coefficient decrease rapidly with the increase of the wavelength (practically the CdS films are perfectly transparent in IR region).

The morphological features of CdS thin films were examined using a A 100 - AFM microscope (from A.P.E. Research, Italy). The microscope was used in the non-contact mode, in air, at a 325 kHz resonance frequency and an approximate 46 N/m constant force. The microscope was equipped with a commercial silicon cantilever (NSC15/AIBS). AFM micrographs were recorded from different regions of the samples, using sampling areas of $5 \mu\text{m} \times 5 \mu\text{m}$.

In Fig. 2 we present some AFM images for the investigated CdS samples.

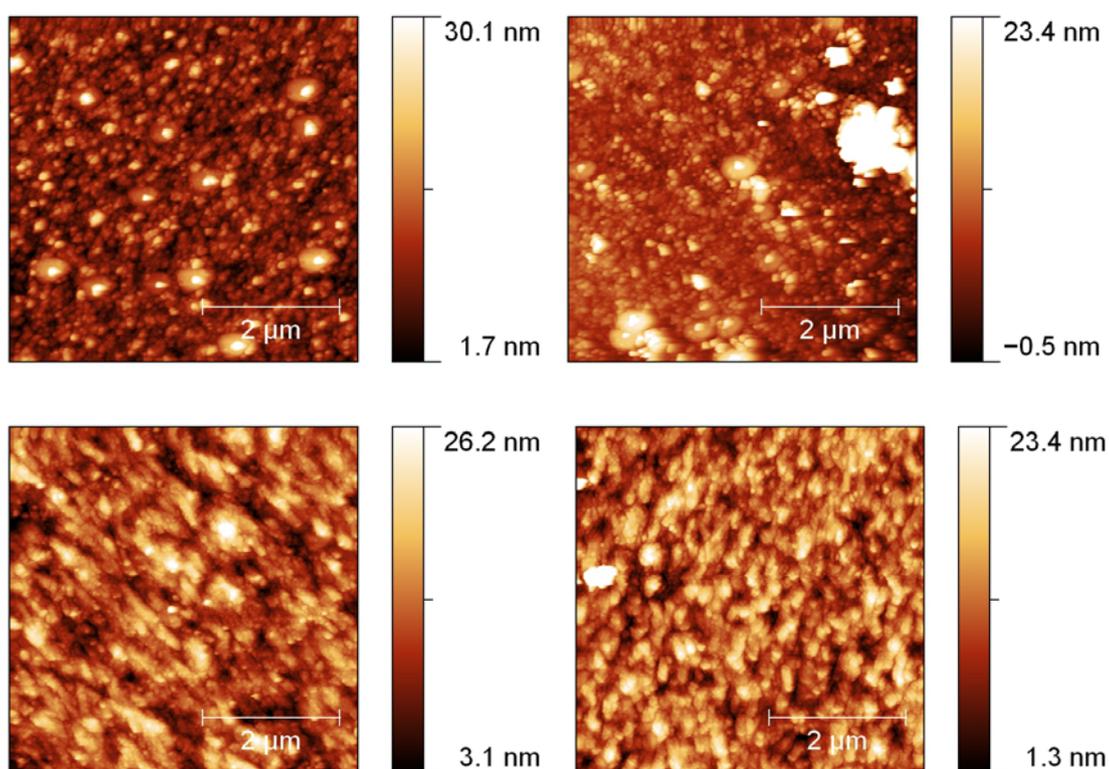


Fig. 2 – AFM bi-dimensional images for two samples: CdS (125 nm thickness) / ITO / glass (up left image), CdS (185 nm thickness) / ITO / glass (up right image), CdS (245 nm thickness) / ITO / glass (down left image) and CdS (185 nm thickness) / IZO / glass (down right image).

AFM images showed that all CdS samples present well defined nanosized grains, having a relatively small roughness (RMS) values, ranging from 3.7 nm to 7.5 nm, as can be seen from the table below.

Table 1.

Sample	RMS (nm)	Ssk	Sku
<u>P 1</u> : CdS (125 nm thickness) / ITO / glass	3.8	1.4	3.9
<u>P 2</u> : CdS (185 nm thickness) / ITO / glass	3.9	0.4	0.3
<u>P 3</u> : CdS (245 nm thickness) / ITO / glass	3.7	0.3	0.2
<u>P 4</u> : CdS (185 nm thickness) / IZO / glass	7.5	2.0	7.1

As can be seen from Table 1, among surface roughnesses (RMS) we calculated another two parameters: the Skewness (Ssk) parameter and the Kurtosis parameter (Sku) [35].

The definition relations of these two parameters are as follows:

$$S_{sk} = \frac{1}{MNS_q^3} \sum_{k=0}^{M-1} \sum_{l=0}^{N-1} [z(x_k, y_l) - \mu]^3 \quad (2)$$

$$S_{ku} = \frac{1}{MNS_q^4} \sum_{k=0}^{M-1} \sum_{l=0}^{N-1} [z(x_k, y_l) - \mu]^4 \quad (3)$$

We have used the Ssk parameter in order to describe the asymmetry of the height distribution histogram. We can see that the Ssk parameter exhibit a positive value greater than value 1 for P1 and P4 samples, suggesting a flat surface with extreme peaks; in the case of P2 and P3 the Ssk parameter have values close to zero, which indicates a symmetric height distributions. Another descriptive parameter is the Kurtosis one: small values of the Sku parameter indicate broader height distributions, whereas values higher than 3.0 indicate sharper height distributions. In P1 and P4 case the Sku parameter exceeded the value 3.9, respectively 7.1, suggesting homogenous surfaces with features having a high sharpness distribution.

All these surface morphology investigations for CdS films were completed with SEM images showed in Fig. 3.

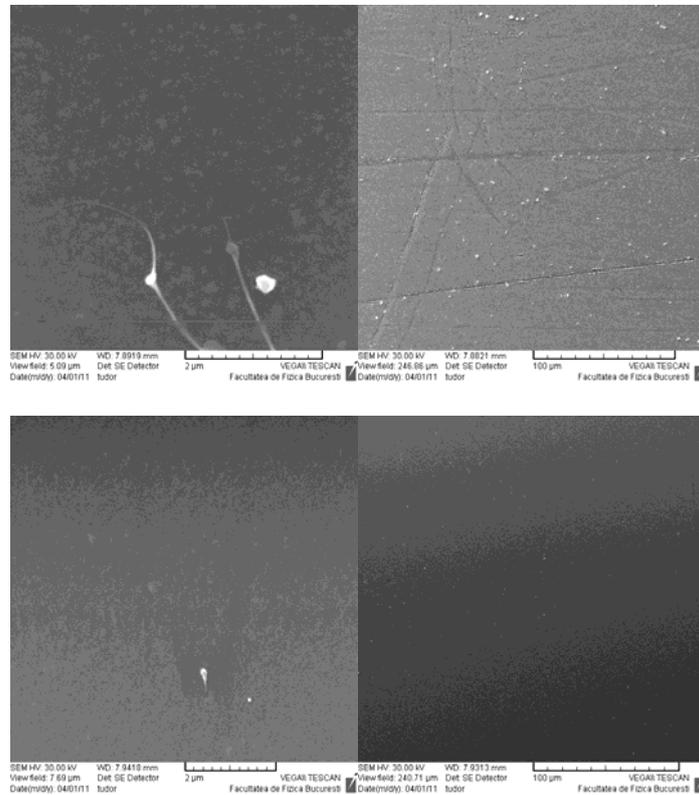


Fig. 3. SEM images for P 1 sample (upper row), respectively, P 3 sample (lower row).

In Fig. 3, we had choose two samples: P 1 sample which represents the material structure CdS (125 nm thickness) / ITO / glass and P 3 sample for the structure CdS (245 nm thickness) / ITO / glass (as in Table 1). For each of these two samples we depicted two SEM images, one at micro scale (hundreds of microns) and one at nano scale (few microns).

As we can see, at micro scale the employed surfaces are relatively smooth and uniform (with the exception of a few scratches). At nano scale, all the samples showed small irregularities which can be seen in AFM 2-D images.

4. Conclusions

We have obtained good quality CdS polycrystalline thin films by thermal vacuum evaporation (TVE) method.

A slight increase of the refractive index with the increase of the CdS films thicknesses was obtained, in direct correlation as AFM studies proved, with the increase of the particle size. From the variations of the extinction coefficients with the incident wavelength, it is observed that the extinction coefficient decrease rapidly with the increase of the wavelength (practically the CdS films are perfectly transparent in IR region).

The AFM images showed that all CdS samples present well defined nanosized grains, having a relatively small roughness (RMS) values, ranging from 3.7 nm to 7.5 nm. The CdS thin films investigated are perfectly suitable for producing relatively low cost and high efficient heterojunction photovoltaic cells.

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