

## Silver doped cadmium sulfide thin films on a PET flexible substrate

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Silver doped cadmium sulphide thin films were deposited on a polyethylene terephthalate flexible substrate through the chemical bath deposition method varying the silver deposition time. In this study we analyzed the absorbance in the visible range between 430 and 800 nm. The direct band gap was calculated with the Tauc method, yielding values of 2.25 to 2.46 eV. The crystallographic structure was determined by X-ray diffraction. An evolution was observed from the original hexagonal cadmium sulphide pattern to the appearance of characteristic signals of metallic silver. Scanning electron micrographs were obtained to describe the morphology of the films's surface. Finally, the electric resistivities measured were in the range of 5.0 and  $12.1 \times 10^7 \Omega \text{ cm}$ .

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### 1. Introduction

Cadmium sulphide is one of the most studied n-type materials used as window layer in solar cell thin films due to its high direct energy band value (2.42 eV) and high chemical stability [1, 2]. Anyhow, CdS is a health risk material upon direct contact [3]. This health risk could be reduced if this material is coated with a innocuous one upon direct contact. Therefore, we chose silver (Ag) as a coating for CdS thin films, which has no negative effects on humans [4].

Several deposition techniques can be employed in the growth of thin films, such as pulsed-laser deposition [5], vacuum thermal evaporation [6], chemical bath deposition (CBD) [7], electrodeposition [8], Spray pyrolysis [9], among others. We chose the CBD technique due to its low cost, simplicity, homogeneity obtained. This technique consists of a solution that contains precursor reagents that after undergoing reactions, adhere to a substrate, which commonly is glass.

Silver (Ag) has been reported to decrease the bandgap energy and electrical resistivity of CdS (of the order of  $10^6$ - $10^7 \Omega \text{ cm}$ ) when used as dopant [10]. In this context, silver acts as a donor dopant which enhances transport properties of II-IV semiconductor films. With silver doping [11] Nazir et al. achieved a decrease in resistivity by three orders of magnitude ( $10^3 \Omega \text{ cm}$ ) with different concentrations of Ag. [12] Dariani et al. established that the band gap energy of Ag-doped samples decreased with respect to the CdS undoped sample. Silver doping forms intermediate energy levels in its band gap, which can be interpreted as its decrease.

Although the commercialization of solar cells with glass substrate is very high [13], transportation care and the breaking risk are also elevated [14, 15]. Thus, we decided to implement polyethylene terephthalate (PET) as a hard to break, flexible and light weight substrate [16, 17] in aqueous solutions which can be performed at a fairly low temperatures [18, 16, 19]. We used PET recovered with indium tin oxide (ITO) for experimental purposes. Above it, we deposited a thin layer of CdS, which typically is used in photovoltaic devices or alternative solar

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cells composed of heterojunctions [16, 20-23]. Our main goal was to dope CdS thin films with silver (CdS:Ag) and compare their responses to those of the CdS thin film.

## 2. Experimental

CdS:Ag thin films have been grown on a PET substrate coated with ITO through the CBD. The reactive substances in the CdS solution were: cadmium chloride ( $\text{CdCl}_2$ ), sodium citrate ( $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ ), potassium hydroxide (KOH), thiourea [ $(\text{NH}_2)_2\text{CS}$ ], a pH 11 buffer system ( $\text{NH}_4\text{OH}/\text{NH}_4\text{Cl}$ ) and deionized water, contained in a 100 ml beaker. The bath was maintained at a constant temperature of 40 °C for 3 hours. The thin films were prepared by dipping a clean PET-ITO substrate slide inside the bath. Then, we waited for the CdS thin films to dry at room temperature and submerged them in a silver ion solution that consisted of: silver nitrate ( $\text{AgNO}_3$ ), potassium hydroxide (KOH), triethanolamine ( $\text{C}_6\text{H}_{15}\text{NO}_3$ ), deionized water, rongalite ( $\text{CH}_3\text{NaO}_3\text{S}$ ), contained in a 100 ml beaker. The bath was maintained at a constant temperature of 40 °C at different depositions times (30, 45, 60 and 75 min.).

The deposited films were homogeneous, with very good adhesion to the substrate and uniform to the eye, while their colors became darker as the deposition time increased. The X-ray diffraction (XRD) spectra of the thin films was obtained with a Rigaku Ultima III-XRD diffractometer for the analysis of its crystalline structure. Optical absorption spectra of the thin films were measured in a Perkin Elmer Lambda 19 spectrophotometer. The morphology was evaluated by Scanning electron microscopy (SEM) using a XL30 ESEM Philips microscope.

## 3. Results and discussion

Thin films of CdS and CdS:Ag at different depositions times were produced using chemical bath deposition. The optical properties of CdS thin films were studied with the absorption pattern and the Tauc's relation to obtain the bandgap of the samples. The absorption spectra were evaluated from 400 to 800 nm, which is important for photovoltaic applications. Fig. 1 shows the absorption pattern of the CdS:Ag thin films at different deposition times grown on PET-ITO flexible substrates through CBD.

The addition of Ag doping at different deposition times caused the absorption to increase and their absorption edges to shift to the longer wavelength region. The absorption edge at a deposition time of 30 minutes was located at 537 nm. This may be due to the adsorption of silver to the CdS thin film. Therefore, we can expect better photovoltaic performance due to the increase in its photoconversion ability. On the range between 537 and 800 nm, a significant difference in absorption of all the samples was observed, compared to the reference CdS sample. For smaller wavelengths, the difference in absorbance became more notorious. Qualitatively, it can be seen that the absorption edges of the silver doped layers shifted to longer wavelengths than that of pure CdS, with a value of 504 nm.

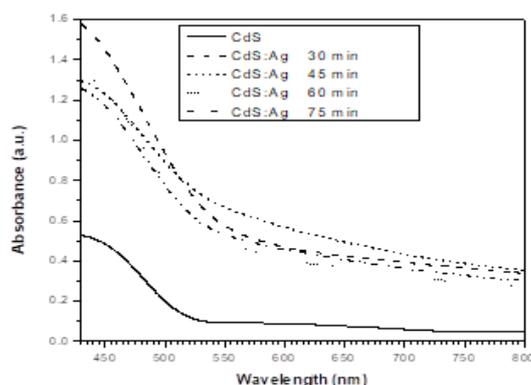


Fig. 1. Absorption spectrum of CdS and CdS:Ag films.

Fig. 2 shows the band gaps of the samples obtained from the absorption spectra calculated with the Tauc method [24]. The band gap energy of thin films with Ag, decreased with respect to the CdS thin film. On the sequence of the samples measured, the band gap energies lowered to 2.28 eV up until 45 min with respect to the reference material (CdS) of 2.46 eV. After that time, the band gap energies rose again at 60 min and remained stable after that at 2.35 eV. The decrease in band gap energy could be due to the doping of CdS with silver. However, the increase in band gap energy could be acquainted to etching due to surface saturation, leading to a higher concentration of precipitate.

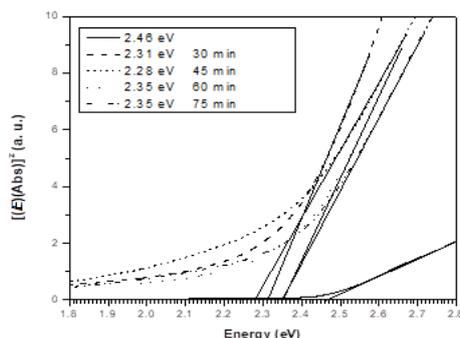


Fig. 2. Band gaps for CdS:Ag thin films with different deposition times on PET/ITO substrate.

The XRD patterns of CdS and CdS:Ag thin films at different deposition times (30 min, 45 min and 60 min), are shown in Fig. 3. The XRD of the CdS film shows a single very intense and wide peak at approximately  $2\theta$  equal to  $26^\circ$ . This peak is characteristic and associated with the hexagonal phase of cadmium sulphide which corresponds to the diffraction plane (002) associated to the crystallographic record PDF#41-1049 (square), which is its preferential growth orientation. It can also be observed that the diffractograms are intensified and widened when Ag is added. The characteristic peak of the (002) plane corresponding to the PDF#41-1049 (represented by a square on Fig. 3) became more prominent and split into two signals. The former, due to the (012) plane that corresponds to the PDF#14-0072 (ovals) record of monoclinic  $\text{Ag}_2\text{S}$ . For the same silver sulphide phase, the planes (ovals) (111) and (122) appeared. Other phases found on the CdS:Ag thin films were: cubic  $\text{Ag}_2\text{S}$  (110) associated to PDF#04-0774 (triangle); cubic Ag (111) associated to PDF#04-0783 (inverted triangle); and hexagonal  $\text{AgNO}_3$  (104) PDF#49-1239 (rectangle).

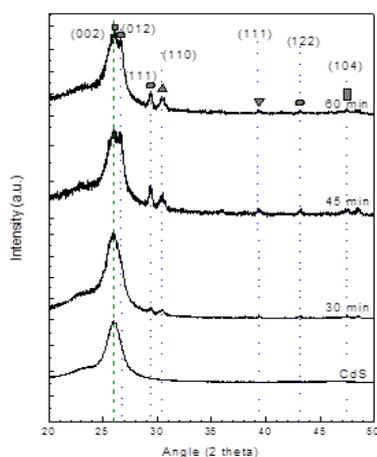


Fig. 3. Optical Rx pattern of Ag doped CdS with different deposition time on PET/ITO substrate. Green line hexagonal CdS, blue line  $\text{AgNO}_3$ .

On the other hand, we recorded top view SEM micrographs where the morphologic difference was observed for the reference sample, and at deposition times of 30 and 60 min. This is shown on Fig. 4, on parts a,b and c, respectively. Part a shows a reference roughness corresponding to CdS. On part b, the roughness is decreased due to the silver chemiadsorption. In addition, silver isolated clusters were observed. Finally, on part c, those clusters grew higher.

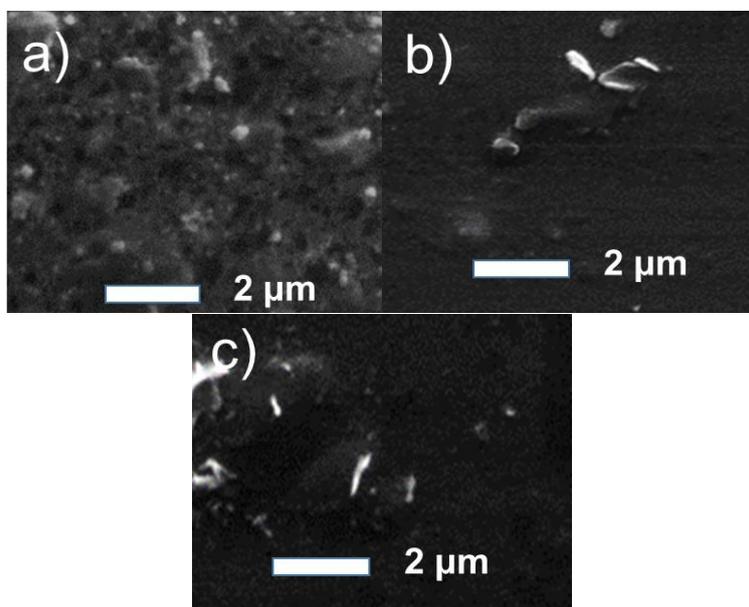


Fig. 4. SEM images of a) CdS thin film; CdS:Ag thin films at deposition times b) 30 min and c) 60 min.

On Fig. 5 we integrated two trends: a) electric resistivities without and with illumination vs immersion time and b) band gap energies vs immersion time. As expected, initially before the CdS samples were immersed, the electric resistivity without illumination was higher ( $12.1 \times 10^7 \Omega\text{cm}$ ) than with illumination ( $8.2 \times 10^7 \Omega\text{cm}$ ). This trend continued for 30 and 45 min of immersion. However, this trend shows only a slight difference. The band gap energy displayed the same trend on its scale.

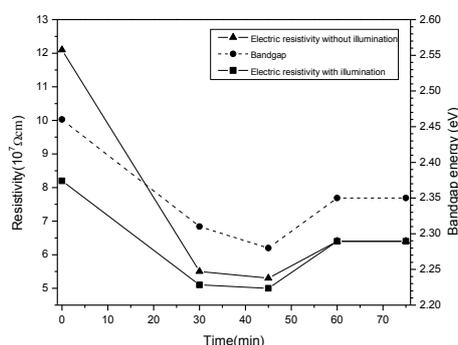


Fig. 5. Electric resistivities (solid lines) measured without illumination (triangles) and illuminated (squares); and band gap energies (dotted line) vs time.

#### 4. Conclusions

The effect of doping of Ag on the physical properties in CdS thin films deposited on a flexible substrate using chemical bath technique at different deposition times were studied. The

doping step consisted only of an immersion at a selected time, which was a very simplified technique once the Ag solution was prepared. The thin films showed good adhesion and were homogeneous. The X-ray diffraction patterns show that the CdS samples have hexagonal crystal structure. On the other hand, upon Ag doping, several phases appeared, yet none of them had Cd-Ag bonds. The band gap energy of Ag doped samples decreases respect to CdS samples. The absorption results promote Ag doped CdS as a good candidate for the window layers in solar cells.

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