

Formation of the band gap energy on CdS thin films growth by two different techniques

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Abstract

The band gap formation during the first stages of growth of CdS thin films, deposited on glass substrates by chemical bath deposition (CBD) and close spaced sublimation (CSS) techniques was studied. To obtain the first stages of growth, we used deposition times between 5 and 40 min for CBD films, and 4–60 s for CSS films. CBD technique with two chemical bath agitation modalities — the traditional magnetic agitation and ultrasonic vibration — was used for film preparation. Morphological, structural, optical, and stoichiometrical results were obtained on each CdS films group. Higher values of the band gap energy (3.2 eV) were obtained for the thinnest films (2–3 nm) by CBD with ultrasonic vibration; others films, showed similar band gap energy values to those reported for polycrystalline CdS films (2.42 eV). Energy vs. α^2 curves, presented strong differences between the two deposition techniques used. The behavior of the optical window effects, the surface roughness, the structural results, and the films thickness related to the deposition techniques are discussed. The CBD technique with ultrasonic vibration produces films with cleaner surfaces, controlled thickness and better optical properties. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cadmium sulfide; Semiconductors; Band gap; Deposition process

1. Introduction

The new technologies for massive production of solar cells, are based on the use of materials with thin film geometry due to the low cost solar energy conversion, low materials consumption and the facility to obtain very small integrated modules [1–4]. In this way, the cost of the produced power/year can be approximately 10 times less than the cost for crystalline silicon technology. For these reasons, thin films are actually the most promising technology for solar cells production. However, a combined solution deposition and thermal

evaporation technology have been found the most promising processes for solar cells mass-production. Considering the different materials for photovoltaic applications, the heterostructure *glass/conductor-oxide/CdS/CdTe/metal* is one of the most low cost efficient converters of solar radiation in electricity (15.8%) [5,6], and much effort has been made on their research and development. Actually, CdTe is one of the most important semiconductors because of the direct band gap energy (1.45 eV), and the high conversion efficiency of terrestrial solar light in electricity. This semiconductor is normally prepared by sublimation, by heating CdTe powder of high purity at 700°C and deposited on a substrate at 500°C. However, CdTe does not grow stoichiometrically [7], having slight Cd vacancies deficiency, consequently growing as p-doped. Thus,

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a natural n-doped material is required as a partner to achieve a good junction with high efficiency in solar conversion. An optimal partner for CdTe is cadmium sulfide, CdS. Normally, CdTe is grown on CdS thin films previously prepared by chemical deposition method. The wider band gap of CdS allows the sunlight to enter the CdTe material more readily, acting as a window effect.

As a rule, CdS thin films grow as n-type semiconductor due to the donor centers formed during deposition. Vacancies of sulfur cause deviations from stoichiometry. However, by means of thermal diffusion of impurities, such as Cu and In, after preparation, it is possible to obtain p-type CdS [8,9].

CdS is normally prepared by a low cost and a low temperature technique: the chemical bath deposition (CBD) [10,11], but is also prepared at high temperature by evaporation-sublimation technique [12], or by spray pyrolysis [13], for the production of large-areas, being the last one an intermediate method between gas phase and solution techniques.

For solar cells manufacturing, typical film thickness suggested is approximately 4 μm for CdTe, and 0.1 μm for CdS. The formed CdTe/CdS interface presents a large mismatch between compounds (10%) [14] and usually, a further heat treatment needs to be made to obtain a good homojunction. The formed junction and the interface characteristics are the key for good development of the solar cell; however, an excessive mix of the materials in the interface can be the reason for the homojunction disappearing and the solar cell performance diminishing [4]. Similar results can be obtained if mixing in the interface is not good, because generated defects can reduce the solar cell efficiency. Therefore, it is necessary to achieve an intermediate mixed conditions such that thin layers of CdS deposited on CdTe only remove the mismatch defects, and maintains the characteristics of the heterojunction.

The band gap energy of the thin films is one of the most important parameters of transparent films for optical window applications. CdS polycrystalline films possess a direct band gap of 2.42–2.45 eV at room temperature (RT). For solar energy applications, CdS films require to have: high optical transparency, low electrical resistivity and high structural orientation at RT, being the first requirement related with this work. Optical transparency depends on the band gap energy value and the thickness measured on the films, and shows a strong dependence with the film preparation procedure.

In this work we studied the formation of the band gap of CdS thin films during the first stages of growth, when they are prepared by CBD and close spaced sublimation (CSS) techniques, and the development of the morphological and the structural properties achieved. The CBD technique was applied with two

modalities: magnetic agitation on the bath solution and by ultrasonic vibration on the whole deposition system. The role of the thickness on the CdS films and its relation with the measured band gap energy for solar applications are discussed.

2. Experimental procedure

CdS films were deposited on Corning glass 7059 substrates (10 \times 15 mm) cleaned with carbon tetrachloride, acetone, and isopropyl alcohol and rinsed with distilled water in each step. Films were deposited by two techniques: chemical bath deposition (CBD) and close spaced sublimation (CSS).

Details of the CBD technique are widely described in the literature [15,16]. Briefly, the chemical bath is formed by an aqueous solution of cadmium chloride (CdCl_2), potassium hydroxide (KOH), ammonium nitrate NH_4NO_3 , and thiourea ($\text{CS}[\text{NH}_2]_2$). The chemical bath solution prepared was maintained at 75°C in a glass-beaker container. The glass substrates were supported by Teflon holders and immersed into the chemical bath with continuous agitation during film deposition. The film deposition starts when the precursor thiourea is added. The samples and holders were retired from the chemical bath after certain deposition times. The resulting films were pale yellow with bright surfaces and presented high adherence on substrates. By using the CBD technique, CdS films were deposited under two modalities:

1. Stirring the solution with a magnetic agitator during deposition. This is a common method used to produce high-quality CdS films, and has been demonstrated to be useful to avoid concentration gradients and precipitation. The effect of the angular velocity of the stirrer has been found to be not important on the film properties [17,18]. In this modality, the chemical bath solution is stirred, meanwhile glass substrates are immersed into the bath.
2. Applying ultrasonic vibration to the chemical bath solution, instead of magnetic agitation. In this new modality, the chemical bath container and samples are immersed into a commercial ultrasonic cleaner vibrating at 42 kHz and maintaining the bath temperature with an electrical heater.

In both modalities, CdS material is deposited on both faces of the substrate.

The second technique used for CdS films preparation was CSS [19]. Films were evaporated into an evacuated chamber with a diffusion pump at 10^{-6} torr. The source material was CdS powder with 99.999% purity from Balzers, and was placed in a graphite crucible. The crucible was heated by Joule effect until CdS

source sublimates at temperature T_f . Vapor species condenses on the substrate, which is located 20 mm above the source. A shutter was used to control the time of growth, i.e. the film thickness. The source temperature (T_f) and the substrate temperature (T_s) were fixed at 700, and 500°C, respectively, while deposition time ranged between 2 and 60 s.

Several atomic force microscopy (AFM) images of each film surface were taken ex situ after growth at atmospheric pressure and room temperature. We used an AFM AutoProbe CP from Park Scientific Instruments in the constant force mode both with a high-resolution scanner ($5 \times 5 \mu\text{m}^2$) and a large area scanner ($150 \times 150 \mu\text{m}^2$). These images were analyzed with the Proscan software, calculating the rms-roughness value.

The CdS film thickness was determined from compositional depth profiles performed by Auger Electron Spectroscopy (AES) technique, with an ESCA/SAM Perkin-Elmer PHI 560 with a double pass cylindrical mirror analyzer with initial pressure of $\sim 2 \times 10^{-9}$ torr. AES profiles were obtained with an Ar^+ beam with 4 keV and $0.36 \mu\text{A}/\text{cm}^2$, yielding a sputtering rate of approximately 10 nm/min.

X-Ray diffraction (XRD) measurements in the grazing incidence mode with 0.5° of beam inclination were performed, using a monochromatic CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$), with a slit of 0.2 mm, in a D5000 Siemens diffractometer. Films were carefully mounted to avoid any misalignment. The scanning step was 0.01° with a counting time of 10 s. Data were sequentially collected in the range between 20 and 60° (2 θ).

Optical absorption measurements were performed with a Jobin-Yvon/Spex H20-VIS spectrophotometer using a 250-W tungsten halogen lamp. The incidence photon flux was normal to the film surface. The investigated wavelength ranged from 300 to 800 nm. The signal was received and processed with a Data Scan-2 controller coupled to a personal computer. Optical analysis of films deposited by CBD was realized after eliminating one of the two CdS faces deposited on the substrate. The band gap energy (E_g) of the transparent films was determined by using the equation:

$$\alpha^2 = \frac{1}{d^2} \ln^2 \left[\frac{I_o}{I} \right] = A(E - E_g) \quad (1)$$

Where α is the absorption coefficient, d is the film thickness, I and I_o are the transmitted and emitted light intensities, respectively; A is a constant, and $E = h\nu$ is the light energy.

3. Results

3.1. Band gap energy formation

Optical properties were measured on CdS films, pre-

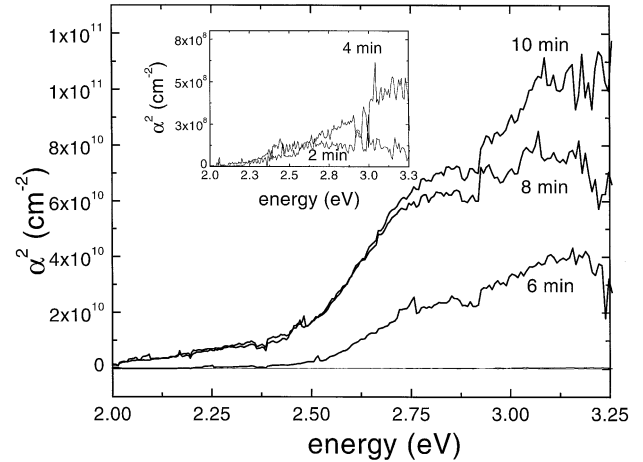


Fig. 1. Energy vs. α^2 curves obtained for CdS films deposited by CBD technique with magnetic agitation for different deposition times. The band gap energy value, E_g , was obtained from the curve slope and its intersection with the energy axis for $\alpha^2 = 0$. E_g formation is clearly seen as the deposition time increases.

pared with different deposition times (i.e. different thickness) by means of the optical transmittance property. Energy vs. squared absorption coefficient (α^2) curves were plotted in order to calculate the E_g value using Eq. (1). Fig. 1 shows the results obtained for the CdS films prepared by CBD with magnetic agitation and different deposition times. The absorption process is directly related to the curves behavior. Curves correspond to films deposited during 2, 4, 6, 8 and 10 min. The absorption process increases with deposition time giving the band gap formation. Inset shows the results for films prepared with minor times and the poor absorption effects. After 10 min of deposition time, the film has reached enough thickness, such that the measured value of E_g corresponds to the typical value for polycrystalline CdS films (2.42 eV) [20,21].

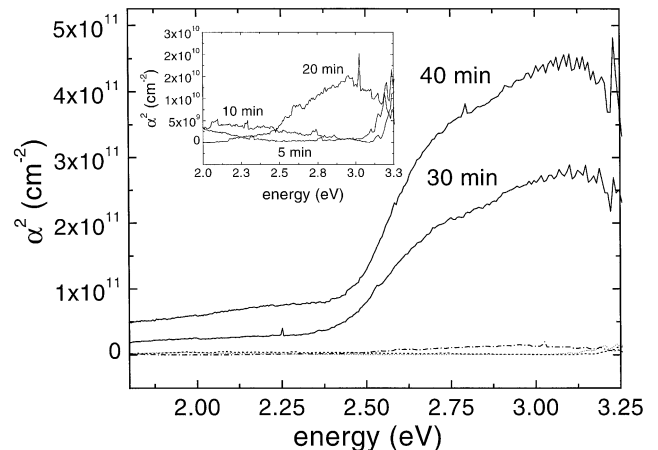


Fig. 2. Energy vs. α^2 curves obtained for CdS films deposited by CBD technique with ultrasonic vibration. E_g values increases with deposition time. Deposition times used in this modality are higher than used for magnetic agitation.

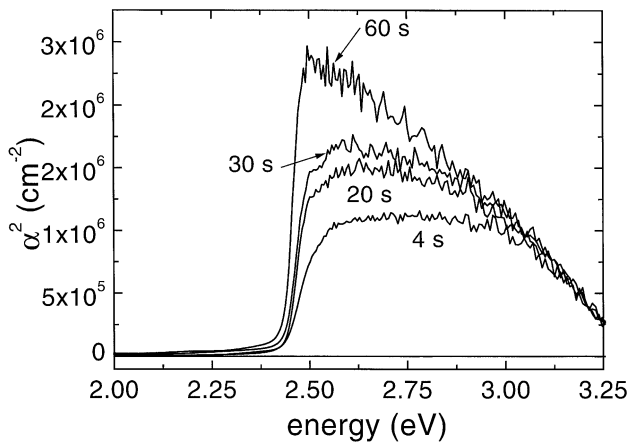


Fig. 3. Energy vs. α^2 curves obtained for CdS films deposited by CSS technique. The profiles obtained here, seem very different than the obtained for CBD technique due to the small deposition times used. E_g formation does not show bigger changes with deposition time.

Similar behavior was obtained for CdS films deposited by CBD with ultrasonic vibration. The results are represented in Fig. 2. In this case, we used higher deposition times than used for magnetic agitation given that ultrasonic effects produces slower deposition rates. Deposition time for films was ranged from 5 to 40 min. After 40 min, the typical E_g value has been reached. Then, by using CBD with ultrasonic vibration, a better controlled and low deposition rates was obtained, because of the higher deposition time used for similar thickness.

The absorption effect seems very different for CdS films deposited by CSS method, as is shown in Fig. 3. The E_g values do not show important variations with deposition time. Thus, the E_g values obtained for deposition times between 4 and 60 s, are closely between them. Results for film preparation with deposition times below 4 s were very hard to obtain and are not plotted. The absorption coefficient curves obtained by CSS technique looks very different than that obtained for films prepared by the CBD technique. Because the slope of the absorption curves for the first seconds is higher, the absorption process is lower.

In all films, the absorption coefficient decreases when deposition time diminishes along with tailing towards lower energies, indicating the presence of smaller crystallites in the films. If these crystallites exist, electrons and holes have a limited geometry to move and their motion only occurs when certain values on energy are present.

Fig. 4 is a resumed plot of the band gap energies, E_g , obtained as a function of the deposition time for CdS films prepared by CBD in the two modalities. For short deposition times, higher values on the band gap energy were obtained, after a certain time, the value was almost constant showing a good agreement with the typical band gap energy for CdS polycrystalline films.

For this case, band gap energy values obtained are 0.7–0.9 eV higher than the corresponding typical value for that films. Note that higher E_g values were obtained for films growth by CDB in the two modalities. However, a most important effect was observed for the thinnest films, i.e. films growth with short times and ultrasonic vibration. From Fig. 4, these higher E_g values were found during the first 5 min of deposition time for magnetic agitation, and during 10 min, for ultrasonic vibration.

Higher values of E_g on films are associated with the quantum confinement effects [22,23], and the values obtained in this work are very similar with the values reported in the literature [24]. This effect is due to the crystallite size and the very thin films obtained for short deposition times. According to the literature, E_g film approaches to E_g bulk for crystalline grain width higher than 50 nm, otherwise, E_g film takes values considerably higher than E_g bulk. This behavior is due to the breaking down of the continuum density of states into discrete levels, such that band gap energy widens compared with the band gap of the bulk.

Values of the band gap energy measured for CdS films growth by CSS technique were similar between them and slightly less than for films deposited by CBD technique. The measured value was approximately 2.40–2.43 eV. The E_g values obtained are similar to the ones reported for CdS films prepared by CSS technique, when the substrate temperature is between

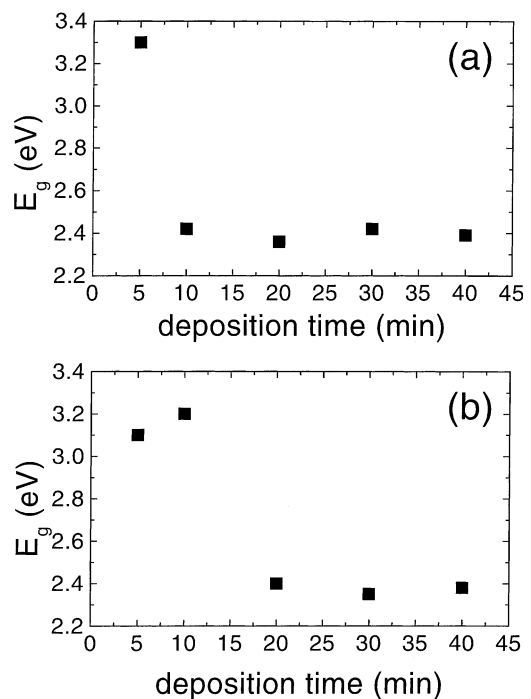


Fig. 4. E_g values as a function of deposition time for CdS films deposited by CBD technique with (a) magnetic agitation, and (b) ultrasonic vibration. Higher values of E_g were found for shortest deposition times (i.e. thinnest films).

200 and 680°C and the source temperature between 650 and 750°C [25] and with 5 min as deposition time. Results enhance the good crystallinity for films prepared for CSS technique for shorter growth times. Now, we will study the deposited films in order to relate the optical properties with the surface morphology and the crystalline structure.

3.2. Films morphology

AFM images were taken in all deposited films in order to study the surface morphology and their relations with other properties, as is shown in Fig. 5.

Fig. 5a corresponds to the AFM images ($1 \times 1 \mu\text{m}^2$) from CdS films prepared by CBD with magnetic agitation modality with 4, 6 and 10 min as deposition time. Viewing the images sequentially, we can observe the thickness formation, by means of the material deposited on the surface. Non-well-defined grains were observed for film growth during 4 min. Peak-to-peak value data was found to be small. With 2 min more on the deposition, formed grains were observed increasing the film thickness. As deposition time increases,

rounded grains size increases and vertical data take larger values, indicating larger roughness and consequently, greater thickness. Uniform CdS films were obtained with longer deposition time.

Comparative AFM images ($1 \times 1 \mu\text{m}^2$) of CdS films prepared with ultrasonic vibration modality, are represented in Fig. 5b with 10, 20 and 40 min as deposition times. In this case, more clean surfaces were obtained, as discussed later. The sequence of CdS film formation shows how the spaces produced by grains separation are filled with time. As time occurs, grains coalesce between them producing larger sizes, with different shapes (not rounded) than the ones obtained with the magnetic agitation modality. It is important to remark the deposition time values used in this modality. To obtain similar thickness, to compare with samples prepared by magnetic agitation, it was necessary to increase approximately 4 times the deposition time. Thus, using ultrasonic vibration we have a more controlled deposition rate. Rms-roughness value measured on CdS films surface prepared by CBD with magnetic agitation ($\sim 9 \text{ nm}$), are double the value obtained for ultrasonic vibration.

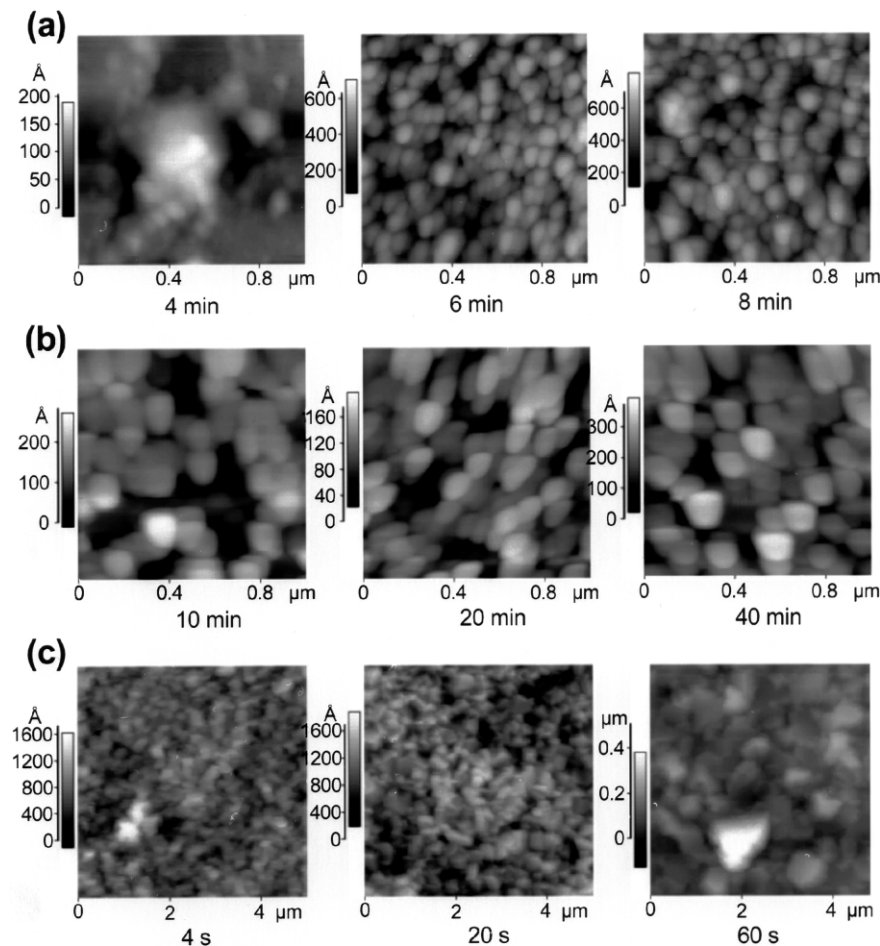


Fig. 5. AFM images of the CdS films as prepared by: (a) ($1 \times 1 \mu\text{m}^2$) CBD with magnetic agitation during 4, 6 and 10 min; (b) ($1 \times 1 \mu\text{m}^2$) CBD with ultrasonic vibration during 10, 20 and 40 min; and (c) ($5 \times 5 \mu\text{m}^2$) CSS with $T_f = 700^\circ\text{C}$, $T_s = 500^\circ\text{C}$ during: 4, 20 and 60 s.

However, Fig. 5c shows a sequence of $5 \times 5 \mu\text{m}^2$ AFM images taken from CdS films surface prepared by CSS technique. Images were larger in size than before due to the characteristics of the growth technique. Here, the grain size is approximately one order of magnitude larger than for the CBD technique. Because this growth technique is the fastest deposition method, we used minor deposition time ranging between 4 and 60 s. Grains shape obtained by CSS seems very different than for grains grown by CBD. Their sizes increase with deposition time, forming grains with well defined faces. In the CSS method, higher temperatures ($T_f = 700^\circ\text{C}$ and $T_s = 500^\circ\text{C}$) were used. A shutter to control the growing time during film deposition was used.

The short times used for films deposition made it possible to obtain very thin films, such that properties such as band gap energy and crystalline structure will be studied as a function of deposition time (i.e. thickness).

3.3. Structural results

Grazing incidence X-ray diffraction was used to analyze the formation of the crystalline phases. Diffractograms of CdS films prepared by CBD with magnetic agitation and ultrasonic vibration modalities are represented in Fig. 6 as a function of the deposition time. When low temperature is applied for CdS film deposition in CBD, they present a cubic structure with a strong orientation in the (111) reflection peak, independently of the agitation modality used. When magnetic agitation is applied, reflection peaks appear after 8 min of deposition time (Fig. 6a); before this time, no peaks were obtained, because of the small thickness values reached on samples with lower deposition time. Three peaks were detected: a strong reflection at (111) and two minor peaks at (220) and (311), which correspond to the cubic structure of Hawleyite [26]. However, CdS films prepared by ultrasonic vibration modality show the formation of the cubic structure after 20 min of deposition time (Fig. 6b). XRD measurements were not attempted in films prepared at lower deposition times, since AFM images showed not well formed grains with very small thickness values.

Crystallite sizes were calculated for all films by Scherrer's method [27]. Their values were approximately 26 nm for CBD in both agitation modalities. Nevertheless, peak intensities are noticeably low for the ultrasonic vibration; as an example, the diffractograms of the samples with 40 min of deposition time, registered at similar conditions, showed peak intensities 5 times greater when the magnetic agitation modality was used, as reported in a previous work [25].

Films thickness measured by Auger technique gives a value of 18–20 nm for CdS films deposited by CBD

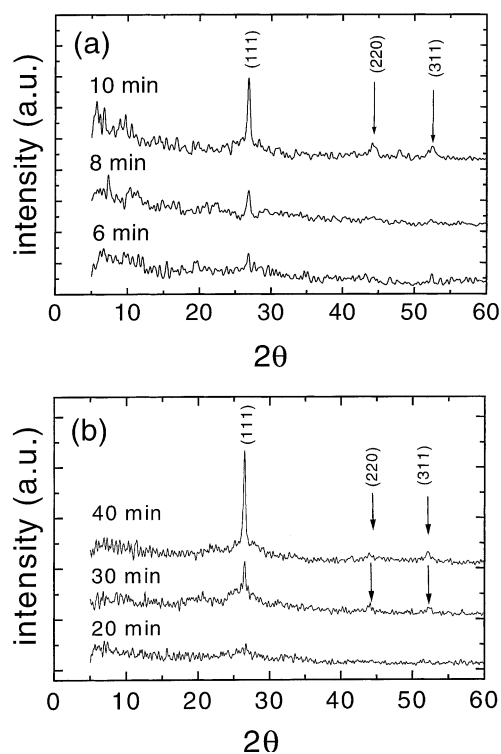


Fig. 6. Crystalline structure formation of CdS films deposited by: (a) CBD with magnetic agitation. The intensity of the cubic (111) peak increases with deposition time. Films with shorter deposition time seem amorphous; (b) CBD with ultrasonic vibration. Similar diffractograms on films deposited with magnetic agitation were observed. After 20 min the cubic (111) peak slightly appears and after that the crystallinity improves.

with magnetic agitation, and 2–3 nm for CdS films deposited by CBD with ultrasonic vibration for identical deposition time (10 min). Thus, this deposition time can be directly related to the film thickness.

When the CSS technique (a high temperature method) is applied for films preparation, the more stable hexagonal phase (Greenockite) was observed. Fig. 7 shows the diffractograms obtained for CdS films deposited with $T_s = 500^\circ\text{C}$, $T_f = 700^\circ\text{C}$, and different deposition times. The (002) main peak always appears for all times. The two small peaks at 24.8 and 28° (2θ) which corresponds to the (100) and (101) orientation, respectively, and obtained for the shortest deposition time, confirms the existence of the hexagonal lattice as reported elsewhere [28].

CdS films prepared by CSS technique always showed diffractograms with stronger intensity peaks, independently of the deposition time. Crystallite size measured on these films, ranging between 37 and 46 nm, have almost double the value obtained for the ones deposited by the CBD technique. Also, the film thickness ranging from 35 to 50 nm when the deposition time was between 4 and 60 s, respectively, were found to be larger.

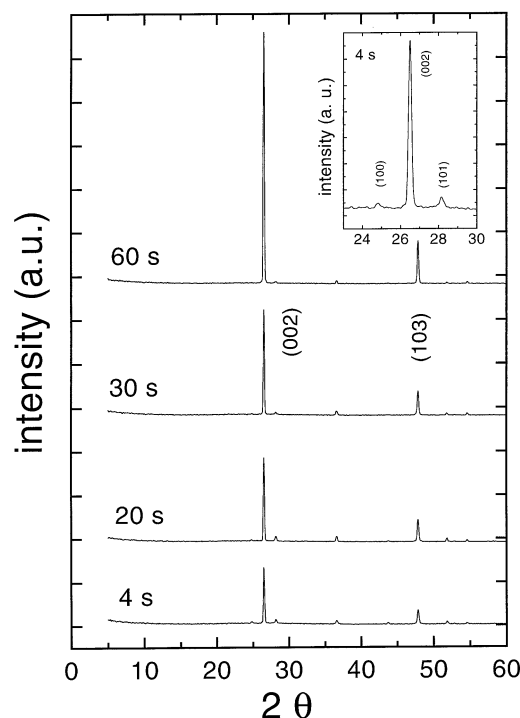


Fig. 7. Typical diffractogram obtained for CdS thin films deposited by CSS technique. The high temperature method produces films with hexagonal structure with a (002) main peak. Small peaks along 2θ axis, confirms the hexagonal crystallinity.

Crystallite sizes measured in all CdS films are in good agreement to the reported values, and the very small thickness films that presented higher band gap energies, induced to think in crystallite sizes less than 25 nm, i.e. with quantum confinement effects, as the band gap energy results showed.

4. Conclusions

CdS thin films were deposited on glass substrate by chemical bath deposition and close spaced sublimation techniques. For films grown using the CBD technique, two modalities for bath agitation was used: magnetic agitation and ultrasonic vibration. For these techniques we used small and crescent deposition times, in order to produce very thin films for the band gap energy formation study, and to obtain the corresponding morphological and structural properties. Morphology of the surface obtained with atomic force microscopy, shows higher differences between growth techniques. Grain sizes and their arrangement can qualitatively explain the optical and structural properties of the films.

Surface roughness obtained, shows that CdS films deposited by CBD technique with magnetic agitation, doubles the value than for films grown with ultrasonic vibration. Roughness value on films is related with the film thickness and the deposition time. Films grown with shorter deposition times make it possible to study

the band gap energy E_g formation. Higher values of E_g (2.31–2.32 eV) in CdS films, prepared by CBD technique, was obtained for the shorter deposition time both with magnetic agitation as for ultrasonic vibration of the bath solution. For longer deposition times (more film thickness) used in this work, it was possible to obtained the typical band gap energy (2.42 eV) of the polycrystalline film. Thus, using ultrasonic vibration instead of magnetic agitation for CdS films deposition presents some advantages that can be used to develop the basic CdS/CdTe solar cell. The band gap energy of the film can be controlled in a better way due to the slow deposition rate achieved with ultrasonic vibration. Moreover, films obtained with this modality seem more transparent and clean (without impurities on surfaces) than other ones. For comparison, we deposited similar films but using the CSS, a high temperature technique. Structural studies on CdS films with X-ray diffraction by grazing incidence method confirms that optical properties obtained are related to the structure formed and the deposition technique. Quantum confinement effects were found for films with smaller thicknesses, giving E_g values between 0.7 and 0.9 eV higher than E_g values for polycrystalline films. Ultrasonic vibration used for bath agitation, can be a useful and a low cost procedure to prepare in a controlled way CdS films to produce optical windows for CdTe solar cells applications.

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