TIMES EFFECT ON MORPHOLOGICAL, STRUCTURAL AND OPTICAL BEHAVIORS OF CDS THIN FILMS FOR PHOTOELECTROCHEMICAL CELLS APPLICATION

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ABSTRACT

Cadmium Sulphide thin films have been successfully electrodeposited on a conducting Indium-Tin-Oxide (ITO) glass substrate, with different deposition time (10 min, 20 min, and 30 min). The Scanning electron microscopy (SEM), UV-Vis spectrophotometry, X-ray diffraction (XRD), and Atomic force microscopy (AFM) were used to characterize the morphological of films obtained. Moreover, Mott–Schottky (MS) measurements and Photoelectrochemical (PEC) measurements were carried out to study their structural, optical and electrical properties respectively. XRD result points to high crystallinity oriented along (002) planes. The studies reveal that the optical transmission increases with decreasing time of deposition. Mott–Schottky and Photoelectrochemical studies indicates that the CdS thin films display n-type semiconductor, which allows used as layer in photovoltaic cell applications.

Keywords: CdS, electrodeposition, semiconductor, properties, Mott–Schottky plots

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1. INTRODUCTION

Nowadays, many studies focused on thin films solar cells such as ZnS [1], ZnSe [2], CdS [3], etc. In these solar cells, to form a p-n junction an n-type buffer layer is constituted. Due to excellent motivating physical and chemical characteristics properties of cadmium sulfide (CdS) may play a vital role in device technology [4].

Cadmium Sulphide belongs to II–VI group and is one of the interesting semiconductors due to its low cost and ease of synthesis [5,7] and an inorganic compound of yellow solid color [8]. It is well known that CdS has a wide band gap semiconductor and has a band gap energy of 2.42~ eV, high transmittance as well as high absorption coefficient [3,9,10]. To improve the optical transmission and to reduce reflection from cell surface, it is recommended to keep CdS as thin as possible (≈100–200 nm), [3,11] because, it has lower refractive index compared to the p-type material.

There is a great importance of CdS due to its various potential applications, such as light emitting diodes [12,13], optoelectronic devices [14], environmental and biological [15], electrochemical sensors [16] and photovoltaics cells [17].

There are many deposition techniques to synthesize the CdS thin film such as Sol – gel deposition [18,19], Dip coating [20], electrodeposition [21,22], Spray pyrolysis [23,24], chemical bath deposition (CBD) [25-27], chemical vapour deposition (PVD) [28,29], hydrothermal [30,31], etc. These techniques could produce high quality CdS thin films exhibiting several properties and for a specific application, these should be optimized.

Among these methods, the electrodeposition is of more interest due to the following characteristics, such as low cost, a large area, and generally lowers temperature and soft processing of materials [32].

This work elaborates the CdS thin films by simple electrochemical deposition and investigates the influence of deposition time, morphological, structural, optical and PEC properties. The various appropriate properties of CdS are also studied to get information about their applications in thin film solar cells and photoelectrochemical cells.
2. EXPERIMENTAL

The electrodeposition (ED) of CdS films is carried out by a solution containing 0.01 M CdCl₂ (Alfa Aesar, 99% Pure) and sodium thiosulphate (Na₂S₂O₃) (Fisher Scientific, 99% pure). The pH of the solution is 1.5–2. The CdS layers are deposited on the ITO surface at different times (10 min, 20 min, and 30 min).

The potentiostat/galvanostat has been used for the electrodeposition that is comprises of a conventional three-electrode cell, and a PGZ-401 Voltalab 40. To select the desired electrochemical technique and to fix the desired parameters, it is coupled with a computer equipped with software (voltamaster 4). The saturated calomel electrode (SCE) is used as a reference electrode. The working electrode used indium tin oxide (ITO), SOLEMS having a resistivity of 50 Ω/cm² and a thickness of 100 nm whereas; the counter electrode is a platinum plate. The experiments have been conducted at a constant temperature (T = 50 °C).

To study the absorption spectroscopy of CdS layers, UV–vis (Shimadzu UV 1800–PC spectrophotometer) has been used. To record the Photoelectrochemical (PEC) measurements, a 500-W halogen lamp has been used as a polychromatic light source with the illumination intensity of 100 mW/cm². Mott–Schottky (MS) measurements have been carried in 0.01M Na₂S₂O₃ solution with a scan rate of 10 mV/s at 0.2 kHz.

The morphology of the deposited layers has been studied by scanning electron microscopy (SEM) model: JEOL, JSM-7001F microscope operating and confirmed by atomic force microscopy (AFM, MFP-3D Asylum Research). X-ray diffraction spectrum is carried out using Rigaku Smartlab X-ray diffractometer with monochromated CuK α1 radiation (λ=1.54056 Å) operated at 20 KV and 10 mA in the 2θ range of 20-80° to identify the phases and crystallographic structure.

3. RESULTS AND DISCUSSION

Cyclic Voltammetry (CV)

The first step of this study is to identify the electrochemical behavior of ITO substrate and to determine its domain of stability and carried out with cyclic voltammetry in 0.1 M Na₂S₂O₃ solution.
(supporting electrolyte) recorded in a potential range of +1 to -1 V vs. SCE at a scan rate of 100 mV.s⁻¹ and at a temperature of 55 °C. The voltammogram is represented in Figure 1.

It is observed from this voltammogram that the substrate is stable in the potential range between +1 and -1 V vs. SCE. So, in the absence of metal ions in the solution, no current associated with an electrochemical reaction at the surface of the electrode is observed; just the reduction of H⁺ ions from -0.8 vs. SCE and the release of oxygen O₂ (from 0.68 vs. SCE). This clearly indicates the inevitable presence of this competing reaction during electroplating in aqueous solution. A first solution of Na₂S₂O₃ has been studied to obtain information relating to its cathodic reaction as shown in Figure 1. On the voltammogram, the cathode peak is observed around 0.395 vs. SCE.

After adding Cd²⁺ ions (0.01M CdCl₂) to the electrolyte bath containing the supporting electrolyte (0.1 M Na₂S₂O₃) and HCl diluted to pH = 1.5, the ITO substrate is immersed; the corresponding cyclic voltammogram is presented in Figure 2 in a potential range from +1.2 to -1.2 vs. SCE, with a scan rate of 100 mV.s⁻¹.

![Fig.1. Cyclic voltammograms of: (a) ITO immersed in the support electrolyte (0.1 M Na₂S₂O₃), (b): ITO substrate immersed in the supporting electrolyte (0.1 M Na₂S₂O₃) with 0.01 M CdCl₂, scan rate of 100 mV s⁻¹, pH = 1.5, T = 55°C](image)

According to this voltammogram, during the sweep of positive potential, there are four reduction peaks. The first peak, an increase in cathode current density begins around -1.2 vs. SCE corresponds to the reduction of sulfur which dissociates from the thiosulfate to a
potential of 0.599 vs. SCE. Whereas, the cathodic electroreduction peak potential of sulfur is observed at 0.395 vs. SCE.

The second peak corresponds to the following reduction in CdS around potential 0.475 vs. SCE. The third peak corresponds to the reduction of Cd\(^{2+}\) ions to metallic Cd\(^0\) following around a potential of -0.162 vs. SCE and the fourth cathode peak (-0.507 vs. SCE) is attributed to the electroreduction of the CdS electrodeposited on the surface of the electrode.

Therefore, the following are the possible sequential electrochemical/chemical reactions involved during electrodeposition of CdS [33, 34]

\[
\text{CdCl}_2 \rightarrow \text{Cd}^{2+} + 2\text{Cl}^- \quad (1)
\]

\[
\text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow 2\text{S}_2\text{O}_3^{2-} + \text{Na}_2\text{O} + 2\text{H}^+ \quad (2)
\]

\[
2\text{S}_2\text{O}_3^{2-} + \text{Cd}^{2+} + 2\varepsilon \rightarrow \text{CdS} + 2\text{SO}_3^{2-} \quad (3)
\]

**Chronoamperometry (CA)**

Figure 2 shows the curves of the current-time variation during the CdS layers deposited on the ITO substrate at different times (10 min, 20 min, and 30 min). The deposition potential is -700 mV between the working electrode (ITO) and the reference electrode at a temperature of 55°C.

The chronoamperograms observed to begin with a current jump which corresponds to the charge of the electric double layer and to the time necessary to form the first nucleation seeds, then it increases to reach the maximum \(i_{\text{max}}\) during time \(t\) equal to \(t_{\text{max}}\). This part ascribes to CdS germs’ growth and their recoveries. Then the current decreases to a limit which is imposed by the diffusion of ions by solution to the surface of electrode. This part is described by the following Cottrel equation [35]:

\[
i(t) = \frac{nFCD^2}{\sqrt{\tau}} \quad (4)
\]

These curves \(i = f(t)\) also indicate a normal dependence with the overvoltage. Therefore, an increase in the current density due to the applied potential is observed and thus enhances the
The visual appearance of CdS thin films a, b, and c of 10 min, 20 min, and 30 min respectively on the ITO substrate is shown in Figure 3. It can be seen that the surface of the film obtained at $t = 10$ min seemed very compact and homogeneous. Moreover, it seemed lighter than the others. This lighter surface could be due to the low roughness of surface. The
surfaces of the films obtained at $t = 10$ min and $t = 30$ min appear very homogeneous and are darker.

![Figure 3: Photograph of the CdS thin films electrodeposited on the ITO substrate from three different times: (a) 10 min, (b) 20 min and (c) 30 min](image)

The CdS thin films thickness is estimated from two distinct methods. Initially, the thickness $d$ of CdS thin films could be controlled by measuring the electrodeposition time and is determined currently from the amount of charge $Q$ according to the following equation [36]:

$$d = \frac{QM}{ZFA\rho} \quad (5)$$

where $Q_A$ is the charge under potentiostatic electrodeposition, $A$ represents the area of electrode $M$ and $\rho$ attribute to molecular weight and specific density of CdS respectively, $z = 0.5$ (number of electrons/CdS per unit), and $F$ is the Faraday constant. The current efficiency is assumed to 100 % during the electrodeposition. The film thicknesses are calculated and summarized in Table 1.

**Table 1.** The total charge passed through the CdS films at various times onto ITO, as well as the corresponding estimated CdS film thickness

<table>
<thead>
<tr>
<th>Temps (min)</th>
<th>Charge (mC)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>375.5</td>
<td>7580</td>
</tr>
<tr>
<td>20</td>
<td>488.1</td>
<td>5833</td>
</tr>
<tr>
<td>30</td>
<td>332.1</td>
<td>5157</td>
</tr>
</tbody>
</table>
Structural characterization

Figure 4 shows the X-ray diffraction spectrum obtained in the films prepared at a fixed temperature of 55 °C for 20 min. The peaks observed in the XRD spectrum could be indexed as hexagonal CdS with wurtzite structure, and are highly compatible with the standard map (JCPDS 41-1049). These are composed of a relatively intense peak located at 26.52° corresponding to the (002) plane, and 29.61° which corresponds to the (101) plane of the hexagonal phase. The peaks marked by stars correspond to the tetragonal phase of (In$_2$O$_3$ doped with SnO$_2$) (ITO). It may be concluded that the CdS films electrochemically deposited using CV and CA are effectively coated on the ITO as a hexagonal wurtzite structure [37-39]. The scanning electron microscope (SEM) and the atomic force microscope (AFM) have been employed to confirm the exact structure of CdS films, and to study its surface morphology as well as its dependence on other properties of these films.

Optical measurements

The variation in the transmittance of CdS films deposited at different deposition times is shown in Figure 5. The figure reveals the transmittance spectra with wavelength ranging from 300 to 800 nm of CdS thin films electrodeposited from different times (10 min, 20 min and 30 min). It may be seen that all the spectra is the same, the optical transmission of the deposits
increases with decreasing time (Figure 5.a). A sharp drop in transmission is observed around ~ 300 nm indicating that the CdS nanostructures absorb light at wavelengths less than this transparency located in the visible range between 450 nm and 800 nm (Figure 5.b). The transmission spectra also make it possible to graphically estimate (extrapolation) the optical gap (Eg) of CdS films from the plot of \((\alpha h\nu)^2\) as a function of \(E=h\nu\). The gap energies of the CdS deposited at different times are shown in Figure 5c.

![Graphs showing transmission and absorbance spectra](image)

**Fig.5.** (a) UV-Visible absorbance, (b) transmittance spectra and (c) Tauc’s plot of the CdS thin films electrodeposition in different times: 10 min, 20 min and 30 min

The obtained optical gaps are 2.49 eV for \(t = 10\) min, 2.45 eV for \(t = 20\) min and 2.42 eV for \(t = 30\) min. It can be seen that the optical gap energy of CdS is slightly increased with the decreasing deposition times up to the maximum value \(E_g = 2.49\) eV for deposition at \(t = 10\) min.
min. The transmission and the energies of the deposited CdS gap at different times are listed in Table 2.

**Table 2.** The transmission and the gap energy of the deposited CdS at different times

<table>
<thead>
<tr>
<th>Times (min)</th>
<th>Transmission (%)</th>
<th>Band gap Eg (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>59.31</td>
<td>2.49</td>
</tr>
<tr>
<td>20</td>
<td>47.36</td>
<td>2.46</td>
</tr>
<tr>
<td>30</td>
<td>41.04</td>
<td>2.42</td>
</tr>
</tbody>
</table>

Mott-Schottky analysis and Photocurrent measurement

Mott-Schottky analysis is one of the methods used to study the electrolytic interface of semiconductors. It provides information about the density of donors or acceptors, $N_A$ and $N_D$ are the acceptor and donor concentration of p-type and n-type semiconductors, as well as the potential of the band flat ($E_{fb}$). It is based on the measurement of capacitance of the space charge of semiconductor layer as a function of potential ($C^2$ vs. $E$) according to the following relation [40, 41]:

$$
\frac{1}{c^2} = \frac{2}{\varepsilon \varepsilon_0 N_D e} \left[ (E - E_{fb}) - \frac{kT}{e} \right]
$$

(6)

where $c$ is the space charge capacitance in the semiconductor, $\varepsilon_0$ is the permittivity in vacuum ($\varepsilon_0 = 8.86 \times 10^{-12}$ F m$^{-1}$), $\varepsilon$ is the dielectric constant of for CdS [42], $E$ is the applied potential, $N_D$ is the donor density of semiconductor, $e$ is the electron charge ($e = 1.6 \times 10^{-19}$ C), $E_{fb}$ is the flat band potential, $k$ is the Boltzmann constant (1.38$ \times 10^{-23}$ J/K), and $T$ is the room temperature (298 K).

Figure 6a demonstrates the Mott-Schottky curves of CdS/ITO films recorded in 0.01M Na$_2$S$_2$O$_3$ electrolyte with a scan rate of 10 mV/s at 0.2 kHz. Figure 6a reveals straight lines with positive slope indicating that all CdS thin films display n-type semiconductor behavior with hole conduction. The obtained flat band potentials ($E_{fb}$) is -0.75 from CdS, similar kind of behavior has already been reported by Divya et al [3].
Fig. 6. (a) Mott-Schottky plots for n-CdS thin films measured in Na$_2$S$_2$O$_3$), (b) photocurrent response of CdS thin films

To confirm the conductivity type of prepared thin films, we studied the photo electrochemical (PEC) performance of the CdS thin films in 0.01M Na$_2$S$_2$O$_3$ solution with an imposed potential of -1000 mV, excited by polychromatic light every 20 s as shown in (Figure. 6b). It can be seen that all the CdS films show anodic (positive) current under light confirming the n-type semiconductor conductivity of these samples [43].

**Surface Morphology Observation**

Figure 7 displays the surface morphology of CdS thin film obtained at different deposition times t = 10 min, 20 min, and 30 min, respectively. In the time of 10 min and 20 min, the SEM micrographs signify spherical surface grains and their size is not homogeneous with the existence of the background voids. whereas in t = 30 min, it is observed that the surface of the films is rough, dense and granular look like crystallites and their sizes are relatively large look like compact hexagonal structures with no voids are observed on CdS layer, (Figure 7c) look like of the flower [44-46], whose size increases with increases of the time of electrodeposition. Therefore, different electrodeposition times play a conclusive role in the morphology, crystallinity and roughness of the CdS thin films.
Fig. 7. SEM images of the CdS thin films obtained at different times: (a, a’) 10 min, (b, b’) 20 min and (c, c’) 30 min

Analysis by atomic force microscopy

Figure 8 represents 2D and 3D AFM images of CdS thin films electrodeposited on an ITO substrate at different times (t= 10, 20, 30 min). These indicate that the surface of CdS layers are regular granular, homogeneous uniform and covers almost the entire surface of the substrate grains. Also, it is important to note that the variation in time of deposition affects
morphology of the deposits. So, the images of the films observed under the atomic force microscope (AFM) are smooth and homogeneous formed of more or less hexagonal grains and very little rough and oriented with a preferential orientation. These observed morphological characteristics suggest that the films are compact and have excellent adhesions to substrates. The 'Root Mean Square' (RMS) values of the average roughness of a surface are given in Table. 3 and indicate that the roughness of the surface of CdS samples is affected by the deposition time. It increases considerably when the latter becomes higher. The RMS roughness values decrease from 119.69 nm to 49.856 nm when the deposition time is increased, with an increase in the grain size, so the maximum roughness is for \( t = 10 \) min, RMS = 119.69 and minimum is for \( t = 30 \) min, RMS = 49.856.

\[ t=10 \text{ min} \quad t=20 \text{ min} \quad t=30 \text{ min} \]

RMS=119.69 nm \quad RMS=91.269 nm \quad RMS=49.856 nm

**Fig.8.** 2D and 3D AFM micrographs of CdS thin films deposited with different times of deposition \( t=10 \) min, \( t=20 \) min and \( t=30 \) min
Table 3. The RMS values of the average roughness of CdS films

<table>
<thead>
<tr>
<th>Times (min)</th>
<th>t=10 min</th>
<th>t=20 min</th>
<th>t=30min</th>
</tr>
</thead>
<tbody>
<tr>
<td>RMS (nm)</td>
<td>119.69</td>
<td>91.269</td>
<td>49.856</td>
</tr>
</tbody>
</table>

Photoelectrochemistry measurements

The photocurrent measurements of CdS thin films at different time (t = 10, 20, 30 min) have been carried out in 0.01M Na$_2$S$_2$O$_3$ solution with an imposed potential of -1000 mV, excited by polychromatic light every 20 s as shown in Figure 9.

The CdS film presents an anodic peak of photocurrent immediately after irradiation. Thus, the prepared CdS films exhibit the behavior of n-type semiconductor [43]. There is a decrease in the generated photocurrent when the times of the deposits increased.

![Figure 9. Current density-time plots of CdS/ITO films with different times of deposition](image-url)
4. CONCLUSION

In this work, we have shown that the CdS/ITO thin layer was successfully prepared with optimal parameters by electrodeposition at three different times: t=10 min, t=20 min and t=30 min. The XRD spectrographs of the prepared films show a high crystallinity and hexagonal (002) structure. The optical gap energy of CdS films is slightly increased with decrease in the deposition times, the film roughness decreases when the deposition time is increased. These films exhibit such promising properties suggesting their possible use in solar Cells and photoelectrochemical Cells.

5. REFERENCES


