Properties of CdS thin films grown by CBD as a function of thiourea concentration

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Abstract

This paper reports a study of the growth rate and optical properties of CdS thin films prepared by the chemical bath deposition technique. For the deposition an aqueous solution of cadmium chloride, ammonium chloride, ammonium hydroxide and thiourea were used, the films were deposited on conducting glass (SnO_2: F). The growth kinetics is relatively fast when the quantity of thiourea is increased in the deposition solution and higher value of band gap is obtained ($E_g = 2.44\,eV$). The films show good transmittance in the visible region.
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1. Introduction

Over the years the CdS thin films have been intensively studied and have been used in electronic and optoelectronic devices. Thin polycrystalline films of CdS can be prepared by different methods such as sputtering, screen printing, physical vapor

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deposition, electrodeposition, chemical bath deposition (CBD), etc. Among these various techniques, the CBD is the most successful method [1], and high-efficiency CdTe and CIGS solar cells were developed with CBD prepared CdS layers. The CBD method is based on the controlled precipitation of the material; the slow release of sulfide ions via the controlled hydrolysis of thiourea and the presence of a cadmium salt and NH_3 in such a way that the precipitation occurs uniformly onto the substrate. Ammonia prevents the undesirable homogenous precipitation by forming complexes with Cd ions, but on the other hand, the effect is to slow down the surface reaction, this implies that an optimum concentration of ammonia can be determined [2,3].

Due to the simplicity and the very economical experimental facilities needed in the film deposition, the CBD is considered as the best method to obtain low-cost CdS thin films that have optimal features for photovoltaic device applications [4]. This work reports the growth rate and optical properties of the CdS films prepared from chemical bath containing different proportions of S and Cd ions and different concentration of ammonia.

2. Experimental

The CdS films were deposited on SnO_2: F conducting glass from a chemical bath containing cadmium chloride, ammonium chloride, ammonium hydroxide and thiourea. The composition of the chemical bath for a set of four representative samples is shown in Table 1. The bath was maintained under constant stirring at a temperature of 75 °C during the process and the deposition times were varied from 5 to 180 min. 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 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. The optical transmission spectra of the samples were recorded in a Shimadzu 3010 PC UV–VIS spectrometer.

Table 1
The concentration of the chemicals used in the bath for the preparation of the CdS-samples

Experiment number	$CdCl_2$ 0.12 mol/l (ml)	NH_3 2 mol/l (ml)	H_2O (ml)	Thiourea 0.3 mol/l (ml)	S/Cd ratio
1	2.5	10	75	2.5	2.5
2	2.5	15	70	2.5	2.5
3	2.5	10	70	7.5	7.5
4	2	30	53	5	6.25

Note: In all cases after the mixing of CdCl2, 10 ml of NH4Cl was added.

3. Results

Optical transmission, deposition time, thickness and band gap value for CdS thin films of experiment 1 are shown in Fig. 1, we observed that as the thickness increase the band gap decrease in agreement with the reports in literature [5]. The first derivative of the Transmission—Energy spectrum (Fig. 2) is shown for the film with 60 min of deposition time (of experiment 1), from this graph, we calculated the band gap by considering that the band gap energy is given by the position where the minimum occurs, the band gap value obtained was 2.40 eV. In similar way the band gap values were estimated in all the cases.

The growth rate for the four experiments is shown in Fig. 3. We can see that in the first 30 min the fastest growth was obtained in experiment 3, where the S/Cd ratio in the bath is 7.5 and the higher value of band gap ($E_g = 2.44$ eV) was obtained, and the lowest growth kinetics was obtained for experiment number 2, where the S/Cd ratio is 2.5 and lower value of band gap ($E_g = 2.38$ eV) was obtained. In the experiments 1 and 3 similar behavior is observed during the period between 30 and 120 min, this can be due to the fast consumption of sulfur ions in the first few minutes in experiment 3, and probably after the first 30 min the quantity of free sulfur ions in the solution is the same as that in experiment 1, where the growth rate is lower in the first 30 min, so in the period of time between 30 and 120 min probably, we have the
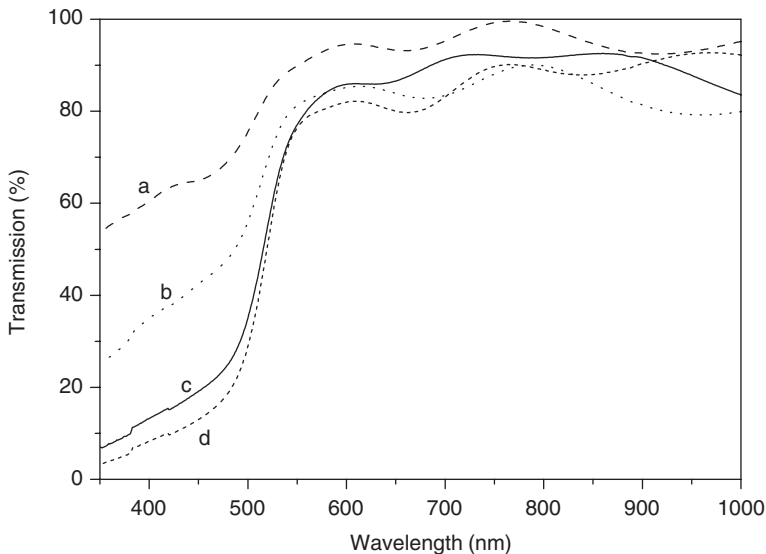

Fig. 1. Optical transmission, deposition time (t_d), thickness (d) and band gap (E_g) values for some CdS thin films of experiment 1. The graph (a) correspond to $t_d = 30$ min, $d = 207$ nm and $E_g = 2.43$ eV, the graph (b) correspond to $t_d = 60$ min, $d = 217$ nm and $E_g = 2.40$ eV, the graph (c) correspond to $t_d = 120$ min, $d = 229$ nm and $E_g = 2.39$ eV, and the graph (d) correspond to $t_d = 150$ min, $d = 280$ nm and $E_g = 2.37$ eV.
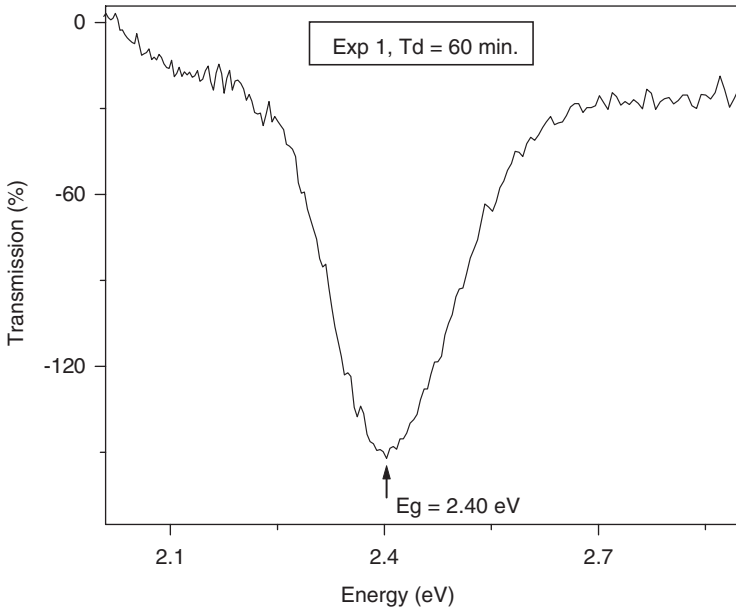
Fig. 2. First derivative of the Transmission—Energy spectrum is shown, for the film with 60 min of deposition time of experiment 1.
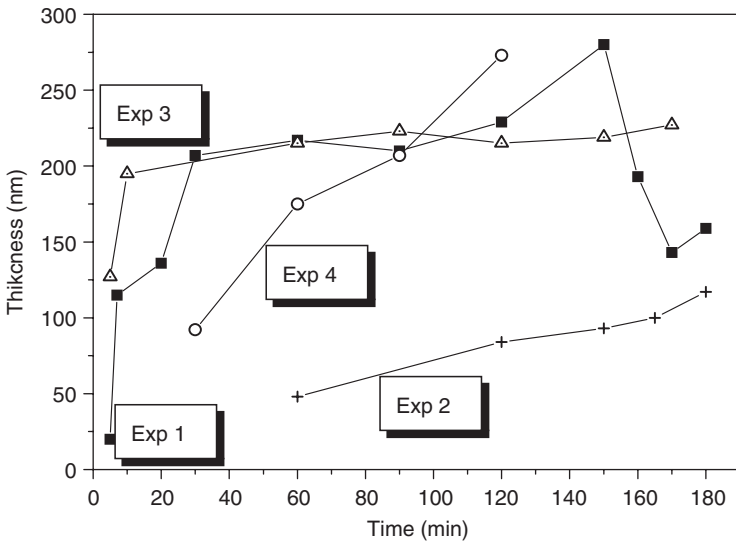

Fig. 3. Growth kinetics of the various CdS samples prepared according to the Table 1.

same quantity of free sulfur ions in the solution. Thicknesses of 100 to 200 nm were obtained in the first few minutes and later there is not much increase in the thickness, this indicates that beyond the first few minutes the quantity of adherent ions that

contribute to the deposition kinetics of the film growth decreases and they get precipitated forming a super saturated solution.

The differences in the chemical bath among these samples are the amount of ammonium and the concentration of S/Cd, apparently both of these parameters affects the rapid growth of the film in the first few minutes, the amount of ammonium affects in the experiments 2 and 4 mainly, and the ratio of S/Cd influences in experiments 1 and 3.

Experiments 2 and 4 are similar and a linear relationship exists between thickness and deposition time, the lowest slope is obtained for the graph corresponds to experiment 2 and the band gap of the CdS was estimated as 2.38 eV. In experiment 4, the growth rate is higher than that of experiment 2, this is due to the double quantity of ammonia used in the solution, in agreement with previous reports [1]. The S/Cd ratio is increased to 6.25 in order to get samples with more stochiometric relation between S and Cd, because it is well known that these films grow with sulfur vacancies [6], and in this way contribute to the formation of a better ternary compound at the metallurgical edge of CdS/CdTe solar cell. The band gap obtained in this experiment was 2.39 eV. Due to the linear relationship in experiments 2 and 4, we can have a better control on the growth kinetics of the films.

In Fig. 4, representative transmission spectra of CdS samples prepared from the four chemical baths is presented, it can be seen that the average transmission for all the samples is about 90% for the wavelengths above 600 nm. In this work we obtained CdS thin films grown by CBD with band gap values that vary from 2.38 eV to 2.44 eV, low S- vacancies and good transmission. Although a different S/Cd
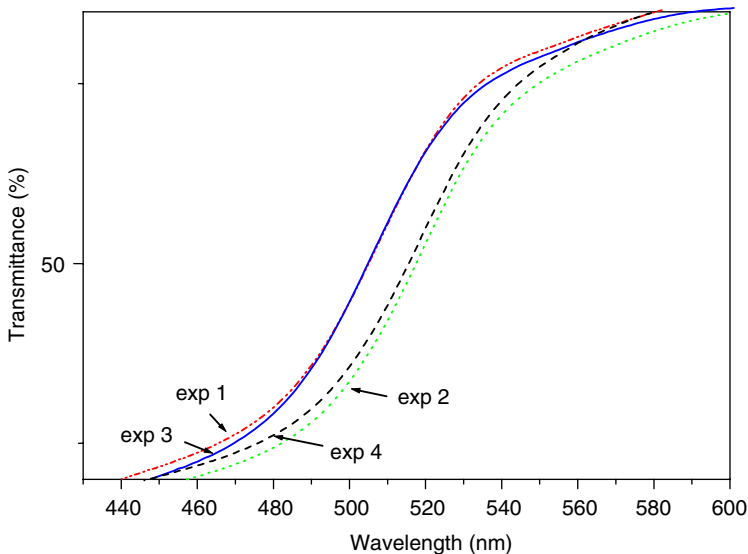

Fig. 4. Representative optical transmission spectra of CdS thin films of different experiments. The graphs; exp 1, exp 2, exp 3 and exp 4 corresponds to typical optical transmission spectra obtained in experiments 1, 2, 3 and 4 respectively.

concentration and ammonium quantity were used the optical transmission curves are very similar for all the experiments.

4. Conclusions

CdS thin films with optimal transmission and band gap values between 2.38 and 2.44 eV were obtained by CBD method. The growth rate was studied and we gained a better knowledge of the growth rate in order to obtain optimal thickness to be used as window material in the solar cells. We observed that the growth rate is faster when the quantity of thiourea is much greater than cadmium chloride concentration in the solution and also when the S/Cd ratio is higher, the band gap value also increases.

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