

Synthesis and Characterization of Thin Films of Chalcogenide Semiconductors Doped With Transition Metals with Photovoltaic Applications

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Abstract. The influence of doping on properties of CdS thin films grown by chemical bath deposition technique is studied. Cu, Co, Ni and La are use as doping elements varying de proportion from 1 to 5%. The synthesis parameters employed were reaction time 120 min; speed stirring 240 rpm at a bath temperature of 75°C and pH are controlled at 10. The doped films with different elements are characterized employed optical and structural techniques such as XRD, UV-Vis and the surface morphology are evaluated through SEM. The films are polycrystalline with a mixture of hexagonal and cubic phases, the slope of absorption edge changes with the elements showing different trends mainly for Cu²⁺ y el La³⁺. The valor of E_g decreases with increase of the metal quantity in case of Cu, Ni and La on the contrary of Cobalt. Films are formed by semispherical cluster, is slightly affected, the size increase in case of Ni and Co, and it is decreases for La and Cu.

Keywords: Doping semiconductors, transition metals, Chemical bath deposition, Optical properties and Crystal structure

1. Introduction

The control of the optical properties of binary II-VI semiconductor materials is important because it enhances their applications, which is why interest in their research has increased [1]. The modification of these properties can be achieved in several ways, among them is the chance in the shape, the deposition technique and the synthesis conditions, the size and the elements that constitute the materials. In recent years some research has focused on studying de doping effect namely introducing an impurity into the crystal structure of semiconductor [2]. CdS thin film have a high transmittance and resistivity because these properties it can be considered as viable material in futuristic device, is currently used in transistors, photoelectric lasers, sensors for ultraviolet radiation and like windows in solar cells [3-4]. Particularly, for the use of solar windows it is necessary that the material have high transparency a low electrical resistivity; control of this property can be done through crystallite size or doping. The good conductivity of CdS is attributed to the native defects or vacancies of interstitial sulfur and cadmium, which is affected by thermal treatments or the introduction of an impurity with valance +2 or +3. Several elements had been studied like: Al⁺³[5], La⁺³[6], Cu⁺²[3], Ni⁺²[4], Co⁺², Mg⁺² [7], Zn⁺²[8], Sn⁺² [9], and Mn⁺²[10], and among others, that are obtained by different synthesis techniques. Pure and doped II-VI semiconductors have been synthesized by multiple techniques, including pyrolysis, laser ablation, SILAR and chemical bath deposition, among others. Using the chemical bath technique has multiple advantages since it is affordable, simple and allows scaling or obtaining thin films on substrates of different dimensions. Therefore, this work is focused the influence on optical and structural properties, as well as the Surface morphology and atomic composition of doping, varying the quantity and type of element (bivalent and trivalent) in CdS films grown by chemical bath deposition technique.

2. Experimental details

In this section, the stages of the experimental procedure of this work are focused on obtaining CdS thin films doped with diverse metals with +2 and +3 valence are described, as well as transmittance and the value of bandgap, using the UV-Vis technique: the crystalline structure, the crystalline size by X-ray Diffraction (XRD) and the surface morphology and atomic

content of the elements, using SEM-EDS. The deposition of the CdS thin films with doping elements was carried out using a chemical bath deposition technique on corning glass substrates. The deposition conditions were as follows: the temperature was kept constant at 75°C; as well as the deposition time in 120 min and stirring speed in 240 rpm, for the reaction to occur to controlled reaction rate, an alkaline pH is necessary, then it was maintained between 10 and 11. For the reaction of CdS as precursors were used $\text{CS}(\text{NH}_2)_2$, CdCl_2 , from S and Cd respectively, like buffer solution and complexing agent NH_4Cl and NH_4Cl are employed. For the doping elements were use salts of La, Cu, Co y Ni, with purities greater than 97%. The percentage doping was varied from 1 to 5% and was adjust in volume ratio respect to cadmium at the same concentration. The substrates were subjected to cleaning with trichloroethylene, acetone and methanol, to eliminate impurities, and promote the formation of nuclei to improve the deposition of the materials of interest.

The optical absorption studies were performed using a Perkin–Elmer UV–vis spectrometer Lambda35, in the range of 1100 to 200 nm using 100% transmittance. The surface morphology of the films was studied using a JEOL Scanning Electron Microscope (model JSM 6300L). XRD spectra were obtained in the range 20 – 60° 2 θ with a Malvern-Panalytical Empyrean diffractometer equipped with a PIXel 1D-Medipix3 detector. The equipment was operated at 45 kV and 40 mA, using the Bragg-Brentano configuration and $\text{CuK}_{\alpha 1}$ radiation ($\lambda=1.5406\text{\AA}$).

3. Results and discussion

This section presents the results obtained of the CdS thin films, grown at 75°C, 120 min, and 240 rpm. The content (1-5%) and type of dopant cation (Co^{2+} , Cu^{2+} , La^{3+} and Ni^{2+}) were varied to evaluate the influence on the optical properties, surface morphology and crystalline structure, as well as the calculation of the crystalline size, which are discussed below.

3.1 Optical properties

In Figure 1 is presented the transmittance spectrum obtained of the pure CdS film, without doping element. It can be observed, the spectrum has a maximum transmittance between 65-68% and shows a well-defined absorption edge; referring to the inflection point of the slope, which to determine the value of the band gap. If the edge is well defined can be assume that the films do not have impurities, or that the number of defects is small, even though they are polycrystalline films, growing by Chemical bath deposition (CBD) [11-12].

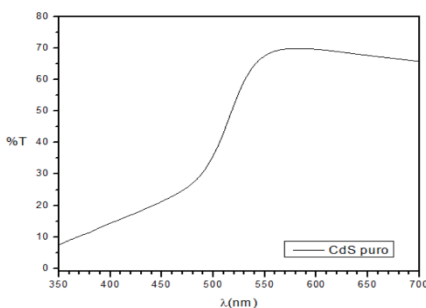


Figure 1. Transmittance spectrum of CdS-pure thin film

Figure 2. Shows transmittance spectra of CdS-pure thin films doped with Co and La grown at 75°C and 120 min. Similarly to the spectrum of pure CdS-pure, the films synthesized with Co (CdS-Co) have well-defined transmittance edges, which suggests that even when introducing a new element with characteristics like Cd, such as Co (CdS-Co) and Ni (CdS-Ni) in small proportions, a little quantity of defects in the films do not strongly influence the transmittance spectra.

However, as the content of Co is increase, a slight shift in the absorption edge towards higher wavelengths is observed, which suggests a decrease in the band gap (E_g), probably related to a diminished in the crystallite size. For this case, the maximum transmittance was obtained for the film grown with 3% Co is 78%. Besides, that the films forms a solid solution as the characteristics of the Co, Cu and Ni atoms obeys Hume Rutherly rules. In the spectra obtained for the films with La, it was observed smaller slopes and greater displacement in absorption edges compared to those obtained for pure CdS, CdS-Co and CdS-Ni, probably due to these films have more defects, as a result of the differences between the properties of the Lanthanum cation such as valence (+3), electronegativity (1.1) and atomic radius 73% greater than Cd^{2+} . Particularly, the

film with 1% La, presents the maximum transmittance around 60%, where a lower impact could be observed due to the small number of atoms incorporated into the CdS-pure lattice.

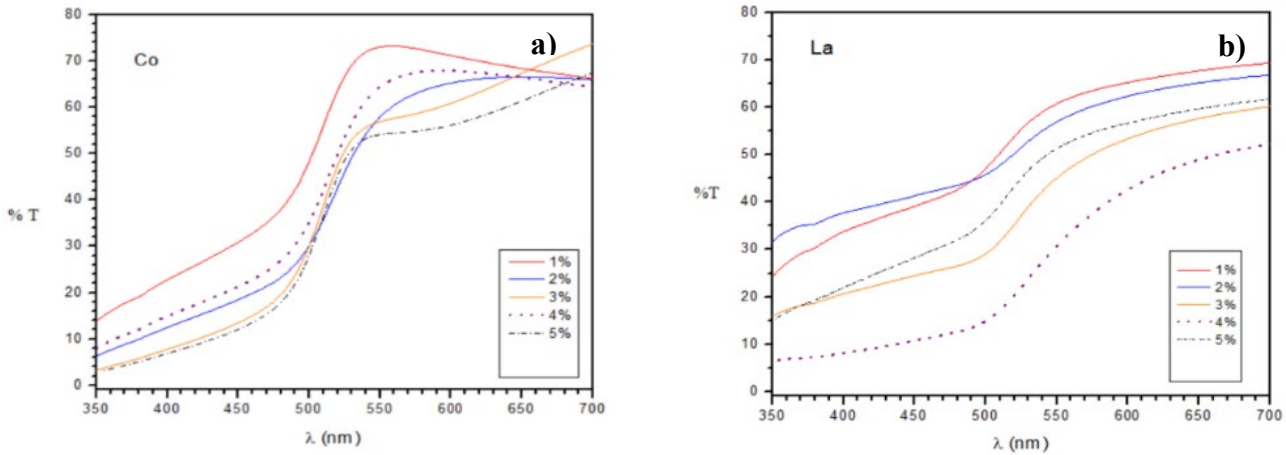


Figure 2. Transmittance spectra of thin film of a) CdS-Co y b) CdS-Ni

Band gap (E_g) calculation

The band gap of the films was calculated using the results obtained in the transmittance vs wavelength graphs, which it is possible to determine the derivative of the optical density (OD) [12]. The OD represents the inflection point that can be maximum or minimum that indicate the value where the energy experiences the maximum rate of change, this point is the value of the band gap. Table 1 summarizes the calculated values of E_g for the CdS-pure, CdS-Co, CdS-Ni, CdS-Cu and CdS-La films. The E_g calculated for CdS-pure thin film was 2.42 eV, this value is consistent with previously reported for bulk samples and for films deposited by different synthesis techniques. [13-14]. The value of E_g decreases slightly as the metal percentage increases for CdS-Ni, CdS-Cu from 2.46 eV to 2.41 and 2.45 eV to 2.40 eV respectively, in agreement with [15-16].

Table 1. E_g for the CdS-pure, CdS-Co, CdS-Ni, CdS-Cu and CdS-La films

Film	E_g (eV)				
	1%	2%	3%	4%	5%
CdS-Co	2.42	2.41	2.46	2.42	2.45
CdS-Cu	2.45	2.45	2.43	2.41	2.40
CdS-La	2.42	2.38	2.38	2.37	2.41
CdS-Ni	2.46	2.42	2.45	2.43	2.41

3.2 Surface morphology

Table 2 shows the micrographs obtained to 1000 nm and 100 nm of resolution for the different samples of CdS-pure, CdS-5%Co, CdS-5%Ni, CdS-5%Cu and CdS-5%La films.

As can be seen, the substrate is almost completely covered by the films, but a few holes are perceived evidencing a lower layer of particles. It has been reported that thin films can follow three different growth mechanisms [17-18], then, from these results it is possible to assume a layered growth (Frank-Van der Merve) or a mixed one known as Stranski-Krastonov. The film CdS-pure is constituted by semispherical clusters of particles with average size from 100 to 250 nm. In the CdS-5%Ni films, no significant difference is observed in the morphology and particle size, with respect to those of CdS-pure.

In the deposition of CdS-Co films, the substrate is completely covered, but the clusters have a diameter 50% larger than those of CdS-pure and CdS-Ni, so it can be assumed that the deposition reaction occurs at a higher growth rate. For CdS-5%Cu the size distribution is smaller, and the particle size ranges from 50 to 100 nm. Finally, regarding the deposits using La as doping cation, it is distinguished that the films are formed by two types of morphologies: the semispherical clusters described in the other films and a kind of flakes-like, that has been reported for films of ternary materials when there is a

cadmium excess in films [19-20]. The above that could be generating the formation of possible impurities, that is, the formation of compounds other than CdS.

Table 2. High resolution SEM micrographs of CdS-pure, CdS-Co, CdS-Ni, CdS-Cu and CdS-La films

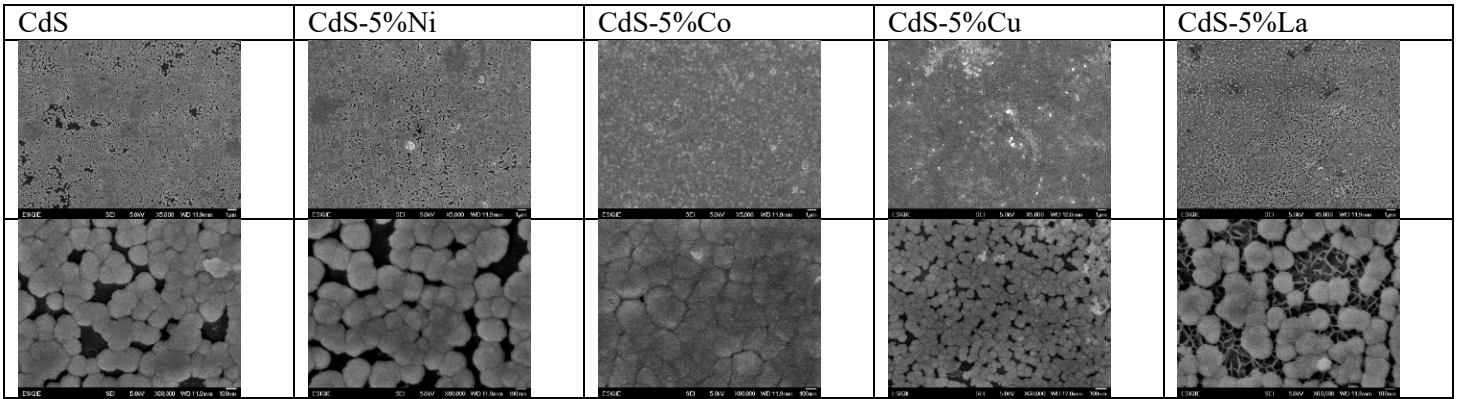


Table 3. Atomic composition of CdS-Co, CdS-Ni, CdS-Cu and CdS-La films

Elemento	5%	10%	5%	10%	5%	10%	5%dopaje	10%dopaje
Cd	0.9918	0.9952	0.9885	0.9957	0.9270	0.8454	0.9873	0.9453
S	1.3821	1.3364	1.8505	1.4304	1.2788	1.1195	1.1890	1.2968
Ni	0.0081	0.0047						
Cu			0.0114	0.0042				
La					0.0730	0.1545		
Co							0.0126	0.0546

Table 3. summarizes the results obtained from energy dispersive spectroscopy EDS, for films grown with 5 and 10% of cation doping. Those with lower doping percentages were not evaluated because the equipment sensitivity does not allow the identification of elements with smaller quantities, clarify that this analysis is semiquantitative. It can be seen there are a sulfur excess in all films, it is known that the films growing by CBD is normally the existence of Cd vacancies and interstitial sulfur. The results show a small or almost no incorporation of the elements Ni and Cu for 5 and 10% of dopant cation, the lower the percentage of doping, the results can be not precises. On the contrary, in the case of Co, the incorporation is reported to be slightly higher than 20%, and almost of 55% for CdS-10%Co. Likewise, CdS-La films the amount of atomic percentage is higher than the theoretical quantity in the bath, this may be because the lanthanum reactivity is greater than that of Cadmium, favoring the incorporation of La or even the replacement of Cd in the lattice of CdS.

3.2 Structural properties

II–VI semiconductor thin films obtained by different techniques indicate that they are polycrystalline in nature with cubic (zincblende), hexagonal (wurtzite), or a mixture of both phases. Figure 3 shows the XRD spectra of the CdS-pure, CdS-5%Co, CdS-5%Ni, CdS-5%Cu and CdS-5%La films. The films synthesized with lower percentage were not analyzed because the detection limit of the diffractometer is 5%. As can be seen, tree peaks with different intensity are defined in the spectra, the peak with the highest intensity is located around $2\theta=26.6^\circ$, it can be related with the (002) plane of the hexagonal (H) phase or the (111) of the cubic (C) phase according to the JCPDS file No. 800006 and 800019 respectively. The other peaks can also be correlated to planes of the same phases located at $2\theta=44.01^\circ$ and $2\theta=52.26^\circ$. However, without a more detailed analysis, it is not possible to determine which phase predominates in the films, so a mixture of phases can be assumed. A slight shift to lower angles is observed in the highest intensity peak. This displacement can be attributed to forming a solid solution [11]. Particularly, in the case of La $2\theta=26.58^\circ$, as described for the UV-Vis analyses, these films may have a greater number of defects that can be attributed to differences in the properties of the metal, mainly in the atomic radius. On the contrary, for doping films with divalent metals, the displacement occurs towards higher angles;

these cations have a smaller atomic radius than cadmium (19-21%) therefore, it could be assumed that the deformation in the crystal lattice is smaller in these films. The value of the crystallite size was estimate using the Scherrer equation using the FWHM of (002) plane from the highest intensity peak without considering the stresses. For all cases the crystal size was less than 20nm, the smallest value being for the film doped with Cu and the largest for the one doped with nickel, there is no clear influence of the doping to crystallite size of the films.

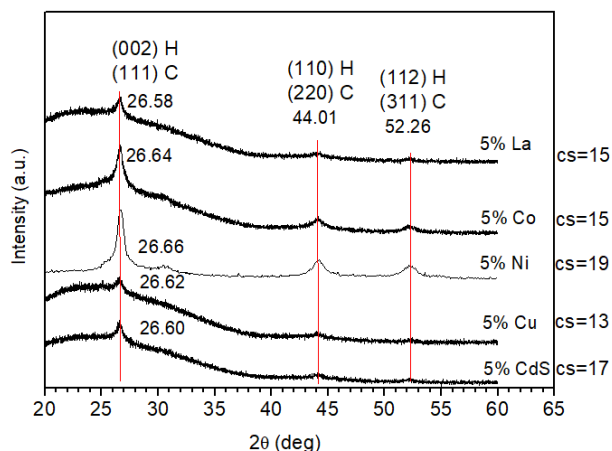


Figure 3. XRD spectra of CdS-pure, CdS-C5%Co, CdS-N5%Ni, CdS-5%Cu and CdS-5%La films

Conclusions

CBD allows the synthesis of thin films of different compounds pure and with various divalent and trivalent dopant cations, it is possible to control and modify the optical properties by varying the bath experimental conditions mainly the ratio of precursors.

Transmittance and the E_g are significantly affect by the content (%) and type of dopant cation, the slope of the absorption spectra is also affected more evidently for the case of Cu^{2+} and La^{3+} . The changes of the properties in CdS-La films are attributed to the differences of valence, electronegativity, crystal structure and atomic radius, in this ion is observed the bigger changes, due to for these films are not forms the solid solution into the CdS lattice according to the Hume-Rothery rules. E_g diminishes as doping percentage increases for Cu and Ni, the contrary effect is observed for Ni and La. the E_g value is less than CdS-pure, in all films the value is greater than 2.42eV. the surface morphology do not present a significantly change with different elements only in the case of La, but the cluster size decrease with the quantity element increase. All films exhibit a mixture of cubic and hexagonal phases, showing a preferential orientation on (111) or (002) plane respectively, a lightly shift to higher angles is observed for all bivalent cations the opposite trend is obtain to CdS-La films.

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