

Annealing Effect of Temperature on the Optical Properties of Nanostructure CdS Films

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Abstract: Cadmium Sulfide polycrystalline thin films were deposited on glass substrates using chemical bath technique at deposition temperature of 60°C from a bath containing cadmium chloride, ammonium chloride, ammonium hydroxide and thiourea. The structure and the crystallite size of these films were studied by X-ray diffraction. The optical properties: absorption, transmission, reflection, band gap, absorption coefficient, extinction coefficient and refractive index as a function of annealed temperature were measured. The influence of thermal treatment under various annealing temperature on the optical properties for some deposited films were studied and discussed.

Keywords: Annealed temperature, as-grown, CdS films, chemical bath technique, optical properties

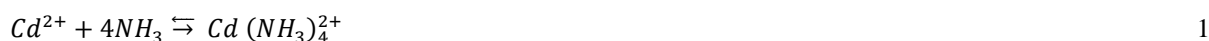
I. Introduction

Nowadays, the products of semiconductor industry spread all over the world and deeply penetrate into a daily life of human being. Thin films are well known for their applications in many physical based industries as instruments for many semiconductor devices [1]. In recent years, interest in the physical properties of thin films has considerably increased because new effects can appear in the film states that are not observed in the bulk samples [2].

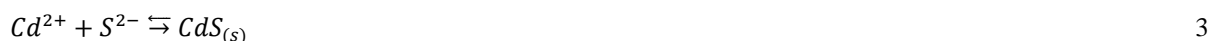
Thin film of cadmium sulfide is a suitable n-type semiconductor for a window layer in CdTe/CdS heterojunction solar cells [3, 4]. CdS is an important material due to its novel properties like photoconductivity, high index of refraction (2.5) and its high electron affinity [5, 6]. Several techniques like vacuum evaporation, sputtering, electro-deposition, radio frequency, pulsed laser evaporation, molecular beam epitaxy (MBE), metal vapour 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 CdS thin films. Among these techniques, CBD has become an attractive technique due to its simplicity, low-cost and having large surface area deposition at low temperature [7].

It has been reported that this technique has been offering an excellent control to deposit uniform thin films and also enhances the performance of CdS window layer as compared to other film growing techniques [8].

The preparation of CdS through CBD involves immersion of the substrate (glass in this case) 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 [9]. The control of deposition temperature, concentrations of the constituent solution which provide Cd^{2+} and S^{2-} ions for chemical reaction, film deposition time, and pH of aqueous solution is required for the deposition of CdS film on the immersed substrate in the chemical bath technique. CdS film is developed through a series of chemical reaction. Hydrolysis of cadmium salt to provide free Cd^{2+} ions which then react with ammonium salt to form the cadmium tetra-ammine complex;



Hydrolysis radical $(OH)^{-1}$ also promotes the thiourea hydrolysis to release the sulphur ions through successive chemical reactions



Hence the presence of the free ions of Cd^{2+} and S^{2-} enables CdS to be formed.

The essence of this research is to investigate the effect of annealing temperature on the optical properties of CdS

thin film deposited by chemical bath technique.

II. Experimental Details

CdS thin films were grown on microscopic glass slides substrates (25.4mm × 76.2mm × 1.0mm) by CBD technique. Cadmium chloride and thiourea were used as precursor sources of Cd²⁺ and S²⁻ respectively. Ammonium hydroxide and ammonium chloride were also used as complexing agent and pH control respectively.

The deposition temperature and time were 60°C and 60minutes respectively. Details of the deposition processes were reported in recent past work [10]. The structure of the film with thickness of 3.69nm was obtained using X-ray diffraction, XRD (Radicon MD 10 mini diffractometer, with Cu- α radiation).

The optical absorption and transmission studies of the film in the wavelength range 300-1100nm were examined using spectrophotometer (model UV-6405, Genway). The thickness was determined by the gravimetric method using Mettler Toledo (PB303) analytical balance. The effect of annealing temperatures of the sample at 70°C, 140°C and 210°C for 1hour under vacuum oven has been investigated.

III. Results and Discussion

Figure 1 shows the x-ray diffraction pattern of the as-grown CdS thin film. The pulses (in arbitrary unit) and diffraction angle (2 θ) were plotted. The broad lump in the range of scanning angle of 20° to 70° is due to the amorphous glass substrate. The planes (001), (002), (042), (107) and (004) indicate the covellite phase with hexagonal crystal structure. It has also been observed that the CdS films are polycrystalline with orientation along different planes and phases. The grain size of as-grown CdS film was evaluated to be between 12.9nm to 15.4nm by using the Debye Scherrer's formula.

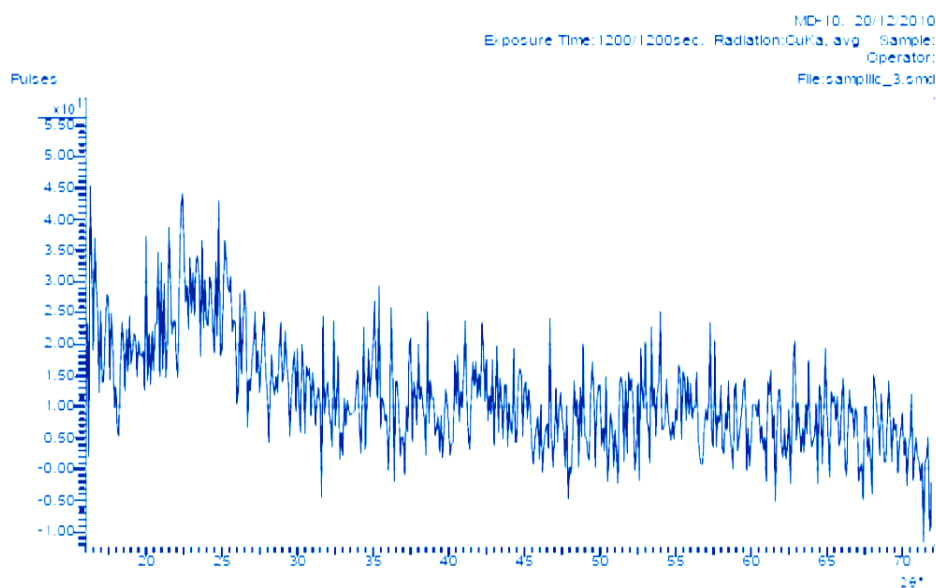


Figure 1: XRD pattern for the as-grown CdS film

In Fig. 2, the absorbance versus wavelength is plotted for CBD-CdS; as-grown and annealed thin films. From the absorbance spectra, it is observed generally that the absorbance of the films decrease with increasing wavelength and absorbance of the film is mainly in the VIS region of the solar radiation spectrum. The sharp absorption edges occurred at wavelength less than 530nm and the absorption edge of the film slightly shift towards longer wavelength with increasing annealing temperature. The highest absorbance values are observed from the annealed samples with the critical annealed temperature for optimum absorbance at 140°C. Similar behaviour was noted by Elmas *et al.* and Abbas *et al.* [11, 12].

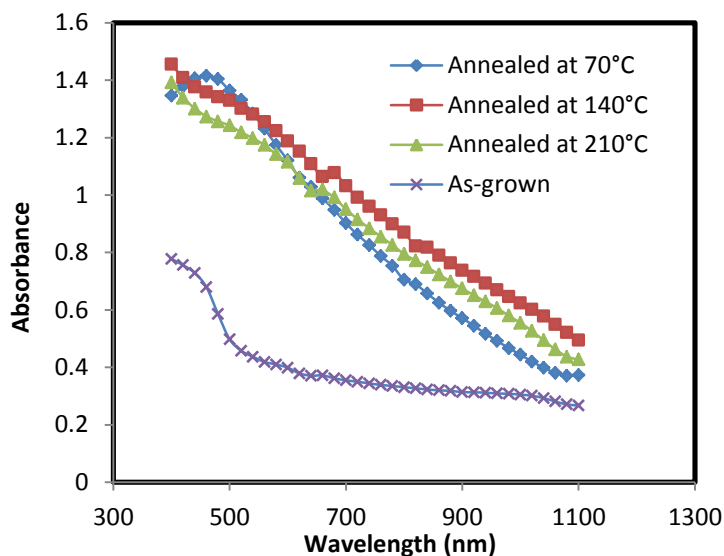


Figure 2: Absorbance as function of wavelength for CdS films at different annealing temperature

The transmission spectra of CdS film of as-grown and annealed films at 70°C, 140°C and 210°C is displayed in Fig. 3. From the transmission spectra, it is observed that the film samples transmit slightly low within UV-VIS regions but moderately high NIR regions for the as-grown films. The minimum transmittance for the films occurred within the UV region from where the transmittance increases with the wavelength towards the NIR region. The transmission spectra also showed that the films annealed at 70°C, 140°C and 210°C have transmittances greater than 25% in the VIS-NIR regions. The as-grown film showed transmittance of less than 60% within the VIS-NIR regions. However the as-grown and annealed films show transmittance that increased exponentially from the UV region towards the NIR region.

It is also observed from the Fig. 3 that increasing thermal annealing tends to reduce transmittance in all the spectrum of solar light energy. This is as a result of formation of denser films because of water evaporation. This behaviour goes in line with result published by Ezema *et al.* [13].

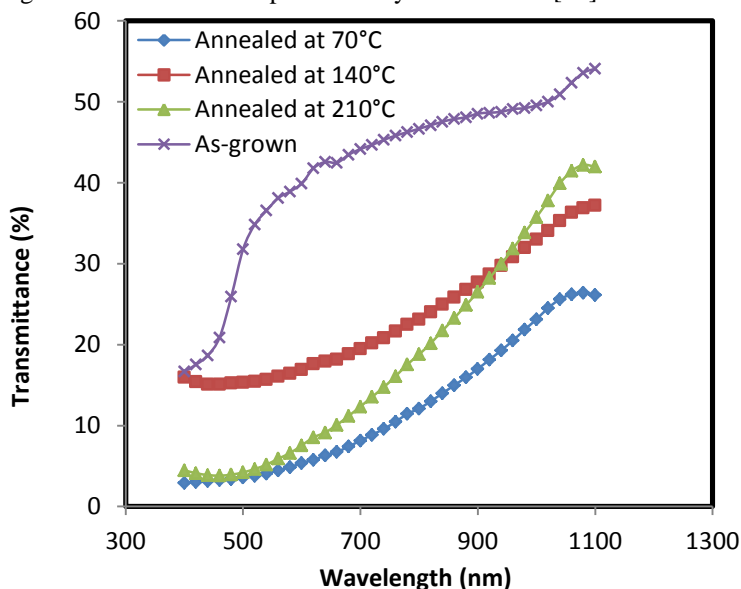


Figure 3: Transmittance as a function of wavelength for CdS films at different annealing temperature

The plots of the refractive index as a function of photon energy are shown in Fig. 4 for as-grown and annealed films. The as deposited film showed a small increase in refractive index up to NIR region before it started decreasing. More also the refractive index of the annealed film decreased uniformly to a maximum value at about 1.83eV, 1.38eV and 1.63eV for 70°C, 140°C and 210°C respectively. This is corresponding to the VIS region of the solar spectrum. However beyond this point, there is increase in the value of refractive index for annealed samples up to NIR region. The highest observed refractive index of 8.26 was observed at photon energy of 3.11eV for the film annealed in air at 140°C. This trend in the behaviour of refractive index with

annealing temperature has also been observed and was attributed to denser films arising from evaporation of water molecules off the films [14].

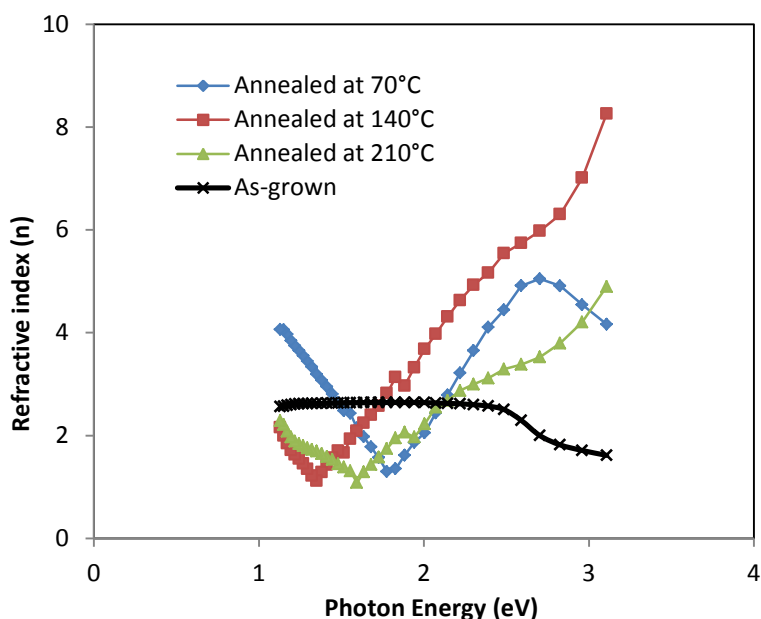


Figure 4: Plots of the refraction index as a function of photon energy at different annealing temperature

The theory of interband absorption shows that at optical absorption edge, the absorption coefficient α varies with the photon energy $h\nu$ according to Awodugba *et al.* [10]. CdS is a typical direct band gap semiconductor. The absorption coefficient for direct band gap material is given by $(\alpha h\nu)^2 = A(h\nu - E_g)$ [15] where α is the absorption coefficient, A is a constant, $h\nu$ is the photon energy and E_g the band gap. The energy band gap was determined by plotting $(\alpha h\nu)^2$ versus $h\nu$ whose intercept on the energy axis gives the energy band gap E_g as shown in Fig. 5. The optical band gap for as-grown and annealed film 70°C, 140°C and 210°C are 2.34eV, 1.95eV, 1.85eV and 1.65eV respectively. This shows that the energy gap decreases with increasing annealing temperature. This trend is possibly due to the evaporation of water molecules off the film and reorganization of the films [13]. The reorganization of the film particles and self-oxidation are the temperature dependence parameters that affect the band gap. These values of band gap obtained are in close agreement to the previous studies by Ezema *et al.*, Cetinnorgu *et al.* and Devi *et al.* [13, 16, 17].

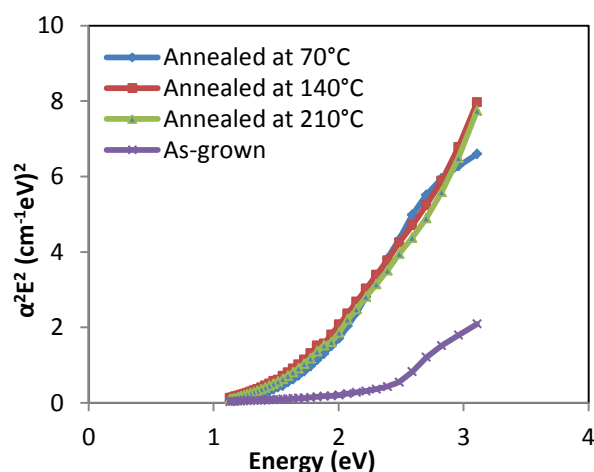


Figure 5: Plot of $\alpha^2 E^2$ against Photon Energy for CdS films

Fig. 6 shows the plot of the reflectance as a function of wavelength for as-grown films and annealed at 70°C, 140°C and 210°C. For as-grown film, the reflectance is increasing in the wavelength range of 400-550nm and a gradual fall in the reflectance in the wavelength range of 600-1100nm was observed. But however in

annealed samples of 70°C, 140°C and 210°C, the reflectance decreases with increasing wavelength toward VIS-NIR regions until a total sharp fall of reflectance value is reached then a sudden rise in reflectance is observed.

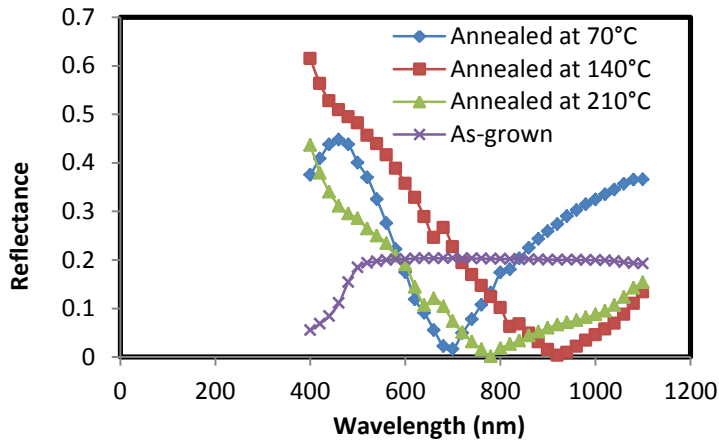


Figure 6: Graph of reflectance against wavelength of CdS thin films

The plots of absorption coefficient against photon energy are shown in Fig. 7. The spectra depict a sharp absorption edge, which are the characteristics of the crystalline state of the film. From the Fig. 7, it is also observed that absorption coefficient increases with annealing temperature. The coefficient of absorption (α) is related to coefficient of extinction (k) by $\alpha = \frac{4\pi k}{\lambda}$ [18] where λ is the wavelength of the electromagnetic wave.

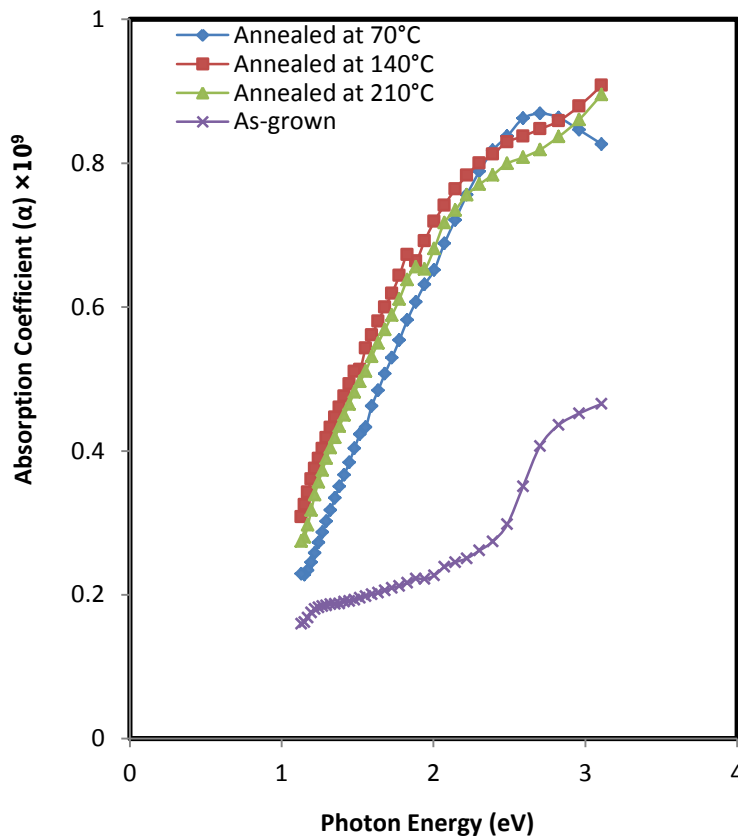


Figure 7: Variation of Absorption Coefficient against Photon Energy for CdS Thin Films

Fig. 8 displays extinction coefficient (k) as a function of photon energy (E). It is observed that annealed film has higher extinction coefficient than as-grown film. The maximum value of k value was observed at 600nm of wavelength.

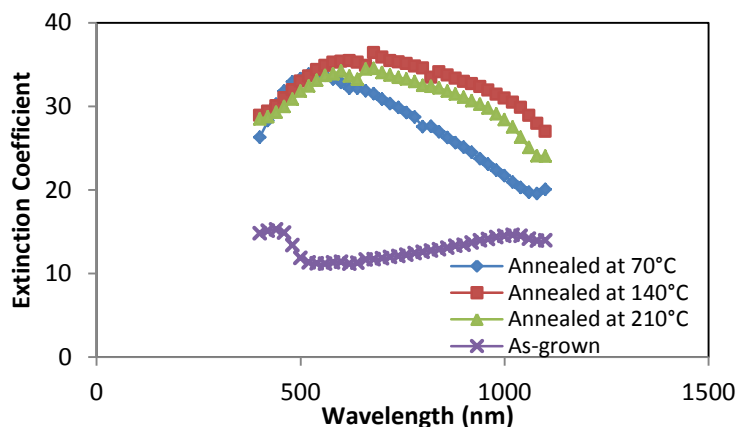


Figure 8: Variation of Extinction Coefficient against Wavelengths for CdS Films

IV. Conclusion

Thin films of CdS were deposited successfully using chemical bath deposition techniques. The effect of annealing temperature on the optical properties of the film has been investigated.

XRD studies of as-grown CdS thin films have a covellite phase with hexagonal crystal structure. The grain size of as-grown film was found to be between 12.9nm to 15.4nm. It was shown that thermal annealing tends to reduce transmittance and increase absorbance in all the spectrum of solar light energy. It was also observed that the energy gap decreases with increasing annealing temperature.

This study confirmed that thermal treatment strongly influence the optical properties of CdS thin films.

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