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Physical properties of chemical bath deposited CdS thin films

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Abstract

Cadmium sulfide films of different thicknesses were deposited by chemical bath deposition (CBD) from a bath containing cadmium chloride, ammonium chloride, ammonium hydroxide and thiourea. The XRD patterns show that the films have a hexagonal phase with a preferential (0 0 2) orientation. The photoluminescence spectra show a defect structure, characteristics of the CdS films obtained by CBD. The electrical behavior in dark and under illumination, the optical properties and the band gap value reported in this work is in agreement with that reported in the literature.

Keywords: Chemical bath deposition; CdS; Thin films

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1. Introduction

Over the years, CdS thin films have been intensively investigated. They have been used in a lot of applications including electronic and optoelectronic devices. Among the several n-type semiconductor materials, it has been observed that CdS is the most promising heterojunction partner for the well-known polycrystalline photovoltaic materials CdTe and CuIn(Ga)Se$_2$ (CIGS). In both cases, a CdS layer is used as the large band gap n-type window material. In these devices, light penetrates the CdS layer and is absorbed in the p-type semiconductor close to the pn junction. Light

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absorbed in the CdS layer, in general, decreases the quantum efficiency in the blue part of the spectrum, and should be avoided. To minimize this loss, the CdS is made as thin as possible [1]. Researchers have tried different techniques to investigate structural and optical properties, but the identification of the best electronic quality for photovoltaic applications is challenging due to the thin film nature of the solar cells [2]. Thin polycrystalline films of CdS can be prepared by different methods such as sputtering, screen printing, physical vapor deposition, electrodeposition, chemical bath deposition (CBD), etc. Among these various techniques, the CBD is the most successful method [3] and the highest efficiency CdTe and CIGS solar cells were developed with CBD-CdS layers. In conventional solar cells, the CdS window layer was deposited onto the conducting glass substrates, whereas in the case of devices on metallic substrates the CdS layer has to be deposited on the absorber layer [4,5]. The CBD method is based on the controlled precipitation of the material in such a way that the precipitation occurs uniformly onto the substrate. Due to the simplicity and the very economical experimental facilities needed in the film deposition, the CBD is the best method to obtain low-cost CdS thin films that have optimal features for photovoltaic device applications [6]. In this work, we present films with good electrical and optical characteristics to be used as window material in CdTe solar cells.

2. Experimental

The CdS films were deposited on microscopic glass slides (25 mm × 75 mm × 1 mm) from a chemical bath containing cadmium chloride, ammonium chloride, ammonium hydroxide and thiourea in suitable proportions. The composition of the chemical bath for a set of five representative samples is shown in Table 1. The bath was maintained under constant stirring at a temperature of 75°C during the deposition. The details of the CBD deposition of the CdS can be found elsewhere [7]. All the solutions were prepared in de-ionized water using Baker Analyzed Reagents. In order to obtain good adherence and uniformity for the films, it is very important to provide clean substrates to the CBD system. The substrate cleaning was done in the following sequence. The glass slides were washed with an

Table 1
The composition of the chemical bath, temperature and the time duration of the film deposition

Experiment number	$CdCl_2$ 0.12 mol/l (ml)	NH_3 2 mol/l (ml)	H_2O (ml)	Thiourea 0.3 mol/l (ml)	Temperature (C)	Time (min)
1	2.5	10	75	2.5	75	60
2	2.5	15	70	2.5	75	60
3	2.5	10	70	5	75	60
4	2.5	15	70	2.5	75	120
5	5	30	53	2	75	120

Note: in all cases after the mixing of $CdCl_2$, 10 ml of NH_4Cl was added.

alkali-free detergent and a piece of gauze and rinsed many times in distilled water. The second step involves the ultrasonic cleaning of the glass substrates in isopropyl alcohol and de-ionized water. Finally, the substrates were dried in nitrogen atmosphere and inserted into the chemical bath.

2.1. Characterization of CdS films

Several techniques were used for the structural, morphological, optical and electrical characterization of the films, these techniques are described below:

1. The thicknesses and roughness, the average dispersion with respect to the average thickness of the film, were determined in a Sloan Dektak II A profilometer.
2. The optical transmission spectra of the samples were recorded in a Shimadzu 3101 PC UV-VIS spectrophotometer with air as reference.
3. The morphology of the surface was analyzed with a Park Scientific Instruments AFM machine with AFM-STM head and ULTRALEVERS of 0.6 μm points.
4. The electrical measurements were performed at room temperature. The $I-V$ characteristics in the planar configuration were determined in the dark and under illumination (100 Watts/m^2). The ohmic contacts were obtained using a paste of graphite–mercury.
5. The diffraction patterns were recorded using the radiation of copper (K_α radiation, with $\lambda = 1.54\,\text{Å}$) in a D-500 Siemens equipment.
6. The photoluminescence spectra were recorded using an Ar^+ laser as the exciting beam ($\lambda = 457.9\,\text{nm}$, 2.71 eV), and with a 1403-SPEX double monochromator. The detector was an RCA-C31034 photomultiplier tube.

3. Results

The difractogram of an as-deposited CBD-CdS sample 2 is shown in Fig. 1. The XRD pattern shows only one line that corresponds to the reflection (0 0 2) of the Greenockita (hexagonal), showing in general that the preferential orientation of the film is along the (0 0 2) direction. However, we can observe also that the films have some amorphous component.

The photoluminescence spectrum (Fig. 2) shows a defect structure characteristic of the films obtained by CBD, the band at 1.7 corresponds to sulfur vacancies [8]. The photoluminescence spectrum was obtained at a temperature of 10 K.

The AFM pictures are presented in Fig. 3, and can be seen that small grains are grouped to form big clusters like a cauliflower. The corresponding grain sizes range from tenths of a micron to 0.5 μm. The pin holes of similar size are also visible in the figure. This behavior is analogous to that observed in other samples prepared in this study, except for small variations with respect to the cluster formation.

In Fig. 4, the transmission spectrum of a CBD-CdS sample (5 in Table 1) is presented; we can note a sharp absorption edge at about 450 nm (dashed line) which corresponds to a band gap of approximately 2.47 eV. The transmittance in the

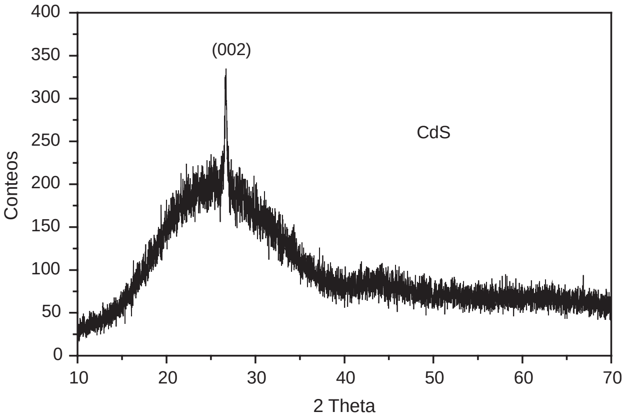

Fig. 1. X-ray spectrum of a typical CBD-CdS sample.

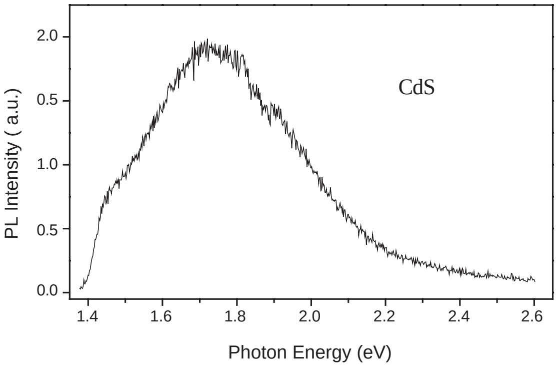

Fig. 2. Typical photoluminescense spectrum of CdS obtained by CBD.

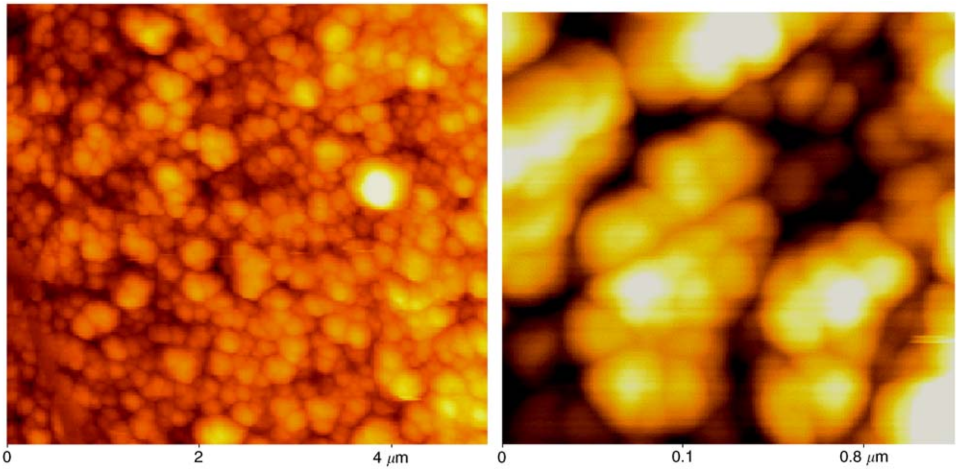

Fig. 3. AFM pictures of sample 5.

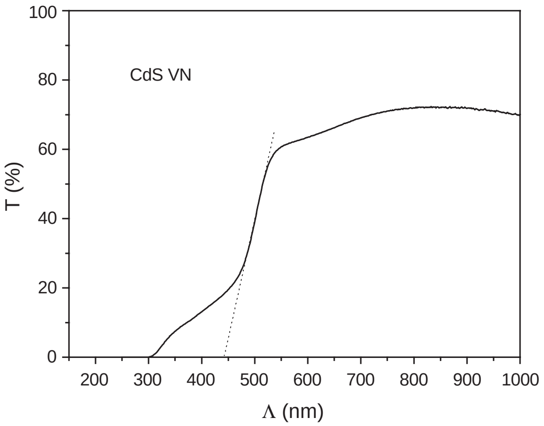

Fig. 4. Transmission spectrum of CdS.

Table 2
Results of optical, electrical, and morphological characteristics of the CBD-CdS films

Sample number	Dark resistivity (Ω cm)	Illumination resistivity (ρ_{illum}) (at 100 mWatt/cm^2) (Ω cm)	Thicknesses (Å)	Roughness (Å)	E_{gap} (ev)	T_{Aver} (%) (400–1000 nm)	Grain size (as-grown) (μm)
1	6.36E+04	2.57E+02	910	36	2.49	61.6	0.148
2	7.34E+03	24.31	1138	50	2.5	67.7	0.065
3	3.63E+05	3.42	538	15	2.41	63.3	0.068
4	2.57E+04	1.25E+02	1255	49	2.45	55.4	0.134
5	1.31E+04	59.54	1870	211	2.47	59.8	0.12

high-energy region extends up to 300 nm, and this is an evidence of disorder effects or presence of amorphous components in the film. The results of the optical, electrical and morphological characteristics of the films are summarized in Table 2. The low ρ_{illum} (resistivity under illumination of 100 mW/cm^2) and high T values are obtained for samples 3 and 2. This CdS film grown by CBD can serve as a good partner for the CdTe with low recombination losses and good optical transmission.

4. Conclusions

Optimal CdS films for photovoltaic devices were prepared by CBD method. The thickness of the films was controlled by the deposition time and the concentration of the bath. We are very confident that the data presented in Table 2 have good characteristics to be used as a window layer for photovoltaic applications.

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