Effect of annealing temperature on the optical properties of nanostructured CdS films prepared by chemical bath deposition technique

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Different concentrations of $CdCl_2$ and $(NH_2)_2CS$ were used to prepare CdS thin films, to be deposited, on glass substrate by chemical bath deposition (CBD) technique employing $CdCl_2$ as source of Cd^{2+} while $(NH_2)_2CS$ for S^{2-} at constant bath temperature 71 °C. Adhesion of the deposited films was found appreciable for all the solution concentrations of both reagents. The films were air-annealed at 360 °C for 1 h. The minimum thickness was observed to be 34.8 nm for air-annealed film. XRD analyses reveal that the films were cubic along with few feeble peaks of hexagonal phase at lower solution concentration. The crystallite size of the air-annealed films was increased from 12 to 50 nm with the increase of solution concentration. Optical energy band gap (E_g), Urbach energy (E_u) and absorption coefficient (α) were chosen as parameters of characterization, calculated from the transmission spectral data and are discussed as function of solution concentration. The best transmission (63 - 98% in the spectral range 350 - 1100 nm) was obtained for the air-annealed films at 0.00125 M thiourea.

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1. Introduction

A number of techniques like electro-deposition, vacuum evaporation, sputtering, radio frequency, pulsed laser evaporation, molecular beam epitaxy (MBE), metal vapor organic deposition (MOCVD), spray pyrolysis deposition (SPD), close-spaced sublimation (CSS), successive ionic layer adsorption and reaction (SILAR), Micelle method and chemical bath deposition (CBD) are being used to develop thin films, since long. These techniques have also been used for the preparation of CdS films. Among these techniques, chemical bath deposition (CBD) has become an attractive route due to its simplicity, being inexpensive and having large surface area deposition at low temperature. This technique is also reported to be offering an excellent control to deposit uniform thin films and is also known as solution growth technique or chemical deposition technique. It is being used to grow CdS films since 1960s [1, 2, 3]. This technique also enhances the performance of CdS window layer as compared to other film growing techniques. The highest efficiency was obtained with the use of chemical bath deposition technique to deposit thin films of CdS as a window layer. Also the highest efficiency was obtained when the CBD technique was used to grow the buffer layer for CdTe and CIGS solar cells [4, 5]. It is also used in the fabrication of the other electronic and optoelectronic devices [6, 7]. CdS is an excellent hetrojunction partner for p-type CdTe, $CuInSe_2$, $Cu(In,Ga)Se_2$ (CIGS) because of the wide optical band gap (2.42 eV). CdS is also important material due to its novel properties like photoconductivity, high index of refraction (2.5) and its high electron affinity [8, 9]. The important properties like uniformity, transparency, crystallinity and good electrical characteristics are required for the use of CdS films in the field of solar cell fabrication. The same properties are also important to fabricate the other sophisticated electronic devices. The substrate is immersed in a bath of alkaline aqueous solution containing Cd^{2+} and S^{2-} resulting from the chemical reaction in the solution to grow CdS film on the immersed substrate [10, 11]. Temperature, film deposition time, relative concentrations of the reactive which provide Cd^{2+} and S^{2-} ions for chemical reaction, PH of aqueous solution is required for the deposition of CdS film on the immersed substrate in chemical bath deposition technique.

CdS film develops through the series of chemical reactions [12]. Firstly, cadmium salt hydrolyses to provide free Cd^{2+} ions. These cadmium ions reasct with ammonia molicules supplied by the ammonium salt to form the cadmium n-amine complex where n = 1, 2, 3…..6.

$$Cd^{2+} + nNH_3 \leftrightarrow Cd(NH_3)_n{}^{2+}$$

Secondly, hydroxyl redical $(OH)^{1-}$ promotes the thiourea hydrolysis to release the sulfur ions via successive chemical reactions

$$(NH_2)_2SC \rightarrow H_2S + CN_2H_2$$

$$H_2S + 2OH^- \leftrightarrow S^{2-} + 2H_2O$$

Finally, the presence of the free ions of Cd2+ and S2- lead to make CdS

$$Cd^{2+} + S^{2-} \rightarrow CdS$$

In this study, CBD technique has been used to deposit nanostructured CdS thin films on microscopic glass slides at the solution concentrations of $CdCl_2$ [0.000312 - 0.005 M] and $(NH_2)_2CS$ [0.000625 – 0.01 M]. The optical and structural properties of CdS films as-deposited and air-annealed at 360 °C are discussed as a function of the solution concentrations.

2. Experimental

All the reagents and solvents used were of analytical grade and procured from Alfa Aesar, Malaysia. Solvents were of 99.9% purity and were used without further purification. Glassware used was of Pyrex, Germany and soaked overnight in 20% nitric acid solution before using following by rinsing with double distilled deionized water and over drying at 70C for 6 h.

Cadmium chloride and Thiourea were used to grow CdS films on microscopic glass slides (76 × 25 × 1.2 mm) as substrate. The substrates were cleaned in acetone and ethanol ultrasonically for 20 minutes. Then substrates were washed with doubly deionized water and dried under N_2 atmosphere. As the source of Cd^{2+} and S^{2-} ions, solutions of different concentrations of $CdCl_2$ i.e. 0.000312, 0.000625, 0.00125, 0.0025and 0.005 M, and thiourea i.e. 0.000625, 0.001250, 0.0025, 0.005 and 0.01 M, respectively, were prepared in doubly distilled deionized water by continuous stirring at room temperature.

The molar ratio of 1:2 for $CdCl_2$: $(NH_2)_2CS$ was maintained throughout the experiment. Five samples by mixing solutions of $CdCl_2$ and $(NH_2)_2CS$ in proportions 0.000312:0.000625, 0.000625:0.00125, 0.00125:0.0025, 0.0025:0.0050 and 0.005:0.01 were prepared for the maximization of transmission spectral data. $CdCl_2$ and $(NH_2)_2CS$ solutions were placed separately in water bath using digital hot plate and temperature was raised upto 65 °C while stirring. Ammonia (NH_3) in aqueous solution was used as a complexing agent. Aqueous NH_3 was added drop by drop in $CdCl_2$ solution to dissolve the white precipitates of $Cd(OH)_2$ formed under constant stirring conditions. pH of the solution was adjusted at 11. Thiourea solution was added in $CdCl_2$ solution in 30 seconds under vigorous stirring. The temperature of resulting clear solution was further raised to 71 °C in 3 minutes followed by immersing cleaned substrates vertically in the solution using special Teflon holders. The container was covered to avoid any evaporation of ammonia. To ensure the uniform stirring and homogenous mixing throughout deposition process i.e. 2 h, magnetic bar was used. Mercury thermometer was also used to countercheck the temperature variations of the solution. Deposited substrates were taken out from water bath after 2 hours deposition time. Deposited substrates were washed in deionized water ultrasonically to remove the loosely adhered CdS particles and were dried at ambient conditions. Deposited films were divided into two sets; one of which was characterized as-deposited while second was air-annealed at 360 °C for 1 h at a heating and cooling rate of 4 °C min^{-1}. Thickness of the films was measured by Ellipsometer. Cu K_α radiation (λ = 1.540598 Å) with PANalytical (Philips) X'Pert Pro PW1830 was used for XRD analysis. The XRD data were analyzed by X'Pert High Score software for the identification of the crystalline phases in the films. Crystallite size (D) was determined using Scherer formula,

$$D = \frac{K(\lambda)}{\beta\cos\theta} \tag{1}$$

where β is the full width at half maximum (FWHM in radians) of the x-ray diffracted peak corrected for instrumental broadening and θ is Bragg angle, λ is the wavelength of X-ray, K is Scherer constant; taken as 0.94 for the calculations [13, 14].

The optical transmission (T) data was measured by double beam spectrophotometer (Shimadzu) over the wavelength range of 350 to 1100 nm. The absorption coefficient (α) was calculated using the equation,

$$\alpha = \frac{Ln\left(\frac{1}{T}\right)}{d} \tag{2}$$

Optical energy band gap (E_g) can be calculated using absorption coefficient (α),

$$\alpha = \frac{A(h\upsilon - E_g)^n}{h\upsilon} \tag{3}$$

where A is constant, $h\upsilon$ is photon energy, n is 1/2 for direct band gap materials as CdS is a direct band gap material [15, 16]. $(\alpha h\upsilon)^2$ is plotted as a function of $h\upsilon$. The linear portion of the curveextrapolated to $(\alpha h\upsilon)^2 = 0$, gives the value of E_g. The absorption coefficient (α) shows a tail for sub-band gap energy. The Urbach energy (E_u), associated with the width of the tail, was measured from the formula [17],

$$\alpha = \alpha_o\, e^{h\upsilon/E_u} \tag{4}$$

where α_o is constant. The inverse of the slope from the plot of $Ln\alpha$ versus $h\upsilon$ gives the value of Urbach energy (E_u).

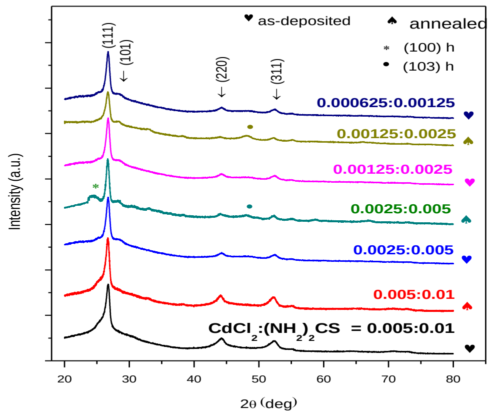

Fig. 1. XRD pattern of CdS films for different concentrations of $CdCl_2$ and $(NH_2)_2CS$.

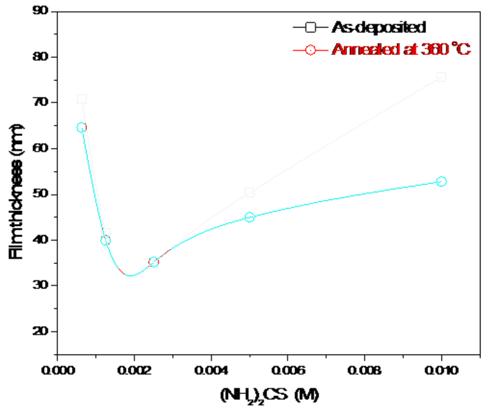

Fig. 2. Variation of thickness with at different concentrations of $(NH_2)_2CS$ (as $CdCl_2$: $(NH_2)_2CS$ = 1:2).

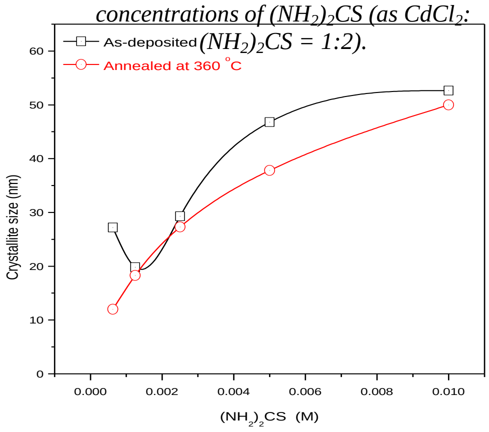

Fig. 3. Dependence of crystallite size at the concentration of $(NH_2)_2CS$ (as $CdCl_2$: $(NH_2)_2CS$ = 1:2).

3. Results and discussion

CdS films prepared from a reaction mixture containing cadmium chloride and thiourea in molar concentration of 0.005 and 0.01 respectively, show polycrystalline nature as shown in XRD pattern, Fig. 1. The prominent peaks for both films, characterized as-deposited and air-annealed at 2θ = 26.7552°, 44.2177°, 52.3606° (ref: 01-080-0019), belong to (111), (220), and (311) cubic CdS, respectively.

The CdS films, as-deposited as well as air-annealed, prepared from mixing the solutions of $CdCl_2$ (0.0025 M) and $(NH_2)_2CS$ (0.005) also show the polycrystalline cubic CdS film but air-annealed films show some small peaks at 2θ = 24.598° (100), 48.0297° (103) (ref: 00-041-1049) related to hexagonal CdS [18, 19]. The CdS films as-deposited, prepared from the solutions of $CdCl_2$ (0.00125M) and $(NH_2)_2CS$ (0.0025) is also cubic in nature but a very small peak is also observed at 2θ = 28.2275° (101) which belong to hexagonal CdS (ref: 00-041-1049). A small peak 2θ = 48.0297° (103) (ref: 00-041-1049) was detected, which belongs to hexagonal CdS for the air-annealed film.

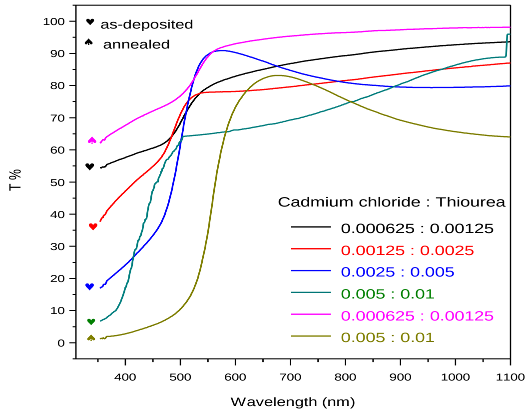

Fig. 4. Transmittance spectra for different concentrations of $CdCl_2$ and $(NH_2)_2CS$ (as $CdCl_2$: $(NH_2)_2CS$ = 1:2).

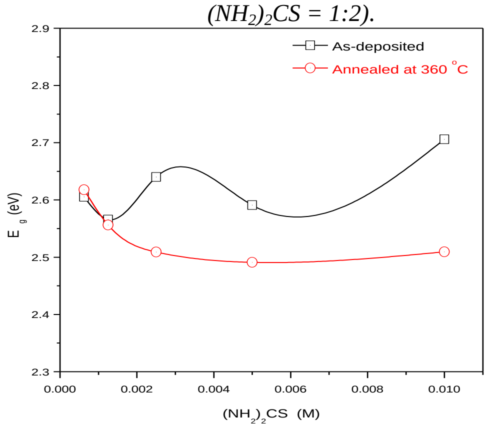

Fig. 5. Variation of E_g with concentration of $(NH_2)_2CS$ (as $CdCl_2$: $(NH_2)_2CS$ = 1:2).

When the concentrations of $CdCl_2$ and $(NH_2)_2CS$ were further reduced to 0.00625, 0.00125 and 0.00312, 0.000625 respectively, the films formed are cubic. These low concentration solutions also exhibited some small peaks related to hexagonal phase of CdS film [20], demonstrating the possibility of hexagonal phase development at the molar concentration $CdCl^2$ (0.00625 M) and $(NH_2)_2CS$ (0.00125 M). Also the development of hexagonal phase were found at $CdCl^2$ (0.000312 M) and $(NH_2)_2CS$ (0.000625 M). The relative percentage error in standard ‘d’ value (3.35498, ref: 01-080-0019) and observed ‘d’ value is below 0.55%. It is also observed that the preferred orientation is (111). The preferred orientation (111) is due to the controlled nucleation process occurring in the growing film in this experiment. This suggests the slow growth rate of the film deposition [21].

Thickness of the as-deposited film samples is observed 70.8 nm at concentrations of 0.000312 and 0.000625 M, for $CdCl_2$ and $(NH_2)_2CS$ respectively (Fig. 2). Thickness of the as-deposited film decreased to 41.5 nm at concentration of 0.000625 and 0.00125 for $CdCl_2$ and $(NH_2)_2CS$, respectively. It is further reduced to 34.8 nm at the molar concentration of 0.00125 and 0.0025. Thickness of the as-deposited film increased to 50.3, 75.7 nm at solution concentrations of 0.0025 and 0.005; 0.005 and0.01, respectively. This indicates that the film thickness is minimum at $CdCl_2$ (0.00125 M) and $NH_2)_2CS$ (0.0025 M). The thickness of the as-deposited film is reduced from 70.8 to 64.6 nm upon air-annealing at 360 ^{o}C for 1h at lower concentrations of 0.000312 and 0.000625 M, respectively for $CdCl_2$ and $(NH_2)_2CS$, (Fig. 2). The thickness of the as-deposited films is reduced from 41.5 to 39.8 nm, 35.2 to 34.8 nm, 50.3 to 44.9 nm, 75.6 to 52.8 nm when air-annealed at $CdCl_2$ and $(NH_2)_2CS$ concentrations of 0.000312 and 0.000625; 0.000625 and 0.00125; 0.00125 and 0.0025; 0.0025 and 0.05; 0.005 and 0.01, respectively. It is observed that the film thickness decreases prominently at higher solution concentrations. The average crystallite size of the as-deposited film was found to be 27.2 nm at concentrations of 0.000312, and 0.000625 M, respectively and is reduced to 19.8 nm for 0.000625 and 0.00125 M solution concentrations, (Fig. 3). It was increased to about 52.6 nm, with the increase of the solution concentration of $CdCl_2$ and $(NH_2)_2CS$ to 0.005 and 0.01 M, respectively as shown in Fig. 3. The average crystallite size reduced with the annealing temperature for all the molar concentrations. The minimum crystallite size (12 nm) was observed at the lower molar concentration of the solutions.

The transmittance spectra of CdS films were recorded over 350 to 1100 nm (Fig. 4). The spectra showed transmittance dependence of film on the molar concentration of thiourea. The transmittance (T %) is about 18% at wavelength of 400 nm for the concentration 0.005 and 0.01 M respectively, of the as-deposited CdS film and increased to a maximum value of 64% at 500 nm wavelength. Its value is increased to about 89 % at wavelength 1100 nm, while transmittance is about 11% at the wavelength 500 nm upon air-annealing. Its transmittance is increased to 83% sharply at 570 nm and decreased to 64 % at 1100 nm. It is observed that the transmission spectra shift towards higher wavelength with the annealing temperature (Fig. 4). This suggests the decrease in optical band gap energy (Fig. 5) [22]. The transmission of films with concentrations of $CdCl_2$ and $(NH_2)_2CS$ 0.0025 and 0.005; 0.00125 and 0.0025 respectively, as-deposited is 82 % at 790 nm. It is observed that the spectra shift towards shorter wavelength with the increase of the concentration, which suggests the decrease in optical energy band gap as shown in the Fig. 5. The transmittance of the as-deposited film is about 70% at 500 nm and is further increased to 94 % at 1100 nm for the concentrations 0.00625 and 0.00125 M, respectively. Its transmission is increased from 69 to 77 % at 500 nm and from 94 to 98% at 1100 nm, when film was air-annealed at 360 ^{o}C for 1 h. The transmission spectra shift towards higher wavelength after annealing, which suggests the decrease in the optical energy band gap, Fig. 5. The best transmission 77% at 500 nm and 98% at 1100 nm at lower concentrations of $CdCl^2$ and $(NH_2)_2CS$, i.e.0.00625 and 0.00125 M is obtained in this experiment.

The graph $(\alpha h\upsilon)^2$ versus photon energy ($h\upsilon$) is shown in Fig. 6. The value of the optical energy band gap (E_g) is 2.60 eV for solution concentrations 0.000312 and 0.00625, respectively, of as-deposited films. It was observed that there is no prominent change in the value of E_g when the film was annealed in air. The value of E_g is 2.56 eV with the increase in concentration to 0.000625 and 0.00125 M, respectively, of the as-deposited films. This value decreased to 2.55 eV after the annealing process. This suggests that the crystallinity of the films was increased with the annealing temperature. It is also clear from Fig. 2 that the film thickness is also increasing with the increase in solution concentration to 0.00125 and 0.0025 M, respectively. Particle size also increased with the increased of molar concentration of the precursor solutions. It is supposed that the loosely adherent collides are formed with the increase of the molar concentration. This may be reason due which the value of E_g. is increased. It is also observed that the value of E_g for air-annealed films decreased as compared to as-deposited films at all solution concentrations. This indicates that the crystallinity is enhanced with annealing. E_u is called Urbach energy and is shown in Fig. 7 and 8 for the as-deposited and air-annealed films, respectively. E_u is also known as band tail width and is due to the disorder in the thin film material. The variation of bond length and bond angle from their standard value in the crystalline material is called disorder [23]. It is clear that the optical band gap is reversely related to the disorder. This behavior indicates that the obtained optical band gap is governed by the disorder variation in the CdS films.

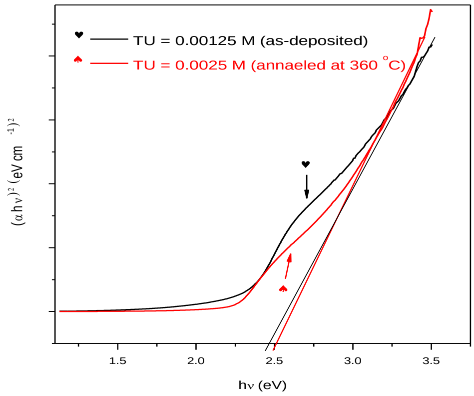

Fig. 6. Variation of $(\alpha h\upsilon)^2$ with $h\upsilon$ at different concentrations of $(NH_2)_2CS$ (as $CdCl_2$: $(NH_2)_2CS$ = 1:2).

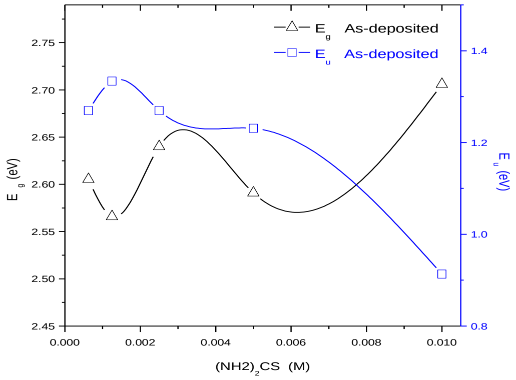

Fig. 7. Variation of E_g and $E_u$with concentration of $(NH_2)_2CS$ of the as-deposited CdS films (as $CdCl_2$: $(NH_2)_2CS$ = 1:2).

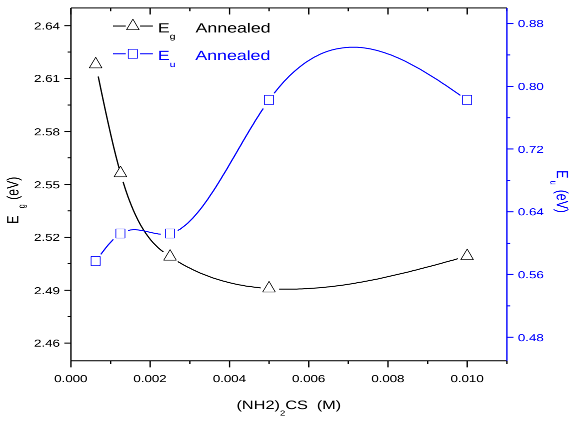

Fig. 8. Variation of E_g and E_u with concentration of $(NH_2)_2CS$ for air annealed (360 °C) CdS films (as $CdCl_2$: $(NH_2)_2CS$ = 1:2).

4. Conclusions

The CdS films were deposited by CBD technique for the different solution concentrations at constant bath temperature. XRD analysis show that the films were in cubic phase along with the few peaks of hexagonal CdS at very low concentrations. The crystallite size was varied with the solution concentration and annealing temperature. The optical band gap is governed by the disordering phenomena in CdS films. The optical transmittance varies with the solution concentration and annealing temperature.

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