# Structural and optical properties of group II-IV Nanofilms by SILAR method

**Jayapriya J, Gunasekaran M and Seenuvasakumaran P**
PG department of Physics, Muthurangam Government Arts College (Aut),
Vellore 632 002, Tamil Nadu, India

*Abstract-:* **Nanostructured thin films have attracted the research community, as they shows looming applications in semiconductor industry, predominantly in fabrication of optoelectronic devices especially, in case of chalcopyrite hetrojunction solar cells, it acts as a buffer layer. In the present investigation $Cd_2ZnBaS_4$ and $Cd_2ZnSrS_4$ thin films are deposited on a glass substrate by SILAR process at room temperature. In this work we have doped Strontium and Barium to the cadmium Zinc sulphide to study the various structural and optical properties of them. The crystalline nature of both nanofilms is confirmed from X-Ray diffraction analysis and has Tetragonal structure. The average particle size calculated using Scherer formula is found to be 51 nm and 91 nm for Ba and Sr doped CdZnS respectively. The strain (ε) and dislocation density (δ) of the materials are calculated as 0.3145& 0.1474 and $3.7674X10^{-14}$ $m^{-2}$ & $1.2029X10^{-14}$ $m^{-2}$ for $Cd_2ZnBaS_4$ and $Cd_2ZnSrS_4$ respectively. The refractive index *n* (*λ*) is 1.6 for $Cd_2ZnBaS_4$ and 1.5501 for $Cd_2ZnSrS_4$ . The energy band gap (E*g*) of both films is 1.48 eV found by using the Tauc relation. The grown thin films are subjected to different excitation wave lengths and their corresponding emission wave lengths are observed from photoluminescence spectroscopy. The SEM pictures revealed the flower like morphology having low optical scattering losses. The thicknesses of grown films (*d*) are 1.594 µm & 0.67799 µm are calculated from Swanepoel method.**

***Key words:*** **- SILAR method, direct band gap, strain, dislocation density, Tauc plot, Swanepoel method.**

## I. INTRODUCTION

Cadmium sulfide (CdS) has been studied extensively for various applications such as solar cells [1, 2], photovoltaic devices [3, 4], and photosensors [5] because of its intermediate band gap (~2.42 eV), high absorption coefficient, electron affinity, low resistivity and easy of making an Ohmic contact [6]. These applications depend on selection of materials, mostly from group II and group IV semiconductors such as Cd, Zn, Ba, Fe, Sr, S. High-quality CdS thin film can be produced by different techniques, which has been already reported by many researchers. But, the fabrication of these types of thinfilms by SILAR technique is of recent research interest because of its simple procedure. In recent years, Zinc is doped with CdS, $Cd_{1-x}Zn_xS$ thin films has been attempted for the improvement of solar cell performance. It also attracted academicians and technologies because of their low energy gap. Thin films of $Cd_{1-x}Zn_xS$ have also been proved to be equally useful in the fabrication of solar cells like CdS [7]. These films can also be prepared by several techniques like Chemical Vapor Deposition, Sputtering, Spray pyrolysis, Chemical Bath Deposition etc [8]. All these techniques are highly sophisticated and at the same time expensive. Therefore, work has been continued to prepare the films by SILAR method so as to reduce cost of solar cell.

Recently there has been extensive work on the deposition of thin film materials such as CdS, CdZnS, and $Cd_2ZnBaS_4$ & $Cd_2ZnSrS_4$ by SILAR method. The Successive Ionic Layer Adsorption and Reaction (SILAR) technique was introduced by Nicolau in the mid-1980 [9]. This method has been employed to grow selected II-VI compounds, especially above mentioned materials [10]. The aim of this work is to promote interest in the SILAR method applied to synthesis of $Cd_2ZnBaS_4$ & $Cd_2ZnSrS_4$ thin films. To the best of our knowledge, for the first time an attempt is made for the preparation of $Cd_2ZnBaS_4$ & $Cd_2ZnSrS_4$ thin films by SILAR because of its large area deposition, easy control on film thickness by adjusting number of deposition cycles, less time consuming compared to other methods [11]. It is based on immersion of substrate in separately placed cationic and anionic precursors and rinsing between every immersion with ion exchange water to avoid wastage of the material [12]. From this work, we expect that, thin films may have apposite properties for application like photo voltaic using different characterization techniques as reported below.

## II. EXPERIMENTAL DETAILS

Microslide glasses of the dimension 75 mm X 25 mm X 1.35 mm are used as substrate. Corning glass slides were boiled in concentrated chromic acid for 1 hour then the glass substrate is rinsed with ethanol for 30 minutes and finally the substrate rinsed in double deionised (2-D) water for 30 minutes [13]. Cadmium nitrate ($Cd\ (No_3)_2\ 4H_2O$), Zinc acetate ($Zn\ (CH_3COO)\ _2\ 2H_2O$) and Barium nitrate ($Ba\ (NO_3)_2$) were taken as a cationic precursor solution. These cationic precursor solutions of known molarity are dissolved in 100ml of double distilled water. The solution was kept in the magnetic stirrer for 15 minutes and the pH was maintained at 4. Sodium Sulphide of known molarity is dissolved in 100ml of double distilled water. This solution was stirred for 15 minutes and the pH was maintained at 12. Sodium Sulphide ($Na_2S\ H_2O$) was taken as anionic precursor.

The pre-cleaned substrate was immersed for 25 seconds in the beaker containing cationic precursor solution, so that the cations get adsorbed on the glass substrate. The drying time was set for 5 seconds. Then the glass substrate was rinsed in second beaker containing deionized water for 5 seconds. This is done to remove the loosely bounded ions and the substrate was dried for 5 seconds. Next the substrate was immersed for 25 seconds in the beaker containing Sodium Sulphide solution, where $S^{2-}$ ions React with the $(Cd_2ZnBa)^{2+}$ ions. Again the substrate was dried for 5 seconds. Finally the glass substrate was again rinsed with double distilled water in the fourth beaker for 5 seconds. This is to remove the unreacted $S^{2-}$ ions from the substrate. Now the substrate is dried for 5 seconds.

Reaction mechanism**,**

The reaction mechanism was observed to be [14],

$$Cd(NO_3)_2 4H_2O + H_2O \rightarrow Cd^{2+} + 2NO_2\uparrow + 5H_2O + O_2\uparrow \qquad \rightarrow 1$$

$$Na_2S + H_2O \rightarrow 2Na^{+} + SH^{-} + OH^{-} \qquad \rightarrow 2$$

$$SH^{-} + OH^{-} \rightarrow S^{2-} + H_2O \qquad \rightarrow 3$$

$$2\,Cd^{2+} + Zn^{2+} + Ba^{2+} \rightarrow Cd_2^{2+}Zn^{2+}Ba^{2+} \qquad \rightarrow 4$$

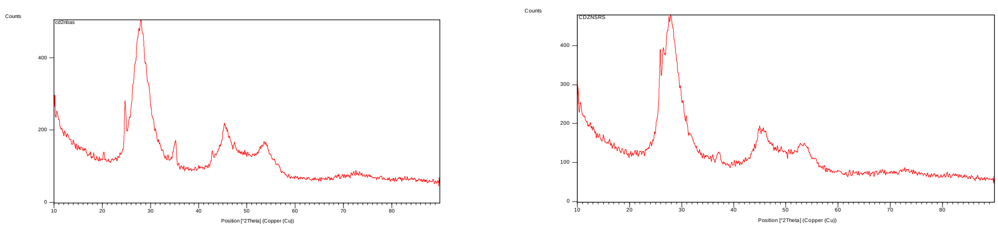
$$Cd_2^{2+}Zn^{2+}Ba^{2+} + 4\,S^{2-} \rightarrow Cd_2ZnBaS_4 \qquad \rightarrow 5$$

The cations and anionic solutions are taken in 1:1ratio.similarly we replaced Ba by Sr and continue the above process we get $Cd_2ZnSrS_4$ thin film.

## III. RESULT AND DISCUSSION

### *A.XRD Analysis*

The crystalline phase of the prepared samples are identified by using powder X-Ray diffractometer with the wavelength λ=1.5406 Å as Shown in fig 1.



(a) (b)

**Fig 1. XRD analysis of $Cd_2ZnBaS_4$ & $Cd_2ZnSrS_4$ thin film**

The broadened diffraction peaks in XRD indicates that the synthesized nanomaterial has very small size crystallites with poly crystalline nature. Using XRD, UV-Visible Spectroscopy data the following values of crystal size [15,16,17], Strain [18], Dislocation density [18] and Energy band gap [26] are found, as shown in table 1.

TABLE I

| S. No | PROPERTIES | $Cd_2ZnBaS_4$ thinfilm | $Cd_2ZnSrS_4$ thinfilm |
|---|---|---|---|
| 1 | Crystal structure & lattice parameters | Tetragonal<br>a=b=8.86 c=8.44Å , α=β=γ=90$^0$ | Tetragonal<br>a=b=11.264 &c=7.624 Å α=β=γ=90$^0$ |
| 2 | Crystal Size (D) | 51nm | 91 nm |
| 3 | Strain ($\varepsilon$) | 0.3145 | 0.1474 |
| 4 | Dislocation Density ($\delta$) | 3.7674X10$^{-14}$ m$^{-2}$ | 1.2029X10$^{-14}$ m$^{-2}$ |
| 6 | Energy band gap Eg) | 1.48 eV | 1.48 eV |

### *B.UV-Visible Spectral Study*

The absorption spectrum was studied in the region 200-1400 nm using UV-Visible spectrometer. In nanomaterials the grown thin films can used for any optoelectronic applications. Then the thin films are continuously evolving, being used for the fabrication of technologically advanced devices covering a wide spectrum of applications such as wear resistant coatings, optical coatings, flat panel displays, photovoltaic cells, sensors and many more. The cutoff wavelengths for both thin films have values of 250 and 320 nm range shown in fig 2(i).

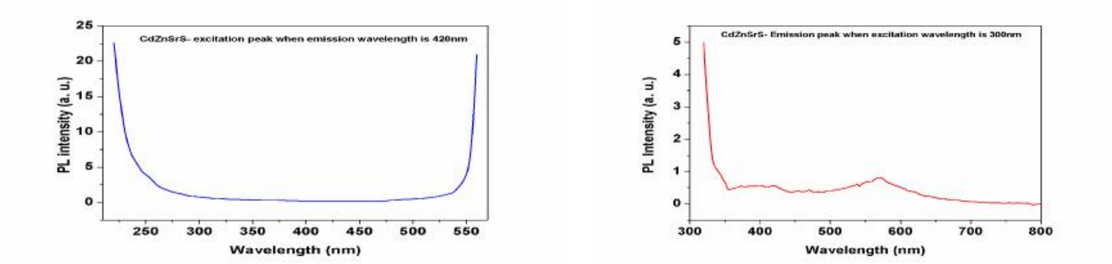

**Fig. 2. (i).Absorbance spectra of (a) $Cd_2ZnBaS_4$ & (b) $Cd_2ZnSrS_4$ thin films. (ii). Plot of ($\alpha$hυ )$^2$ vs. hυ for (a)$Cd_2ZnBaS_4$, (b) $Cd_2ZnSrS_4$ thin film thin films**

The refractive index and thickness of a thin film can be calculated from a simple transmittance spectrum using the Swanepoel method. This method can only be applied to thin films deposited on transparent substrates several orders of magnitude thicker than the film. When film thickness is uniform, interference effects give rise to the typical transmittance spectrum with successive maxima and minima. Practical application of this method entails, as a first step, the calculation of the maximum and minimum transmittance envelope functions, *TM* (λ) and *Tm* (λ), *M m* respectively[19],[20] . From these functions the refractive index *n* (λ) found to be 1.600 for $Cd_2ZnBaS_4$ and 1.5501 for $Cd_2ZnSrS_4$ thin films .The film thickness, d, a number of thicknesses are calculated using Swanepoel equation [21] [22] and the average of d is calculated for $Cd_2ZnBaS_4$ and $Cd_2ZnSrS_4$ thin films which are about 1594.46 nm & 677.99 nm.

An approximate functional dependency of the energy of the incident photon (hv) is given by the expression $\alpha = \alpha_0 (h\upsilon - E_g)^n / h\upsilon$ where $\alpha_0$ is a dimensional constant, Eg the optical band gap, and n is an index representing the transition order[23]. For a direct optical band gap, n = 2 and the curve (**α**hv)2–hv tends asymptotically towards a linear section, other values of n (generally 1/2) suggest an indirect optical band gap. The nanostructured thin films prepared in this study has a direct optical band gap [24],[25] as shown by the plot of (**α**hv)2 versus hv in fig 2(ii). Consequently, Eg is the intersection with the hv axis of a fit to the linear section of the (**α**hv)$^2$–hv curve [26].The intercepts of these plots on the energy axis reflect the energy band gaps. When the straight line intercept portion of the graph of ($\alpha$hυ)$^2$ vs. hυ gives the transition gaps and the energy gap of both thin films is observed to be 1.48 eV range.

### *C. Photoluminescence*

Light emission from compound semiconductors has been an important phenomenon due to its technological applications [26]. The optoelectronic devices such as light emitter or photo detectors can be fabricated using the semiconductors having a direct energy band gap and high efficiency like $Cd_2ZnBaS_4$ and $Cd_2ZnSrS_4$ thin films. These films can also be used in solar cells as light absorbing panels. Photo Luminescence (PL) analysis of these thin films over glass substrate was performed to analyze the purity of deposition [27]. The photoluminescence study ranges between 300-800 nm for emission and 200-600 nm for excitation peaks for Ba and Sr deposited thin films as shown in fig 3. In the spectra for $Cd_2ZnSrS_4$ thin film when the excitation wavelength is 300nm, we find two major PL peaks for Sr doped film at 560 nm and 580 nm as shown in fig 3 (a). Here, these peaks correspond to the emission of near band edge excitonic peaks which exhibits green band corresponding to the defect related luminescence emission



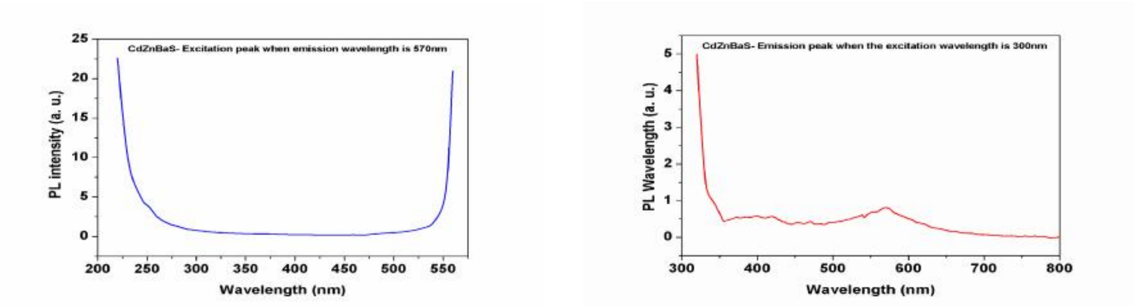
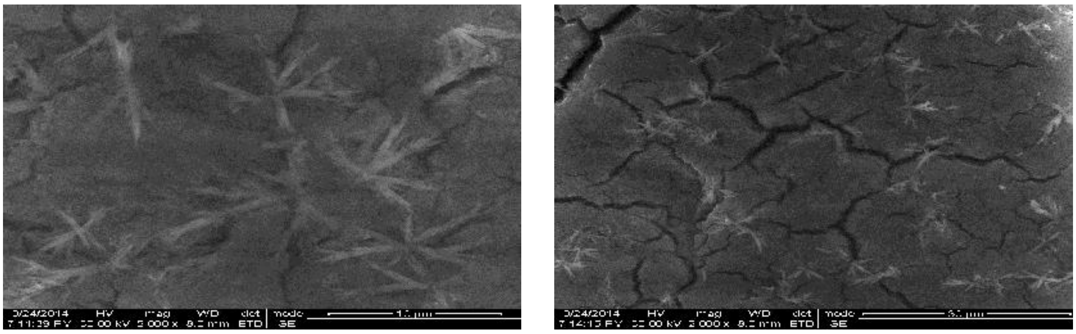



**Fig 3. PL studies of (a) $Cd_2ZnSrS_4$ and (b) $Cd_2ZnBaS_4$ thinfilms**

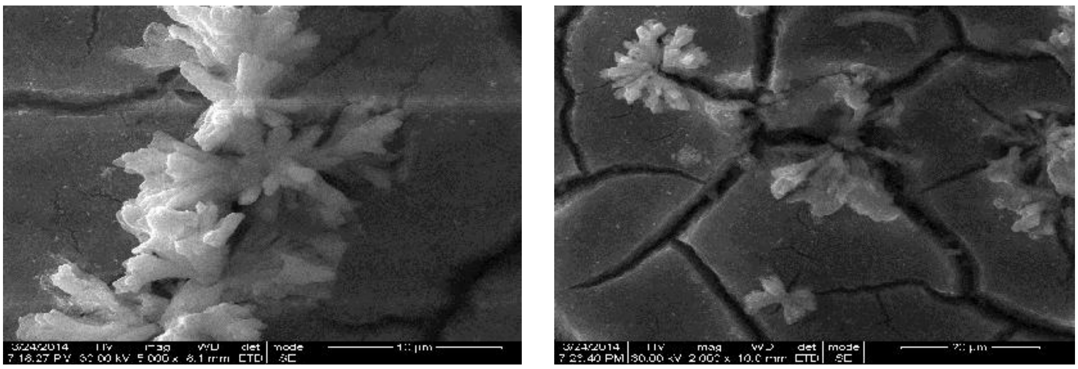
The PL spectra of $Cd_2ZnBaS_4$ exhibits many lower energy emission peaks for certain excitation wavelength. The excitation is less in the region from 300nm to 550 nm as shown in fig 3 (b) similar to Sr doped thinfilms. There is blue and green emissions as shown in figure 3a & 3b are due to photon transitions at 420 nm, 580 nm and 560 nm respectively. We find a major peak at 580nm which corresponds to the emission of near band edge exitonic peaks.

### *D. Surface Morphology*

The morphological studies of the nanomaterials have been carried out from scanning electron microscope (SEM). Thin film of $Cd_2ZnBaS_4$ at 10µm range &30µm range shown in fig 4 (a).which shows the grown films have some Pinholes, cracks and small flower-like particles. As a result, nano-sized homogeneous and smooth thin films have been obtained.



**(a)**



**(b)**

Figure 4 , SEM images of grown (a) $Cd_2ZnBaS_4$ & (b) $Cd_2ZnSrS_4$ thin film

Fig 4(b) shows the SEM image of $Cd_2ZnSrS_4$ thin film at 10µm range, 20µm range shows the film is deposited on glass substrate is homogeneous with high purity with cauliflower structure and the nano particles can occupy the glass substrate without any space in the grown film also there are macroscopic defects like void, pinhole, peeling or cracks on the film surface. In spite of these, from the featureless surface morphology of the deposited thin films, we can anticipate that these films will exhibit very low optical scattering losses and should therefore be suitable for optoelectronic applications[28].

## IV.CONCLUSION

The $Cd_2ZnBaS_4$ and $Cd_2ZnSrS_4$ thin films are deposited on a glass substrate by SILAR process at room temperature. The structure of $Cd_2ZnBaS_4$ and $Cd_2ZnSrS_4$ is Tetragonal. The average particle sizes of $Cd_2ZnBaS_4$ and $Cd_2ZnSrS_4$ are 51 nm & 91 nm and the strain (ε) is found to be 0.3145 & 0.1474 respectively. The change in the strain may be due to the predominant crystallization process in the nanomaterials. The dislocation densities 'δ' have been calculated as $3.7674X10^{-14}$ $m^{-2}$ for Zinc Barium and $1.2029X10^{-14}$ $m^{-2}$ for Zinc strontium doped with Cadmium sulphide thin films. The refractive indices n (λ) is found to be1.6 & 1.5 and thickness of the films (*d*) are 1.594 µm & 0.67799 µm are calculated from Swanepoel method for $Cd_2ZnBaS_4$ and Cd2ZnSrS$_4$ respectively. The energy band gap (E*g*) for the films at the edge of absorption band is calculated as 1.48 eV range by the Tauc relation. The grown thin films are subjected to different excitation wave lengths and their corresponding emission wavelengths are studied. This type of films finds applications in making antireflection coatings and solar cells. Especially II-VI compounds have attracted a great interest, because of their good quality and cheaper. SEM pictures have reveals the flower like morphology.

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