Preparation and Characterization of CdS Thin Films

H. Moualkia [1,*], N. Attaf [2], L. Hadjeris [1], L. Herissi [1], N. Abdelmalek[1]

[1] Laboratoire des matériaux et structure des systèmes électromécaniques et leur Fiabilité, Faculté des sciences et de la technologie, Université Larbi Ben M'Hidi de Oum El Bouaghi, Algérie

[2] Laboratoire de couches minces et interfaces, Faculté des sciences, Université Mentouri de Constantine, Algérie

Corresponding author: moualkia88@ yahoo.fr

ABSTRACT

In this work we report the structural, optical and electrical properties of CdS thin films prepared by chemical bath deposition (CBD) under the effect of solution temperatures. The solution temperatures used vary between 55 and 75 °C. The XRD patterns show that the films have a hexagonal phase with a preferential (002) orientation. The structural parameters such as the grain size, dislocation density and strain are calculated. The transmission spectra, recorded in the UV visible range, reveal a high transmission coefficient (85%) of the prepared films and an optical band gap values of 2 - 2.4 eV. The electrical measurements show that the dark conductivity values increase from 10^{-7} to 10^{-4} $(\Omega.cm)^{-1}$ at higher temperature (Ts > 65°C). It is found that the photoconductivity of the deposited films is two to five decades larger than the dark conductivity, and the photoconductivity to the dark conductivity ratio obtained at 3000 Lx vary from 10^2 to 10^5. From these results we inferred that the elaborated CdS thin films exhibit good properties intended for solar cell window layers.

Index Terms-CdS, Thin films, Chemical bath deposition (CBD), Photoconductivity, Solar cell

1. INTRODUCTION

Solar Energy is one of the abundant, non polluting renewable energy of our planet. During the last three decades considerable progress has been made in developing technologies to harness electricity from solar radiation. The most commonly used solar cell material is crystalline silicon (Si) and naturally the cost is an obstacle to terrestrial applications. The development of thin film solar cells is an active area of research at this time. Recently, much attention has been paid to the development of low cost, high efficiency thin film solar cells. Cadmium sulphide (CdS) is one of the low cost materials of this kind. CdS is known to be an excellent heterojunction partner for p-type cadmium telluride (CdTe) and p type copper indium diselenide ($CuInSe_2$) due to its wide band gap, high absorption coefficient and photoconductivity. It has been widely used as a window material in high efficiency thin film solar cells based on CdTe or CIGS [1, 2].

Moreover, the latter application needs CdS thin film with (i) high structural orientation, (ii) high optical transmittance to allow the sunlight to enter the absorbing material more readily, (iii) relatively large conductivity to reduce the electrical solar cells losses and higher photoconductivity that causes a smaller series resistance in the cells.

Several methods were used to prepare CdS thin films such as electrodeposition, spray, sputtering and chemical bath deposition (CBD). Among these methods chemical bath deposition is well investigated and widely employed to obtain CdS films for photovoltaic applications [4]. Indeed, J. N. Ximello-Quiebras [4] has investigated the physical properties of chemical bath deposited CdS thin films. J.Y. Choi [5], using different chemical reagents and ultrasonic agitation, achieves hexagonal CdS films oriented in the (101) direction. C. Guillén et al. [6] reported that the CdS films prepared by CBD method using low cadmium salt concentration and a high thiourea one in the bath, exhibited a high transparent CdS films. U. S. Jadhav at al. [7] have studied the effect of Cd:S ratio on photoconductivity of CdS films. This research work aims at studying the influence of solution temperature on the structural, optical and electrical properties of CdS thin films deposited by CBD. The samples are illuminated at different light intensity of 220, 630 and 3000 Lx in order to understand the influence of the latter parameter on the photoconductivity of the elaborated films.

2. EXPERIMENTAL DETAILS

The CdS thin films are deposited onto glass substrates by chemical bath deposition technique. The used solution is prepared in 100 ml beaker by the sequential addition of distilled water, ammonia NH_4OH (2M) cadmium acetate $Cd(CH_3COO)_2 2H_2O$ (5.10^{-3} M), Thiourea $SC(NH_2)_2$ (2.10^{-2} M). A total volume of 78.5 ml of the chemical bath was formed after mixing the different components. Before deposition, the glass substrates are cleaned in acetone and methanol ultrasonically, rinsed in distilled water and dried in hot air. Then, the glass substrates are vertically immersed into the chemical bath solution. The solution temperatures are vary from 55 to 75°C. The deposition time is 60 min for each film. After deposition, the film is retired from the chemical bath, cleaned with distilled water and dried in air at room temperature.

The films' thicknesses are measured using a profilometer DEKTAK 3ST. The structural characterization of the films is carried out by the X-ray diffraction (XRD) technique using an X-ray diffractometer (Philips X'Pert) with $Cu\,K\alpha$ radiation. The optical transmittance of the films is studied using a Shimadzu 3101 PC UV-visible spectrophotometer. The optical gap is deduced from the recorded transmittance spectra. The electrical conductivity and the photoconductivity of the films are measured in a coplanar structure obtained by evaporation of two golden strips on the film surface. For the photoconductivity measurements, the samples are illuminated by unfiltered white light from a halogen lamp whose light intensities are 220, 630 and 3000 Lx

3. RESULTS AND DISCUSSION

3.1 Structural properties

Figure 1 shows the XRD patterns of the samples deposited at different temperatures. The diffraction patterns show a diffraction peak located at 26. 75° corresponding respectively to (002) plane of hexagonal CdS according to the JCPDS data (6-314) [8]. The same structure in the CdS thin films deposited by CBD has been reported by earlier reports [9-12]. Note that for solar cell applications, hexagonal CdS thin films are preferable due to their excellent stability [13].

From the DRX pattern, it is clear that the (002) diffraction peak disappears at 75°C. This is due probably to the defect formation such as sulphur vacancies Vs and cadmium interstices Icd at higher temperature as can be seen in more detail below. It is well established that the defects formation reduces the crystalinity [14, 15, 16, 17].

The grain size (D), dislocation density (δ) and the strain (ε) are calculated using respectively the relations 1, 2 and 3 given below and reported in table 1:

$$D = \frac{0.9\,\lambda}{\beta\cos\theta} \qquad (1)$$

$$\delta = \frac{1}{D^2} \qquad (2)$$

$$\varepsilon = \frac{\beta\cos\theta}{4} \qquad (3)$$

Where, λ is the wavelength of the incident X-rays, θ is the incidence angle and β is the full width at half maximum (FWHM) of the diffraction peak.

Approximately similar structural parameters values were reported in the literature [9, 18].

Table 1

Structural parameters of the CdS films (Grain size (D), dislocation density(δ), strain(ε))

Sample temperature Ts (°C)	D (nm)	δ (×10^{15} (lines/m^2))	ε (10^{-3})
55	20,93	2,282	1,654
60	17,56	3,243	1,972
65	18,35	2,969	1,888
75	-	-	-

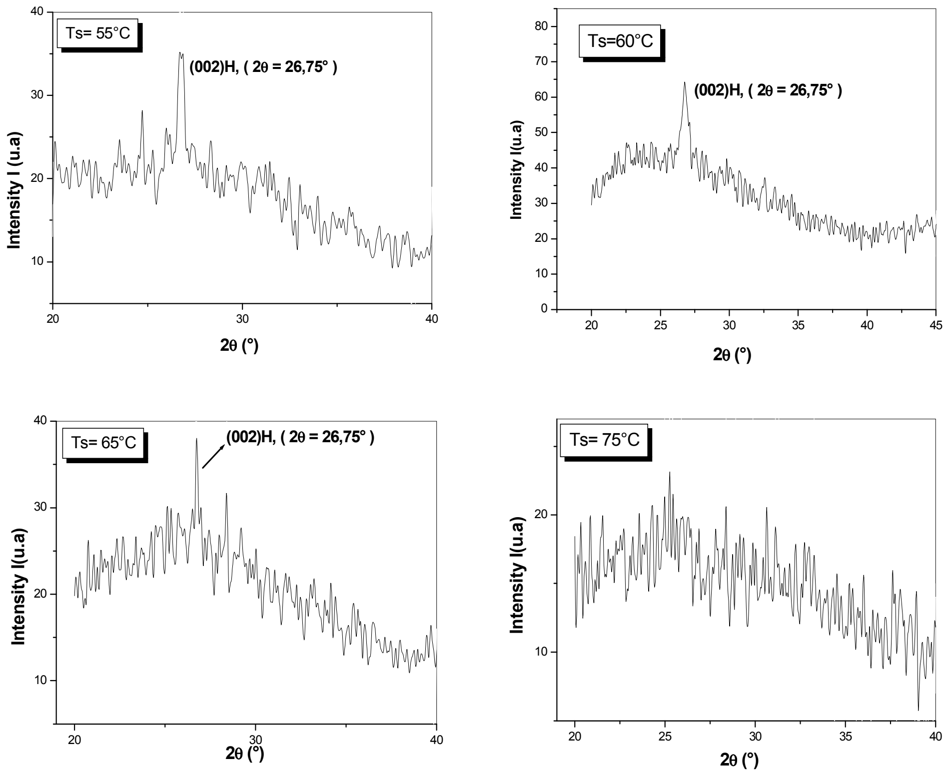

Figure 1: XRD spectrum of CdS thin films under different solution temperatures

3.2 Optical properties

Figure 2 shows the optical transmittance of CdS films deposited at various solution temperatures. It is clear from the figure that the transmittance increases sharply in the range 400-450 nm. Then all films exhibit optical transmittance more than 60 % above 500 nm, which is one of the prerequisites for solar cells window layer [19]. We note that the transmittance is extended to lower wavelength up to 300 nm. This is due probably to the disorder effects or to the presence of the amorphous components in the film [4]. The absorption coefficient α of CdS thin films is calculated from the transmittance spectra using the Beer-Lambert approximation.

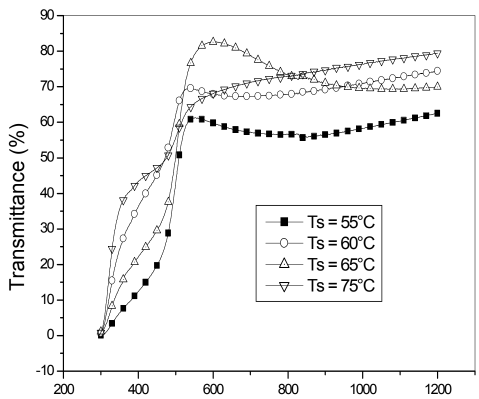

Figure 2: Influence of solution temperature on the optical transmittance of CdS films

The absorption coefficient α can be expressed by the standard expression for direct transition,

$$\alpha = \frac{A\sqrt{h\upsilon - Eg}}{h\upsilon} \qquad (4)$$

Where *A* is a constant, *Eg* is the energy band gap, υ is the frequency of the incident radiation and *h* is Plank's constant. The energy gaps of the films have been determined by extrapolating the linear portion of the plots of $(\alpha h\upsilon)^2$ against $h\upsilon$ to the energy axis. The obtained values are in the range of (*Eg* = 2 - 2.4 eV) (see table 2) in agreement with earlier findings [18, 20].

3.3 Electrical properties

The conductivity is measured in the dark at different temperatures. The variation of the dark conductivity and its activation energy E_A as a function of the solution temperature are presented in figure 3. The E_A values are deduced from the variation of the conductivity versus temperature as shown in our previous work [21].

The electrical activation energy $E_A = E_C - E_F$, indicates the Fermi level position E_F regarding the minimum of the conduction band E_C and thereafter the free carriers concentration variation. To determine the Fermi level position in the forbidden band, one calculates the ratio $(2E_A/Eg)$. The results are presented in table 2.

As can be seen from table 2, the $(2E_A/Eg)$ values are less than the unity for all solution temperatures indicating that the deposited films are of n-type. This is in agreement with earlier findings [13, 22].

Table 2: Optical bandgap (Eg) and $(2E_A/Eg)$ ratio of CBD-CdS films.

Sample temperature (°C)	*Eg (eV)*	E_A	$(2E_A/Eg)$
55	2,3	0.24	0.208
60	2,2	0.32	0.290
65	2,4	0.40	0.333
75	2	0.13	0.13

As shown in figure 3, for solution temperature $Ts \leq 65$°C, the dark conductivity varies from 10^{-6} to 10^{-7} $(\Omega.cm)^{-1}$. This low dark conductivity may be interpreted by a decrease of the carrier concentration since the electrical conductivity depends on the number of charge carriers. It may also be due to the presence of structural disorders and dislocations as interpreted by D. Padiyan and al [23].

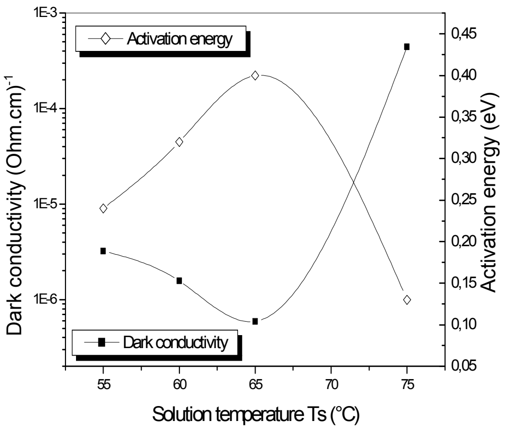

Figure 3: Dependence of dark conductivity and electrical activation energy on the solution temperature.

In the high temperature region (Ts > 65°C), the dark conductivity increases from 10^{-7} to 10^{-4} $(\Omega.cm)^{-1}$. This increase of the dark conductivity is due principally to the sulphur deficiency which is due either to the presence of hydroxide cadmium $Cd(OH)_2$ [24], since the dominating growth mechanism is cluster by cluster at higher temperature [25], and to the sulphur volatility.

Consequently, we suggest that CdS films deposited at high temperatures contain a high concentration of sulphur vacancies Vs and cadmium interstices Icd which act as donor's defects in CdS films.

3.4 Photoconductivity properties

The dark conductivity (σdark) and the photoconductivity (σphot) as function of solution temperature at different light intensities 220, 630 and 3000 Lx are reported in figure 4. The photoconductivity of the films increases with increasing light intensity.

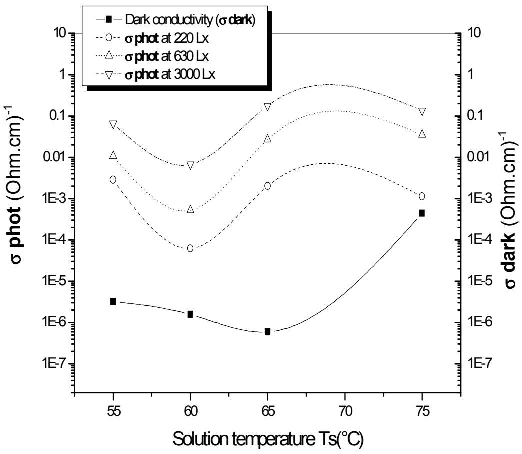

Figure 4: Variation of the photoconductivity σphot at different light intensities 220, 630 and 3000 Lx as function of solution temperature.

It is also seen from figure 4 that the photoconductivity of the deposited films is two to five orders of decade larger than the dark conductivity. The photoconductivity to the dark conductivity ratio obtained at 3000 Lx varies from 10^2 to 10^5. Similar results are reported by C. Guillen et al. [6] in the same temperature range.

The photoconductivity evolution as a function of light intensity and temperature can be interpreted as fellow:

- As the films are prepared by the chemical bath deposition method, some oxygen can be absorbed onto the surface and/or in the grain boundaries of the CdS films [9, 26]. The absorbed oxygen acting as an acceptor impurity and as a trap for carriers. This explains the low photoconductivity at 220 lx.

- At higher light intensities (630 and 3000 lx), the oxygen is desorbed from the samples, resulting in the rise of the photoconductivity [6, 27]

- The low photoconductivity in the film deposited at Ts = 60 °C is due to the recombination velocity of the photocarriers. At this solution temperature, the obtained films present relatively high structural defects as reported in table 1.

4. Conclusion

In this study, the CdS thin films were grown by chemical bath technique. Structural, optical, and electrical properties of the CdS thin films have been investigated as a function of solution temperature in order to optimize their optoelectronic properties and prepare promising films for window layer applications in photovoltaic solar cells. The structural studies revealed that the films have preferential orientation along the (002) plane of the hexagonal phase with good crystallinity and grain size of about 17 nm. The optical investigations showed that the CdS films have good band gap in the range of 2-2.4 eV and high optical transmission (85%) in the visible range. It is found that solution temperature had obvious effect on the dark conductivity. The increase of solution temperature beyond 65°C improves the dark conductivity of the CdS thin films. The photoconductivity was found to increase with increasing light intensity. These results indicate that the elaborated CdS thin films exhibit good properties intended for solar cell window layers.

5. References

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