Elaboration and Characterization of Cadmium Sulfide (CdS) Thin Films Prepared by Chemical Bath Deposition (CBD)

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Abstract—Our work consists in elaboration and characterization of cadmium sulfide (CdS) thin films. Indeed, in order to deposit a series of these films, we have adopted a simple and cheap technique, such as the chemical bath Deposition (CBD). The series of samples of CdS was deposited on glass substrates by varying the deposition bath temperature from 55 to 75 °C and by keeping the deposition time fixed (25 min).

Our investigation is focused on the understanding and study of the effect of the deposition temperature on the physical properties of the thin films to which it was referred. For this purpose, we used two characterization techniques which are: the X-ray diffraction (PANalytical X-ray diffractometer) for determining the structure of the films and also, the UV-Vis spectroscopy (UV-3101 PC-SHIMADZU double beam spectrophotometer) for determining their optical properties. Thicknesses (d) of CdS films was measured with gravimetric weight different method using a sensitive electronic microbalance and were confirmed by using a profilometer of the type KLA-TENCOR P6.

The structural characterization indicates that the structure of CdS films obtained is cubic or hexagonal with preferential orientation in accordance with the plane (111) or (002), respectively. The optical characterization shows that these films have a fairly high transparency which varies between 55 and 80% in the visible range of the optical spectrum, the optical gap value of which can reach 2.2 eV. It can be suggested that these properties make these films perfectly suitable for their use as window film in solar cells in thin films.

Keywords: Thin films; Chemical bath; Cadmium Sulfide; Optical Properties; and Structural Properties.

I. INTRODUCTION

The history of the machines and the technology of material deposit in thin films evolved much since the Sixties. That can be explained by the growth of the industrial demand for materials in thin films. Semiconductor nanocrystals (NCs) have attracted much attention during the past decades. Among them, CdS is one of the most interesting because it is of great interest for applications in optoelectronics, photovoltaics, catalysis, and biological sensing [1]. The techniques allowing realizing materials in thin films are very several: evaporation [2], sputtering [3], spray pyrolysis [4], electrodeposition [5], CBD [6], pulsed laser deposition [7]. Parallel to the variety of the methods of deposit, the types of materials produced in thin films are very several: insulators, semiconductors, polymers, superconductors, etc. Their applications extending on several disciplines: micro-electronics, optics, mechanics, biomedical chemistry, etc [8].

In this work, our attention focused on the elaboration of Cadmium Sulfide (CdS) thin films and studied of their some physical properties. CdS is an II°VI° semiconductor material which possesses excellent physical properties such as: Structural and optical properties, which make of him a good candidate for the fabrication of film buffer (window) in solar cells (CdS/CuInSe₂ [9], CdS/CdTe [10], CdS/CIGS [11], CdS/CuS [12]) and allow, also, to use it in other optoelectronics and photovoltaic applications such as: photo detectors, gas sensors, optical filters, [13] transistors [14], photo resistance (LDR: Light Dependant Resistor), photometer, as coloring for textiles and papers and it is useful in medical diagnosis [15].

The fabrication of homogenous, adherent and nanostructure CdS thin films is realized by adopting a chemical, simple and inexpensive technique, namely, the chemical bath deposition (CBD). The CBD is a technique in which the thin films are deposited on substrates immersed in solutions sources of the metallic ions (Cd²⁺) and chalcogens ions (S²⁻). A complexing agent (a base) is added to limit the hydrolysis of the metallic ion and to give certain stability to the bath. This method is based on the controlled precipitation of the material; the slow release of the chalcogens ions (S²⁻) in the solution in which the free metallic ion (Cd²⁺) is complexed in low concentration. The formation of uniform CdS film on the substrate takes place when the ionic product [Cd²⁺][S²⁻] exceeds the product of solubility Kₘ₉ = 10⁻²⁸ [16]. The cadmium source agents reported included cadmium sulfate, cadmium acetate, cadmium chloride, [17] cadmium nitrate [18], while cadmium ions were complexed by ammonia, EDTA, triethanolamine [15]. Thiourea, sodium sulfide, sodium thiosulfate, thioacetamide were used as sulfur source agents [16].

II. EXPERIMENTAL DETAILS

A. Thin film fabrication

Thin films of cadmium sulfide have been deposited on glass slide (36 × 14 × 1.6) mm² by chemical bath deposition method. Before the deposition the substrates must be cleaned using, successively, distilled water, acetone, and methanol followed by second clean in the distilled water for 15 min and finally dried in air.
Fig. 1 shows the scheme of the simple and effective experimental set-up (CBD) realized to manufacture CdS thin films.

The CdS thin films are formed from the reaction between aqueous solutions of 1 M cadmium salt (CdSO₄, 8/3 H₂O), 1 M thiourea (CS(NH₂)₂) in 60 ml distilled water and 9.5 M ammonia was used as complexing agent. The pH of the alkaline solution was adjusted about to 11 in the beginning of each deposition.

The introduction of solutions in the beaker was made in the following order (Fig. 2):

a. Dionized water,

b. Cadmium sulfate solution (CdSO₄, 8/3 H₂O),

c. Ammonia or ammonium hydroxide (NH₄OH),

d. Thiourea solution (CS(NH₂)₂).

The series of samples was prepared by varying the deposition temperature from 55 to 75 °C and by keeping the deposition time fixed at 25 min (tab.1).

<table>
<thead>
<tr>
<th>Code of sample</th>
<th>Molarity solutions (mol/l)</th>
<th>Deposition temperature T (°C)</th>
<th>Deposition time t (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS 1</td>
<td>1M</td>
<td>9.5M</td>
<td>1M</td>
</tr>
<tr>
<td>CdS 2</td>
<td>1M</td>
<td>9.5M</td>
<td>1M</td>
</tr>
<tr>
<td>CdS 3</td>
<td>1M</td>
<td>9.5M</td>
<td>1M</td>
</tr>
<tr>
<td>CdS 4</td>
<td>1M</td>
<td>9.5M</td>
<td>1M</td>
</tr>
<tr>
<td>CdS 5</td>
<td>1M</td>
<td>9.5M</td>
<td>1M</td>
</tr>
</tbody>
</table>

The color of CdS film was yellow at low deposition temperature and orange at high deposition temperature. All the CdS films enjoyed a good adherence with the glass substrate or the walls of the beaker and this was tested by adding concentrated hydrochloric acid to the film or using scotch tape where we note that the film is difficultly detached.

B. Characterization techniques of thin films

The thickness (d) of CdS film was measured with gravimetric weight different method using a sensitive electronic microbalance and employing ‘(1)’ [19]:

\[ d = (m_2 - m_1)/(\rho S) \]  

(1)

Where \( m_1 \) (g) is the mass of glass substrate before each deposition, \( m_2 \) (g) is the mass of the film and substrate after deposition, \( \rho \) the density of the CdS (4.84 g/cm²) and \( S \) (cm²) is the area of the film. The results of “d” were confirmed by using a profilometer of the type KLA-TENCOR P6.

A XPERT Powder, PANalytical X-ray diffractometer operated at 40 kV and 40 mA in the scanning range of 20 from 20 – 70° with Cu Kα radiation of wavelength 1.5406 Å; was used for the structural analysis of the CdS films of different thicknesses. The, grain sizes (D), strain (ε), dislocation density (δ) and number of crystallites per unit area (N) of CdS thin films were inferred from experimental XRD.

A UV-3101 PC-SHIMADZU double beam spectrophotometer was used for optical studies in the wavelength range 200–800 nm. The optical properties studied include: Transmittance (T %), energy band gap (Eg) and Urbach energy (EU).

III. RESULTS AND DISCUSSION

A. Kinetic study and growth mechanisms

The obtained films thicknesses range from 250 to 500 nm with increasing bath temperatures (Fig 1, in inset). Generally, the film thickness is the most reported parameter rather than the deposition rate. From the variation of the thickness, we deduced the growth rate which is the report thickness at the deposition time. In figure 1 we have reported the variation of the deposition rate of CdS thin films as a function of the bath temperature. As seen, the deposition rate is an increasing function of the bath temperature indicating a significant dependence of the growth rate on temperature. The highest growth rate, equal to 19.46 nm/min; was obtained for films grown at 65 °C; however, at low temperature the deposition rate is around 10 nm/min. As shown, the influence of the temperature divides, at least, in three phases:

- Phase I (nucleation and growth), that which corresponds to temperatures lower than 65 °C. In this range, the growth rate increases nearly-linearly or regularly, as function of the deposition temperature. The deposition rate obtained at 65 °C is equal to 19.46 nm/min, and it is, approximately, two times higher than that obtained at 55 °C. This influence is due to the activation of the chemical reaction between the species which contribute to the formation of the films on the substrates from an alkaline solution. The formation and growth of thin films can occur through several mechanisms such as ion by ion or cluster by cluster. Indeed, the deposition temperature motivates, on the one hand, the slow decomposition of the thiourea (“(2)”), which is responsible for the production of sulfur chalcogen ion (S²⁻) ;
and on the other hand, it releases metal ions (Cd$^{2+}$) by dissociation of complexing compound Cd(NH$_3$)$_4$$^{2+}$ ("(3)"):

\[
\text{Cd(NH}_3\text{)}_4^{2+} = \text{Cd}^{2+} + 4 \text{NH}_3
\]

whence, the formation of this compound is an intermediate reaction, necessary to control the hydrolysis of the metal ion (Cd$^{2+}$) and to give a certain stability to the bath ("(4)"). It is for this reason that the addition of the solution of ammonium hydroxide in the bath is primordial.

\[
\text{NH}_4^+ + \text{HO}^- = \text{NH}_3 + \text{H}_2\text{O}
\]

\[
\text{CdSO}_4 = \text{Cd}^{2+} + \text{SO}_4^{2-}
\]

\[
\text{Cd}^{2+} + 4 \text{NH}_3 = [\text{Cd(NH}_3\text{)}_4^{2+}
\]

Consequently, the free ions obtained of Cd$^{2+}$ and S$^{2-}$ react between them by ionic reaction (mechanism ion by ion) to forming nucleus or molecules of CdS ("(5)").

\[
\text{Cd}^{2+} + \text{S}^{2-} = \text{CdS}
\]

These nucleus cover the surface of the substrate (nucleation or incubation period) and become stable when the solubility product ($K_{sp}$=10$^{-28}$) of CdS in the alkaline bath, is reached. Then, the growth is carried out on these first nucleus, simultaneously with a continuity of production of other new small nucleus to creating a thin film of this material (period of growth of the film). The deposited film is strongly; adherent to the substrate and it has a yellow color.

During the decompositions of thiourea and the release of Cd$^{2+}$ ions become stronger by increasing the deposition temperature from 55 to 65 °C, causing the increase in the molar concentrations of the free ions (Cd$^{2+}$ and S$^{2-}$) in the bath, and therefore, the increase of the growth rate ($V_d$) of films (Fig. 2) and of their thicknesses (Fig. 2, in inset).

During the experiments of deposit of these films and for this range of temperature (phase I), the formation of heterogeneous precipitates on the substrates is, clearly seen.

![Fig. 2. Variation of the deposition rate of CdS thin films as a function of the bath temperatures.](image-url)

These precipitates are more remarkable, with the eye, and denser compared to those which are formed in solution (homogeneous precipitation). It is deduced that, the highest concentration of the reactants, participates in the formation of the films with higher thicknesses and this is perhaps due to the free energies of the nucleation of CdS in solution and on the substrate.

- Phase II (saturation), in this case, it is noted that the growth rate reaches saturation (~20 nm/min) at 65 °C of which the thickness of film extended, in its turn, its maximum value, due to the strongest decomposition of cadmium sulfate and thiourea.

- Phase III (reduction), once the reactants are exhausted, the growth starts to slow down and stop thereafter. We can consider the temperature of 65 °C as a critical temperature corresponding to the appearance of a mixed mode of growth, among which both mechanisms ion by ion and cluster by cluster, coexist (at this temperature, the mechanism of growth changes of ion by ion into cluster by cluster).

However, at temperatures higher than 65 °C, the three precursors are, immediately, mixed; we remark a fast formation of CdS in the form of clusters in solution as well as on the immersed substrate. This observation allows us to suggest that the growth of the films is carried out, probably by the cluster by cluster mechanism, which nucleation step is less obvious. However, the formation of a film passes, initially, by the production of an intermediate phase Cd(OH)$_2$ coming from the dissolution of the ammonium hydroxide ("(6)").

\[
n \text{Cd}^{2+} + 2 n \text{HO}^- = [\text{Cd(OH)}_2]_n
\]

and secondly, by the replacement of HO$^-$ by S$^{2-}$ in order to form a particles of CdS ("(7)").

\[
[\text{Cd(OH)}_2]_n + n \text{S}^{2-} = n \text{CdS} + 2 n \text{HO}^-
\]

By increasing the temperature from 65 to 75 °C, a decrease in growth rate is observed (up to 11.084 nm/min), accompanied by a reduction in a film thickness. This is due to the impoverishment of the solution after just the first minutes of the deposit, because of the fast consumption of the reactants while contributing, at the homogeneous growth, as well as heterogeneous, of CdS colloids. In fact, at very high temperatures (> 65 °C), we feel a pungent odor of ammonia (NH$_3$), evaporated during chemical reactions, which led us to limit the temperature of the solution at 75 °C. The presence of NH$_3$ in the bath is essential to control the chemical reactions and to stop the creation of these colloids in solution. Moreover, the evaporation of NH$_3$ and therefore, the rich solution of HO$^-$, prove that the film growth is controlled by cluster by cluster; a dominant mechanism, in this phase. From another point of view, the reduction of growth rate and of thickness may have other origins, such as:

- the dissolution of unstable nuclei adsorbed on the surface area of the film,
or the detachment of the film, considering its high weight and its vertical position.

The variation of the growth rate has been reported and studied extensively by several authors as a function of different deposition parameters such as: deposition temperature [20], deposition time [20], pH of the solution [21] and thiourea [22] or cadmium concentrations [23]. The shape of this variation is an intrinsic characteristic of the CBD technique, contrary to the other deposition techniques of thin films [16].

Fig. 3, shows two possible mechanisms of formation and growth CdS thin films: ion by ion and cluster by cluster.

Fig. 3. Diagram of the CBD process. The CdS film is formed by a mechanism ion by ion (blue) or a cluster by cluster (red) or both simultaneously (at the same time) (homogeneous precipitation in solution or in volume (green) and heterogeneous precipitation on the substrate (blue and red)).

B. Structural analysis

• Structure and Orientation

In Fig.4, we presented the X-ray diffraction patterns (XRD) of CdS thin films deposited at different solution temperatures: 55 to 75 °C. The XRD spectrum of the CdS film deposited at 55 °C shows that the structure of this film is amorphous and it becomes monocrystalline and polycrystalline in the films prepared at higher temperatures. The peaks of diffraction which were recorded for the films deposited at 65 °C are: C(111)/H(002), H(103) and C(222)/H(004) located at the angles: 25.4°, 48.1° and 54.17°, respectively. These peaks are relating to the CdS material of cubic or hexagonal structure and were identified while being based on the standard files (JCPDS data: 80-0019 and 41-1049), respectively. The same results were mentioned in several published works [24,25]. These spectra show also the presence of a broad peak in the form of a bump, indicating that the structure of CdS is amorphous in which, of small poly-crystallites (cubic or hexagonal) are embedded. It is noted that the intensity of the peak located at 25.4° increases with temperature deposition (up to 65 °C) and then it decreases. This result is in good agreement with the variation of the films thicknesses as a function of the deposition temperature. However, Ramaiah, Bhatnagar, Pilkington, Hill and Tomlinson [26], are mentioned that only the observation by MET confirms the nature of the crystalline phase. Moreover, the studies reported in the literature show that several factors can affect the crystalline structure; among which may be mentioned [16]:

• nature, position and design of the substrate,
• pH of the solution,
• concentrations and natures of the solutions used in the bath
• and stirring speed.

Surfaces of the prepared films are, homogeneous and sometimes rough.

• Growth rate and grain size

The grain size of the CdS film was calculated from the middle-height width of the peak C(111)/H(002) using the Scherrer’s equation for all samples prepared by this technique ("(8") [27]:

\[ D = \frac{(0.94 \lambda)}{(\Delta(2\theta_{hkl}))} \cdot \cos \theta_{hkl} \]  

(8)

Where D: crystallite size, \(\Delta(2\theta_{hkl})\) = \(\beta\): full width at half maximum (FWHM) of the diffraction peaks, \(\theta\): diffraction angle, \(\lambda\): wavelength of the \(\lambda\alpha\) ray (Cu)= 1.54 Å.

Fig. 5 represents the variation of the growth rate and the grain size of the CdS films as a function of the temperature deposition. The grain size varies inversely with the variation of the growth rate, which leads us to suggest that the temperature deposition affects the grain size through its influence on the growth kinetics. In other term, the film growth rate becomes relatively high with the increase in the temperature (from 55 to 65 °C), which creates the cause of a high number of nucleation centers (rapid nucleation). Consequently, the high concentration of juxtaposed nucleus limits their enlargement and form very small grain sizes. Contrary, in the case where the growth rate decreases, the nucleus adsorbed on the surface of the substrate, where it have sufficient space to expand and produce a large grains.

• Growth rate and strain

Fig.6 illustrates the evolution of the growth rate and the strain in films prepared at different deposition temperature. We calculate the deformations (\(\varepsilon\)) by the following ratio ("(9") [19]:

\[ \varepsilon = \frac{(\Delta(2\theta_{hkl}))}{4} \cdot \cos \theta/4 \]  

(9)

with: \(\Delta(2\theta_{hkl})\) = \(\beta\): width at half maximum of the diffraction peaks C(111)/H(002).

As can be seen on fig. 5, the variation of the strain follows that the growth rate and it is in opposite direction compared to that of the grain size, as a function of deposition temperature.

As we have previously reported, the increase of the growth rate by increasing the temperature of the solution (from 60 to 65 °C) causes the appearance of a strong strain in the elaborate CdS films. By increasing the temperature even more than 65 to 75 °C, the atoms are organized increasingly by reducing the
strain due to the decrease of the growth rate and therefore, the enlargement of the particle size.

As shown in fig. 7, the strongest peak situated at 25.4 ° is slightly horizontally offset from the position of the standard peak (26.6 ° from JCPDS data). This allows us to deduce the nature of our stress where it is the compression (Fig. 8).

**Fig. 4.** X-ray diffraction spectra obtained for CdS films prepared at different deposition temperature.

**Fig. 5.** Growth rate and grain size as a function of deposition temperature.

We can, also, deduced the nature of the strain (extension or compression) from the shift direction of the intense peak C(111)/H(002) (Fig. 3).

**Fig. 6.** Evolution of the growth rate and that the strain with different deposition temperatures.
However, strains vary in the opposite direction compared to the variation of the grain size (fig. 7). The increase of the number of crystallites and the reduction of their sizes, with increasing the temperature deposition (60 to 65 °C), are at the origin of the appearance of a high density of grain boundaries or dislocations (see Tab. 2). The presence of this strong density of defects in the films, resulting in the increase in the concentration of deformation and strain in the networks of the prepared films. But, the enlargement of the grain sizes in the temperature range from 65 to 75 °C, causes the reduction of empty spaces existing between the grains which leads to growth of the film with a weak deformation or strain. The size of the larger grain and the lowest strain were noted for the film prepared at 75 °C.

C. Optical analysis

Optical characterizations were based on the transmission spectroscopy in the UV-Visible region. Fig. 9 presents the variation of transmittance as a function of the wavelength for the samples prepared at different deposition temperatures. All our films have a high transmittance whose value varies between 55 and 80 % in the visible range. This result supports the application of the CdS as buffer (window) film in solar cells [28].

Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Deposition temperature T (°C)</th>
<th>Density of dislocations ( \delta \left(10^{-4}\text{line.nm}^{-2}\right) )</th>
<th>Number of crystallites/unit of surface ( N \times10^{4} \left(\text{nm}^{-2}\right) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS 1</td>
<td>55</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CdS 2</td>
<td>60</td>
<td>15.25</td>
<td>220.53</td>
</tr>
<tr>
<td>CdS 3</td>
<td>65</td>
<td>25.507</td>
<td>626.86</td>
</tr>
<tr>
<td>CdS 4</td>
<td>70</td>
<td>1.92</td>
<td>9.107</td>
</tr>
<tr>
<td>CdS 5</td>
<td>75</td>
<td>1.657</td>
<td>5.91</td>
</tr>
</tbody>
</table>

Tab. 2 contains the different values of the density of dislocations and numbers of crystallites in the CdS films deposited at different deposition temperatures. The two formulas (“10)” and “(11)” used to calculate these two quantities are [19]:

\[
\delta = \frac{1}{D^2} \tag{10}
\]

\[
N = \frac{d}{D^3} \tag{11}
\]

In these spectra, we also note the absence of the interference fringes in the region of high wavelengths (between 500 and 800 nm). Therefore, we can deduce that the surfaces of our films are rough except for the films deposited at 65, 70 and 75 °C which begin to have surfaces approximately smooth due to the start of appearance of large interference fringes in their spectra.

This figure shows also that the transmittance decreases with increasing thicknesses of the films deposited at 55, 60
and 65 °C and then increases again, with the decrease in thicknesses for those which are deposited to 70 and 75 °C. The last film deposited at 75 °C is the best candidate for use as a buffer film in sandwich structure of solar cells, because of its high transmittance and also because he enjoys a thickness, on the one hand, not too thick to prevent the passage of the free electrons of the transparent film to that which is absorbing, and on the other hand, not too thin, for not create an electrical short-circuit between these two films.

- **Optical band gap and Urbach energy**

The exploitation of the transmittance spectra enables us to calculate the optical band gap (Eg) and the Urbach energy (EU) of the elaborate CdS films. The defects are manifested by the appearance of continuous states near the band edges. These states are called localized states and formed band tail at the borders of the band gap in the valence and the conduction bands. Also, it is known by the term "disorder" or "Urbach energy". The band gaps and Urbach energy of the prepared CdS thin films are determined from (12) [27] and (13) [29]:

\[
\alpha h v = A (h v - E_g)^n \quad (12)
\]

\[
\alpha = a_0 \exp \left( \frac{h v}{E_U} \right) \quad (13)
\]

where A is a constant. Eg is the band gap of the material, n = ½ for direct band gap and α is the absorption coefficient.

Fig. 10 reports, variations of these two parameters: optical band gap and disorder. It is noted that these two quantities, vary in opposite manner with increasing deposition temperature.

The value of the optical band gap of the films deposited at various temperatures passes by a minimum at 65 °C corresponding to the highest disorder and that in turn, is synonymous with the highest growth rate due to the mixed growth mechanism or the change of the type of mechanism from ion by ion into cluster by cluster. However, for the film prepared at 75 °C, the value of the band gap is ~ 2.2 eV, near to that of CdS material, while its optical disorder and strain are less weak compared with those of our other prepared films.

Otherwise, it is well-known that the high disorder (and consequently, a high concentration of defects) causes the formation of the grains of small sizes. The size of the largest grains (77.67 nm) and the lowest disorder (180.28 meV) correspond to the film prepared at 75 °C.

IV. CONCLUSION

We can consider the temperature 75 °C as an optimal parameter to deposit a film with better optical and structural characteristics allow to use it as buffer film in solar cells and in other photovoltaic applications.

**References**


