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Crystallographic, optical and electrical properties of low zinc content cadmium zinc sulphide composite thin films for photovoltaic applications

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ABSTRACT

In this paper a screen-printing method has been employed for the deposition of low zinc content cadmium zinc sulphide ($Cd_{0.9}Zn_{0.1}S$) composite thin films on ultra clean glass substrate. Cadmium sulphide, zinc sulphide and cadmium chloride have been used as the basic source material. With these basic source materials, the optimum conditions for preparing good quality screen-printed films have been found. X-ray diffraction studies revealed that the films are polycrystalline in nature, single phase exhibiting wurtzite (hexagonal) structure with strong preferential orientation of grains along the (1 0 1) direction. SEM/EDAX analysis confirms the formation of ternary compound. The optical band gap (E_g) of the films has been studied by using reflection spectra in wavelength range 350–600 nm. The DC conductivity of the films has been measured in vacuum by a two probe technique.

1. Introduction

Recent investigations have evoked considerable interest in the II–VI semiconducting compounds because of their wide use in the fabrication of solar cells and other optoelectronic devices [1]. II–VI compound semiconductors, which are based on the elements cadmium, zinc, and mercury in combination with sulphur, selenium and tellurium, can be formed either by co-precipitation or as a composite [2]. II–VI semiconductors with a variable band gap have interesting optical applications such as solar cell, photodetector and laser. Cadmium and zinc compounds are suitable materials for photovoltaic applications since they are direct band gap semiconductors and have high absorption coefficients [2].

Films of $Cd_XZn_{1-X}S$ have found extensive applications in various optical, electronic and opto-electronic devices. The reason is the possibility of tailoring its semiconductor properties between the values corresponding to the pure binaries. This fact allows us to adapt the material properties to the device requirements [3].

Cadmium zinc sulphide thin films have been widely used as a wide band-gap window material in hetrojunction solar cells and in photoconductive devices [4]. In solar cell system, where CdS films have been demonstrated to be effective, the replacement of CdS with higher band gap ternary CdZnS has led to a decrease in window absorption losses resulting in an increase in the short circuit current in the solar cell [5].

Generally CdS and ZnS form solid solution over the entire composition range from $X = 0$ to $X = 1$. However, the use of CdZnS thin films as a window layer also presents a challenging problem due to the change in zinc concentration within the compound changing the lattice parameter. Moreover, a higher zinc concentration leads to a high resistive material increasing the sheet resistance [6]. For best solar cell efficiency, the composition of $Cd_XZn_{1-X}S$ thin film must be in the range $X = 0.9$ to $X = 0.8$ [7]. Therefore this study is focused on the deposition of $Cd_XZn_{1-X}S$ film with low zinc content.

There are various techniques to produce thin films of $Cd_XZn_{1-X}S$ thin films such as chemical bath deposition [8,9], spray pyrolysis [10,11], successive ionic layer adsorption and reaction (SILAR) [12], vacuum evaporation [2,13], dip coating method [14], solution growth technique [1] and screen printing and sintering [15].

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This communication is in continuation of previous research work of the authors [15] in which structural and optical properties of sintered $Cd_XZn_{1-X}S$ films with composition (X = 0, 0.2, 0.4, 0.6, 0.8, 1) were studied. In the present work authors have synthesized the screen printed $Cd_{0.9}Zn_{0.1}S$ films with low zinc content and have investigated the structural, optical and electrical properties of the films. Our intention is to employ this material for the fabrication of photovoltaic devices.

Screen-printing is a very simple and viable technique compared to other costly methods. It is less time consuming, less polluting and ensures optimum material utility and offers a suitable method for preparing films on large area substrates [16,17].

2. Experimental details

Commercially available CdS, ZnS, anhydrous $CdCl_2$ and ethylene glycol of high purity (99.999%) have been used to prepare $Cd_{0.9}Zn_{0.1}S$ screen printed films. $Cd_{0.9}Zn_{0.1}S$ alloy has been prepared by taking stoichiomatric ratio of CdS and ZnS compounds. The different compounds have been taken as follows:

$$\text{Wt. of CdS} = 144.476 \times (0.9)\,\text{g} = 130.0284\,\text{g}$$

$$\text{Wt. of ZnS} = 97.446 \times (0.1)\,\text{g} = 9.7446\,\text{g}$$

$$\text{Wt. of CdCl}_2 = 10\%\,\text{wt of}\,(\text{CdS} + \text{ZnS})\,\text{g}$$

All these weights being very large; were reduced proportionately. All the three compounds were mixed and dispensed thoroughly. Few drops of ethylene glycol have been added to convert it into a paste. Cadmium chloride has been used as an adhesive and ethylene glycol as a binder. The paste thus prepared has been screen-printed on ultra-clean glass substrates, cleaned by emery powder, acetone and finally washed with distilled water. The samples thus prepared have been dried on a hot plate at 120 °C for 4 h in open air. The reason for drying the samples at lower temperature was to avoid the cracks in the samples. The removal of organic materials takes place at about 400 °C, so sintering temperature cannot be less than 400 °C. Cadmium chloride is hygroscopic and its melting point is 568 °C. However, the evaporation of cadmium chloride starts above 400 °C. To get stable films, cadmium chloride and ethylene glycol must not be present in the samples. Optimization of sintering temperature and time has been carried out by performing the experimental process for different values of these parameters. It has been concluded that the samples should be sintered at 500 °C for 10 min in a temperature controlled furnace [18]. The controlling of stoichiometric changes during the sintering of CdZnS films has been reported earlier by the authors [18]. The XRD patterns show that there is no crystal structure with oxides. The problem of diffusion arises due to the temperature gradient during the cooling process, due to upper surface being exposed to air and lower surface being in contact with glass substrate. Hence a temperature gradient is produced between upper and lower surface. Since the diffusivity of Cd is greater than that of Zn, hence due to temperature gradient, diffusion of Cd atoms is more than that of Zn atoms. This result in formation of CdS dominated films. To minimize the problem of diffusion due to the temperature gradient during the cooling of films after sintering, the films have been covered with the glass plates of exact size of substrate [19]. All the films of $Cd_{0.9}Zn_{0.1}S$ system have been deposited under the same experimental conditions. The thickness of films has been determined after sintering by weighing. The thickness of various films has been found to be of the order of 5 μm.

3. Techniques of characterization

The crystallographic study of the films has been performed by a Philips PW 1140/09 X-ray diffractometer using CuKα radiation of wavelength λ = 1.5418 Å. The diffraction patterns have been recorded automatically with scanning speed of 2°/min. Surface morphology has been characterized using a JEOL-VP-4835 scanning electron microscope. The optical reflectance spectra versus wavelength of the films have been recorded in the range of 350–600 nm using a Hitachi U-3400 UV–vis spectrophotometer. The reflection attachment has a 5° specular reflection arrangement. We have used spectrophotometer in repetitive wavelength scanning mode with a scanning rate of 120 nm/min and a band pass of 2 nm. The energy band gap of $Cd_{0.9}Zn_{0.1}S$ film sintered at 500 °C for 10 min has been determined by reflection spectra. The dark DC electrical conductivity of the films has been measured in 300–400 K temperature range by using Keithley two probes set up.

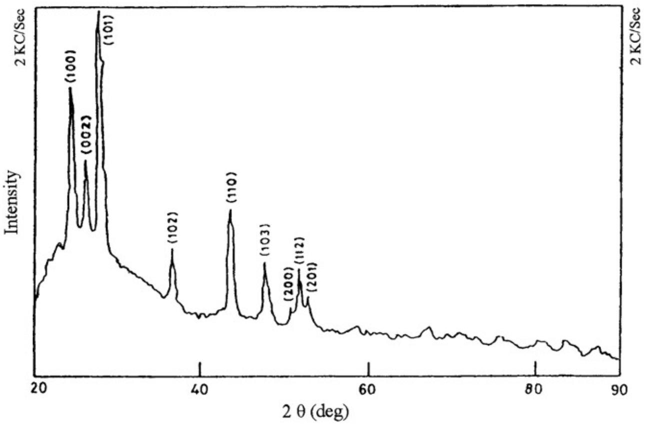

Fig. 1. X-ray diffraction pattern of $Cd_{0.9}Zn_{0.1}S$ screen-printed film.

4. Results and discussion

4.1. XRD studies

X-ray diffraction studies have been carried out on these samples and diffractograms have been analyzed to obtain the information about various crystallographic aspects. XRD traces of all the samples have been taken at room temperature and found to show almost similar trends. The XRD pattern of $Cd_{0.9}Zn_{0.1}S$ screen printed films deposited onto the glass substrate is shown in Fig. 1. The presence of sharp structural peaks in these XRD patterns confirmed the polycrystalline nature of the films. The experimental d-values for $Cd_{0.9}Zn_{0.1}S$ alloy have been calculated from the Bragg's relation $2d_{hkl}\ \sin\theta = n\lambda$, by taking θ values from the peaks of XRD patterns. These d-values have been compared with the standard JCPDS card no. 24-1136 or data obtained from Vegard's law for $Cd_{0.9}Zn_{0.1}S$ alloy for the confirmation of the structure of the film material. The prepared $Cd_{0.9}Zn_{0.1}S$ films have been found to exhibit wurtzite (hexagonal) structure with a preferred orientation along certain crystallographic planes which have been identified as (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (2 0 0), (1 1 2) and (2 0 1) planes respectively, of which the intensity of the (1 0 1) orientation is predominant. In literature, cadmium chalcogenides films have been found to grow in cubic (zinc-blende) or wurtzite (hexagonal) structure [20]. In present work we report the wurtzite (hexagonal) structure of $Cd_{0.9}Zn_{0.1}S$ material. The grain size of the samples have been estimated by 'Scherrer' formula:

$$D = \frac{0.94\lambda}{\beta \cos\theta},$$

where λ is the wavelength of the X-ray source, β is the broadening of the diffraction line measured at half of its maximum intensity (FWHM) and θ is the Bragg's angle in degrees. The estimated size of $Cd_{0.9}Zn_{0.1}S$ crystallites was 10 nm.

4.2. SEM/EDAX analysis

Scanning electron microscopy is a convenient method for studying the micro structure of thin films. Fig. 2 shows SEM image of $Cd_{0.9}Zn_{0.1}S$ screen printed film sintered at 500 °C. SEM indicates that microstructure is polycrystalline, granular and porous in nature. The SEM image clearly illustrates the formation of crystallites distributed more or less uniformly over the surface.

The EDAX (Energy dispersive X-ray analysis) of this micrograph has been consistent with the formation of ternary compound. The approximate elemental ratios have been estimated from peak area analysis as 8:2:10 for Cd:Zn:S respectively.

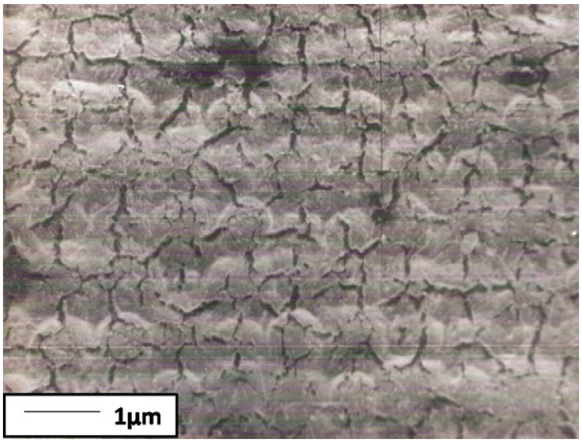

Fig. 2. SEM image of $Cd_{0.9}Zn_{0.1}S$ screen-printed film.

4.3. Optical studies

The optical band gaps of these films have been determined with the help of reflection spectra. Almost all II–VI compounds are direct band gap semiconductors. According to Tauc relation [21], the absorption coefficient for direct band gap material is given by:

$$\alpha h\nu = A(h\nu - E_g)^{1/2},$$

where $h\nu$ is photon energy, E_g is the band gap and A is constant which is different for different transitions. The absorption coefficient α may be written in terms of reflectance as [22].

$$2\alpha t = \ln\left[\frac{R_{\max} - R_{\min}}{R - R_{\min}}\right],$$

where t is the thickness of the film and R is reflectance for any intermediate photon energy. The reflectance falls, from $R_{\max}$ to $R_{\min}$ due to absorption of light by material.

A graph has been plotted between $(\alpha h\nu)^2$ or the square of $h\nu \ln[(R_{\max} - R_{\min})/(R - R_{\min})]$ (as ordinate) and $h\nu$ (as abscissa), which is a straight line. The extrapolation of straight line to $(\alpha h\nu)^2 = 0$ axis gives the value of the band gap of film material. Fig. 3 shows the reflection spectra $Cd_{0.9}Zn_{0.1}S$ screen-printed film. In Fig. 4 a graph has been plotted between the square of $h\nu \ln\left[(R_{\max} - R_{\min})/(R - R_{\min})\right]$ and $h\nu$, for the determination of band gap. In authors previous report on $Cd_XZn_{1-X}S$ screen printed films, it has been reported that band gap of this $Cd_XZn_{1-X}S$ alloy varies from 2.44 eV (for $X = 1$) to 3.5 eV (for $X = 0$) [15]. It has been also concluded that energy band gap of $Cd_XZn_{1-X}S$ alloy increases with increase in zinc concentration. In present study the band gap of $Cd_{0.9}Zn_{0.1}S$ screen-printed film comes out to be 2.53 eV from this plot (Fig. 4). This value of band gap is in good agreement with authors' earlier conclusion and the value reported elsewhere [6].

The mode of optical transitions in these films is of band-to-band direct type. This has been confirmed by plotting $\ln(\alpha h\nu)$ versus $\ln(h\nu - E_g)$ for direct allowed type transitions [23] as shown in Fig. 5. The variation yields a straight line with a slope equal to 1/2.

As given above the absorption coefficient of the film material is proportional to $\ln[(R_{\max} - R_{\min})/(R - R_{\min})]$. The magnitude of α is high and is of the order of 10^4 cm^{-1}. The absorption coefficient increases sharply with photon energy beyond the fundamental absorption edge. The high absorption coefficient and tunable band gap of $Cd_XZn_{1-X}S$ films will be an added advantage with respect to their applications in photovoltaic devices.

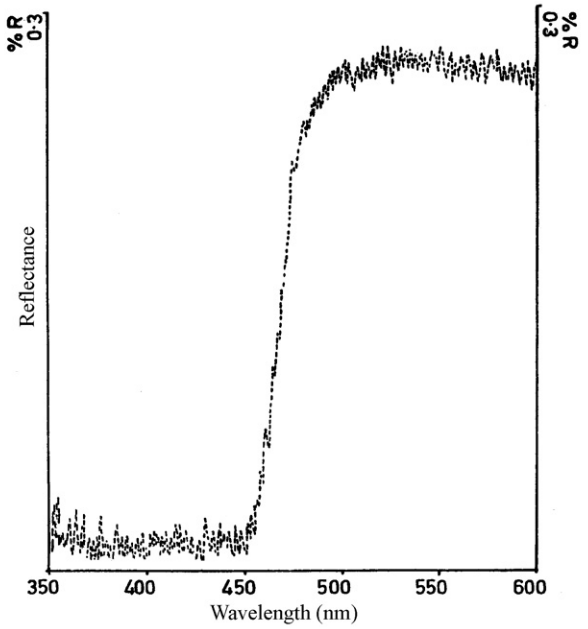

Fig. 3. Reflection spectra of $Cd_{0.9}Zn_{0.1}S$ screen-printed film.

4.4. Electrical studies

The electrical transport properties are of great importance in determining whether the studied material is congruent with our necessities or not. The electrical properties are dependent on various film or growth parameters such as composition, thickness, and substrate temperature and deposition rate. For photovoltaic application, important properties include electrical conductivity [16,17].

The electrical conductivity of screen-printed $Cd_{0.9}Zn_{0.1}S$ films has been measured in temperature range 300–400 K using the Keithley DC two point probes set up in vacuum. Fig. 6 shows the temperature dependence of dark conductivity of the screen-printed

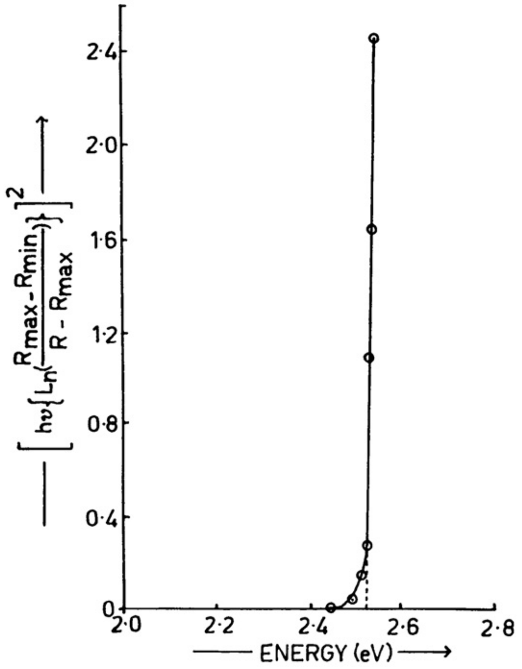

Fig. 4. Energy band gap determination of $Cd_{0.9}Zn_{0.1}S$ screen-printed film from reflection spectra.

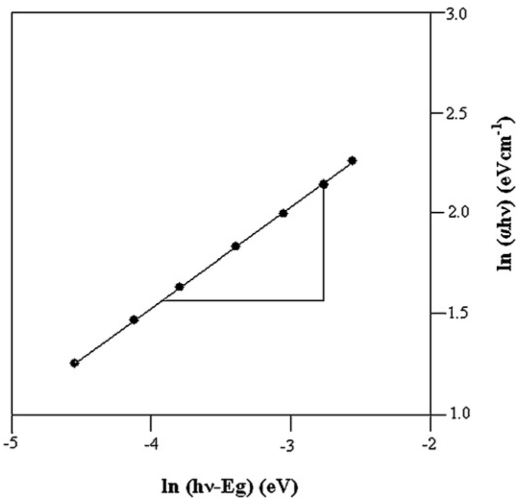

Fig. 5. Plot of ln($\alpha h\nu$) versus ln($h\nu - E_g$) of $Cd_{0.9}Zn_{0.1}S$ screen-printed film.

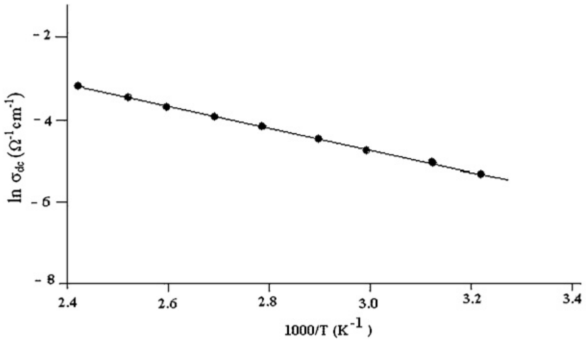

Fig. 6. Temperature dependence of DC conductivity of $Cd_{0.9}Zn_{0.1}S$ screen-printed film.

$Cd_{0.9}Zn_{0.1}S$ film. It has been observed that conductivity increases non-linearly with the increase in temperature. This increase in conductivity can be explained on the basis of the growth of grain size and increase in carrier density. The electrical conductivity depends on the structure of the films. It has been noticed that thick films thus prepared contain lattice defects and randomly oriented grains with the appearance of grain boundaries [24]. An increase in temperature affects the structure of films due to increase of grain size, removal of defects on the surface of films and decrease of grain boundary area. This can be attributed to the migration of smaller crystallites and joining of similarly oriented grains. This brings a decrease in scattering of electrons, which leads to an increase in mobility of charge carriers [24]. The DC conductivity of a semiconductor at temperature T is given by the Arrhenius relation:

$$\sigma_{DC} = \sigma_0 \exp\left(\frac{-\Delta E}{kT}\right),$$

where σ_0 is the pre-exponential factor, ΔE is the activation energy and k is Boltzmann constant.

Linear behavior of plot (Fig. 6) shows that the film conductivity is in good agreement with the Arrhenius relation. The plot of ln σ_{DC} against 1000/T for $Cd_{0.9}Zn_{0.1}S$ film is a straight line indicating that conduction in the film is through thermally activated process. The straight line nature of this plot suggests that grain-boundary limited conduction is the dominant conduction mechanism. The grain boundaries are consequence of imperfections associated with the polycrystalline nature of the films [16,17]. Seto [25] explained the high temperature conduction mechanism in semiconductors. In the present investigation, the dark conductivity of $Cd_{0.9}Zn_{0.1}S$ film comes out of the order of $10^{-3}\ \Omega^{-1}\ \text{cm}^{-1}$ and value of activation energy comes out about 0.17 eV.

5. Conclusions

The method of preparing thin films of low zinc content i.e. $Cd_{0.9}Zn_{0.1}S$ alloy by screen printing method is cost-effective, reasonably accurate and efficient. The structural, optical and electrical studies of these films indicate that the films are quite suitable for photovoltaic device fabrication. The prepared films of $Cd_{0.9}Zn_{0.1}S$ alloy have been found to be polycrystalline in nature and have hexagonal (wurtzite) structure. The energy band gap of $Cd_{0.9}Zn_{0.1}S$ screen-printed comes out to be 2.53 eV. The absorption coefficient of these films is high and is suitable for efficient absorption in the visible region of solar spectrum. It has been observed that the dark DC conductivity of $Cd_{0.9}Zn_{0.1}S$ films comes out of the order of $10^{-3}\ \Omega^{-1}\ \text{cm}^{-1}$ and value of activation energy comes out about 0.17 eV. The conduction in $Cd_{0.9}Zn_{0.1}S$ films is through thermally activated process.

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