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EFFECTS OF THE ANNEALING AND $CdCl_2$ TREATMENT ON THE STRUCTURAL AND OPTICAL PROPERTIES OF AMMONIA-FREE AND AMMONIA CdS THIN FILMS BY CHEMICAL BATH DEPOSITION

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CdS thin films, with and without ammonia, were prepared using the chemical bath deposition method (CBD), with bath temperature of 70^0C, 20 and 60 min times of reaction and different complexing agents. We study the effects of $CdCl_2$ treatment and annealing on these films. The thin films were characterized by X-Ray diffraction (XRD), Scanning Electron Microscopy (SEM), optical absorption spectroscopy and Atomic Force Microscopy (AFM). The XRD measurements showed that the films have polycrystalline nature, hexagonal structure and the crystallites are oriented preferentially with the (002) and (110) planes. The optical absorption measurements show the presence of direct transition with energy band gaps of 2.55 eV and 2.44 eV and after diminished to 2.37 eV and 2.36 eV.

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1. Introduction

The deposition and characterization of thin films of CdS have been widely investigated for its potential application in the electronic and optoelectronic devices [1,2]. Polycrystalline thin films of CdS are commonly used as window layer in thin film solar cells of the type CdS/CdTe and has been attracting much research attention worldwide [3]. There are many methods for making CdS thin films, such as electro-deposition [4], chemical bath deposition (CBD) [5], close space sublimation (CSS) [6], chemical vapour deposition of metal organic (MOCVD) [7], screen printing (SP) [8]. Among them, Chemical bath deposition (CBD) is one of the most convenient methods to produce CdS thin films for photovoltaic applications because no requirement for sophisticated instruments, simplicity, economical way of large area deposition, etc. and facilities the betters orientation of the crystallites with improved grain structure [9]. Solar cells with record efficiency of 16.5% have been reported for CdTe/CdS thin film solar cells using CBD CdS films [10]. However, pinholes presented in thin CdS thin films and small nanocrystalline grains severely affect the performance of CdTe/CdS solar cells. Depending on the deposition process, the as-deposited CDS thin film is either in an amorphous state, in metastable cubic, or in a mixed cubic/hexagonal phase [3]. For high-efficiency thin film solar cells of the type CdS/CdTe,

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prepared by techniques such as CBD, electrodeposition, physical vapour deposition MOCVD, requires a $CdCl_2$ heat treatment after depositing CdTe film for to improve the crystalline quality, optimizing the recrystallization process and improve the structural and electrical properties [11,12, 13]. On the other hand, it is clear that the preparation of CdS by CBD represents a serious contamination problem because of the employment of large amounts of ammonia, which is toxic and highly volatile, harmful for environmental and some research has been done to reduce this environmental problem [14,15,16]. In this work, two samples of CdS were grown by CBD. We study the effects of $CdCl_2$ treatment and annealing on structural and optical properties of CdS thin films with different complexing agent, with and ammonia-free.

2. Experimental

Two different formulations were used to deposit CdS thin films by CBD technique. The different types of CdS thin films were labeled as: X- CdS, Y- CdS. All CdS thin films were deposited on glass substrates. For the deposition of X-CdS samples, the glass substrate was introduced into a solution consisting of 25 ml of $CdCl_2$ at 0.1 M, 20 ml $C_6HO_7Na_3.2H_2O$ to 1 M, 15 ml NH_4OH to 4M, 10 ml of $CS(NH_2)_2$ (thiourea) at 1 M and 30 ml of deionized water, prepared in a 100 ml beaker [17]. The Y-CdS thin film was raised in a reaction solution prepared with the following compounds: 10 ml of $CdCl_2$ at 0.05 M, 20 ml of $C_6H_5O_7Na_3.2H_2O$ at 0.5 M, 5 ml of KOH (potassium hydroxide) at 0.3 M, 10 ml of $CS(NH_2)_2$ at 0.5 M and 55 ml of deionized water. The types of films were grown at a 70^0C reaction temperature, but the deposition time was 20 and 80 minutes respectively. Table 1 shows a summary of all the components. The CdS thin films showed a yellow color, uniformity and good adhesion to the substrate and they have a thickness of approximately 100 nm. The samples were introduced into a solution of $CdCl_2$ at 0.3 M for 10 minutes, after which time the films were dried with N_2 (nitrogen) and immediately introduced into an oven for 30 minutes. The annealing applied to the CdS thin films was the following values: 400, 420 and 450^0C. The crystal structure of all films was determined from the diffraction patterns of X-rays with a Rigaku D/max-2100 diffractometer. The Optical transmission spectra of the films were recorder with a spectrometer TekTM Film 3000. The morphology of the samples surface were investigated by a scanning electron microscope (SEM) using a XL30 ESEM Scanning Electron Microscope Philips.

Table 1. Summary of all components of X-CdS and Y-CdS thin films.

Component	X-CdS (ml)	Y-CdS (ml)
$CdCl_2$	25 (0.1M)	10 (0.05M)
$C_6HO_7Na_3.2H_2O$	20 (1 M)	20 (0.5M)
$CS(NH_2)_2$	10 (1M)	10 (0.5M)
KOH	-	5 (0.3M)
NH_4OH	15 (4M)	-
Deionized water	30	55

3. Results and discussion

3.1 Structure properties

Fig. 1 shows the XRD patterns, between 20^0 and 60^0, for 2θ, without $CdCl_2$ treatment before and after the annealing for samples X-CdS and Y-CdS. The diffraction spectra exhibit a strong diffraction peak at approximately $2\theta = 26.7^0$, which coincides with the diffraction line (002) hexagonal crystalline phase of CdS. Fig. 2 shows XRD patterns of the X-CdS and Y-CdS samples after $CdCl_2$ treatment and annealing. For 450^0C the diffraction spectra exhibits four high XRD

peaks at near 24.7^0, 26.7^0, 28.1^0, 48^0 and others, which correspond to the diffraction lines (100), (002), (101) and (103) of hexagonal phase CdS. From the diffraction spectra it has been found that X-CdS and Y-CdS samples are polycrystalline in nature with hexagonal structure having the preferential orientation along crystal direction [002].

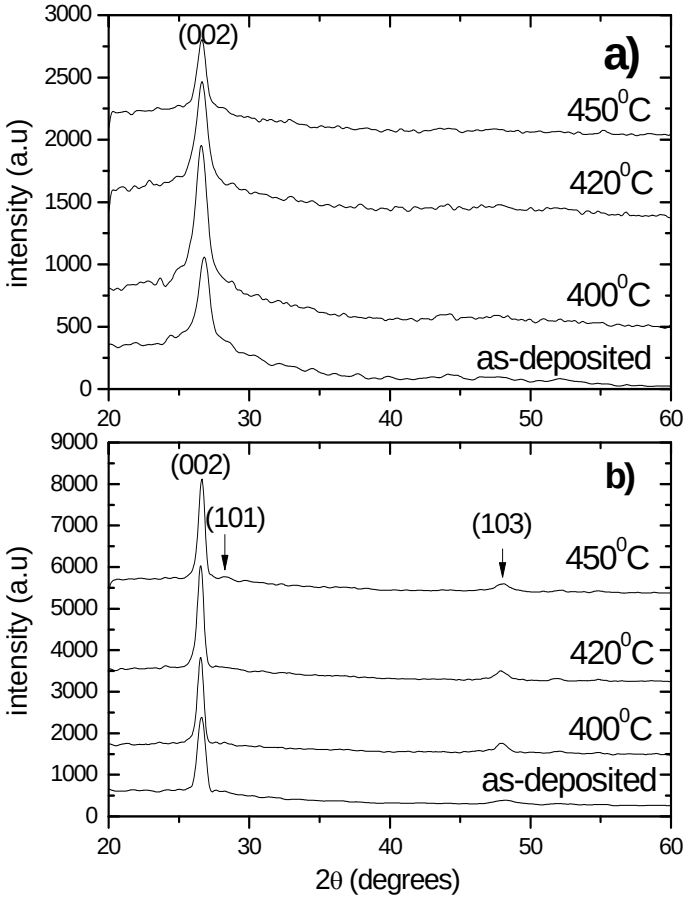

Fig. 1. a) XRD spectra of X-CdS thin film and b) XRD spectra of Y-CdS thin film. All without $CdCl_2$ treatment and annealing.

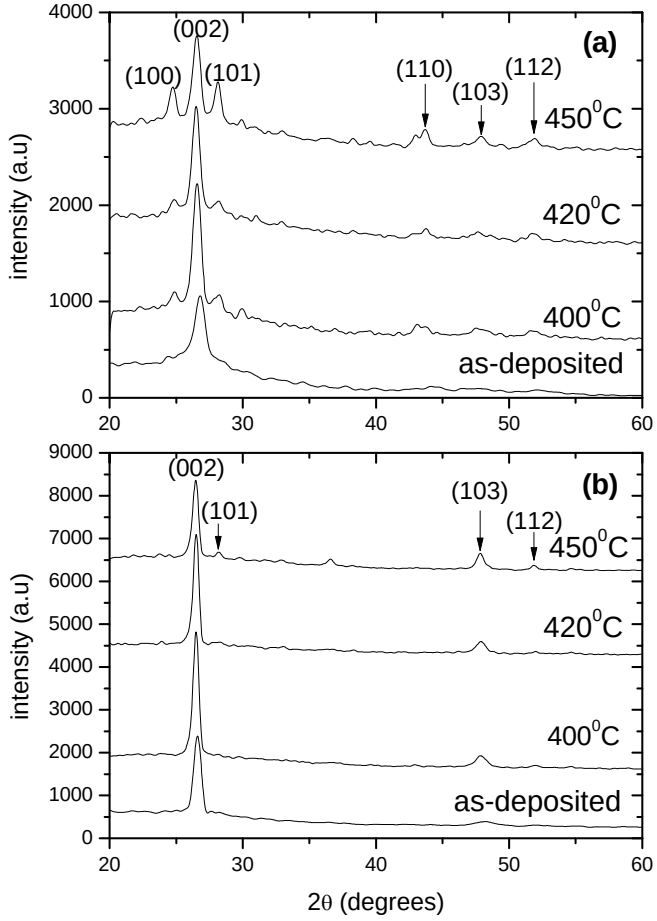

Fig. 2. a) XRD spectra of X-CdS thin film and b) XRD spectra of Y-CdS thin films. All samples with $CdCl_2$ treatment and annealing.

The crystalline sizes of sample films are of the order 10-17 nm (see Table 2).

Table 2. Grain size of X-CdS and Y-CdS thin films

Temperature (^{0}C)	X-CdS (nm)	X-CdS ($CdCl_2$) (nm)	Y-CdS (nm)	Y-CdS ($CdCl_2$) (nm)
as-ground	10.15	10.15	11.82	11.82
400	9.34	11.74	16.27	16.15
420	9.08	12.62	15.85	16.93
450	11.64	12.25	16.22	16.35

The surface morphology of CdS films was obtained by SEM. Images 3a and 3c show the surfaces of X-CdS and Y-CdS film as ground, while Fig. 3b and 3d correspond to the surfaces of the samples X-CdS and Y-CdS with annealing at 450^{0}C with $CdCl_2$ treatment. In the 3b image we see that X-CdS shows a granular structure with grain boundary well defined, there is also the presence of large aggregates dispersed on the surface, which becomes more evident when the film

is annealing with $CdCl_2$ treatment, here the grain size grows. It has been shown by TEM measurements that these grains are composed of CdS crystallites smaller. The images of the films produced in an ammonia-free system with and without annealing at 450^0 C with $CdCl_2$ treatment show much smoother surface with much smaller grains. In these images there is also added on the surface of the film, yet they are present in smaller amounts.

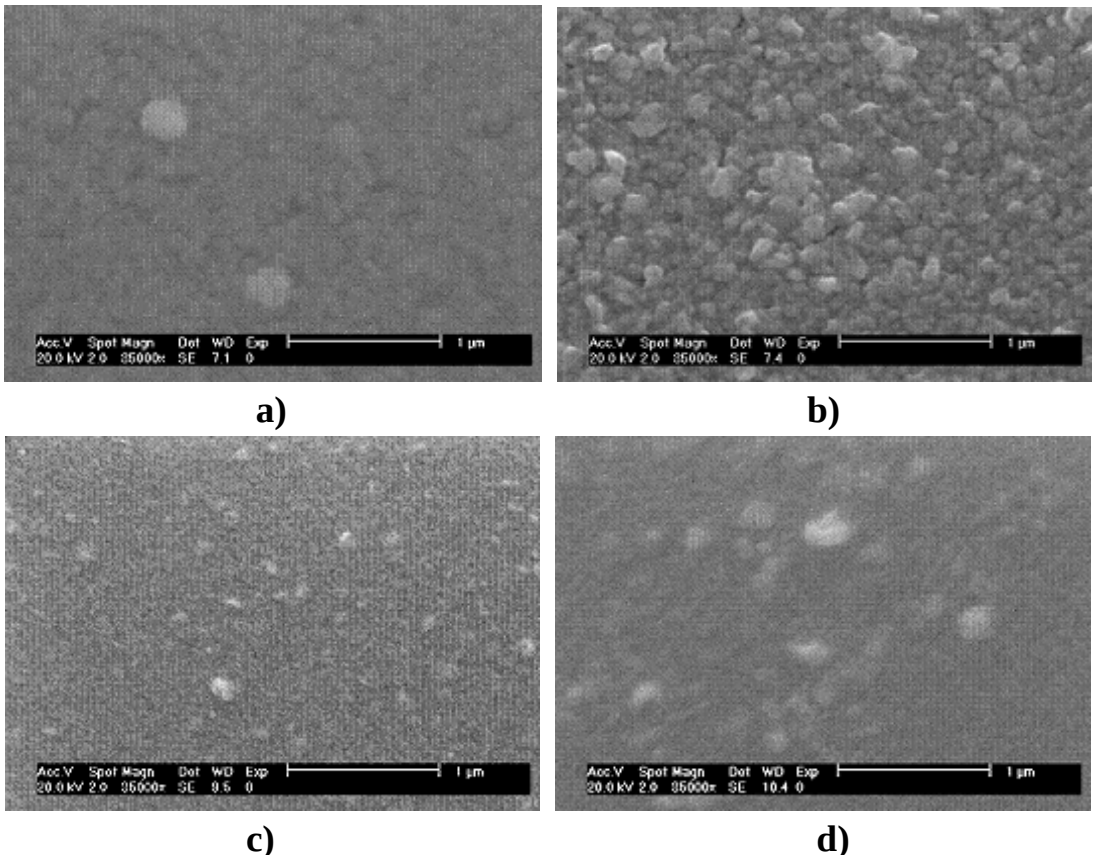

Fig. 3. X-CdS thin film: a) as ground and without $CdCl_2$ treatment and b) with $CdCl_2$ treatment and 450^0C annealing; and Y-CdS thin film: c) as-deposited without $CdCl_2$ treatment and d) with $CdCl_2$ treatment and 450^0C annealing.

3.2 Optical analysis

The transmission spectra of the X-CdS and Y-CdS films is shown in the Figure 4 (before and after annealing, without and with $CdCl_2$). The transmission spectra of CdS films were adjusted considering a two-layer system represented by the glass substrate and the CdS film. In these spectra shows that the absorption edge of the films X-CdS and Y-CdS with $CdCl_2$ treatment are shift slightly longer wavelengths and the transmission rate is reduced, i.e., there is a red shift effect of the transmission spectra after annealing, which means that there is some decrease of the band gap value after annealing. Effectively, Eg = 2.55 eV before annealing and 2.37 eV after annealing for X-CdS samples without $CdCl_2$ treatment [see a) and b) of Fig. 4]; and Eg = 2.44 eV before annealing and 2.36 eV after annealing for Y-CdS thin films with $CdCl_2$ treatment [see c) and d) of Fig. 4]. The transmission spectra were used to determine the band energy gap, Eg, of all films. For this, we use the model of intrinsic absorption of light to direct transitions. Eg values are shown in Table 3. We can see that the forbidden energy band of all CdS films decreases when heat treated with and without $CdCl_2$.

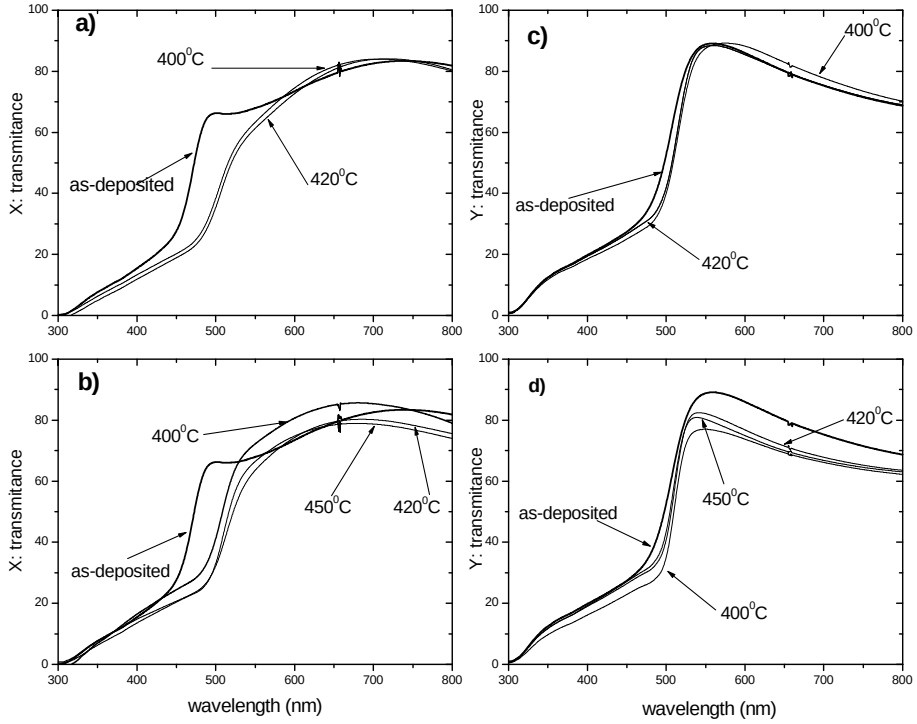

Fig. 4. a) y b) transmittance spectra of X-CdS thin film without and with $CdCl_2$ treatment, respectively; c) and d) trasmitance spectra of Y-CdS thin films without $CdCl_2$ treatment, respectively.

Table 3. Band gap of X-Cds and Y-Cds thin films.

Temperature (^{0}C)	X-CdS band gap (eV)	Y-CdS band gap (eV)
as ground	2.55	2.44
400	2.39	2.36
400 ($CdCl_2$)	2.40	2.38
420	2.37	2.35
420 ($CdCl_2$)	2.35	2.38
450	2.34	2.36
450 ($CdCl_2$)	2.37	2.36

4. Conclusions

Two sets of CdS thin films were prepared by CBD with different complexing agents, one with ammonia and other ammonia-free. We studied the effect of annealing and $CdCl_2$ treatment on the structural and optical properties. The films are polycrystalline in nature with hexagonal structure. The annealing and $CdCl_2$ treatment causes the reduction of band gaps. Both samples have a similar structural and optical property, however, the Y-CdS thin film does not contain ammonia, eliminate its toxicity.

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