CdS THIN FILMS DEPOSITED BY A MODIFIED CHEMICAL BATH DEPOSITION METHOD

Ngamnit Gaewdang* and Thitinai Gaewdang

Photonic Materials Research Laboratory, Department of Applied Physics, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang, Bangkok 10520, Thailand.

ABSTRACT

CdS thin films were deposited on glass slide substrates by a modified chemical bath deposition technique using $CdSO_4$ as the cadmium source, SC $(NH_2)_2$ as the sulfur source and NH_3 as the complexing agent in deionized water bath. The modification to the traditional technique consists in applying the rotated substrate holder with controlled speed instead of using magnetic stirer or a bath stirred by an impeller. As-deposited films were thermally annealed in a controlled N_2 atmosphere. The annealing temperature was varied from 100- 500 °C. Scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD) techniques were used to determine the morphology, compositions and crystalline structure of the films. The gradual structural transition from zincblende for the as-deposited CdS to wurtzite structure for the film annealed at 400 °C, the critical point of the phase transformation, was observed by XRD and optical transmission studies. Electrical sheet resistance of CdS thin films as a function of annealing temperature were also investigated. The appearance of the minimum sheet resistance of samples annealed at 200 - 300 °C, being around 4.6×10^4 Ω / square, was obtained in the darkness and under illumination conditions by using an ELH halogen lamp.

KEYWORDS: CdS thin films, chemical bath deposition, optical transmission

1. INTRODUCTION

Extensive research has been done on the deposition and characterization of Cadmium Sulfide (CdS) semiconducting thin films due to their potential application in the area of optoelectronic device fabrication [1- 4]. Polycrystalline CdS thin films have good optical transmittance, wide band gap and electrical properties suitable for their application to solar cell fabrication [5] . CdS-based solar cell structure such as CdS/CdTe and CdS/Cu (In, Ga)Se_2 exhibits conversion efficiency about 15.8 % and 18.8 % respectively [6, 7].

*Corresponding author, Address: Department of Applied Physics, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang, Tel: 0-2326-4339 ext. 285, Fax: 0-2326-4413, E-mail: kwngamni@kmitl.ac.th

Direct band gap CdS thin films have been the subject of intensive research because of its wide band gap, high absorption coefficient, low resistivity, high photosensitivity response, easy ohmic contact fabrication and finally the structure of CdS thin films can be grown with cubic or hexagonal phase depending on the deposition conditions [8]. It is well known that hexagonal CdS invariably grows with columnar structure along the c-axis perpendicular to the substrate [3]. This means that there are no grain boundaries parallel to the junction which would impede the flow of photogenerated excess carriers to the grid. Reasonable conversion efficiency, stability and availability of low cost deposition technique attracts the usage of CdS as window electrode in solar cell structure.

In recent years, high priority has been given to develop low cost deposition technique to deposit CdS thin films [9]. Though various deposition techniques such as electrodeposition, screen printing, spray pyrolysis, photochemical deposition and chemical bath deposition (CBD) have been reported. The CBD technique has attracted much attention since it is confirmed as a simple and most economic technique to obtain good quality polycrystalline CdS thin films [10].

The aim of this work is to highlight the modifications CBD by using the rotated substrate holder with controlled speed instead of using traditional magnetic stirer or a bath stirred by an impeller. The effect of thermal annealing on crystal structure, optical band gap and electrical properties performed in the dark and illuminated condition measurements with a commercial ELH halogen lamp have been investigated in order to better understand the growth conditions that give rise to films for optimum device performance.

2. MATERIALS AND METHODS

CdS thin films have been deposited on glass slide substrates using CBD technique. Glass slide substrates of dimension 12 x 25 mm^2 were cleaned with detergent, degreased with ethanol in an ultrasonic cleaner, etched in a 4 % HF solution for 10 min and dried in nitrogen. Finally, they were introduced in oven at 80 °C for 20 min. The cleaned substrates were vertically mounted on a specially designed substrate holder providing 8 maximum glass substrates fixed together (Fig. 1). This can be rotated around vertical axis with desired speed during the entire deposition in order to obtain homogeneous heat transfer to the total surface of the substrate for uniform film growth. Each experimental solution contained 150 ml of deionized water in a 200 ml beaker containing 0.01 M $CdSO_4$, 0.05 M SC $(NH_2)_2$, 1.5 M NH_3 (25%) and pH value around 11.4 [11]. The beaker was placed in a water bath at a constant temperature of 80 °C. The mixture of $CdSO_4$ and 16 ml of NH_3 as well as dissolved thiourea in 10 ml deionized water were separately prepared. After that, they were simultaneously introduced in a beaker. Finally, the deionized water were added into the beaker until attained the calculated value. The substrate holder, with a radius of 15 mm, was rotated with a chosen speed about 60 rpm. The deposition rate of the films was very small when the solution was not stirred. The rate was drastically increased even by slow speed but could not increase more with further increase in the speed. However, the glass slide substrates will be easily detached from the substrate holder when the speed higher than 60 rpm. The colour of the bath solution changed from pale yellow to orange and the films deposition started to appear on the substrate surface. Under these conditions, the chemical reaction and deposition completed after 30 min and a uniform film deposition on glass slide substrate was achieved. Deposited films were detached from the holder and were washed with deionized water in ultrasonic bath to remove the existing surface radicals on the films. These samples were dried in N_2 atmosphere and preserved in a desiccator in order to avoid form surface contamination. As-deposited films were annealed in N_2 atmosphere to investigate the annealing effect on the structural, optical and electrical properties. The crystal structure of these films was checked by the X-ray diffraction technique with a Bruker D8 diffractometer using CuK_α radiation. Surface morphology, film thickness and EDS measurements were examined by JEOL model JSM- 6400 scanning electron microscope on

bare-surfaced samples without coating by gold before analysis. The optical transmission spectra were obtained by means of a UV/VIS Jasco 7800 spectrophotometer in the range 400- 1000 nm. Identical glass slide substrate was used as a reference during the optical transmission studies. The sheet resistance was performed at room temperature, after be careful check ohmic contact, in the darkness and also under illumination conditions by using an ELH halogen lamp.

3. RESULTS AND DISCUSSION

The obtained films were pale orange, smooth, reflecting, homogeneous and adherent. In our previous work, CdS thin films were prepared by CBD technique in the bath stirred by an impeller [12, 13]. The film thickness was about 50 nm within 30 min of deposition time. However, the film thickness obtained in present investigation is about 80 nm. It may indicate that the rotation of glass slide substrate propably reduces the powder existing on the surface during deposition process. Consequently, the higher growth rate was promoted. Moreover, the film obtained from the latter shows more shiny and more smooth surface than the one obtained from the former. Multiple depositions, where the same substrate was repeatedly coated, was also investigated to obtain the thicker film. The film thickness about 120 and 150 nm were observed, by SEM microgarphs, from the double and triple coating bath. Obviously, increasing the film thickness as a function of number of deposition did not give rise to a linear behavior.

3.1 STRUCTURAL CHARACTERIZATION

Fig.2 shows the X-ray diffraction patterns of as- deposited and thermally annealed CdS films. At the bottom, the spectrum of the as-deposited film shows a small peak at 2θ about 26.5 °. This diffraction peak is produced by the (111) crystalline plane of the cubic zincblende structure or the (002) crystalline plane of the hexagonal wurtzite one. It has been reported that both lines coincide within one per cent [1]. From previous reports [1, 14, 15] we can be assured that the crystalline stracture of the as-deposited sample is the zincblende one. The high orientation of the CdS crystallites along the [111] direction reduces considerably the intensity of other diffraction peaks. This peak becomes more intense and sharper after thermal annealing. For the 400 °C - annealed film, it can be also observed the formation of additional peaks at 2θ equal to 24.9, 28.3, 43.7 and 51.8°. These peaks are related to the (100), (101) (110) and (112) crystalline planes of the CdS hexagonal structure respectively and can be seen more clearly in the spectrum of CdS sample annealed at 500 °C.

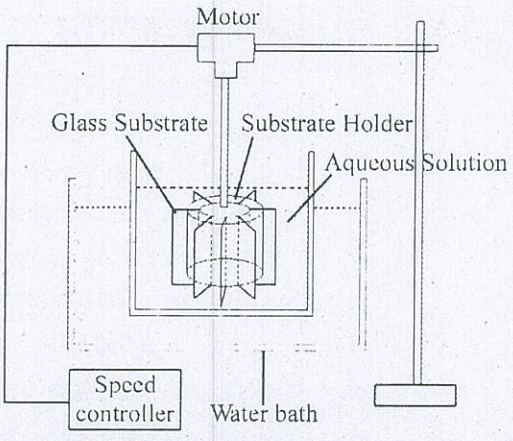

Fig. 1 Shematic illustration of the experimental setup of the modified CBD technique.

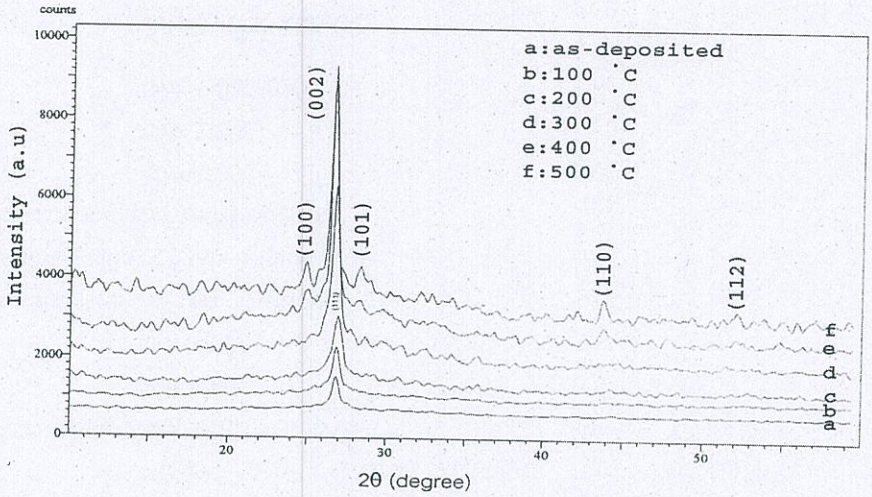

Fig. 2 X-ray diffraction patterns of as-deposited (80 °C) and thermally annealed CdS films.

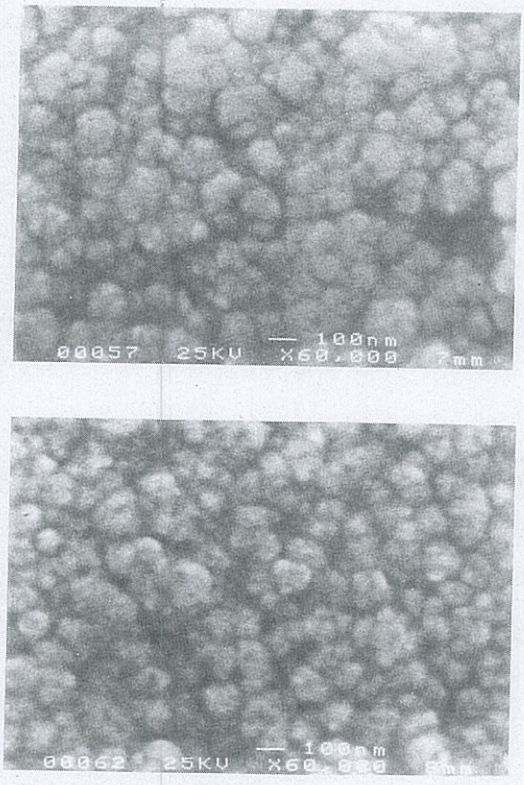

Fig. 3 SEM micrographs for CdS films : as- deposited (upper) and annealed at 500 °C. (lower).

Thus, the formation of the diffraction peaks associated with the hexagonal phase in the spectra of the 100 - 500°C annealed CdS films indicates an evolution of the sample structure from the cubic phase to the hexagonal one.

Fig. 3 shows scanning electron micrographs (SEM) of the as-deposited films and the films annealed at 500 °C. As can be seen from the figure, the as-deposited films are formed by different size of clusters of nanoparticles. The thermally annealed films, cluster size is seemingly decreased as the increase in annealing temperature. The 500 C°- annealed film exhibits to be composed of irregular shaped granules with maximum diameter around 100 nm. The EDS results were consistent with the CdS compound deposited on a glass slide substrate. The peaks of Si, Ca and Na elements are associated with the glass slide substrate .

3.2 OPTICAL CHARACTERIZATION

All films were optically transparent, pale orange in colour. The annealed films exhibit a pronounced colour change from pale orange to brownish orange while the annealing temperature increases to 400 °C. Then, it becomes to pale orange at annealing temperature higher than 400 °C.

Fig. 4 shows typical optical transmission spectra. The absorption edge is observed near 500 nm for all the samples, but the position of the edge was shifted by the annealing conditions. The band gap of the films were determined before and after annealing. The linear dependence of $(\alpha\ h\nu)^2$ with energy (eV) was indicative of direct band gap material where α is the absorption coefficient and $h\nu$ is the photon energy. Extrapolation of the linear region of the absorption profile from the plot of $(\alpha\ h\nu)^2$ against energy (eV) provided band gap value of as-deposited films being 2.43±0.01 eV (Fig. 5), a value that agrees with the value generally accepted for bulk CdS. Fig. 6 clearly shows a shift of the band gap of the annealed films to lower energy value from 2.43±0.01to about 2.31±0.01 eV. The CdS sample annealed at 400 °C has the minimum band gap being 2.32± 0.01 eV. For higher annealing temperature the band gap of the films increases up to 2.38± 0.01 eV at 500 °C which corresponds to the band gap of hexagonal phase [1].

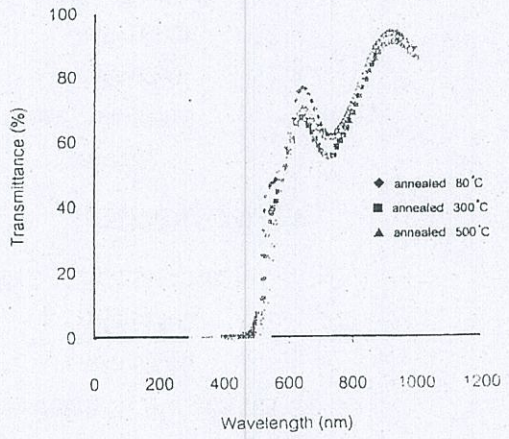

Fig. 4 Optical transmission spectra for the as-depositedand N_2 – annealed CdS films.

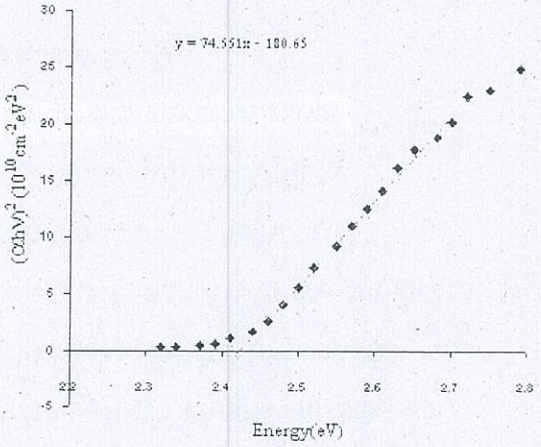

Fig. 5 The optical absorption of the as- deposited CdS film for the band gap determination.

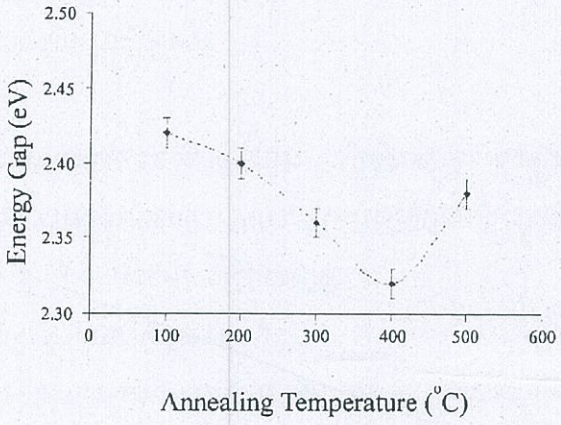

Fig. 6 Relationship between the annealing temperature and the band gap determined from the optical transmission data for CdS films.

The annealing temperature at which the band gap of the films is a minimum has been considered as a critical temperature associated with the structural transition [1, 14- 16]. The origin of the alteration in the band gap of annealed CdS films has not been fully understood. Ramirez- Bon et al. [1] have reported, by means of AFM, the phase transition from cubic phase to hexagonal one occuring at 300 °C. However, Tomas et al . [17] reported the influence of the annealing conditions, in various gas atmosphere, on the band gap shift in CBD- CdS films. From photoacoustic absorption spectra. The phase transition from cubic to hexagonal phase is assumed to occur around 350 °C.

Hernandez et al. [15] reported the similar annealing behavior of the band gap of CBD-CdS. With increasing annealing temperature, the band gap once decreases and then increases. However, the band gap begins to increase at 300 °C, a temperature considerably lower than the one observed in the present study, and the increase is much more gradual. We may suppose that their films already include hexagonal CdS in the as-deposited state and thus can be transformed to the hexagonal phase gradually at a relatively low temperature. This thermal annnealing behavior was also observed on photochemical deposition CdS thin films reported by Ichimura et al. [16]. Our results are in good agreement with their work at which phase transition occurs around 400 °C .

3.3 ELECTRICAL CHARACTERIZATION

At room temperature, the dark sheet resistance and the illuminated sheet resistance of as-deposited films are about 3.2×10^5 and 1.2×10^5 Ω/ square. The decrease in sheet resistance under illumination is probably due to the excess carriers in the grains introduced by the absorption of above band gap radiation and the lowering of potential barriers at gain boundaries [18]. Fig. 7 shows the sheet resistance of CdS films as a function of annealing temperature without illumination and under illumination by a ELH halogen lamp. As annealing temperature increases, the dark sheet resistance value of films decreases from 3.2×10^5 to 4.6×10^4 Ω/ square, saturated in the range 200-300 °C and then increases from 6.8×10^4 to 3.5×10^5 Ω/ square.

Under illumination conditions, the similar behavior was also observed. The decrease in sheet resistance as the increase in annnealing temperature probably is due to the enhancement of the particle size and crystallinity [16, 19]. However, annealing temperature beyond 300 °C the formation of some defects such as sulfur vacancies or complexes can play a significant role in enhancement of sheet resistance [17, 18]. These phenomena were also observed by some authors [14, 17]. All the films obtained during the present investigations have shown in n-type conductivity.

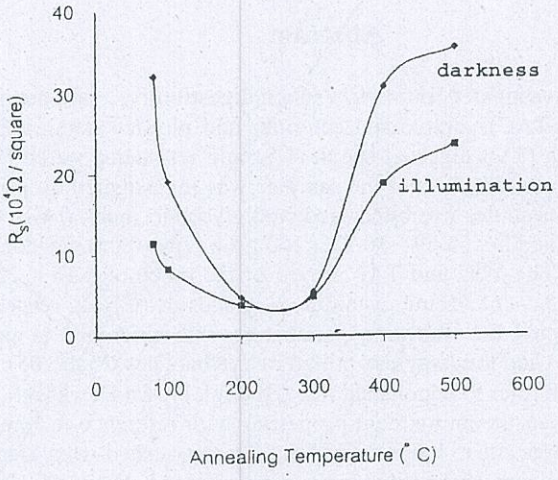

Fig. 7 Sheet resistance as a function of N_2 - annealing temperature.

4. CONCLUSION

CdS thin films have been successfully deposited by the modified chemical bath deposition using an aqueous solution of cadmium sulfate, thiourea and ammonia at 80 °C. The as - deposited films are dominantly of cubic zincblende phase with a preferential orientation along (111) plane of reflection and the CdS films annealed at higher 400 °C has the hexagonal phase with a preferential orientation along (002) direction growth. The band gap of annealed CdS films seems to shift to lower energy for low annealing temperature (100- 400 °C). Thus, the critical point of the phase transition is definitely close to 400 °C. Relationship between electrical sheet resistance and the annealing temperature is also investigated. The decrease in sheet resistance as a function of annealing temperature ranging 100- 200 °C is seemingly to the increase in particle size and the improvement of crystallinity.

However it moves back to higher value for the annealing temperature ranging 400- 500 °C is possibly attributed to the sulfur vacancies or complexes. We have found that the CdS films display low sheet resistance and high band gap when exposed to N_2 annealing atmosphere about 200 °C. CdS films with these characteristics play an important role because they can be used in the development of low resistivity CdS/Cu (In, Ga)Se_2 and CdS/CdTe solar cells with high quantum efficiency . Thus, they are real candidates for high conversion efficiency solar cells.

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