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On the Bandgap Energy and Refractive Index of Cd Zn S Thin Films Deposited By Two Methods

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ABSTRACT

Cadmium Zinc Sulphide thin films were prepared at room temperature using Successive ionic layer adsorption and reaction(SILAR) and chemical bath (CBN) techniques. The solution is made of solution of Cadmium Sulphide (CdS) as a source of Cd^{2+}, Zinc Sulphate (Z_nSo_4) as a source of Z_n^{2+}, thiourea [CS($NH_2)_2$ as a source of Sulphide ion and ammonia (NH_2) as the complexing agent. The grown films were annealed at temperature of 200 K and 300 K in each case in order to investigate the effect of annealing temperature on the deposited thin films. The films grown by both techniques were studied using X-ray Diffractometer (XPERTPEA) and UV-ViS Spectropholometer. Extrapolation of the linear portion of the plots to the energy axis yielded the direct bad gap values of 2.9-3.0 eV for CBD deposited films and 3.49-3.50 eV for SILAR deposited films and the range of band gap obtained from the CDB deposited film were in close agreement with that of other authors. Also, the index of refraction was found to be in the range 1.05-1.15 eV for CBD deposited film and 1.5-2.65 eV for SILAR deposited films.

Keywords: Temperature, SILAR, impurities, Energy Bandgap and Index of refraction, absorption coefficient

INTRODUCTION

Cadmium Sulphide (CdS) and Cadmium Zinc Sulphide ($Cd_{1\_x}Z_{nx}S$) have properties in between CdS and Zinc. Addition of Z_n^{2+} to CdS buffer materials that promotes the electronic and refractive properties of the Film leading to new widows in the application of the Films in device production. The large band gap of Cadmium Zinc Sulphide thin Films makes the material much more attractive for the fabrication of solar cells. The thin Film is widely used as a wide bandgap widow material in heterojunction photovoltaic solar cells and photoconductive devices [1-10].

Following the above features more attention is being given in producing good quality CdS thin Films for various applications. There are various methods which are used to deposit CdS and CdZnS thin Films such as electrode position, successive ionic layer adsorption and reaction (SILAR),Vacuum evaporation, spray pyrolysis and chemical bath deposition (CBD) [1,7]. In this research, successive ionic adsorption and reaction (SILAR) and chemical bath deposition (CBD) method was used because it aid thin Film deposition of various temperature. It is important due to layer-by-layer growth comprises excellent material utilization efficiency, good control over deposition process along with Film [1,6]

Cadmium sulphide thin film is an n-type of semiconductor, (9) that can be manufactured with metal-organic vapour phase epitaxy methods [7]. CdS thin films are used in some photo resistors and solar cells [1,3]. Cadmium sulphide semiconductor is a material having a direct band gap of 2.42eV [5,9]. Cadmium sulphide is used as a photo-resistor because its conductivity increases when irradiated with light [4,9]. Cadmium Sulphide thin films can combine with a p-type semiconductor to forms an essential compound for photovoltaic solar devices. The first efficient cell to be reported was made of CdS/Cu_2S solar cells [2]. In thin-film form, CdS can be combined with other semiconductors for use in other types of solar cells [2]. CdS is also one of the first semiconductor materials used for thin-film transistors (TFTs). Cadmium sulphide thin films have been seen to be piezoelectric and have also been used as transducers which can operate at frequencies in the GHz region [4]. Synthetic cadmium pigments based on cadmium sulphide have many desirable qualities which make them valuable. These qualities include good heat stability, light and weather fastness, chemical resistance and high capacity [5,8].

MATERIAL AND METHODS

Thermal treatments were carried out on three synthesized thin films at temperature of 473K, 573K and 673K respectively and 0.05M of cadmium chloride pentahydrate ($CdCl_2.5H_2O$) solution was prepared by dissolving 1.14gram of the salt in 100ml of distilled water and 0.05M of zinc chloride ($ZnCl_2$) solution was prepared by dissolving 0.68g of ZnCl in l00ml of distilled water and this solution served as the cationic precursor. Then 0.05M of NH_4Cl was prepared by dissolving 0.27g in 100m1 of distilled water and 2M of NH_4OH were prepared by diluting 11.73ml of ammonia solution (analytical grade) with 88.27ml of distilled water these serves as complexing agents. 0.1M of thiourea (NH_2CSNH_2) was prepared by dissolving 0.76g of NH_2CSNH_2 in 100ml of distilled water this serves as anionic precursor. Synthesizing of CdZnS by this method involved the following steps: Four pre-treated substrate were immersed in a cationic precursor solution that is contained in beaker (a) for 30secs. Cadmium and zinc ions were absorbed on the surface of the substrates. The substrates were rinsed in high purity distilled water that is in beaker (b) for 5secs to remove the non-adhesion. The substrates were then immersed in the anionic precursor solution contained in beaker (c) for 30secs which provides the sulphide ions that react with the absorbed Cd^{2+} and Zn^{2+} to form the CdZnS thin films. Finally the substrates were rinsed again in the fourth beaker (d) for 5secs to remove non-adhesion thin films. This four steps above makes one complete cycle and it was optimized at thirty (30) cycles.

RESULT AND DISCUSSION

The plot of refractive index (n) against wavelength for the CdZnS deposited by chemical bath and SILAR techniques and annealed at different temperatures of 200°C, 300°C and 400°Cfor CBD and SILAR method are shown in Figures 1 (A – CBD and B- SILAR) respectively. The index of refraction n was calculated using the relation,

$$n = \left(1 + \sqrt{R}\right)\left(1 - \sqrt{R}\right)^{-1} [7] \qquad (1)$$

where n is the index of refraction and R is the reflectance. The index of refraction was found to be in the range of 1.05 – 1.15 for CBD deposited film and 1.5 – 2.65 for SILAR deposited film. The plot equally showed that as the annealing temperature increases the index of refraction increases. However, the SILAR deposited film displayed a lot of slopes and steps in the curves when compared to the CBD deposited film. The range of n obtained was in close agreement with that obtained by [1][5][9].

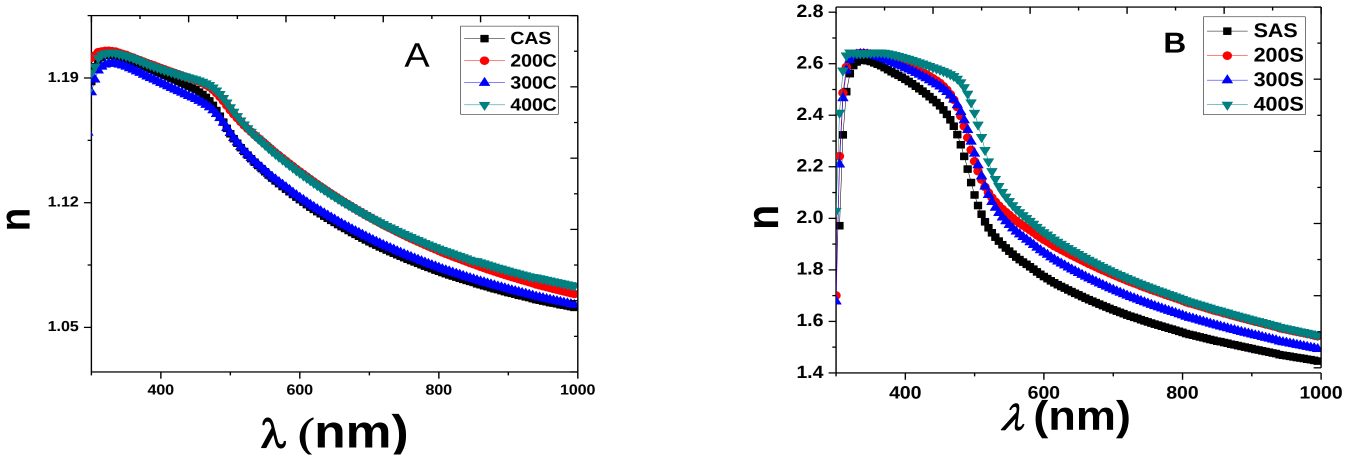

Fig.1: Refractive index against Wavelength **(A – CBD and B- SILAR)**

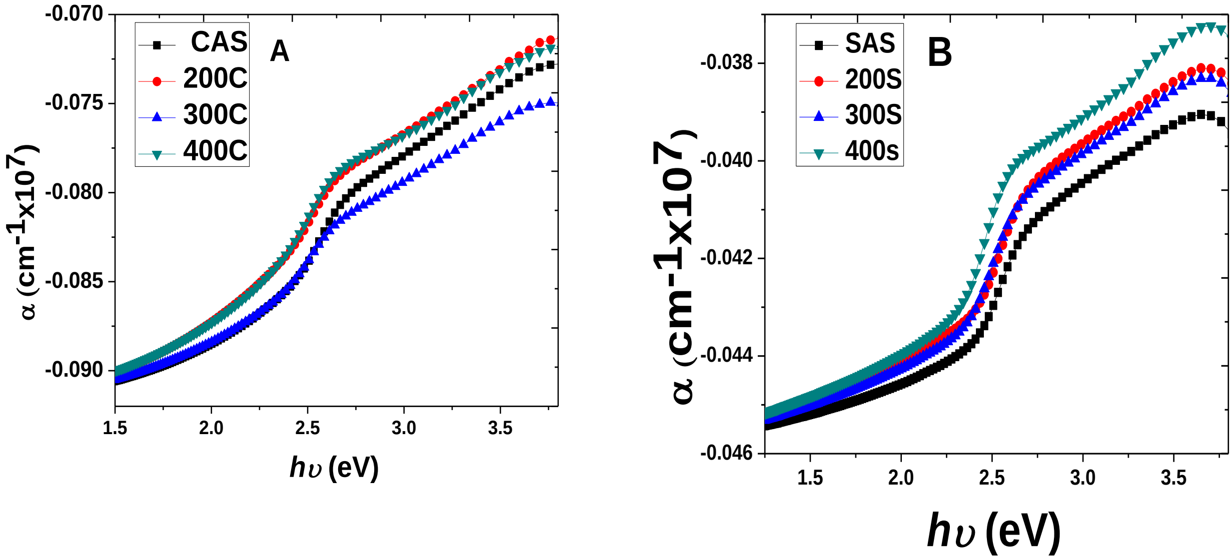

Fig.2: Absorption coefficient against photon energy **(A – CBD and B- SILAR)**

The plot of absorption coefficient against wavelength for the CdZnS deposited by chemical bath and SILAR techniques and annealed at different temperatures is shown in figures 2. The absorption coefficient was from the spectra of transmittance using the expression;

$$\alpha = \frac{4\pi k}{\lambda} \qquad (2)$$

Where k is the extinction coefficient, which is a measuere of how well the material absorbs electromagnetic radiation and λ is the wavelength. In figure 2 A, it is observed that the absorption coefficient increased almost linearly with photon energy for all the films. However, the film annealed at 300^{0} C have lowest value of absorption coeffient when compared to others. The plot also showed a little sudden rise in absorption coeffiecient immediately after photon energy of 2. 67 eV. This could be the absorption edge for the films under review. Simillar trend is displayed for the films deposited using the SILAR method except that the films displayed loer value of absorption coefficient when compared to those deposited using the chemical bath technique. This could be attributed to te fact that the SILAR method is based on sequential reaction at the substrate surface.coupled with rinsing which follows each reaction and this enables heterogeneous reaction between the solid phase and the solvated ions in the solution resulting to a better films formation [6.7].

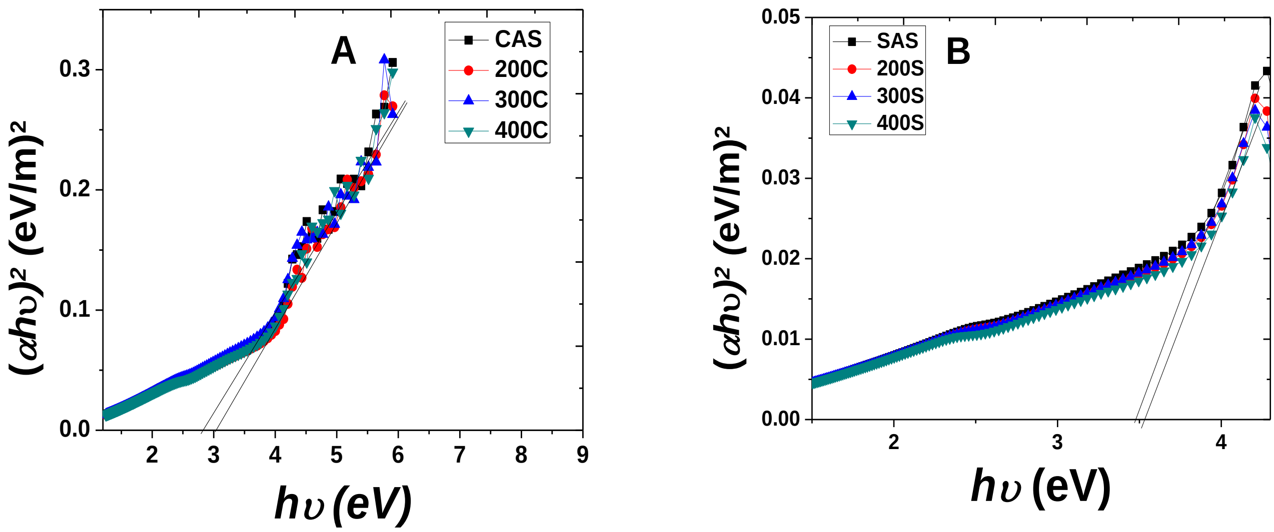

Fig.3: Plot for determination of bandgap energy (**A – CBD and B- SILAR)**

The plot of $(\alpha h\upsilon)^2$ against hv for the CdZS deposited by chemical bath and SILAR techniques is as shown in figures 3A and 3B respectively. For direct transitions;

$$\alpha h v = A (\alpha h v - Eg)^{n} \qquad (3)$$

In optical processes, n has the value ½ for the direct allowed transition, 3/2 for forbidden direct allowed transition and 2 for the indirect allowed transition. By extrapolating the straight portion of the graph of $(\alpha h v)^n$ at α = 0 the intercept gives the transition band gaps [9]. The region of higher values of α that is $\alpha > 10^6 m^{-1}$ correspond to transition between extended state in the conduction and valance bands while for lower values where $\alpha \leq 10^6 m^{-1}$ is the region where absorption present a rough exponential behavior [5,7]. The values of bandgap energy ranged between 2.8 – 3.0 eV for films deposited using chemical bath technique while for the films deposited using the SILAR method,the value of the bandgap energy varied between 3.5 – 3.62 eV. The variation may be caused by the change in garin size of the films due to different depositional method. Litterature has shown that variation in grain size affects the value of bandgaps [10]. The values of the optical parameters obtained for the CdZS thin films deposited in this work suggests that it can be applied in wide areas such as opto-electronics, solar energy harvesting etc.

CONCLUSIONS

A ternary alloy of cadmium Zinc sulfide (CdZnS) thin films were successfully synthesized on glass substrates using chemical bath deposition (CBD) and successive ionic layer absorption reaction (SILAR) technique. Thermal treatments were carried out on the synthesized thin films to determine the effect on optical properties of the films such as refractive index (n), absorption coefficient and band gap energy (E_g). This shows that deposition method and thermal treatment have effect on the properties of the deposited film. The bandgap energy values ranges from 2.8eV to 3.00 eV, for the thin films deposited by CBD while that deposited by SILAR method, band gap energy values ranges from 3.34eV to 3.62 eV which makes the films good materials for applications in laser diodes and Photovoltaic applications.The properties of films synthesized possess the same quality as films reported by other scholars

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