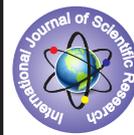


Band gap and thickness variation with temperature of solid solution II-VI CdZnS₂ thin films by spray pyrolysis



Physics

KEYWORDS: :- CdZnS₂ thin films, spray pyrolysis, band gap energy.

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ABSTRACT

Spray pyrolysis is a simple and inexpensive method to prepared thin films on large substrate area. CdZnS₂ thin films were prepared by spraying the films on pre-heated glass substrate using aqueous solution of cadmium chloride, zinc chloride and thiourea. Band gap energy decreases and thickness increases upto the optimised temperature (3000C). Further increase of temperature optical band gap increases and thickness decreases. This is due to higher evaporation the initial ingredient. The band gap energy decreases from 3.17 eV to 3.12 eV as temperature increases. CdZnS₂ thin films show direct allowed transition.

1. Introduction:- II-VI group of semiconductor materials is attributed to their wide spread use for the opto-electronic devices as well as solar cells fabrication process. It is a ternary compounds including cadmium, zinc and selenide have attracted much attention in the field of solar cells due to their interesting properties of band gap by composition parameter. This group of compounds can also be used in hetero-junctions, IR detectors, switching devices and schottky barriers etc. The II-VI group compounds particularly CdZnS₂ are attracting a lot of attention due to their potential application in producing photo-voltaic devices, and wide use in the IR devices. CdZnS₂ is a semiconductor that has been considered attractive for use in solar energy conversion. The photo-electronic properties of CdZnS₂ thin films are greatly influenced by both native and foreign contaminated in the lattice during the films preparation which can cause a considerable change in electrical and optical properties of semiconducting films without causing a major change in the crystal structures. CdZnS₂ thin films ternary compounds is also potentially useful a window material for the fabrication of p-n junctions without lattice mismatch in the devices based on materials. Thin films can be prepared by various method such as flash evaporation, vacuum evaporation, r.f. sputtering, molecular beam epitaxy, chemical bath deposition and spray pyrolysis. Among these spray pyrolysis is one of the most used methods, compared to the other methods. Spray pyrolysis has the following advantages simple and continuous operation, economical uniform particle size distribution, controllable size and controllable anion and cation concentration or droplets.

The aim of this study it is to investigate the effect of temperature on optical band gap energy and thickness of the films.

2. Experimental details:- CdZnS₂ thin film were prepared by spraying the aqueous solution of cadmium chloride, zinc chloride and thiourea on pre-heated glass substrate. Molarity of each solution was 0.02 M. Chemical were used as AR-grade. Temperature of the substrate was varied from 250°C, 275°C, 300°C and 325°C in the interval of 25°C. It was measured by pre-calibrated copper-constantan thermo-couple. The glass sprayer was mechanically move to and fro to avoid the formation of droplets on the substrate and insure instant evaporation. The solution were taken in the proportion 1:1:3.2 by volume. The thin films shows a sulphur deficiency if the ratio of solution of proportion was taken as 1:1:2 by volume. The distance between the sprayer nozzle and substrate was kept at 30 cm. The spray rate was maintained at 3.5ml/min at a pressure 12kg/cm². Thickness of the films were measured by weight difference method on unipan microbalance and Michelson interferometer. In both method thickness of the films were found to be nearly same, only difference was observed as 0.003µm. Transmission were taken on UV-1800 Shimadzu spectrophotometer.

3. Optical study:- Figure 1 shows the transmission verses wavelength of as deposited CdZnS₂ thin films. prepared at different temperature. Transmission were recorded within the wavelength range between 350 nm to 800 nm for all films.

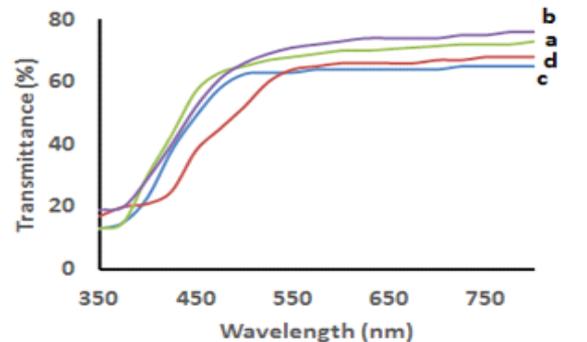


Fig.1 The transmission verses wavelength of as deposited CdZnS₂ thin films prepared at different temperature a) 250°C b) 275°C c) 300°C and d) 325°C.

From the figure 1, It was observed that onset of decrease of transmission towards the lower wavelength side if the preparation temperature of the films increases. This indicates the optical band gap energy changes if the temperature changes.

From the transmission curve, the absorption coefficient (α) were calculated for each wavelength is given by the relation,

$$\alpha = 1/t \ln(I_0/I) \quad (1)$$

Where I_0 and I be the intensity of incidence and transmitted radiation respectively, t -the thickness of the films.

To calculate the exact value of band gap energy of all films was estimated using the Tauc-radiation (2,3).

$$\alpha = A/h\nu (h\nu - E_g)^n \quad (2)$$

Where $h\nu$ -the photon energy, E_g -the band gap, A is constant which is different for different transitions, $n=1/2$ for direct band gap transition and $n=2$ for indirect band gap transition.

4. Results and Discussion:- The energy band gap is measured with the help of absorption spectra. To calculate the exact value of band gap, a graph $(\alpha h\nu)^2$ verses $h\nu$ is plotted of all the films as shown in the figure.2.

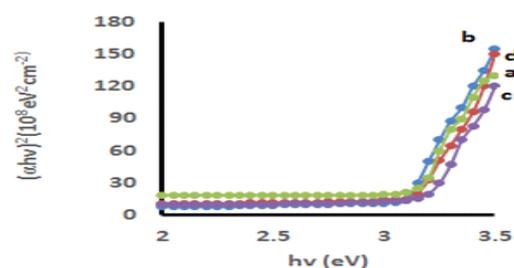


Fig.2 The graph between $(\alpha h\nu)^2$ versus $h\nu$ of as deposited CdZnS₂ thin films prepared at different temperature a) 250°C b) 275°C c) 300°C and d) 325°C

Each graph has linear portion which intercept on $h\nu$ axis gives the value of band gap. Calculated band gap with temperature is shown in table.1.

Temperature T (°C)	Band gap Eg (eV)	Thickness of the films t(μm)
250°C	3.17	0.1635
275°C	3.14	0.1795
300°C	3.12	0.1950
375°C	3.13	0.1870

The calculated value of band gap greater less than Saliha Ilcan et al (4). They have reported the optical band gap at optimised temperature was of 3.04 eV. Our calculated value also match with the value reported by Feng et al (5). It was observed that if the temperature increases the band gap value decreases upto the optimised temperature 300°C. After increase the temperature the band gap value slightly increases. Similar results also reported by sprayed CdIn₂S₄ thin films (6) and CdZnSe thin film (7). Calculated value of thickness with temperature of as deposited films is shown in table.1. It was observed that if the temperature increases, the thickness also increases upto the optimised temperature (300°C) if further increase the temperature, the thickness of the films slightly decreases. This shows that the temperature less than 300°C may not be sufficient to decompose the sprayed droplets from solution. Therefore the deposited results into a low thickness was estimated. This is due to higher evaporation the initial ingredient (6). Similar results also reported by Tembhurkar (9) for CdSe, ZnSe, CdTe thin films. Thus CdZnS₂ thin films shows a good stoichiometric in semiconducting nature. CdZnS₂ thin films shows direct allowed transition.

Conclusion:- Spray pyrolysis is a simple, inexpensive and easy to prepare thin films on large substrate area. If the temperature increases the band gap decreases and thickness increases upto optimised temperature. CdZnS₂ thin films shows a direct allowed transition.

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