OPTICAL PROPERTIES OF SPRAY PYROLYSIS DEPOSITED CDS:Al THIN FILMS

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ABSTRACT

Aluminium doped cadmium sulphide thin films were prepared on glass substrate using aqueous solution of cadmium sulphide and thiourea salts by spray pyrolysis deposition (SPD) technique. Its optical properties were analyzed as a function of doping concentration. The direct energy band-gap of Al-doped CdS films was estimated in the range of 2.25 to 2.48 eV. The optical spectra of $Cd_{1-x}Al_xS$ ternary system exhibit high absorption near visible region and transmission throughout the near-infrared region (600 - 1200 nm). Thus so obtained hetero-junction films are suitable for fabrication of photo detectors, solar cells and other optoelectronics devices.

Key words: CdS:Al, Optical properties, Spray pyrolysis

INTRODUCTION

Focused interests in the material properties of metal-metal chalcognide materials (Thangaraju and Kaliannan 2000), are mainly due to their high efficiency in solar energy conversions such as photo-electrochemical solar cells fabrication (Uda *et al.* 2003). CdS thin films can be prepared by different techniques such as chemical bath deposition (CBD) (Whitley *et al.* 1994), electrodeposition (Fan *et al.* 2003), laser ablation (Raviprakash *et al.* 2009), sputtering (Ubale *et al.* 2007), and vacuum evaporation (Naumov *et al.* 2006). Among these methods, SPD is a very attractive method to produce CdS films for photovoltaic applications for which large-area devices and low-cost processes are involved. Due to the excellent electrical, optical and structural properties, group II-VI semi-conducting materials such as CdS is a prominent material in optoelectronic applications as transparent electrodes, gas sensors (Khan *et al.* 2009), light emitting diodes (LED's), laser systems (Vazquez *et al.* 1998, Natha and Jayasheela 2000) and heterojunction solar cells (McGregor *et al.* 1996) etc. light emitting diodes, photo resistor, optical memories, optical sensors (Takahashi *et al.* 2002), infrared lasers (Shono *et al.* 2000) and as a window (Lozada-Morales and Zelaya-Ange 2004) or an interface layer to produce high efficiency in thin film solar cells owing to its suitable properties. A variety of techniques has been employed to prepare CdS thin films, amongst which spray pyrolysis is simple, inexpensive and enables doping and solid solutions to be
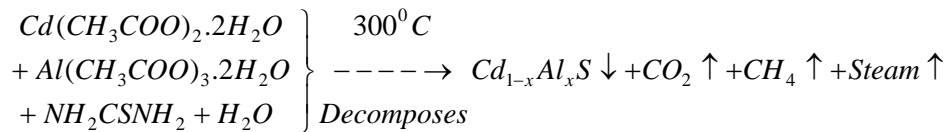
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accomplished. In doping of group III element into II-VI compound has been widely used to decrease the dark resistivity of CdS thin films grown by SPD (Isah *et al.* 2008). In this work, in doping of SPD-CdS using group III elements, namely Al, is investigated. Their material properties are usually affected by the addition of dopant elements. Such impurity affects the band gap tunibility and changes in optical properties have been reported by many researchers (Ilican and Caglar 2007). Although many studies concerning chemically-sprayed CdS thin films are reported in the literature, a lack of information exists concerning the Al variations. Previously we studied the structural and electrical transport properties of CdS and Al-doped CdS thin films (Hasnat and Podder 2012). Transmittance, absorbance, bandgap energy of doped films were carried out in the present work to study the effect of Al doping on the optical properties of SPD-CdS. In section 2 experimental procedure and in section 3 the optical properties of CdS:Al were described.

MATERIALS AND METHODS

The SPD-CdS:Al thin films was carried out in a locally made reaction chamber. Glass substrate was previously cleaned by 24 hours immersion in chromosulphyric acid and rinsed with acetone and double distilled water. In order to prepare $Cd_{1-x}Al_xS$ thin films the aqueous solution of Cadmium acetate [$Cd(CH_3COO)_2.2H_2O$] (Jachon *et al. 2007*), Aluminum acetate [$Al(CH_3COO)_3.2H_2O$] and thiourea [NH_2CSNH_2] (Elangovan and Ramamurthy 2003) were used as the precursor solution. In the work, the concentration of the solution was kept at 0.1 M (Baykul and Balcioilu 2000). The substrate temperature was kept 300^0C and substrate to spray nozzle distance was 25 cm and flow rate of solution was kept constant as 0.5 ml/min, the pressure of the carrier gas (air) was kept constant at 0.5 bar throughout the experiment. All the films annealed at 450°C for one hour (Bagnall *et al.* 2001). The thicknesses of the films were measured by the setup of Fizeau fringes method (Cheng *et al.* 2003). The possible chemical reaction that takes place on the heated substrate to produce $Cd_{1-x}Al_xS$ ternary system may be as follows:

$$\left.\begin{array}{l} Cd(CH_3COO)_2.2H_2O \\ + Al(CH_3COO)_3.2H_2O \\ + NH_2CSNH_2 + H_2O \end{array}\right\} \begin{array}{c} 300^0C \\ \dashrightarrow \\ Decomposes \end{array} Cd_{1-x}Al_xS \downarrow + CO_2 \uparrow + CH_4 \uparrow + Steam \uparrow$$

RESULTS AND DISCUSSION

The optical transmittance spectrum for the $Cd_{1-x}Al_xS$ thin films has been shown in Fig 1. All the films demonstrate more than 75% transmittance at wavelengths longer than 500 nm, which is comparable with the values for the $Cd_{1-x}Al_xS$ thin films deposited by others (Jaehyeong 2004), using chemical bath deposition method. Below 500 nm there is a sharp fall in the T of the films, which is due to the strong absorbance of the films in this

region. Absorbance in the ultraviolet region is high. Absorption increases with the increasing incorporation of Al in the CdS films. Variation of absorbance coefficient (α) as a function of wavelength for $Cd_{1-x}Al_xS$ thin films are shown in Fig. 2. It has been observed that the fundamental absorption edges shift towards the longer wavelength with increasing Al incorporation. Thus the value of absorption coefficient may be calculated from the equation (1) (Hong *et al.* 2005).
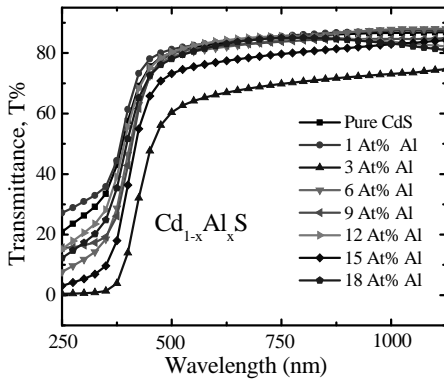
$$\alpha = \frac{\ln(\frac{1}{T})}{t} \tag{1}$$

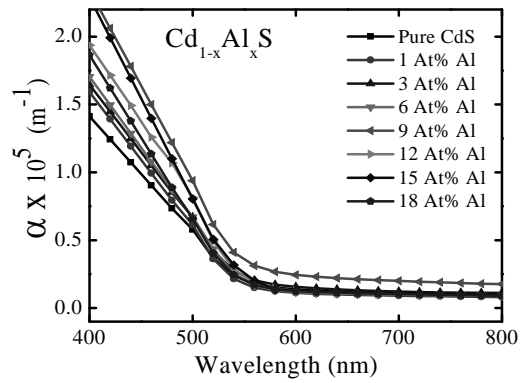Fig. 1. Variation of transmittance as a function of wavelength for $Cd_{1-x}Al_xS$ thin films.

Fig. 2. Variation of absorbance coefficient (α) as a function of wavelength for $Cd_{1-x}Al_xS$ thin films.

In Fig. 3 (a) the variation of $(\alpha h\nu)^2$ vs. photon energy for $Cd_{1-x}Al_xS$ thin films are shown. The optical transmission data were analyzed using the classical relation for near edge of the optical absorption using the relation (2) (Bordas *et al.* 2003) (for $\alpha > 10^4$ cm^{-1}).

$$(\alpha h\nu) = B(h\nu - E_g)^n \tag{2}$$

Where B is a constant in the optical frequency range and E_g is the optical band gap, and n is an index related to the density of state curves for the energy band. This n is determined by the nature of the optical transition involved in the absorption process. Analysis of the data has been made using both n = 1/2. The energy gap in a semiconductor is responsible for the fundamental optical absorption edge. The fundamental absorption process is one in which a photon is absorbed and an electron is excited from an occupied valance band to an unoccupied conduction band. If photon energy is less than the gap energy, such process is forbidden and photon energy will not be absorbed. Such inter band absorption processes are possible only if the photon energy is higher than the gap energy. Since absorption coefficient, is used to describe the reduction in intensity of light in a medium as a function of distance, therefore higher

values of   is an indication of more reduction h   curve. The band gap of the films varied between 2.29 and 2.44 eV. Similarly the indirect band gap of the films has also been calculated from (h)$^{1/2}$ vs. h   curve in Fig. 3 (b).
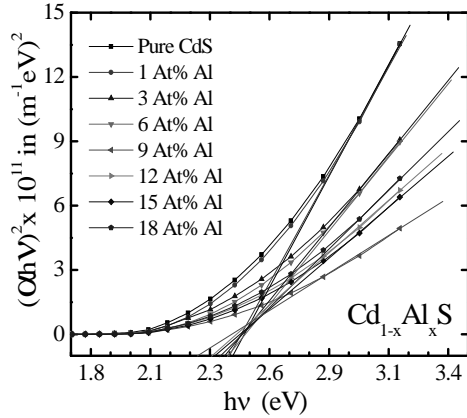
Fig. 3 (a). Variation of (h)^2 vs. photon energy for $Cd_{1-x}Al_xS$ thin films.
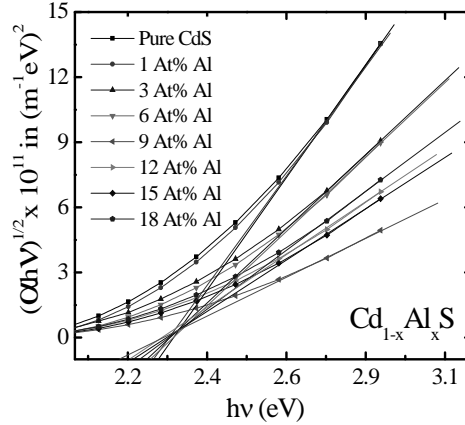
Fig. 3(b). Variation of (h)$^{1/2}$ vs. photon energy for $Cd_{1-x}Al_xS$ thin films.
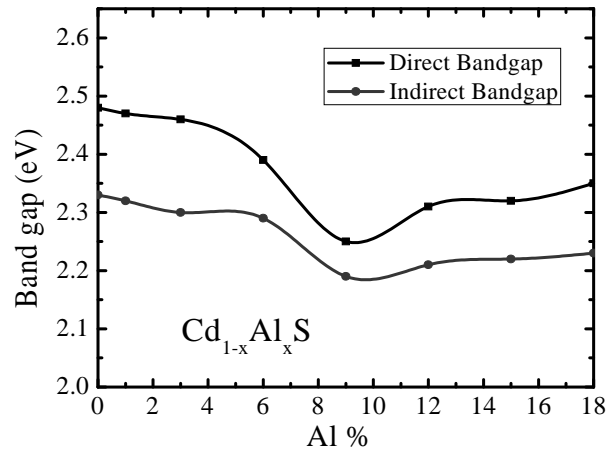
Fig. 3(c). Variation of direct and indirect band gap (eV) with concentration of Al of $Cd_{1-x}Al_xS$ thin films.

It was observed that the band gap of the doped films decreases to minimum of 2.26 eV at a ratio of 0.09, then slightly increases and finally saturates at 2.35 eV as the [Al]/[Cd] ration exceeds 0.18. The undoped film has a band gap of 2.44 eV which agrees well with the 2.42 eV band gap of single crystal CdS (Kumar *et al.* 2008). Incorporation of Al as well as sulfur deficiency in Al-doped films gives rise to donor levels in the band gap of CdS. As the concentration increases which in turn increase the sulfur deficiency, the donor levels become degenerate and merge in the conduction band of CdS, causing the conduction band to extend into the band gap which reduces the band gap. The nature

of this variation in the band gap energy may be useful to design a suitable window material in fabrication in solar cells. Our obtained Eg values are in good agreement with the band gap of $Cd_{1-x}Al_xS$ films deposited by other techniques (Fraas and Ma 1977). The variations of direct and indirect optical band gap with different film concentrations are shown in Fig. 3(c).

CONCLUSIONS

Aluminium doped CdS using SPD proves to be successful. The band gap of doped films was found to decrease at first with the Al concentration and then slightly increases and finally saturates at 2.48 eV. The minimum direct band gap observed was 2.25 at [Al]/[Cd] ratios of 0.09 and this value of band gap is in good agreement with value reported by other workers. Optical transmittance spectra for the $Cd_{1-x}Al_xS$ thin films reveals that all the films demonstrate more than 75% transmittance at wavelengths longer than 500 nm and absorbance is high in the ultraviolet region.

ACKNOWLEDGEMENTS

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