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DENSIFICATION KINETICS OF CdS THIN FILMS ANNEALED AT LOW TEMPERATURE

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A systematic study of growth, annealing, and characterization of cadmium sulfide (CdS) thin films obtained by chemical bath deposition is presented. The aim of this work is to elucidate the densification kinetics and the annealing effect on microstructure, optical behavior, and band gap of annealed CdS films in the temperature range of 373.15-523.15 K, using nitrogen atmosphere. Film characterizations were performed by profilometry, X-ray diffraction, X-ray photoelectron spectroscopy, and atomic force microscopy techniques. Additionally, optical properties and band gap of films were determined by UV-visible spectroscopy. CdS films intended for solar cell applications grown to an average thickness of 118 nm, exhibited band gap values in the range of 2.38 eV to 2.45 eV. Lastly, annealing process allows a densification degree increase up to 64 % and the kinetic study reveals that the densification process of CdS obeys to fractional order rate law with activation energy of 43.09 Kcal/mol.

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1. Introduction

Recent advances in soft solution processing of inorganic semiconductor materials offer technical advantages to develop large area manufacturing technologies for solar cells. In particular, nanostructured semiconductor materials offer better light absorption than semiconductor monocrystalline or polycrystalline silicon [1, 2]. Cadmium sulfide (CdS) is an attractive semiconductor material and it can be deposited as thin layers on a substrate (commonly glass or silicon) allowing less material consumption [2]. Additionally, CdS is used a suitable window layer for CdTe solar cells, gaining a leading role on the thin film photovoltaic technology [3-5].

CdS thin films have been synthesized and deposited by several methods, such as: chemical bath deposition (CBD) [6], pulsed laser deposition (PLD) [7, 8], atomic layer deposition (ALD) [9], and magnetron sputtering (MS) [10]. Among these methods, the CBD technique is considered an excellent approach to produce thin films for electronic applications due to low cost, scalable process, and simple technique [11]. On the other hand, the thermal treatment (annealing) deposition in CdS thin films can offer a way to improve their electrical and optical performance.

Even though CdS has been studied for many years, research is needed to optimize fabrication methodologies for industrial applications. The present work is intended to understand

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the effect of annealing on CdS properties and improve the CdS thin film densification, usually obtained at high temperatures, resulting on lower process costs.

2. Description of the experimental process and setup

CdS thin films were synthesized in a beaker of 100 mL. Reagents in solution were placed into beakers by sequential addition of 31 mL of deionized water, 4 mL of cadmium nitrate tetrahydrate ($CdNO_3 \cdot 4(H_2O)$) 0.1 M, 5 mL of glycine 0.1, 2 mL of pH buffer 11(NH_4Cl 1M + NH_4OH non-diluted), 5 mL of thiourea 1M, and 13 mL of deionized water to obtain 60 mL of solution. Film depositions on glass substrates were carried out at 343.15 K for 30 minutes without stirring. Then, samples underwent two ultrasonic cleaning cycles of five minutes each, in a Branson 2510 ultrasonic cleaner. A solution of acetone/deionized water in a 1:1 ratio was used to remove excess CdS material from the deposited films. Then, films were thermal treated in a BLUE M vacuum furnace under a controlled nitrogen atmosphere at a pressure slightly above atmospheric pressure. In order to determine the kinetics of the densification process during the thermal treatment (annealing), temperature and time were varied. Temperature and time combinations reported in this work were (373.15, 423.15, 473.15 and 523.15 K) and time (30, 60, 90, and 120 minutes) resulting on 16 combinations. Finally, as deposited and annealed samples were prepared for their characterization by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), profilometry, and UV-VIS spectroscopy techniques accordingly.

XRD characterizations were performed in an Empyrean PANalytical diffractometer operated at 45 kV and 40 mA using CuKα (with a wavelength of 1.5406 Å). Analyses were achieved using the grazing angle technique with an incident angle of 0.5°. Characterizations by XPS spectroscopy were carried out in a Perkin Elmer PHL 5100 double source (Al/Mg). AFM characterizations were achieved in a Nanosurf Easy Scan 2 with a 10 μm resolution. Also, a Bruker Dektak XT Profilometry equipment was used to measure film thickness. Finally, optical characterization and band gap were determined by UV-vis spectroscopy in a Perkin-e Elmer Lambda 19 in the visible spectrum range of 300 to 900 nm.

3. Results and discussion

3.1. Microstructural behavior

The microstructural characterization of CdS films started with the identification of phases by XRD, followed by the analysis of chemical composition, as atomic percent, through XPS technique. Observation of the surface characteristics and roughness of CdS deposits were performed by AFM.

Fig. 1 shows the XRD patterns corresponding to as deposited and annealed films grown by CBD method.

As shown in Fig. 1, the representative XRD patterns for as deposited and annealed (thermal treatment parameters: 523.15 K for 120 minutes) thin films indicate that all reflections correspond to CdS phase with hexagonal crystalline structure (PDF 01-079-3167, cadmium sulfide (CdS) or Greenockite, syn; hexagonal, a=b=4.31 Å, c=7.02 Å; 23.825°, 25.351°, 27.038°, 41.897°). Also, it is possible to identify, on the XRD patterns for as deposited and annealed films, the main peak of the hexagonal phase of CdS at 27.038° of 2θ. The last mention peak corresponds to (101) crystallographic plane, which indicates a preferential orientation of the deposited and annealed films in the mentioned plane.

According to those results, in the study range for densification kinetics, changes in crystalline structure are not observed. This behavior is attributed to the CdS thermal stability in the range of 373.15 to 523.15 K, which presents a melting point around to 2023.15 K. It is worth mention that annealing process was used for the densification of CdS films and the glycine removal (complexing agent). Considering that decomposition temperature of glycine is 506.15 K, the maximum densification temperature used in this work was 523.15 K. Under this condition,

densification and glycine removal were achieved. However, XRD results revealed that there is not changes in the crystalline structure of CdS and it remains as Greenockite. In addition, a comparison of obtained results under the tested condition with those conditions reported by Ichimura [13] (473.15-723.15 K) and Islam [14] (673.15-773.15 K) confirms that it is possible to reach a good densification degree at lower temperature, and temperatures up to 523.15 K are not required.

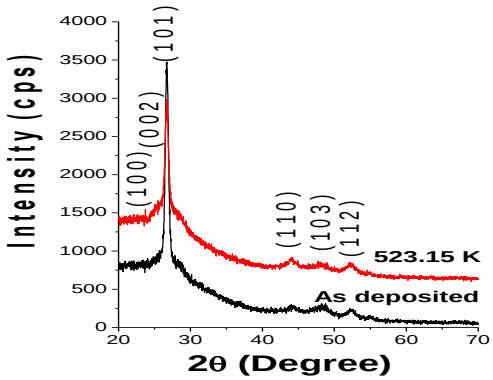

Fig. 1. Representative XRD patterns corresponding to as deposited and annealed (thermal treatment parameters: 523.15 K for 120 minutes) thin films of CdS.

Nevertheless, it is possible to observe an increase of main full-width at half-maximum (FWHM) in XRD patterns of CdS samples as function of temperature, and the FWHM widening is associated with the increase of the crystal size in CdS films. Measurements of the average crystallite sizes of CdS thin films from XRD patterns using Debye-Scherrer's formula, show changes in crystallite size from 13.87 to 22 nm for as deposited and annealed films, respectively. The increase of the crystallite size is attributed to the coarsening of the tiny crystals with high reactivity at relatively high temperatures (523.15 K).

In Figure 2, illustrates the XPS spectra for CdS thin films, deposited and annealed at various temperatures (373.15, 423.15, 473.15 and 523.15 K). The qualitative XPS analyses are shown in Table I and confirm the presence of Cd and S in the deposited material by CBD.

The quantitative chemical analyses by XPS for as deposited and annealed CdS thin films show that the thermal treatment has an effect on the composition of the CdS deposits, as follows: The as deposited phase presents the chemical formula: Cd0.53S0.47. Then, when temperature increase from 373.15 to 423.15 K, a diminishing in the cadmium amount promotes a change in the global composition and the chemical formula can be represented as Cd0.51S0.49, reaching the stoichiometric composition (Cd0.50S0.50) at 473.15 K. Above that temperature, the concentration of cadmium increase until 54.00 atomic percent at 523.15 K, reaching a final composition of Cd0.54S0.46. The current behavior in composition of CdS can be associated with the different removal stages of the volatile phases and the remaining reagents used in the synthesis.

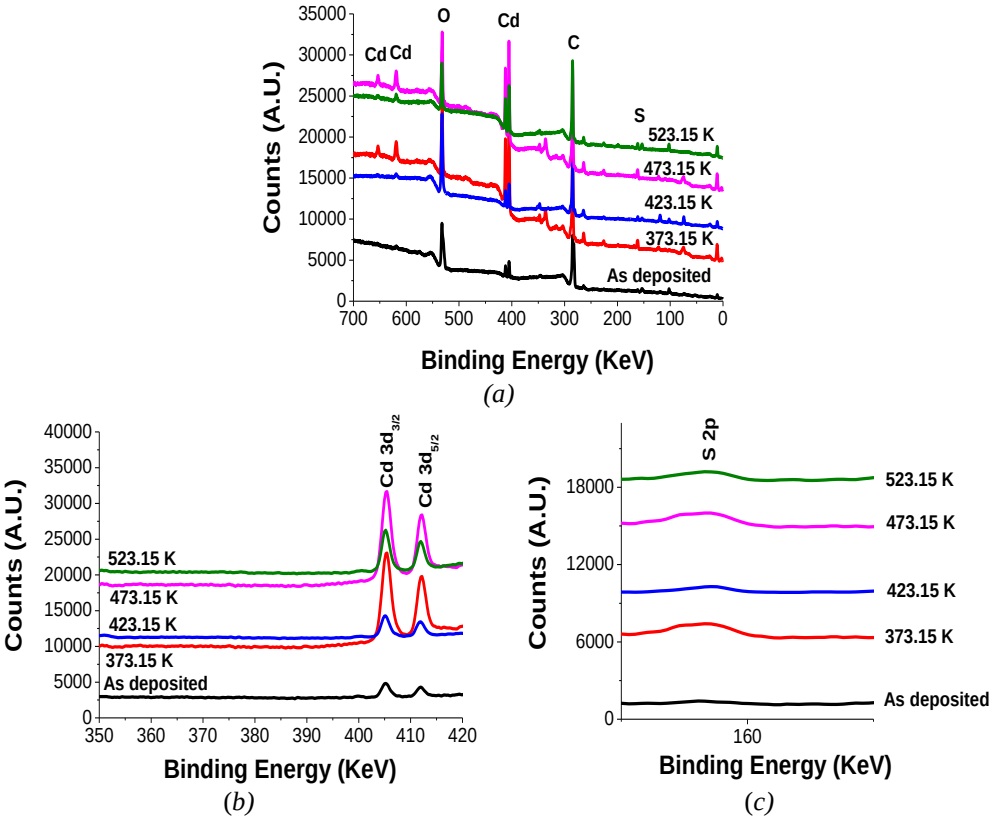

Fig. 2. XPS results of CdS nanostructured films as deposited and annealed at 373.15, 423.15, 473.15, and 523.15 K. (a) XPS survey spectra, (b) Cd 3d binding energy spectra, and (c) S 2p binding energy spectra.

Table 1. Chemical composition of CdS thin films determined by XPS analysis.

Annealing temperature	Cd (Atomic %)	S (Atomic %)
As deposited	53.00	47.00
373.15 K	52.00	48.00
423.15 K	51.00	49.00
473.15 K	50.00	50.00
523.15 K	54.00	46.00

Observation of the surface characteristics and roughness of CdS deposits performed by AFM are presented below. Fig. 3 shows AFM results that corresponds to images of CdS phase for as deposited and annealed films and Table 2 shows RMS roughness values for each sample (as deposited and annealed at four different temperatures and times). The error associated with RMS roughness measurements for the present study is ±0.6 nm.

AFM images and RMS roughness results indicate that the annealing process promotes, in most cases, a decrease in the roughness degree. The lowest roughness degree (RMS roughness: 9.56 nm) is reached when densification process is carried out at 523.15 K for 120 minutes. Hence, given that the densification process is a thermal activated phenomenon, AFM results confirm that high temperatures and long times promote a reduction on the roughness degree. The decrease in the RMS roughness can be associated to the displacement and the reorganization of the crystallites, as well as, to the increase of the densification degree of CdS thin films.

Table 2. RMS roughness values obtained by AFM.

Temperature (K)	Annealing Time (minutes)			
	30	60	90	120
373.15	9.44	9.17	11.61	11.50
423.15	14.50	8.23	10.25	12.50
473.15	10.13	9.88	13.50	13.91
523.15	9.92	9.94	11.47	9.56

*As deposited Roughness: 16.05 nm

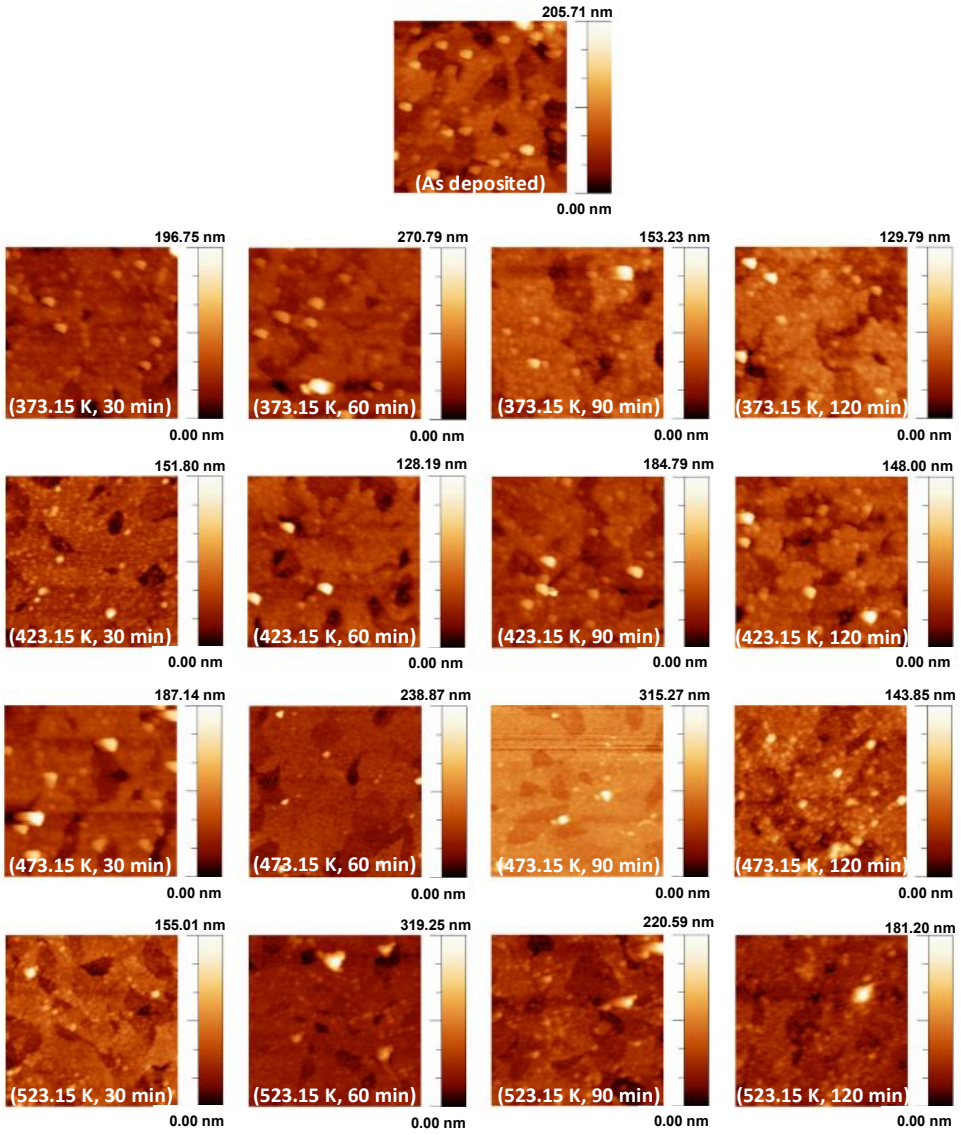

Fig. 3. Representative images of CdS nanostructured films obtained by AFM and WSxM software [15] as deposited and annealed at 373.15, 423.15, 473.15 and 523.15 K for 30, 60, 90 and 120 min. 10μm scan.

3.2. Optical properties and band gap

CBD-CdS films are yellowish with varied homogeneity as function of processing conditions (time and temperature). These films present suitable adhesion at Corning® glass substrate and have average thickness values of 112 nm (measured by profilometry) for a deposited and annealed (373.15, 423.15, 473.15 and 523.15 K in times to 30, 60, 90 and 120 min.) films.

Optical transmittance spectra of CBD-CdS nanostructured films as a function of annealing are shown in Figure 4. Transmission curves for deposited and annealed films, exhibit a response in the visible spectrum with transmittance values from 60 to 70 % in wavelength range from 500 to 800 nm. Films with a similar response have been suggested for solar cell applications with relatively high efficiency. Given that, under these conditions, more light can penetrate into the active region of the solar cells [16, 17]. Furthermore, the optical band gap (Eg) was determined using Tauc relation [18] (Fig. 5). Based in Tauc plot, the intersection with the x-axis of the plot of $(\alpha h\nu)^2$ versus $h\nu$ corresponds to the Eg. Here α es the absorption coefficient, and $h\nu$ is the photon energy.

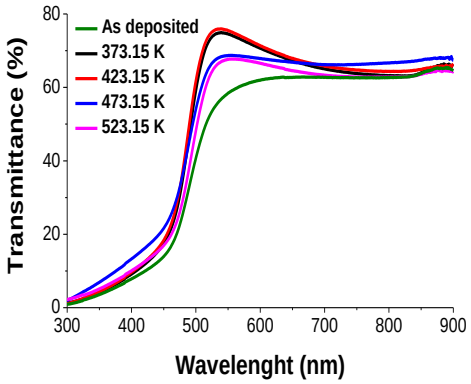

Fig. 4. Transmittance spectra of CdS films of as deposited and annealed films.

According to optical characterization and analysis of results, films as deposited present an optical band gap of 2.45 eV. After thermal treatment, band gap of the films can be varied in the range of 2.45 to 2.34 eV with increasing annealing temperature from 373.15 to 523.15 K, respectively. Hence, the change of band gap values is indirectly proportional to annealing temperature. Band gap behavior can be associated to coarsening phenomena, that it is a thermal activated process, which promotes the growing of grains of nanostructured films.

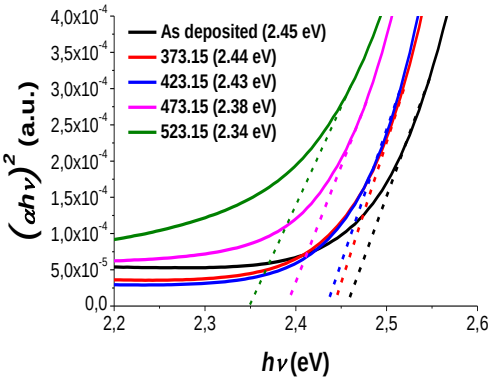

Fig. 5. Plot of $(\alpha h\nu)^2$ versus $h\nu$ of CdS films as deposited and annealed at different temperatures.

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3.3. Densification kinetics

Study of densification kinetics of CdS thin film in nitrogen atmosphere (to avoid oxidation) were based on the variation of thickness (see Figure 6) of annealed specimens at different temperatures (373.15, 423.15, 473.15 and 523.15 K) and times (30, 60, 90, and 120 minutes).

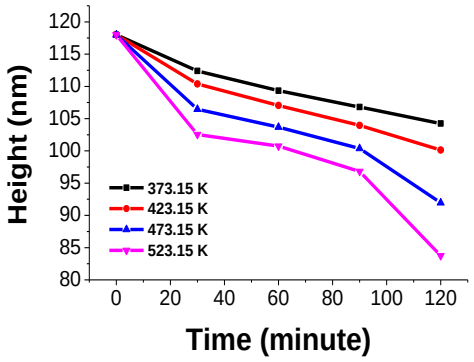

Fig. 6. Thickness plot showing the values obtained after annealing at various temperatures.

As expected, the annealing process affects film thickness resulting on a variation range from 118 nm up to 84 nm. According to the differential method, densification rate equations at tested annealing temperatures for this study are:

373.15 K	$y = 0.0651x + 2.0172$	$R^2 = 0.8855$	(1)
423.15 K	$y = 0.0631x + 2.0098$	$R^2 = 0.9493$	(2)
473.15 K	$y = 0.061x + 2.0008$	$R^2 = 0.9487$	(3)
523.15 K	$y = 0.062x + 1.992$	$R^2 = 0.9264$	(4)

The densification process of CdS thin film in a nitrogen atmosphere within a range of temperatures from 373.15 to 523.15 K, obeys a fractional order rate law. After solving the Arrhenius equation [19], the activation energy (Ea) for the densification process for CdS films was obtained and it corresponds to 43.09 Kcal/mol (180.30 KJ/mol). The densification degree under this condition can reach up to 64%, which leads the authors to consider the densification process as highly efficient and low temperature. Quality of films at low temperature (523.15 K) is improved requiring less energy. Usually higher temperatures (up to 773.15 K) and large amount of energy [20, 21] (heat) is typically needed for inorganic materials.

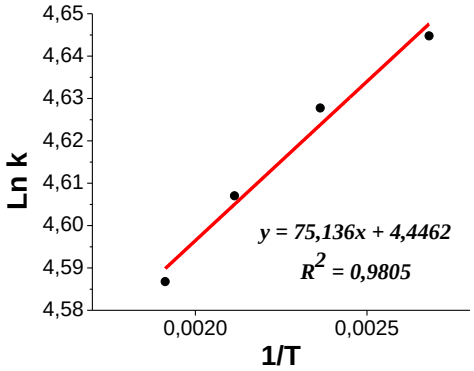

Fig. 7. Arrhenius plot for densification of CdS in nitrogen atmosphere in temperature range from 373.15 to 523.15 K.

4. Conclusions

Annealing process conditions have a strong effect on microstructure, optical behavior, and band gap of CdS thin films synthesized by CBD method using glycine as ligand. According to results, glycine plays an important role as binder and allows the densification of CdS thin films at relative low temperatures (523.15 K), given that it support the formation of liquid phase and improve densification process. Kinetics study indicates that densification is a thermally activated process that obeys a fractional order rate law and requires relatively low activation energy of 43.09 Kcal/mol (180.30 KJ/mol).

The described densification process, carried out under the experimental conditions, promote an increase of densification degree on CdS films up to 64 % at relatively low temperatures (523.15 K). Methods requiring higher annealing temperatures result on thin films with lower optical band gap values, because of that, it is important to propose methodologies that allows CdS film densification at low temperature, such as, this case. Lastly, CdS films with the obtained properties and characteristics can find potential application on optical and electrical devices, such as, solar cells for cars or home windows.

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