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Tunability and Graded Energy Band Gap of Chemical Bath Deposited Cadmium Sulfide (CdS) Thin Film for Optoelectronic Applications

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Abstract: CdS thin films have continued to receive scientific and technological attention due to their potential applications in efficient solar energy conversion and utilization in device fabrication. In this research, CdS thin films were deposited on indium doped tin oxide (ITO) substrates of dimension 2.3 by 2.4 cm^2. Three different aqueous bath solutions of CdS were formed by increasing the concentration of cadmium acetate as a source of cadmium while the concentration of ammonium chloride and thiourea as a source of sulfur remained constant in the reaction bath as against the usual convention to ascertain the strength of the constituents in the reaction. The energy band gap of the films decreases with increase in the concentration of cadmium as a constituent of the bath while the films optical transmittance was found to increase with increase in concentration. This indicates that the energy band gap of the films can be predetermined by the choice of the constituent of the concentration in the chemical bath deposition technique (CBD). The increase in the transmittance for both as deposited and annealed CdS confirms the suitability of the films as window layer device, solar cell and optoelectronic applications.

Keywords: Fabrication of CdS Thin Film, Chemical Bath, Thermal Treatment, Bang Gap Reengineering, Optical Properties

1. Introduction

Recently, the realization of interesting properties of group II, III, V and VI semiconductors such as wide band gap, high absorption coefficient, high chemical stability etc., have been attributed to the chemical solution-based synthesis route being a low cost and environmentally friendly fabrication techniques [1-3, 5]. Several methods have been employed in the synthesis of compound semiconductor materials [4-9]. Chemical Bath Deposition (CBD) has received considerable attention due to its capability of adjusting and re-engineering semiconductor materials properties [10, 11]. In this research work, chemical bath deposition was employed in the growth of Cadmium sulfide (CdS) thin film. CdS has gained a worldwide prominence due to its optical properties such as wide energy band gap (2.45 eV), high transmission, good absorption coefficient [12] etc. It has also received tremendous attention because of its potential applications in efficient energy conversion from sunlight to electric energy [13, 14]. The suitability of CdS for photovoltaic applications depend on the deposition parameters such as pH, deposition temperature, duration of deposition and ionic concentration [15]. The potential of CdS thin film has been realized by the optimization of its preparative parameters [16, 17]. CdS has been known as the most promising heterojunction partner for prominent polycrystalline photovoltaic materials such as CdTe and Cu (In, Ga)Se_2 [17]. Tremendous improvement has been made on cadmium telluride (CdTe) based solar cell when CdS is used as a window layer [18].

The formation of CdS requires optimized preparation

techniques and CBD is known to meet this requirement [9]. Some major advantages of the formation of CdS compound semiconductor on the transparent conducting oxide (TCO) using CBD include proper adhesion. This results to free pinholes, fewer carrier trapping, chemical stability and high transparent layer capable of housing polycrystalline photovoltaic materials [19-22]. In this work, indium doped tin oxide (ITO) was employed as the substrate while the CdS thin films were obtained via the chemical bath deposition technique. The precipitation of CdS occurs when the ionic product is higher than solubility product [23]. In most of the previous researches on CdS, the source of sulfur (S) often varies while the source of cadmium (Cd) is kept constant [24]. The uniqueness of the present work is that the source of sulfur is kept constant while the source of cadmium is varied. The onus here is to ascertain the actual strength of the constituents in the reaction bath and their contribution in the adjustment of the properties of materials.

2. Material and Method

Chemical bath deposition technique was employed for the preparation of Cadmium sulfide (CdS) thin films. The reagents used for the preparation were analytical grade which include cadmium acetate (99%,), Thiourea (99.5%) and ammonium chloride (98%). The aqueous bath solution was prepared by dispensing 0.42 g of cadmium acetate (Cd $(CH_3COO)_2.2H_2O$), 0.62g of thiourea ($CS(NH_3)_2$) and 1.4 g of ammonium chloride (NH_4Cl) as a complexing agent into 500 ml beaker contained 400 ml of deionized water to produce 0.0045 M of $CH_3COO)_2.2H_2O$, 0.02 M of $CS(NH_3)_2$ and 0.065 M of NH_4Cl. The solution was magnetically stirred for 2 hours for the formation of homogeneous solution of the admixed solutes. The bath alkalinity was controlled to 9.0 using a pH meter and ammonium solution. Different samples of CdS were obtained by varying the concentration of Cd $(CH_3COO)_2.2H_2O$). Three sets of samples were obtained with 0.0046, 0.0097 and 0.014 M of Cd $(CH_3COO)_2.2H_2O$). The bath aqueous solution was heated up to a bath temperature of 90°C before the previously degreased substrate was immersed and deposition takes place. After the precipitation of CdS thin film on ITO substrate, the samples were immersed into deionized water for 10 minutes to remove the presence of chlorine and dried using hand dryer at 50°C. The prepared samples were characterized for their morphological using scanning electron microscopy (SEM), elemental composition using energy dispersive x-ray spectroscopy (EDX) and optical properties using ultraviolet visible spectrophotometer (UV-vs).

3. Results and Discussion

3.1. Morphological Properties

The grain size and the shape of the deposited CdS as revealed by SEM were obtained through imagej analyzer to be $100 \pm 20\,nm$ and round shape (columnar shape), respectively. The grains are uniformly distributed as shown in SEM micrograph (Figure 1). Nevertheless, little agglomeration of the grains is noticed in the films which could be due to the duration of deposition resulting to over growth of CdS nucleation and bath temperature. However, the film was more uniform and strongly adherent to the substrate when heat treated at a substrate temperature of 350°C in 20 minutes (Figure 1). This agrees with previous research [25-27].

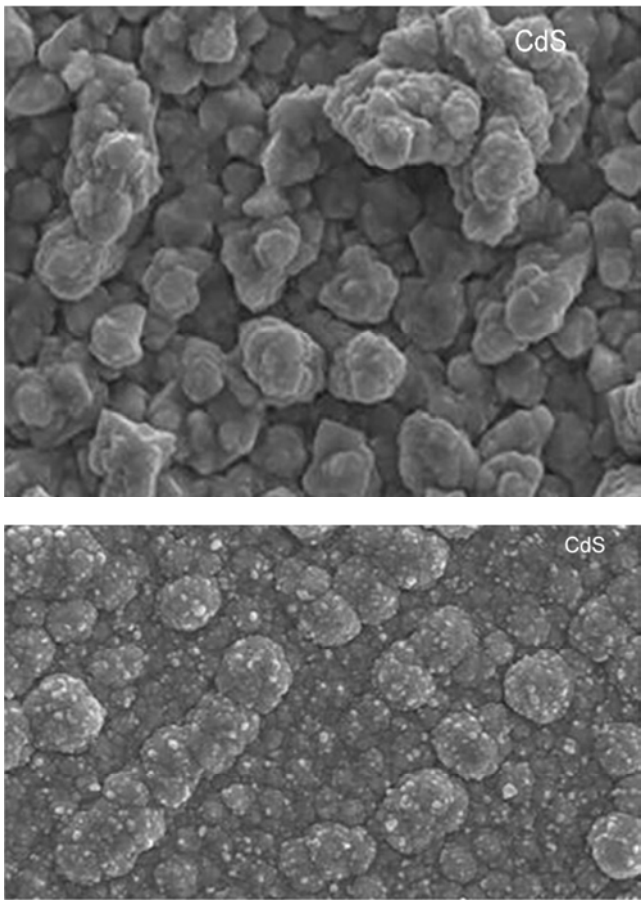

Figure 1. *SEM for the CdS thin films deposited.*

The EDX study revealed the presence of Cadmium (Cd), Sulfur (S) and indium (In) respectively. These elements were taking according to the Kα and Lα spectra energy levels. Cd has energy value of Lα = 3.13 KeV, S has the energy value of Kα = 2.307 KeV and In has its value as Lα = 3.207 KeV. However, the presence of indium as revealed by the EDX spectrum was not cleared but it could be suggested to have come from the substrate used. The quantitative atomic percentage of the compositional elements in CdS thin films are given as insert of Figure 2. It is important to note the presence of indium in the films as revealed in the EDX (Figure 2); Cd, S, being the primary constituents of the samples. In previous researches this peak had been constantly repeated as Cd probably due to the proximity of the energy value/atomic mass of In and Cd. In addition, the substrate glass used in the research is made of indium. Hence the In indicated could have been injected into the film from the substrate.

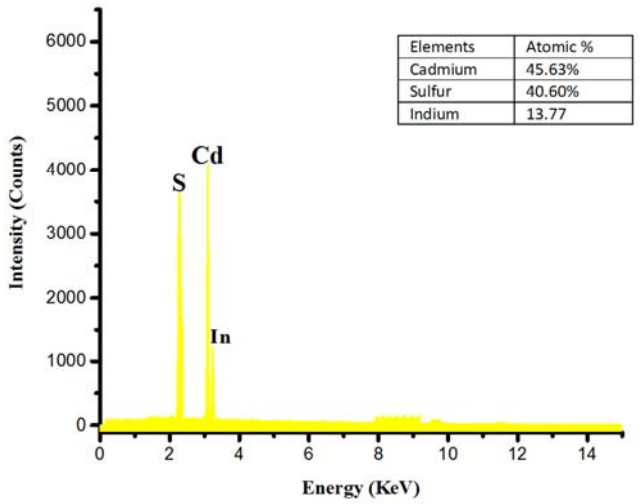

Figure 2. *Energy dispersive x-ray analysis (EDX) of CdS thin films.*

3.2. Analysis of Energy Band Gap

The energy band gap of the CdS thin films for both as deposited and heat-treated films as shown in Figures 3 and 4 were calculated by plotting $(\alpha hv)^2$ against hv. In this study, the energy band gap of CdS decreases as the concentration of cadmium acetate increases and also decreases when heat - treated. CdS has been characterized with a direct energy band gap. The energy band gap was obtained from the interception of the straight line on the hv axis as shown in the graph. This is achieved by extrapolating the linear portion of the graph. The plot of $(\alpha hv)^2$ against hv as proposed by Tauc and Mott [28-29] was used to determine the energy band gap of the synthesized films

$$\alpha hv = A\left(hv - E_g\right)^n$$

where A is a constant usually unity, E_g is the energy band gap and n is the transition between valence band and conduction band, n is equal to 0.5 and 2 for direct and indirect transitions respectively.

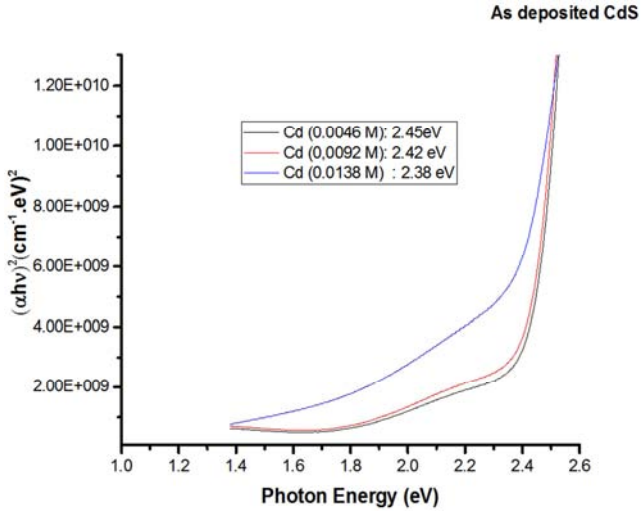

Figure 3. *Comparison of energy band gap of as deposited CdS thin films via a chemical bath deposition with Cd molarity variation.*

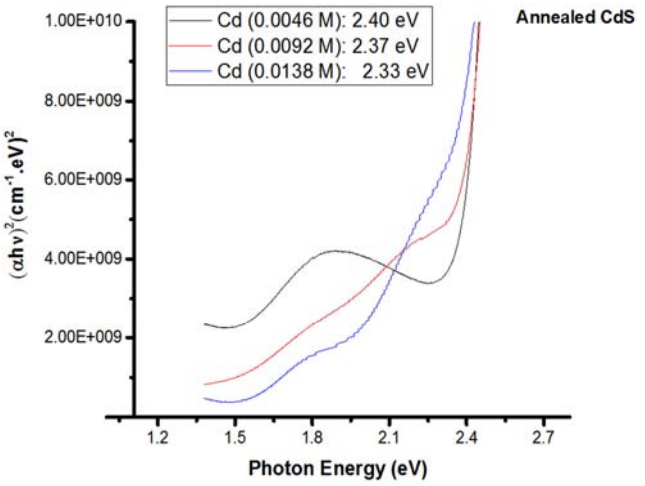

Figure 4. *Comparison of energy band gap of heat-treated CdS thin films at substrate temperature of 350°C in 20 minutes via a chemical bath deposition with Cd molarity variation.*

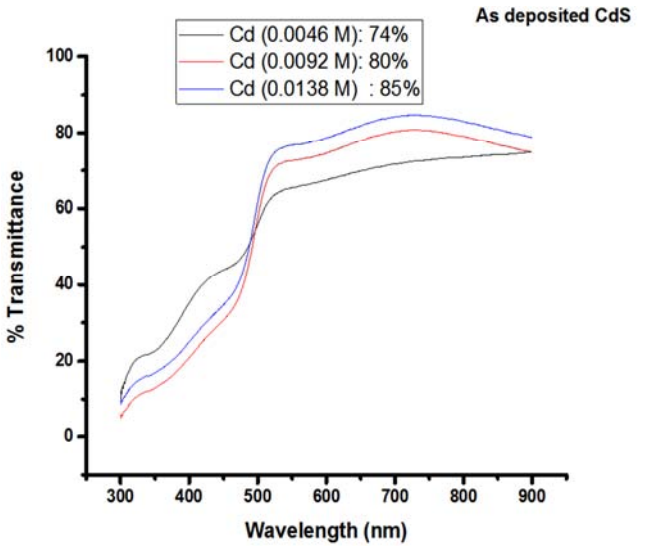

Figure 5. *Comparison transmittance spectra percentage of as deposited CdS thin films via a chemical bath deposition with Cd molarity variation.*

When a semiconductor material is heat-treated, the material's properties changes [29]. Evidence of this is noticed in the band gap of the heat-treated films. Similar phenomena have also been reported in previous researches [30-32]. Subsequent energy band gap was achieved as the concentration of Cd increases in the sample. Consequently, graded band gap energies of the films were achieved by successive and careful selection of Cd concentration in the fabrication of the material. Therefore, the utilization of CdS for solar and optoelectronic application can be tuned for specific functions.

The average transmittance of CdS films as shown (figures 5 and 6) increases with increase in Cd concentration and more pronounced when heat-treated. The usual decrease in the defect density due to the heating process could have favoured the improvement in the transmittance of the heat-treated samples [29]. Improvement in the crystallinity of materials was noticed with heat treatment [33]. Such

treatment in most cases heals worked samples and enhances the realignment of particles that are thrown off their lattice sites as a result of machining during fabrication. This phenomenon has been attributed in previous research on CdS as a result of surface irregularity and defect density [34]. Furthermore, the treatment of materials after fabrication at temperature is believed to promote recrystallization; nevertheless, at high temperature and long annealing duration, material loss becomes an important factor [29, 35]. The percentage of transmittance of as deposited and heat-treated films is more pronounced above the wavelength of 500 nm and such behaviour has been reported previously as one of the prerequisites for optoelectronic devices, especially for solar cell window layers [36, 37]. Specifically, the increase in the percentage transmittance is noted to be rapid within the wavelength range of 350-550 nm as evidence in the spectrum (Figure 6). The occurrence of the transmittance is an evidence for the formation of dense films on the surface of the substrate [38, 39].

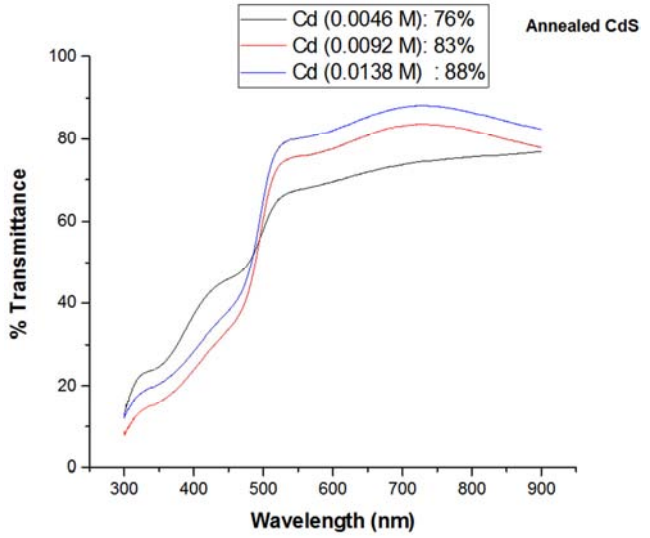

Figure 6. *Comparison transmittance spectra of heat-treated CdS thin films at substrate temperature of 350°C in 20 minutes via a chemical bath deposition with Cd molarity variation.*

4. Conclusion

In this work attempt had been made to deposit and synthesize CdS through CBD route with varied Cd concentration. The grain size and the shape of the film as obtained by SEM is an indication that the film was evenly distributed, and the elementary components of the film was revealed by EDX as Cd and S. The ultraviolet visible spectrophotometer for the film optical properties, revealed that the thicker the film, the higher the band gap but the lesser upon heat treatment. Such changes in the optical band gap of nanostructured materials can be explained based on quantum size effect. The result revealed that graded energy band gap could be obtained for specific optoelectronic device applications. All CdS thin films deposited showed good transmission as the transmittance spectra increases with wavelength. The rapid increase in the transmission above 500 nm revealed that the material showed potentials for good window layer for heterojunction solar cell and optoelectronic device applications.

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