Synthesis and characterization of chemically deposited CdS thin films without toxic precursors.

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Abstract. Al doped and undoped CdS thin films (CdS:Al) were deposited on glass, copper and bronze substrates by chemical bath deposition technique in an ammonia-free cadmium-sodium citrate system. The structural and optical properties of the CdS films were determined by X-ray diffraction (XRD), scanning electron microscope (SEM), and simultaneous transmission-reflection spectroscopy. It was found that the properties of the films depend on the amount of Al in the growth solutions and deposition time. The increase in Al content in the reaction solution led to a smaller crystallite size and higher energy band gap that varies in the range 2.42 eV - 2.59 eV depending on the Al content.

1. Introduction
Over the years, the study of optical and electrical properties of Cadmium Sulphide (CdS) has been the subject of intense research due to the wide variety of technological applications, such as opto-electronic devices [1] and thin film solar cells [2]. For thin film solar cells based on CdTe and Cu(InGa)Se2 (CIGS) absorber layers, CdS is the most commonly used optical window material because of its high optical transparency, wide band gap (2.42 eV), n-type conductivity and thickness of about 100 nm [3].

Now, one of the most inexpensive and scalable methods to prepare CdS thin films is chemical bath deposition (CBD), which uses a controlled chemical reaction to grow thin films by precipitation. To achieve this, substrates are vertically immersed in an alkaline solution containing the chalcogenide source, the metal ion and a complexing agent. Many studies on the deposition of CdS using this technique employ a highly toxic material which is ammonia in the chemical bath as complexing agent and hydroxide source [4, 5].

In terms of introducing impurities in the films, doping agents on CdS thin films synthesized by CBD alter their optical, electrical and structural properties, as it has been reported in [6, 7, 8, 9]. These authors reported a decrease in the band gap of doped CdS films for some specific ratios between the concentrations of doping agents and Cd. It is important to note that in all these studies, ammonia is one of the main components of the chemical bath. In this sense, the aim of this research is to study optical, structural and mechanical properties of CdS:Al thin films that were grown by CBD in an ammonia-free system and to provide information on the surface morphology of CdS films grown by CBD on metal substrates.
2. Experimental procedure
Several sets of CdS films were grown by chemical bath deposition (CBD) on glass, copper and bronze substrates (25 mm × 75 mm × 1 mm). Before the process of deposition, the glass substrates were previously cleaned with deionized water and then dried at room temperature. On the other hand, copper and bronze substrates were previously cleaned with ciclohexane, then rinsed with deionized water and dried at room temperature. The formula to prepare CdS films is described in [10], referred as AF films, and it is based on a mixture of the following precursors dissolved in an aqueous solution: Cadmium Chloride, 0.05 M; Sodium Citrate, 0.5 M; Potassium Hydroxide 0.5 M; Thiourea 0.5 M. Also, pH 10 Borate buffer and deionized water is added to the beaker. The films were grown by vertically immersing the substrates in the aqueous solution at a temperature of 70°C for 120 minutes.

In the case of glass substrates, the doping of the CdS films was performed by adding Aluminium chloride (AlCl₃) to the mixture with a different molar ratio in the solution, \( R = [\text{Al}]/[\text{Cd}] \) (0.00, 0.05, 0.10), where the initial concentration of Cd at 0.5 M remains constant.

In order to determine the surface morphology, the films were analyzed by a scanning electron microscope (SEM) using a Jeol microscope model 6610LV. The nanomechanical properties were determined through nanoindentation technique using a HysitronTriboindenter model TI-900 with a Berkovich indenter tip. Additionally, the structural properties of the CdS:Al films were determined through X-ray diffraction measurements (XRD) using a Bruker Endeavor D4 unit with Cu-Kα radiation, \( \lambda = 0.15406 \) nm (Voltage 40 kV with 20 mA flux and measuring angle (2) varying from 20° to 70°).

Optical properties of the films were determined using a reflectometer Filmetrics model F10-RT, which measured the reflectance and transmittance simultaneously in the wavelength range from 380 - 1050 nm. The film thickness was calculated using a software Filmmeasure, which uses a mathematical model [11] to adjust the spectral data in order to determine the films thickness.

3. Results and Discussion
In the glass substrates, the CdS:Al films were yellowish, homogeneous, and their color slightly changed for different Al contents becoming more orange-colored as Al concentrations increased. Besides, it is observed that the more Al content, the better the films adhered to the substrate.

Conversely, the films deposited on copper and bronze substrates had a low adhesion and they were inhomogeneous. CBD applied to grow CdS films on metals produces oxides during the deposition that prevent a pure CdS film from growing unless we perform a thin film deposition on metal and characterize the surface morphology using SEM and Nanoindentation.

In Fig. 1 it is shown the SEM micrographs of CdS films deposited on copper and bronze substrates. We observed a vertical orientation of CdS grown on metal sheets due to the metal lamination process. The films were inhomogeneous and they did not reflect specularly, but they had yellowish regions as well as in the glass substrates, implying that a CdS film is grown by CBD process. This is different from the CdS:Al films deposited on glass substrates which were homogeneous, hard, and they adhered better to the substrate. In Fig. 2, we show in the SEM images of CdS:Al films. A dense layer of small grains that had less than 60 nm in diameter was observed and large particles of about 200 - 300 nm were embedded in the surface, which were absorbed by the it because of colloids formed in the solutions. In this case, CdS can appear heterogeneously in the solution, via an ion-by-ion process forming the film first layer and then through the cluster-by-cluster process, as it is reported in [10].

In the Figs. 3 and 4 it is shown 2D images obtained from the data of the tip scanning performed in the Nanoindenter. Nanoindentation consists in the penetration of a Berkovich tip that applies many cycles of load and unload to the CdS film measuring the hardness and the elastic modulus of each sample. The data is resumed in the Table 1.

The films bad adhesion to the metal substrates is deduced from the data because the measured
Figure 1. SEM images with different magnifications of CdS films deposited on metal substrates. (a) CdS on Bronze (100X); (b) CdS on Bronze (10000X); (c) CdS on Copper (100X); (d) CdS on Copper (10000X).

Figure 2. SEM images of CdS:Al films deposited on glass substrates. (a) R=0.00; (b) R=0.05; (c) R=0.10.

Hardness and elastic modulus are close to the reported values of bronze and copper. Then, the Berkovich tip penetrated the substrates and the lamination process of the metal sheet fabrication used in the deposition resulted in many regions with no deposition shown as the vertical lines in the SEM images. On the other hand, CdS:Al films grown on glass are homogeneous and had a good adhesion to the substrate. We observed that the elastic modulus and hardness measured using the nanoindentation technique had similar values. Besides, the penetration depth of the indentation can be controlled taking into account that the films have a thickness of about 100 nm. The tips penetration depth is 10 to 20 nm, therefore the indentation process was carried out in the films and not in the glass.

Structural properties of CdS:Al films were studied by X-ray diffraction and the diffraction
Figure 3. 2D images of CdS films deposited on metal substrates obtained from the tip scanning in the Nanoindenter in an area of 15 µm x 15 µm (a) CdS on Bronze; (b) CdS on Copper

Figure 4. 2D images of CdS:Al films deposited on glass substrates obtained from the tip scanning in the Nanoindenter in an area of 15 µm x 15 µm (a) R=0.00; (b) R=0.05; (c) R=0.10.

Table 1. Hardness and elastic modulus of CdS thin films grown on different substrates obtained from nanoindentation.

| Film Substrate | Hardness (GPa) | Elastic modulus (GPa) |
|----------------|---------------|-----------------------|
| Bronze         | 123.00 ± 15.01| 2.112622 ± 0.341433  |
| Cooper         | 180.19 ± 29.12| 1.910959 ± 0.284137  |
| Glass (R=0.00)| 81.76 ± 6.82  | 3.292905 ± 0.343220  |
| Glass (R=0.05)| 87.13 ± 7.07  | 3.150583 ± 0.079346  |
| Glass (R=0.10)| 81.32 ± 8.26  | 3.091134 ± 0.103674  |
Table 2. Average interplanar distance \( d_{(002)} \) and crystallite size \( D \) of CdS:Al thin films obtained from XRD.

| Molar ratio [Al]/[Cd] in solution | Average interplanar distance (nm) | Crystallite size (nm) |
|----------------------------------|----------------------------------|----------------------|
| R=0.00                           | 3.34365                          | 32.58835             |
| R=0.05                           | 3.32884                          | 21.45239             |
| R=0.10                           | 3.34973                          | 16.09833             |

patterns are shown in Figs. 5, 6 and 7. In all the samples the observed peak at \( 2\theta = 26.63^\circ \) corresponds to the hexagonal structure of the CdS (wurtzite) and belongs to the plane (002), which has the lowest surface energy in CdS. Besides, an increase in the full width at half maximum (FWHM) is observed as the Al doping increases. This result can be due to Al atoms inducing dislocations and/or defects inside the crystalline structure of CdS and this causes a modification in the XRD pattern. According to the Bragg’s law \( n\lambda = 2d\sin\theta \) the average interplanar distance \( d_{(002)} \) was calculated, where \( \lambda \) is the X-ray wave length and \( \theta \) is the peak angle. Besides, we obtained the crystallite size through the Scherrer equation \( D = \frac{0.9\lambda}{\beta\cos\theta} \), where \( \beta \) is the FWHM in radians. These results are resumed in Table 2.

Figure 5. X-ray diffraction pattern of undoped CdS thin film (R=0.00).

Figure 6. X-ray diffraction pattern of CdS:Al thin film (R=0.05).

Figure 7. X-ray diffraction pattern of CdS:Al thin film (R=0.10).

The ionic radius of \( \text{Al}^{3+} \) is 0.53 Å and it is smaller than the ionic radius of \( \text{Cd}^{2+} \) (0.95 Å) [12]. Therefore, the difference in the interplanar distance may be due to \( \text{Al}^{3+} \) ions were replaced substitutionally in the lattice with the \( \text{Cd}^{2+} \) ions producing a decrease in the interplanar distance, which is observable when \( R=0.05 \). Except when the ratio [Al]/[Cd] is 0.10, \( \text{Al}^{3+} \) ions are also incorporated in the interstitial states of the lattice, which implies that the interplanar distance begins to increase. We also observed a decrease in the crystallite size when the Al content in the bath solution increased, as it was also reported in [8] with CdS:Al films synthesized by CBD using ammonia as one of the precursors.

Optical properties of the CdS:Al thin films were measured with a light incidence of \( 0^\circ \), obtaining absorbance, transmittance and reflectance spectrum simultaneously. We also calculated the thickness using the software Filmmeasure that numerically fitted the spectrum, taking into consideration the film structure deposited on the substrate and a mathematical model for the dielectric constants, in this case the Lorentz oscillator was used. The absorbance, reflectance and transmittance of the CdS:Al films are shown in Figs. 8, 9 and 10. Film thicknesses are resumed in the Table 3. We did not present the spectra of thin films grown on metal
Table 3. CdS:Al film thickness calculated with software Filmmeasure using the measured spectra.

| Molar ratio [Al]/[Cd] in solution | Film thickness (nm) |
|-----------------------------------|---------------------|
| R=0.00                            | 73.13               |
| R=0.05                            | 99.91               |
| R=0.10                            | 162.70              |

substrates because the non uniformity of the films and the deformation of copper and bronze do not let us perform accurate measurements with this apparatus.

In order to calculate the band gap for CdS:Al films (the energy gap between the valence band and the conduction band), we used the measured absorbance \( \alpha \). This value depends on the incident photon energy \( h\nu \) in a semiconductor as:

\[
\alpha(h\nu) = K (h\nu - E_g)^{n/2}
\]  

where \( K \) is a constant, \( \nu \) is the photon frequency, \( E_g \) is the optical band gap, and \( n \) is equal to 1 for direct band gap materials such as CdS [18]. Then, the band gap was determined for each film by plotting \( \alpha^2 \) vs \( h\nu \) and then extrapolating the straight-line portion of the curve to intercept the energy axis as it is shown in Fig. 11. The band gap value of R=0.00, R=0.05 and R=0.10 thin films were found to be 2.374, 2.369, and 2.357 eV, respectively.

We observed a decrease in the band gap of the films as the Al content in the solution increased. These results are similar to those reported in [13]. We believe that this is related to previous reports of Lokhande and Pawar in [9], who suggested that Al\(^{3+}\) ions substitute Cd\(^{2+}\) in the lattice. Also the sulfur deficiency gave rise to donor levels that became degenerate and merged with the conduction band extending the conduction band to the band gap and therefore reducing the latter.

4. Conclusions
CdS films were deposited on bronze and copper substrates by CBD process. The films obtained were inhomogeneous due to metals highly malleability. The deposition took place in regions of
Figure 11. Plot of $\alpha^2$ vs vs $h\nu$ for $R=0.00$ (Black), $R=0.05$ (Red) and $R=0.10$ (Blue). Dashed lines are the linear fit of the straight-line portion of the curves.)

the substrates shaped by a lamination process leaving many regions with no CdS deposition. We believe that CBD is not a good technique to synthesize semiconductors thin films on metal, and is highly recommendable to employ another technique to carry out this process, such as physical vapor deposition. SEM images and 2-D nanoindentation images show a very inhomogeneous film and the hardness or elastic modulus cannot be determined because the Berkovich tip penetrates the substrates and removes the CdS.

For CdS:Al films deposited on glass, we obtained a film with (002) hexagonal phase and there was no modification in the crystalline structure by Al doping. We only observed a decrease in the crystallite size and a change in the interplanar distance because Al$^{3+}$ ions were replaced substitutionally or interstitially depending on the Al content in the solution. No considerable differences are observed in the hardness and elastic modulus of films, which suggest that a low concentration of Al in the films composition does not modify the mechanical properties of the thin films.

The optical properties of the films deposited on glass showed a decrease in the band gap energy when the Al content increased due to Al$^{3+}$ ions, which induced donor levels when merging with the conduction band and consequently the band gap was reduced. The reflectance spectrum was also modified, probably because of the high reflectivity of Al which alters the color of the films and the light reflectance in the UV region.

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