OPTICAL CHARACTERIZATION OF AS-DEPOSITED AND AIR-ANNEALED 
CdS FILM GROWN BY CBD TECHNIQUE

Z. RIZWAN, N. KAMILAH SA’AT, A. ZAKARIA
National Textile University, Sheikhpur Road, 37610 Faislabad, Pakistan
Department of Physics, Faculty of Science, University Putra Malaysia, 43400 Serdang, Selangor D.E., Malaysia

CdS thin films were deposited on commercial glass substrate using CBD technique from bath with low solution concentrations of cadmium chloride and thiourea. The film adherence was excellent for all samples. The films samples were air annealed at 200 °C for 60 minutes. The observed minimum film thickness was 34.8 nm. XRD analyses results show that the film samples were cubic CdS in as-deposited film samples. Very feeble peaks of hexagonal phase were observed in all air-annealed samples except the samples at higher solution concentration. Crystallite size was increased from 27.2, 19.8 to 52.6, 70 nm with the increase of cadmium chloride and thiourea concentration for thin film samples as-deposited and annealed samples, respectively. $E_g$, $E_{\infty}$ and $\alpha$ was determined from the transmittance data. The best transmittance (> 96 %) was obtained for longer wavelength range in this experiment.

(Received April 1, 2017; Accepted October 10, 2017)

Keywords: CBD, CdS, Optical properties, air-annealing

1. Introduction

Several techniques are being used to grow thin films e.g., sputtering, electro-deposition, vacuum evaporation MBE, MOCVD, CSS, pulsed laser evaporation, radio frequency, SILAR, SPD and chemical bath deposition (CBD). CBD technique has an attractive due to its simplicity, low deposition temperature, large area deposition and low cost. CBD technique also has tremendous control to grow thin films uniformly [1]. This technique increases the efficiency CdS window layer. Maximum efficiency was also achieved when this technique was used to develop buffer layer for CdTe, CIGS and photovoltaic cells [2-5]. This popular technique is also used in the fabrication of sophisticated electronic [6-7]. Cadmium sulfide is an admirable heterojunction partner for the p-type CuInSe$_2$, CdTe, Cu(In,Ga)Se$_2$ due to the wide energy band gap that is 2.42 eV. It is also significant because of its unique properties for example, high refractive index having the value 2.5, photoconductivity and higher electron affinity [8-11]. The substrate was dipped in aqueous solution having alkaline nature in chemical bath which contains S$^2$- and Cd$^{2+}$ ions produced by the chemical reaction in solution [12, 13]. pH of aqueous solution, temperature, time for thin film deposition, relative concentrations of reactive which provide ions for the chemical reaction are main parameters to control growth rate of film.

This excellent CBD technique has been carried out to grow CdS films on commercial glass slides with the solution concentrations of cadmium chloride [0.000625 - 0.005 M] and thiourea [0.00125 - 0.01 M] in this study. The structural and optical properties of CdS thin films as-deposited and air-annealed have been discussed with the increased solution concentrations.

*Corresponding author: azmizak@upm.edu.my
2. Experimental

CdCl₂ [Alfa Aesar, 4N purity.] and [(NH₄)₂CS (Alfa Aesar, 3N purity)] were used to grow CdS thin films on microscopic commercial glass slides as substrate. Substrates were immersed in 4% HCl for cleaning and the further cleaned with acetone and methanol, ultrasonically.

All calculations in this experiment are molar solution concentrations. About 55 ml aqueous solution of CdCl₂ [0.00312, 0.000625, 0.00125, 0.0025 and 0.005] and (NH₄)₂CS [0.000625, 0.00125, 0.0025, 0.005 and 0.01] were prepared in a glass beaker in doubly deionized H₂O to obtain the source of Cd²⁺ and S²⁻ ions, respectively under constant stirring at the room temperature. The ratio of CdCl₂ to (NH₄)₂CS = has been kept constant as 1:2 as in our previous papers [14, 15]. The beaker of the solution of CdCl₂ was placed in a temperature bath to achieve temperature up to 69 °C while stirring. The aqueous solution of ammonia (NH₃) as complexing agent was used. Aqueous NH₃ was used drop by drop in aqueous solution of CdCl₂ to dissolve precipitate of CdOH. The pH of the solution was stabilized at 11. Temperature of the solution of Thiourea was maintained at 69 °C in second temperature bath placed on digital hot plate. Aqueous solution of (NH₄)₂CS was dropped slowly in aqueous solution of CdCl₂ at vigorous conditions of stirring. The temperature of the mixture was raised to 71±1 °C, rapidly. Cleaned substrates were dipped vertically in the solution with the help of self-made special holders. The container of solution was shielded to avoid the ammonia evaporation. Constant stirring was obtained using magnetic bar for the deposition time of 120 minutes. The constant stirring was necessary to ensure the homogeneous thickness of deposition at 71 °C±1 °C. Samples of thin films were taken out after 120 minutes of deposition time. All microscopic glass slide were washed ultrasonically in deionized water to eliminate loosely adhered particles of CdS. All samples were air dried in open atmosphere as in our previous paper [14]. One thin film sample from every solution concentration was air-annealed at a temperature 200 °C for 60 minutes. As-deposited thin film samples were marked as A₀, [CdCl₂ (0.00312), NH₄)₂CS (0.000625)], A₁ [CdCl₂ (0.000625, NH₄)₂CS (0.00125)], A₂ [CdCl₂ (0.00125, NH₄)₂CS (0.0025)], A₃ [CdCl₂ (0.0025, NH₄)₂CS (0.005)] and A₄ [CdCl₂ (0.005, NH₄)₂CS (0.01)]. Air annealed samples are marked as B₀ [CdCl₂ (0.00312), NH₄)₂CS (0.000625)], B₁ [CdCl₂ (0.000625, NH₄)₂CS (0.00125)], B₂ [CdCl₂ (0.00125, NH₄)₂CS (0.0025)], B₃ [CdCl₂ (0.0025, NH₄)₂CS (0.005)] and B₄ [CdCl₂ (0.005, NH₄)₂CS (0.01)]. Ellipsometer was used to measure the thickness of the films. Radiation Cu Kα (λ = 1.540598 Å) was used for structural analysis using x-ray diffraction technique through (PANalytical X’Pert Pro PW1830). X’Pert High Score software were used to identify the crystalline phases of the films. Crystallite size (D) was calculated using the following Scherer formula;

\[ D = \frac{0.94 \lambda}{\beta \cos \theta} \]  

(1)

where β is FWHM. Peaks of XRD were corrected for instrumental broadening. Theta (θ) is Bragg’s angle, λ is the wavelength of the used x-ray, Scherrer constant (K=0.94) [16, 17, 24]. Optical transmittance (T) data was captured by double beam Photospectrometer (Shimadzu) for the wavelength range from 350 to 1100 nm. The absorption coefficient (α) was calculated by the following equation;

\[ a = \frac{\ln T}{d} \]  

(2)

Using absorption coefficient (α), Optical energy band gap (Eᵥ) was calculated by the equation;

\[ a = \frac{A(h\nu-Eᵥ)^n}{h\nu} \]  

(3)

Here A is constant, photon energy (h\nu), n = 0.5 for direct allowed transitions because cadmium sulfide material is a direct band gap [18]. The parameters (ah\nu)^{2} are plotted as a function of photon energy (h\nu). The linear portion of the plotted curve was extrapolated to energy axis as
(ahv)² = 0. This gives the value of E_g. Absorption coefficient (α) explains a tail for sub-band gap photon energy (hv). E_∞ is the Urbach energy related with the width of tail and E_∞ can be determined from the fit of the data [19]:

\[ a = a_0 e^{hv/E_∞} \]  

Here \( a_0 \) is constant. The values of \( Lna \) against the photon energy (hv) were plotted. The inverse of the slope from this graph gives the value of \( E_∞ \).

3. Results and discussion

XRD pattern of the thin films as-deposited and air-annealed show polycrystalline nature, Fig.1. The x-ray diffraction graphs have been scaled to a smaller size. Six graphs have been shown in one figure. Various small peaks have been lost in this presentation. All the peaks observed in these graphs are described in comprehensive detail.

All peaks of the sample A, are cubic except the peak at 2θ = 28.1544° having plane (101) which belongs to the hexagonal phase (ref: 00-065-3414). The clear peaks for the sample B, at 2θ = 26.26707°, 44.2172°, 52.4116° belongs to (111), (220) and (311) planes of cubic CdS, respectively (ref: 01-080-0019). Very small peaks which cannot be seen in the given graph for this sample at 2θ = 24.6780°, 28.384°, 58.4528°, 66.698° (ref: 00-001-0783) belongs to (100), (101), (202) and (203) belongs to hexagonal phase of CdS, respectively. The clear peaks for sample A, at 2θ = 26.7277°, 44.1346°, 52.3619° belongs to (111), (220), (311) cubic phase of CdS (ref: 01-080-0019), respectively. Three peaks at 2θ = 26.1618°, 28.2306° and 48.1229° (ref: 01-080-0006) belongs to (100), (101), (103) hexagonal phase of CdS. Peaks for the sample B, at 2θ = 26.8079°, 44.4133° and 52.7364° belongs to the (111), (220), (311) planes of the cubic CdS, respectively (ref: 01-075-0581). Four peaks at 2θ = 26.9810°, 28.6450°, 58.4937°, and 66.7578° (ref: 01-080-0006) belongs to (111), (101), (202), (203) hexagonal phase of CdS. This indicates the hexagonal phase is more prominent after heat treatment for this concentration of the solutions. A peak is also observed at 2θ = 21.3924° which belongs to monoclinic CdSO₃ (ref: 01-078-1874), [20, 21]. The peaks for the sample A, at 2θ = 26.7405°, 44.2257°, 52.3939° and 54.9616° can be related to the (111), (220), (311) and (222) planes of cubic CdS, respectively (ref: 01-075-0581). Only one peak at 2θ = 28.1468° belongs to plane (101) of hexagonal phase CdS, (ref: 01-072-2306). Peaks for the sample B, at 2θ = 26.7670°, 44.4147°, 52.4847° are related to (111), (220), (311) planes of cubic CdS, respectively (ref: 01-080-0019). Three peaks only that are very small at 2θ = 28.7526°, 58.4426°, 66.6771°, belongs to (101) hexagonal phase CdS (ref: 01-072-2306). This indicates the as-deposited films have very small peaks but three peaks after heat treatment are slightly clear. The peaks for the sample A, at 2θ = 26.7247°, 44.2043°, 52.4544° and 55.0273° belong to the (111), (220), (311) and (222) planes of cubic CdS, respectively (ref: 01-075-0581). Only one peak at 2θ = 28.5542° (ref: 00-001-0783) belongs to (101) hexagonal CdS. Peaks for the sample B, at 2θ = 26.7520°, 44.5644° (ref: 01-080-0006) are related to the (111), (220) cubic CdS, respectively. Only three very small peaks at 2θ = 24.9624°, 26.6230°, 28.5050°, 48.2758°, 58.9330°, 67.0811°, 73.2655° (ref: 01-080-0006) belong to (111), (111), (101), (103), (202), (203), (114), hexagonal phase CdS, respectively. This indicates the as-deposited films have one very small peak but seven peaks after heat treatment are detected. This indicates that the heat treated samples have prominent hexagonal phase. Peaks for sample A, at 2θ = 26.7552°, 30.3602°, 44.2143°, 52.3606°, 55.0631° are related to the (111), (200), (220), (311) and (222) planes of cubic CdS, respectively (ref: 01-080-0019). No peak related to hexagonal phase was detected. Peaks detected for B, at 2θ = 26.7674°, 30.4024°, 44.3195°, 52.4880°, 54.8619° and 73.1410° belong to (111), (200), (220), (311), (222) and (420) planes of cubic CdS, respectively (ref: 01-080-0006). No peak related to hexagonal phase was detected but peaks at 2θ = 26.7674°, 52.4880°, 54.8619° may overlap with cubic phase that may not be distinguished separately. The XRD characterization propose that the hexagonal phase of CdS film developed prominently at the air-annealed samples for these solution concentrations [22]. The observations indicate that preferred orientation of the plane is (111).
Preferred orientation (111) is due to the nucleation controlled process that arises in the growing film. This proposes that the growth rate is slow in the film deposition process [23].

The thickness of film samples as-deposited and air-annealed at the temperature 200 °C is discussed with the reference of CdCl₂ molar concentration. The film thickness is 70.8 nm at CdCl₂ concentration of 0.000312 M and is decreased to 42 nm at the CdCl₂ concentration of 0.00625 M of the as-deposited sample. The film thickness is minimum i.e. 34.8 nm for the 0.00125 molar concentration of CdCl₂ of the as-deposited sample as shown in fig. 2. Then the thickness is increased to 75.7 nm that is maximum value at the molar concentration 0.005 of CdCl₂ of the as-deposited sample.

This specifies that the thin film thickness has minimum value for the 0.00125 molar concentration of CdCl₂. The thickness of air-annealed film is 56.8 nm at molar concentration 0.000312 of CdCl₂. This thickness is less about 14 nm in comparison with the film thickness of as-deposited sample. Again the thickness of annealed film is less about 14.4 nm at the higher concentration of CdCl₂. The film thickness has the same values for the both as-deposited and annealed samples at the CdCl₂ molar concentration of 0.00625, 0.00125 and 0.0025 that is 42, 35 and 50 nm, respectively. This shows that the film thickness of the as-deposited and annealed for the ratio CdCl₂ : (NH₄)₂CS = 1:2 is the same specifically at the ratio [CdCl₂ (0.000625, (NH₄)₂CS (0.00125)], [CdCl₂ (0.00125, (NH₄)₂CS (0.0025)] designated sample names as A₁, A₂, A₃ and B₁, B₂, B₃, respectively.
Crystallite size (D) of the as-deposited thin film was 27.2 and 19.8 nm for concentration 0.000312, 0.000625 of CdCl₂, respectively fig. 3. It was increased to 52.6 nm when the concentration of CdCl₂ was increased for the as-deposited film samples. Crystallite size was 26 nm for the annealed film sample at the ratio CdCl₂:(NH₂)₂CS = 0.000312:0.000625. The thickness is increased to about 70 nm with the increase of the molar concentration at the higher molar ratio. The crystallite size increases prominently with increase of molar ratio. It is also very prominent difference in crystallite size for the as-deposited and air-annealed thin film samples.

Transmittance (T) spectra of CdS films of as-deposited and annealed film samples were recorded in the range of 350 nm–1100 nm. The transmittance (T) dependence of spectra on the molar concentration of solutions is discussed for both as-deposited and annealed film samples. Transmittance for the low solution concentration [CdCl₂ (0.00312 M), thiourea (0.00625 M)] was observed 78, 83, 86% at wavelengths 550, 850 and 1050 nm for the as-deposited samples, respectively. This Transmittance was increased to 93, 98 and 99% at the same wavelengths when samples were air-annealed at 200 °C as shown in fig. 4. No significant effect of annealing was observed for the solution concentration of [CdCl₂ (0.000625), (NH₂)₂CS (0.00125)] and [CdCl₂ (0.00125), (NH₂)₂CS (0.0025)]. Transmittance for the high solution concentration [CdCl₂ (0.005 M), Thiourea (0.01 M)] was observed 65, 72, 88% at wavelengths 550, 850 and 1050 nm for the as-deposited samples, respectively. This Transmittance was significantly increased to 94, 98 and 98% at the same wavelengths when samples were air-annealed at 200 °C as shown in fig. 5.
The dependence of $\alpha$ on the $\lambda$ is shown in fig. 6 at the different concentrations of the solution. The value of $\alpha$ is increased with the annealing as shown in fig. 6. The value of $\alpha$ was increased with the increase of concentration of solution. It is also observed that the value of $\alpha$ was appreciably increased at all the wavelengths at the higher concentration of the solution fig. 7. $E_g$ was calculated from the plot $(ah\nu)^2$ against photon energy $(h\nu)$ [23, 24]. The optical energy band gap is discussed here with reference to the solution concentration fig. 8. The value of $E_g$ is 2.65 eV for the ratio CdCl$_2$:(NH$_3$)$_2$CS = 0.000312:0.00625 of the as-deposited film and is slightly reduced to 2.59 eV for the air-annealed samples. $E_g$ was decreased with the increase of solution concentration and again increased with the further increase of solution concentration. The value of the $E_g$ is 2.59 eV and 2.56 eV for both the samples as-deposited and annealed samples at the concentration [CdCl$_2$ (0.0025, (NH$_3$)$_2$CS (0.005)]. The $E_g$ increased from 2.59 to 2.86 eV for the as-deposited sample with the increase of solution concentration from [CdCl$_2$ (0.0025 M, Thiourea (0.005)] to [CdCl$_2$ (0.005 M, Thiourea (0.01 M)]. No significant difference in the value of $E_g$ was observed at higher solution concentration when the sample was air - annealed at 200 °C. Urbach energy ($E_{\omega}$) is shown in for the annealed samples fig. 9. $E_{\omega}$ is also acknowledged as band tail width and this is because of the disorder in thin film sample material. The variation of bond angle and bond length from their standard values in crystalline material is known as disorder [25, 26, 27]. The optical band gap behavior is opposite to disorder. This behavior suggests that the observed optical energy band gap ($E_g$) is administrated with the variation of disorder in the film samples.

4. Conclusions

The CdS thin films were grown by CBD technique at different solution concentrations of CdS and (NH$_3$)$_2$CS. The bath temperature remained constant throughout the experiment. XRD characterization shows that all the grown films were in CdS cubic phase in as-deposited and few feeble peaks of hexagonal phase are present in all annealed film samples.

The crystallite size was increased with the increase of solution concentration. Also crystallite size enhanced with the annealing temperature. Optical band gap energy ($E_g$) was administrated with the phenomena of disordering. The optical Transmittance was varied with solution concentration and annealing temperature of the thin film samples.

Acknowledgement

This work is financially supported by the Higher Education Ministry of Malaysia and University Putra Malaysia through FRGS Project # 01-01-16-1835FR.
References