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STRUCTURAL AND OPTOELECTRONIC PROPERTIES OF PYRALYTICALLY SPRAYED CdZnS THIN FILMS

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Sulfides of Cadmium and Zinc have been extensively used as a wide band gap window material in heterojunction solar cells and photoconductive devices. CdZnS thin films of different substrate temperature have been prepared by the conventional Spray Pyrolysis method. The XRD pattern of the CdZnS thin films deposited at different temperature confirms the hexagonal structure with preferred orientation along the (002) plane. The lattice parameter a and c evaluated from the XRD data are well in agreement with the JCPDS data. The mean grain size of the CdZnS thin film calculated from the XRD data lies between 50 and 250 nm. The influence of substrate temperature on the sheet resistance and resistivity of the CdZnS films has been studied and reported. The maximum and minimum optical transmittance of the CdZnS films has been found to be 80% and 20% respectively. The band gap energy of the doped CdS films was 3.3 – 3.5ev. The influence on Substrate Temperature on the structural, electrical, optical and surface properties of the CdZnS thin films have been investigated and the results are elaborately discussed.

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1.Introduction

In the past years, II-IV semiconductor thin films have attracted considerable attention from the research community because of their wide range of application in the fabrication of solar cells and other opto-electronic device with much interest shown in the use of CdS window layer in solar cell architecture. However, the absorption of the blue portion of the solar spectrum by CdS window results in a decrease in the current density of such solar cells and UV laser diodes. For the high performance of solar cell device, it is imperative to use an appropriate window material. Ternary CdZnS thin films often exhibit improved chemical, structural and optical properties and hence are potentially useful as a window layer in solar cell.

CdZns thin films have been prepared by various techniques, such as electro-deposition(1), successive ionic layer adsorption and reaction (SILAR) (2) chemical bath deposition (3,4), spray pyrolysis(5) and metalorganic chemical vapour deposition (6). Among these, spray pyrolysis method is economical, simpler and more versatile than the others and gives the possibility of obtain films with suitable properties for optoelectronic applications and also when large areas are needed. The method is well studied and produces films that have comparable structural and optoelectronic properties to those produced using other sophisticated thin film deposition techniques (4, 7). The technique has been applied in producing emerging materials for solar cells, sensors, laminated sheet glass for transport, protective coating, soar thermal controls in buildings and is being adopted in mass industrial production (8, 9). In this report, the optoelectronic, structural and surface properties of the spray deposition ternary semiconductor thin films of CdZns are presented.

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2. Experimental

Spray pyrolysis is basically a chemical process (5), in which a precursor solution is sprayed onto a substrate held at high temperature, where the solution reacts and forms the desired thin film. Cadmium Chloride, thiourea and Zinc Chloride (Merck brand) are used as starting material for the source of Cd, S and Zn. The precursor solution has been prepared by mixing appropriate amounts of cadmium chloride and zinc chloride in thiourea solution. The optimized coating parameters used in the present work as Substrate – nozzle distance – 30cm, Flow rate of the precursor solution – 20cc/minute and concentration of Cd and S – 1:1. The films have been prepared at different substrate temperature ranging from 325and 450 °C. The developed CdZnS films have been annealed at 300 °C for 2 hours in ambient condition. The precursor solution is prepared by mixing aqueous solution of 0.5 M cadmium chloride, 0.5 M of thiourea and 0.5 M zinc chloride, to get CdZnS thin films with stochiometry $Cd_{1-x}Zn_xS$, (x = 0.006). The CdS and $Cd_{1-x}Zn_xS$ thin films are prepared by spraying the solution onto glass substrates kept at 325 to 450 °C. All films are annealed at 300 °C for 2 hours and 30 min. The film thickness was measured by weight gain method.

The structural properties of CdZnS films are studied by using X-ray diffractometer (XRD) using Cu-Kα radiation with wavelength 1.5418 Å. Surface morphology was examined by Scanning Electron Microscope (SEM). The absorption coefficient (α) and the band gap is determined using the transmission measurement carried out in an UV-VIS Spectrophotometer in the wavelength range 300nm – 900nm.

3. Results and discussion

3.1. Structural Analysis

The XRD pattern of CdZnS thin films deposited at different temperature is shown in fig.1. The XRD pattern shows that the as-grown film possess good crystallinity compared to the annealed films. The planes (101), (002), (100) exhibited the wurtzite (hexagonal type) structure and is well in agreement with with the standard JCPDS data file No. 80.0006. The low intensity peaks observed in the XRD pattern indicate that the films are composed of fine crystallies or nano crystallites. The (002) diffraction peak gives the lattice matching to the chalcogenide semiconductor material, which are used in photovoltaic solar cell (11) and optoelctronic applications. The average crystallite size of the films is calculated from the recorded XRD data using Scherrer relation (1).

$$D = 0.89\lambda/\beta\cos\theta \, . \qquad (1)$$

Where D is the average crystallite size, λ is the wavelength of the incident X-ray, β is the full width at half maximum and θ is the Bragg's angle (5). The average crystallite size of the CdZnS thin film is found to lie between 50 nm and 250 nm(13). The lattice constant a and c are calculated (5) from XRD data using the following relation (2).

$$1/d^2 = 4/3\,(h^2+hk+k^2)/a^2+l^2/c^2 \qquad (2)$$

It is also observed that the lattice constant gradually decreases (10) as the substrate temperature increases (Table 1). We have found that the resistivity of the deposited CdZnS thin films increase from 95 to 10^3 (Ω-cm) as substrate temperature increases from 325 to 450 °C as shown in Table 1.

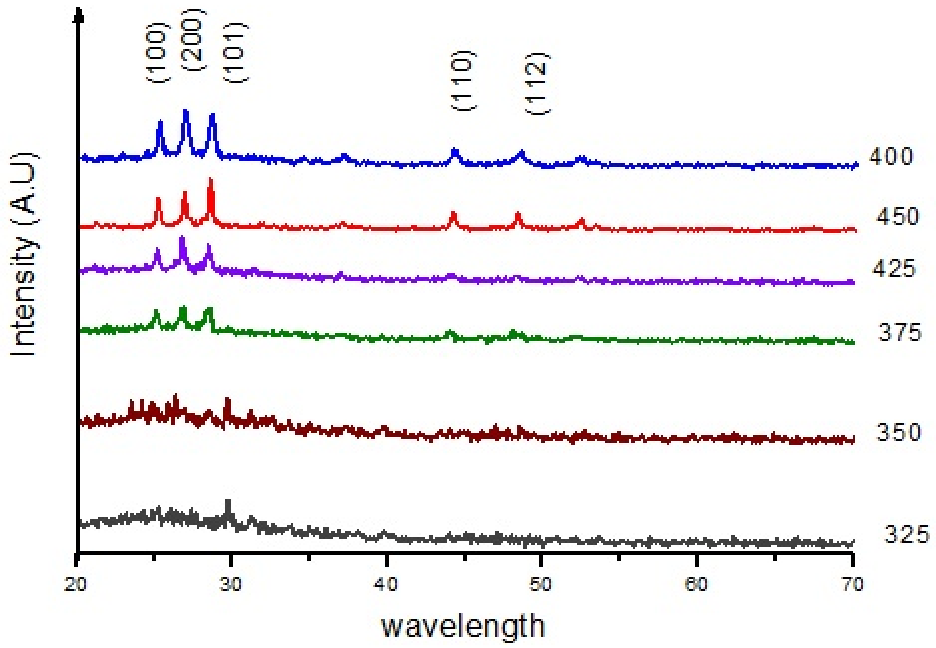

Fig. 1. X-ray diffractrograms of CdZnS thin films deposited at different substrate temperatures 325, 350, 375, 400, 425 and 450 °C.

Table 1. Lattice constant, grain size, optical bandgap and resistivity of the CdZnS thin films deposited at different substrate temperature.

Substrate Temperature	Lattice constant		Grain size nm	Band gap E_g (ev)	Resistivity ρ (Ω-cm)
	a Å	C Å			
325	4.1023	6.6616	250	3.05	95
350	4.0854	6.6324	125	3.35	135
375	3.9580	6.6208	85	3.4	215
400	3.8952	6.5208	75	3.42	750
425	3.7980	6.4035	55	3.45	973
450	3.7045	6.2912	50	3.5	1155

3.2 . Surface Analysis

The surface morphology of the CdZnS thin films is characterized by scanning electron microscopy (SEM) . SEM is a promising technique for the topography study of samples, as it gives important information regarding the growth mechanism, shape and size of the grains. Figure. 2 (a, b, c and d) shows the SEM images of the CdZnS thin films deposited at the substrate temperature 375, 400, 425 and 450 °C. SEM images show that Zn doping has significant effect on the surface morphology of the CdZnS thin film. There are some spheroid shapes growth appears as the creation of nucleation centre on the film surface. These shapes are more visible in fig 2(c) and fig 2(d). These are most probably aggregated due to colloidal particles formed in solution and then adsorbed on the film (10).

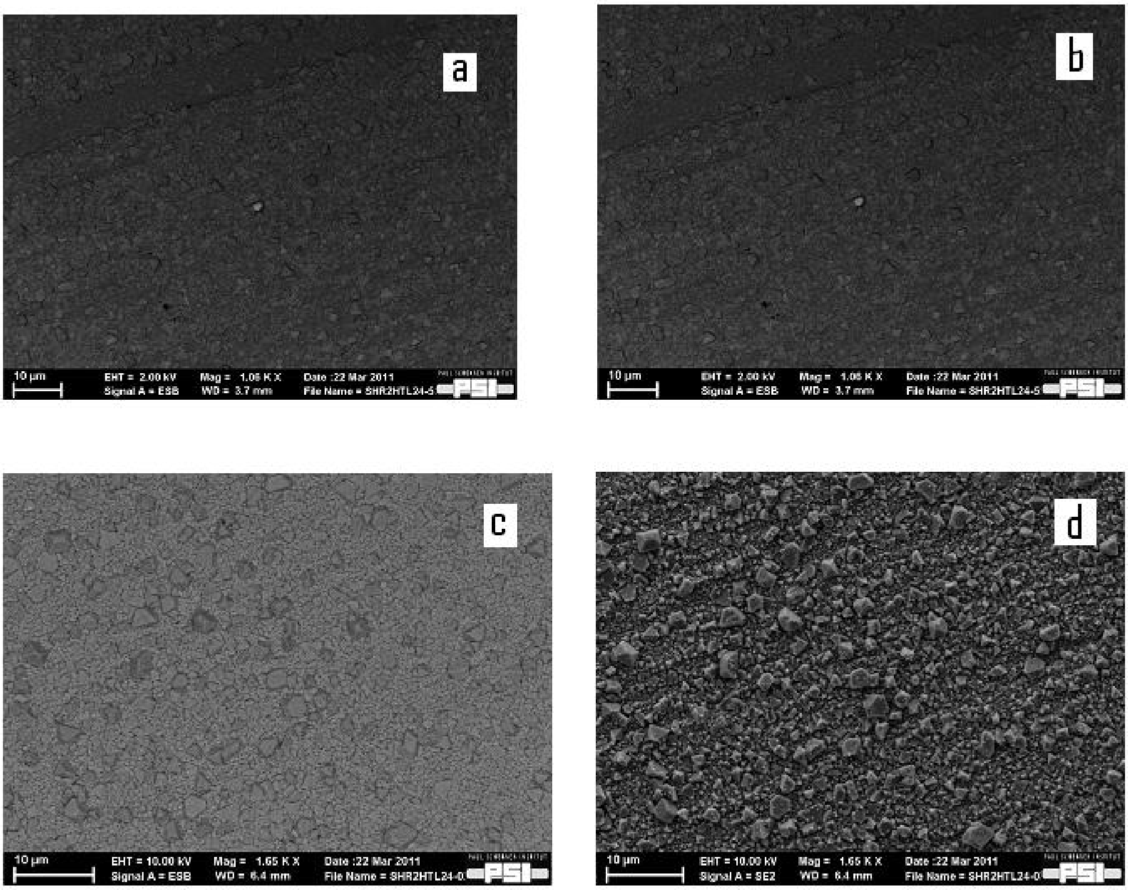

Fig. 2.(a),(b),(c) and (d). SEM micrograph of the CdZnS thin films Spray deposited at the Substrate temperature 375, 400, 425 and 450 °C.

3.3. Optical characterization

The optical Transmission of the CdZnS films are recorded using double beam UV-Visible spectrometer in the wavelength range 300 nm – 800 nm and the transmission spectra is presented in fig. 3(a). The optical data is used to evaluate the absorption coefficient (α), energy band gap (E_g) and nature of transition involved. Optical energy band gap (Eg) can be calculated using absorption coefficient (10). The spectra shows that the adsorption edges are blue shifted. Blue shifting of the absorption edge confirmed that the crystallites in the films decreased with Substrate Temperature. The experimental values of $(\alpha)^2$ plotted against (E) photon energy for CdZnS thin films deposited at different substrate temperature is shown in Fig. 3(b). All the films show high absorption coefficient. The optical band gap vary from 3.05 to 3.5 eV (4). The variation of optical band gap with different substrate temperature is shown in Table.1. It is observed that % Transmittance increases with the increase in substrate temperature of the deposited CdZnS thin films.

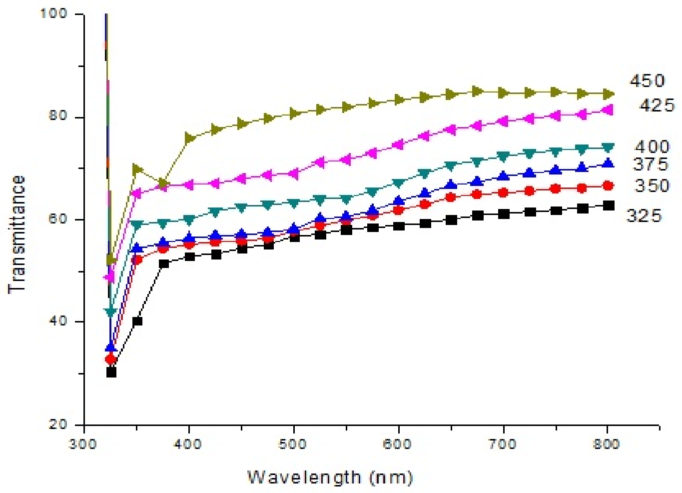

Fig. 3a. Transmission spectra of CdZnS thin films deposited at different substrate temperatures

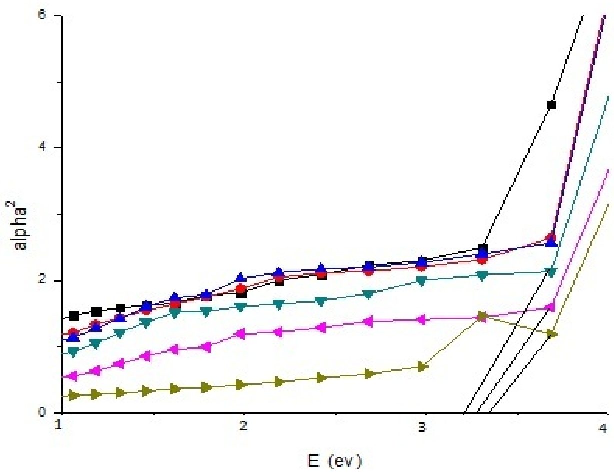

Fig. 3b. Variation of square of the absorption co-efficient with Photon energy

4. Conclusion

CdZnS thin film are deposited on glass substrates using aqueous solution of $CdCl_2$, $ZnCl_2$ and $(NH_2)_2CS$ by spray pyrolysis technique. The XRD study confirms the hexagonal phase of CdZnS thin films. The intensity of the (002) peak is found to be improved for the CdZnS thin films deposited at 425 and 450 °C. The grain size is observed decreasing with the increase in substrate temperature. The (002) peak is found to be dominant for all the CdZnS thin films, indicating the lattice matching to chalcogenide semiconducting materials, which are used in photovoltaic solar cell and optoelectronic devices. Optical study confirms the energy (direct band gap) and is found to decrease with substrate temperature. The range of band gap energy for the mixed films may be helpful in designing a suitable window material in fabrication of solar cells and sensors. The % transmittance is observed to increase with the increase in substrate temperature of CdZnS thin films.

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