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CHARACTERIZATION OF CdS NANOCRYSTALLINE THIN FILMS GROWN BY CBD TECHNIQUE AT VERY LOW SOLUTION CONCENTRATIONS

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CdS films were deposited on glass substrate by chemical bath deposition (CBD) from a bath containing very low concentrations of $CdCl_2$ and $(NH_2)_2CS$. The adhesion of the deposited films was very good for all solution concentrations. The films were thermally annealed in air at the temperature 240 ^oC for 1 hour. The maximum and minimum film thickness 75.6 nm, 33 nm was observed, respectively. XRD analyses show that the films were cubic along with few feeble peaks of hexagonal phase at lower solution concentrations. The crystallite size was increased from 17 to 51 nm with the increase of the solution concentration. The optical energy band gap (E_g), Urbach energy (E_{oo}) and absorption coefficient (α) was calculated from the transmission spectral data. The best transmission (> 94 %) was obtained in this experiment.

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1. Introduction

Many techniques are used to grow thin films like vacuum evaporation, sputtering, electrodeposition, molecular beam epitaxy (MBE), metal vapor organic deposition (MOCVD), close-spaced sublimation (CSS), radio frequency, pulsed laser evaporation, spray pyrolysis deposition (SPD), successive ionic layer adsorption and reaction (SILAR) and chemical bath deposition (CBD). These techniques have been reported for the preparation of CdS films. Among these techniques, chemical bath deposition (CBD) technique has become an attractive route because of its simpleness, low temperature, cheap and large area deposition method. CBD technique is appropriate for the coating of large surface areas. So, this technique is very popular for the large surface area deposition industrial application. This technique also offers an excellent control to deposit uniform thin films. CBD is also known as solution growth technique or chemical deposition technique. This technique is being used to grow the Cadmium sulfide (CdS) films since 1960s [1, 2]. 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 CBD 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 [3, 4]. It is also used in the fabrication of other electronic and optoelectronic devices [5, 6]. 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 [7, 8]. 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

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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 [9, 10]. 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 CBD technique. In this study, CBD technique has been used to deposit nanostructured CdS thin films on microscopic glass slides at very low solution concentrations of $CdCl_2$ [0.0003112 - 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 are discussed with respect to the solution concentrations.

2. Experimental

Cadmium chloride [$CdCl_2$, 99.99 % purity Alfa Aeser] and Thiourea [$(NH_2)_2CS$, 99 % purity Alfa Aeser] were used to grow CdS thin films on commercial microscopic glass slides (76 × 25 × 1.2 mm) as a substrate. The substrates were dipped in the diluted HCl (4%) and then washed with deionized water. Substrates were cleaned ultrasonically in ethanol for 20 minutes, washed with doubly deionized water and dried in air. Aqueous solution (55 ml) of Cadmium chloride [0.005, 0.0025, 0.00125, 0.000625, 0.000312 M] were prepared in a beaker using doubly deionized water for the source of Cd^{2+} ion at room temperature under continuous stirring. Also aqueous solution(55 ml) of Thiourea [0.01, 0.005, 0.0025, 0.00125, 0.000625 M] were prepared using doubly deionized water in beaker for the source of S^{-2} at room temperature under continuous stirring conditions. The molar ratio, $CdCl_2$: $(NH_2)_2CS$ = 1:2 was kept constant during the experiment. The samples of 5 different molar concentrations, $CdCl_2$:$(NH_2)_2CS$ = 0.005:0.01, 0.0025:0.005, 0.00125:0.0025, 0.000625:0.00125, 0.000312:0.000625 were used in this experiment. $CdCl_2$ solution was placed in temperature bath to raise temperature upto 60 ^oC while stirring. Digital hot plate was used for this purpose. Ammonia (NH_3) in aqueous solution was used as a complexing agent. Aqueous NH_3 was added drop by drop in the $CdCl_2$ aqueous solution to dissolve the white precipitate of CdOH under constant stirring conditions. PH was stabilized at about 10.5. The temperature of 55 ml solution of $((NH_2)_2CS$ was maintained at 60 ^oC in second temperature bath using digital hot plate. Aqueous solution of Thiourea was added in the $CdCl_2$ aqueous solution in 1 minute under vigorous stirring. The temperature was raised to 71 ^oC in few minutes and then cleaned substrates were immersed vertically in solution using special Teflon holders. All solutions that were used for deposition process were clear solutions. The container was covered to avoid the evaporation of ammonia. The magnetic bar was used for constant stirring throughout the 2 hours deposition time to ensure the homogeneous distribution of the chemicals in solution at constant bath temperature 71 ^oC ± 1 ^oC. Mercury thermometer was also used to monitor the temperature variations of the solution. Samples were taken out from the bath after 2 hours deposition time. Substrates were washed in deionized water ultrasonically to remove the loosely adhered CdS particles and dried in air. One sample from each concentration were air annealed at the temperature 240 ^oC for 1 hour at a heating and cooling rate of 4 ^oC 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*) can be determined using Scherer formula,

$$D = \frac{0.94\,(\lambda)}{\beta \cos\theta} \tag{1}$$

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 Scherrer constant taken 0.94 for the calculations [11]. The optical transmission (T) data was measured by double beam photospectrometer (Shimadzu) in the wavelength range from 350 to 1100 nm. The absorption coefficient (α) was calculated using the equation,

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

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 0.5 for direct band gap materials as CdS is a direct band gap material [12]. $(\alpha h\upsilon)^2$ is plotted as a function of $h\upsilon$. The linear portion of the curve is extrapolated 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_{oo}) associated with the width of the tail and can be measured from the formula [13],

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

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_{oo}).

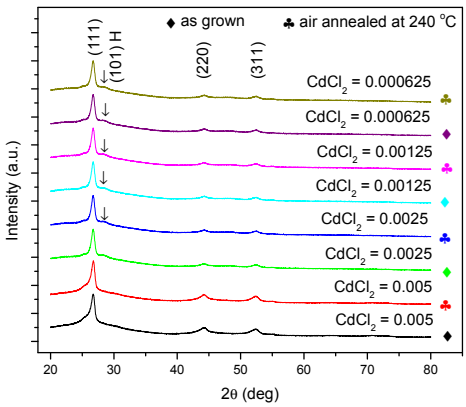

Fig. 1: XRD pattern of CdS film for different concentrations of $CdCl_2$

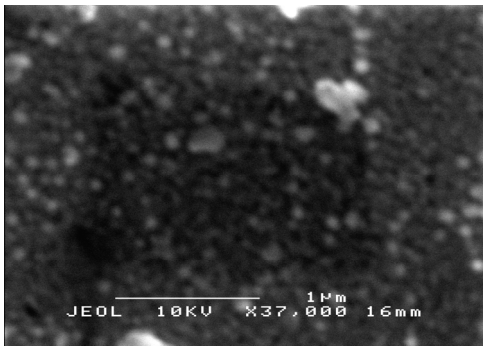

Fig. 2: SEM image of as–deposited film at $CdCl_2$ (0.005M)

3. Results and discussion

XRD pattern of CdS films as-deposited and air annealed from the $CdCl_2$ (0.005 M) and $(NH_2)_2CS$ (0.01 M) show polycrystalline in nature. The prominent peaks for both samples at 2θ = 26.7522°, 44.2177°, 52.3606° (ref: 01-080-0019) belongs to (111), (220), (311) cubic CdS, respectively, Fig. 1. The CdS films as-deposited and air annealed grown from the solution concentration $CdCl_2$ (0.0025 M) and $(NH_2)_2CS$ (0.005 M) also show the polycrystalline cubic CdS film [14, 15]. The prominent peaks for both samples as-deposited and air annealed at 2θ = 26.7925°, 44.2394°, 52.4816° (ref: 01-080-0019) belongs to (111), (220), (311) cubic CdS, respectively, For molar concentration $CdCl_2$:$(NH_2)_2CS$ = 0.00125:0.0055, very small peaks are also observed at 2θ = 28.7302°, 48.1229° which belong to (101), (103) hexagonal phase (ref: 01-080-0006). When the molar concentration was further reduced to $CdCl_2$:$(NH_2)_2CS$ = 0.00625:0.00125, the peaks observed for both samples as-deposited and air annealed are at 2θ = 26.8176°, 44.4089°, 52.4616° (ref: 01-080-0019) belongs to (111), (220), (311) cubic CdS,

respectively. Few peaks were also observed at 2θ = 24.2463°, 28.4096°, 48.1075° which belong to (100), (101), (103) hexagonal phase (ref: 01-080-0006). The further low solution concentrations also showed some peaks related to hexagonal phase of CdS film. This suggests that the hexagonal phase developed at the low solution concentrations only [16]. The relative percentage error in standard d value (3.35498, ref: 01-080-0019) and observed d value is below 0.45%. 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. This suggests the slow growth rate of the film deposition [17]. No pin hole was seen in the micrograph but few clusters were observed in film sample at higher solution concentrations as shown in the Fig. 2.

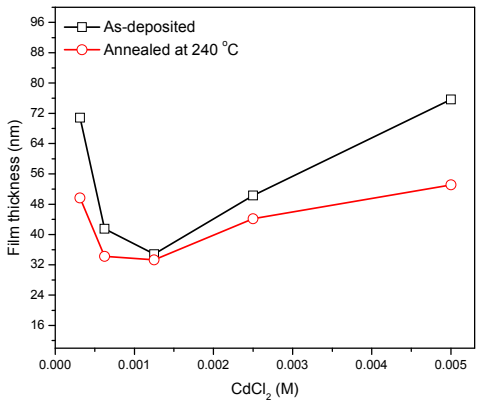

Fig. 3: Variation of thickness with concentration of $CdCl_2$

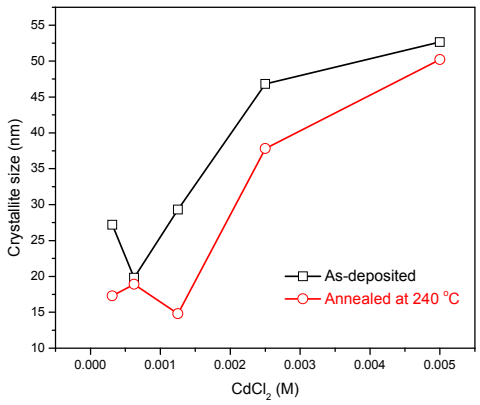

Fig. 4: Variation of crystallite size with concentration of $CdCl_2$

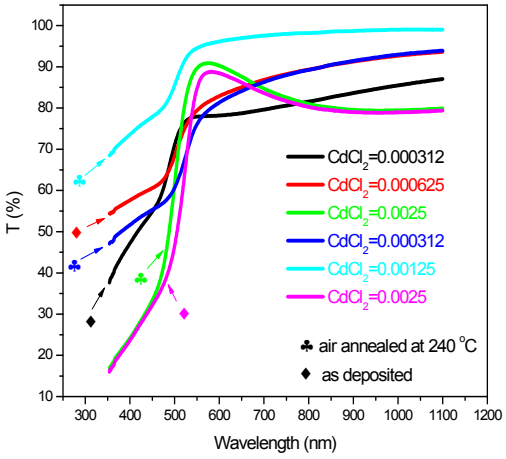

Fig. 5: Transmittance spectra for different concentrations of $CdCl_2$

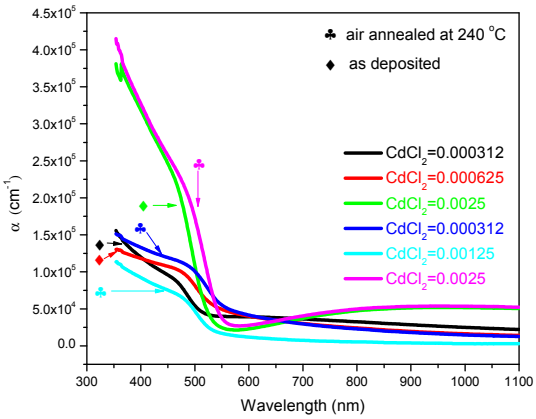

Fig. 6: Absorption coefficient (α) for different concentrations of $CdCl_2$

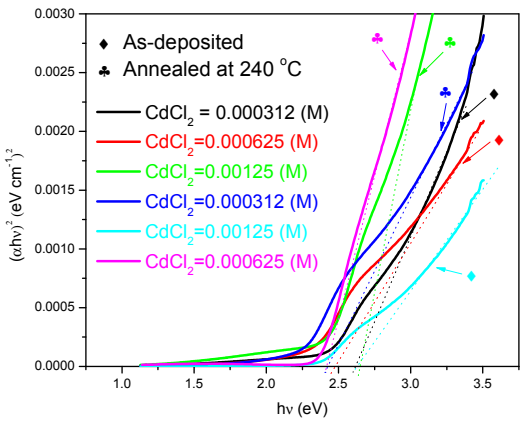

Fig. 7: Variation of E_g with hυ at different concentrations of $CdCl_2$.

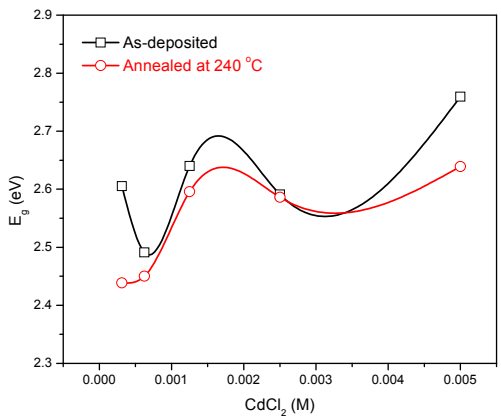

Fig. 8: Variation of E_g with concentration of $CdCl_2$

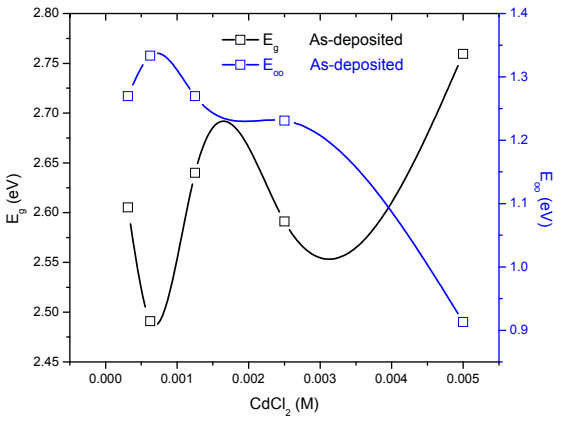

Fig. 9: Variation of E_g and E_{oo} of as-deposited films with $CdCl_2$

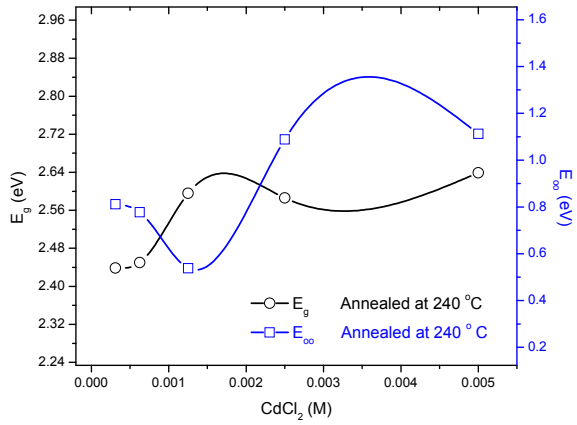

Fig. 10: Variation of E_g and E_{oo} of annealed films with $CdCl_2$

Thickness of the as-deposited film samples is observed 70.8 nm at molar ratio $CdCl_2$:$(NH_2)_2CS$ = 0.000312:0.000625 and is decreased to 34.8 nm for the molar ratio $CdCl_2$:$(NH_2)_2CS$ = 0.00125:0.0025 nm, Fig. 3. Then thickness increased to 75.6 nm with the increase of the solution concentration for the as deposited film sample. This indicates that the film thickness is minimum at molar concentration of $CdCl_2$:$(NH_2)_2CS$ = 0.00125:0.0025. The thickness of air annealed films is 49.6 nm at the low concentration and is decreased to 33.2 nm with the increase of solution concentration to $CdCl_2$:$(NH_2)_2CS$ = 0.00125:0.0025. Thickness increased to a maximum value 53 nm at the molar concentration of $CdCl_2$:$(NH_2)_2CS$ = 0.005:0.05. The average crystallite size of the as-deposited film was 27.2 nm, 19.8 nm for the molar concentration of $CdCl_2$:$(NH_2)_2CS$ = 0.000312:0.000625, $CdCl_2$:$(NH_2)_2CS$ = 0.000625:0.00125, respectively, Fig. 4. It was increased to about 52.6 nm with the increase of the solution concentration to $CdCl_2$:$(NH_2)_2CS$ = 0.005:0.01 for the as-deposited film. The average crystallite size was 17.2 nm for the annealed film at the molar ratio $CdCl_2$:$(NH_2)_2CS$ = 0.000312:0.000625 and increased to about 50.2 nm with the increase of the molar concentration. The transmittance spectra of CdS films were recorded from 350 to 1100 nm, Fig. 5. The spectra show transmittance dependence of the film on the molar concentration of the solutions for the deposition time of 2 hours. The transmission (T) was about 15 % at the wavelength 350 nm for the molar ratio.$CdCl_2$:$(NH_2)_2CS$ = 0.0025:0.005 of the as-deposited CdS film . The transmission increased to 89 % sharply at the wavelength 577 nm. It was constant at about 80 % for the higher wavelength range. The transmission was increased to ~91 % at the 560 nm wavelength after annealing. The transmission spectra slightly shift towards shorter wavelength, Fig. 5, with the annealing temperature. This suggests the increase in the optical band gap energy, Fig. 8 [18]. The transmission of the films with molar concentration $CdCl_2$:$(NH_2)_2CS$ = 0.000312:0.00625 as deposited was 39 % at the wavelength 350 nm and increased to 87 % at the wavelength 1100 nm. The transmission of annealed film was increased from 48%, 94 % at 350 nm and 1100 nm, respectively. The maximum transmission was found at the molar ratio $CdCl_2$:$(NH_2)_2CS$ = 0.00125:0.0025 for annealed film at 240 ^oC. The observed transmission was 80 %, 94 % at 470 and 550 nm, respectively. The best transmission (~ 97 %) was obtained from 550 to 1100 nm for this annealed thin film, Fig. 5. The variation of the optical absorption coefficient (α) with wavelength is shown in Fig. 6 for the different molar concentrations of the $CdCl_2$. The value of α is lower for the $CdCl_2$ solution concentration 0.00125 M for the annealed film sample. The graph $(\alpha h\upsilon)^2$ versus photon energy ($h\upsilon$) is shown in Fig. 7. The value of optical energy band gap (E_g) is 2.60 eV for the molar ratio $CdCl_2$:$(NH_2)_2CS$ = 0.000312:0.00625 of as-deposited films. This value decreased to 2.49 eV with the increase of the molar ratio to $CdCl_2$:$(NH_2)_2CS$ = 0.000625:0.00125 of the as deposited samples, Fig. 8. Its value increased to 2.76 eV with the further increase of the molar ratio of as-deposited films. This suggests that the Crystallinity of the films were decreased with the increase of the solution concentration. It is also clear from Fig. 3 that the film thickness is also increasing with the increase of the molar ratio. Particle size also increased with the increased of molar ratio of the precursor solutions. It is supposed that the loosely adherent collides are formed with the

increase of the molar ratio. Some clusters can be seen from the SEM micrograph Fig. 2. This may be the reason of the increased value of E_g. It is also observed that the value of E_g for the annealed films decreased as compared to the as-deposited films at all solution concentrations. This indicates that the crystallinity is enhanced with annealing. E_{oo} is called Urbach energy and is shown in the Fig. 9 and Fig. 10 for the as-deposited and annealed films, respectively. E_{oo} 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 [19]. It is clear that the optical band gap is opposite to the disorder. This behavior indicates that the obtained optical band gap is governed with the disorder variation in the film samples.

4. Conclusions

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

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