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Optical Properties of Screen Printed Thick Films of $Zn_xCd_{1-X}S$ Solid Solutions Prepared by Flux Technique

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Abstract: $Zn_xCd_{1-x}S$ [$0.1 \leq x \leq 0.9$] solid solutions have been prepared by flux method using Na_2S-S system as a flux. Thick films of each composition are prepared by screen printing technique. UV-vis spectrometry is used to study the optical absorption of the samples. UV-vis spectrometery showed a shift in the absorption edge towards the shorter wavelength side with increasing Zn.

Key words: $Zn_xCd_{1-x}S$, flux method, thick films, screen printing, optical absorption, solid solutions

Introduction

Cadmium sulphide and zinc sulphide, are of widely important in various applications such as optical, electronics, opto-electronics, phosphors and photoconductor etc (Vankar *et al*., 1978; Ballentyen and Ray, 1961; Cherin *et al*., 1970). Mixed crystals of ZnS and CDs have direct band structures with wide bandgap useful for various optoelectronics devices by controlling there composition (Yasuhiro *et al*., 1972). Zn/Cd ratio may be varied to obtain larger bandgaps (Fahrenbruch, 1977). $Zn_xCd_{1-x}S$ films are of considerable interest in heterojunction solar cells and photovoiltaic application (Romeo *et al*.,1978; Burton *et al*., 1979). Energy gap of $Zn_xCd_{1-x}S$ is the controllable function of composition. Studies on preparation and properties of electrodeposited $Zn_xCd_{1-x}S$ films are carried out by Edamura and Muto (1993). $Zn_xCd_{1-x}S$ thin films grown by ion-beam deposition reported by Kuroyanagi (1994). Chemically prepared thin films of (Cd,Zn)S for photovoltaic devices are investigated by Yamaguchi *et al*. (1996). A simple method to determine the optical constants and thicknesses of $Zn_xCd_{1-x}S$ thin films have been reported by Torres *et al*. (1996). Preparation and Optical properties of $Zn_xCd_{1-x}S$ films are reported by Shimaoka and Suzuki (1997). Structural, compositional, optical and electrical properties of solution-grown $Zn_xCd_{1-x}S$ films have been reported by Kuhaimi and Tulbah, (2000). Studies on $Zn_xCd_{1-x}S$ nanocrystals have been carried out by Zhong *et al*. (2003). High quality $Zn_xCd_{1-x}S$ nanocrystals are reported by Zhong *et al*. (2004).

Many of the II-VI compounds, such as ZnS and CDs form solid solutions over the complete composition range (Aven and Prener, 1967). There are various methods for preparation of $Zn_xCd_{1-x}S$ solid solutions (Scheel, 1974; Patil *et al*., 1998a,b; Garner and White, 1970). The solid solution $Zn_xCd_{1-x}S$ have been prepared by flux techniques (Bidnaya *et al*., 1962; Patil and Wani, 2001; Patil *et al*., 1998a,b) to form a continuous series of solid solutions. Flux techniques is very convenient and simple method to prepare high quality homogeneous solid solutions with potentials of up- scaling. This technique permits solid solutions well below the melting point of material. Doping with suitable elements can be easily achieved. Non-stoichiometric forms of solid solutions are obtainable. Equipments required are simple and within the financial scope of the most laboratories. Efforts are made to understand optical absorption of $Zn_xCd_{1-x}S$ in thick film form.

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This study describe the method of preparation of solid solution and thick film of $Zn_xCd_{1-x}S$ of entire range by flux method. The variation of energy gap with the thick films of mole percent of ZnS was investigated by studying optical absorption of $Zn_xCd_{1-x}S$.

Materials and Methods

Preparation of $Zn_xCd_{1-x}S$ Solid Solutions by Flux Method

The hydrated sodium sulphide ($Na_2S.9H_2O$), high purity sulphur and an appropriate wt.% of coarse zinc and cadmium powders were used as starting materials. Preparation procedure of one of the compositions (x = 0.1) is explained as follows.

Preparation of $Zn_{0.1}Cd_{0.9}S$

High purity hydrated $ZnCl_2$ [0.9M] and $CdCl_2$ [0.1M] were mixed throughly into an appropriate amount of sulphur and $Na_2S.9H_2O$. The mixture was transferred into platinum crucible. The crucible was placed in kanthol wound muffle furnace. The space around and above the crucible was filled with coarse corrundum powder. The furnace temperature was increased to 600°C. This temperature was then maintained for an hour. The furnace was then cooled to room temperature. Excess sulphur evaporated and removed the residual oxygen and water as SO_2 and H_2S, respectively. The product in the crucible was washed with double distilled water. Sodium polysulphides got dissolved in water and separated out easily. The final product was dried. Same procedure was adopted to synthesize the other compositions (x = 0.2 to 0.9). CDs and ZnS powders were also prepared using the same procedure.

Preparation of $Zn_xCd_{1-x}S$ Thick Films

Thick films of each composition were prepared by screen printing technique. The powder of a particular composition prepared using the method as mentioned above was ball milled in ethanol for 24 h to ensure sufficiently fine particle size. The thioxotropic paste was formulated by mixing fine solid solution powder with solution of ethyl cellulose (a temporary binder) in a mixture of organic solvents such as butyl cellulose, butyl carbitol acetate and terpineol (Amalnerkar *et al*., 1980; Yang and Im, 1986; Patil *et al*., 1998a,b; Fu *et al*., 1985a,b). The ratio of inorganic part to organic part was kept as 75:25 in formulating the paste. The paste was screen printed on glass and alumina substrate in the pattern suitable for measurements. The films were fired at 550°C in air for 10 min.

UV-vis Spectrometry Analysis of the Film

UV-vis spectrometry was used to study the optical absorption of the samples. Band gap energy of each sample were determined from the corresponding absorption spectra.

Results

UV-vis Spectrometry

Figure 1 represents the absorption spectra of CDs, $Zn_xCd_{1-x}S$ (x ranging from 0.1 to 0.9) and ZnS. It is clear from Fig. 2 that absorption edges go on shifting towards shorter wavelength side with increasing Zn content in the composition. Figure 3 represents gradual increase in band gap energies from 2.41 eV (CDs) to 3.72 eV (ZnS) with increasing Zn content.

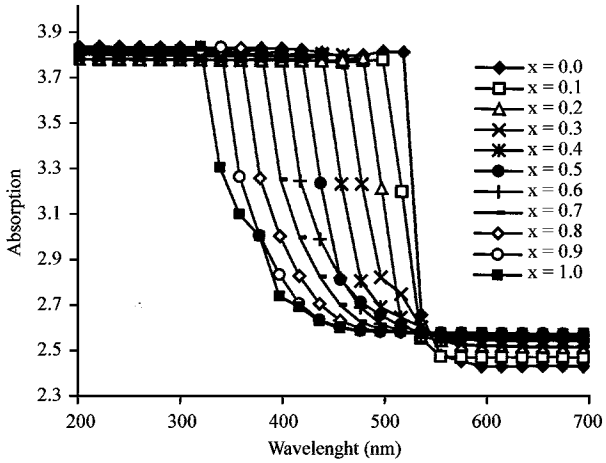

Fig. 1: Absorption spectra of $Zn_xCd_{1-x}S(0 \le x \le 1)$ thick films

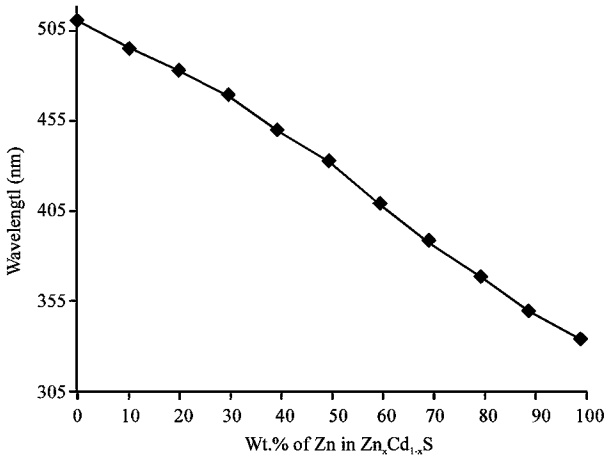

Fig. 2: Shifting of absorption edge with wt.% of Zn in $Zn_xCd_{1-x}S$

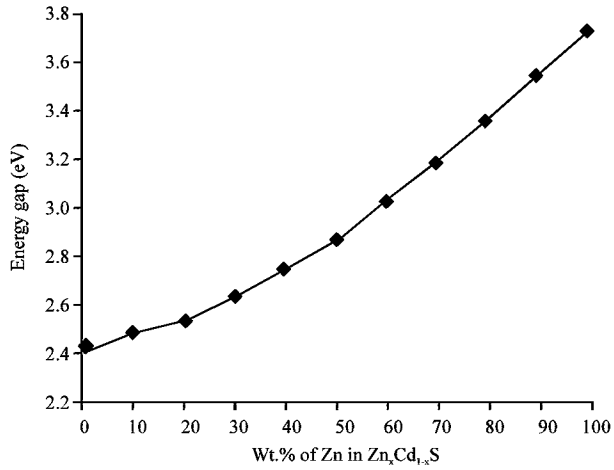

Fig. 3: Variation of energy gap with wt.% of Zn in $Zn_xCd_{1-x}S$

Discussion

Homogeneous $Zn_xCd_{1-x}S$ solid solution was prepared by flux technique using Na_2S_x as fluxing agent. High purity $ZnCl_2.H_2O$, $CdCl_2.H_2O$, sulphur and Na_2S_x were mixed in appropriate proportion and then heated slowly upto certain temperature followed by slow cooling (Patil and Wani, 2001). The $Zn_xCd_{1-x}S$ compound could be possible as :

$$(ZnCl_2)_x+(CdCl_2)_{1-x}+S+Na_2S_x \xrightarrow{\text{Heat}} Zn_xCd_{1-x}S+xNaCl$$

The end product was washed with distilled water to remove the NaCl. Extra amount of sulphur would evaporate during heating. XRD confirmed the homogenity and single phase of the $Zn_xCd_{1-x}S$. The compounds so prepared was screen printed to obtain thick films. The optical absorption of as prepared compounds were studied. It is clear from Fig.1 that the absorption edge goes on shifting towards smaller wavelength side with the increase of wt% of zinc in $Zn_xCd_{1-x}S$. There is the blue shift of absorption edge with the increase of zinc. The band gap energy goes on increasing with the increase of zinc in $Zn_xCd_{1-x}S$ (Fig. 3). The band gaps of some of the compositions from $Zn_xCd_{1-x}S$ have been reported in literature (Oktik *et al*., 1982). These reported values are matching well with the estimated values of present article. The band gap of CDs and ZnS are 2.41 and 3.72 eV, respectively. The band gap energy of member compounds from $Zn_xCd_{1-x}S$ (x = 0.1 to 0.9) was observed to vary from 2.41 to 3.72 eV. Thus it is possible to obtain the materials having band gap energies from 2.41 to 3.72 eV.

Conclusions

- Flux method is the simplest and economical method to obtain sulphides.
- Thick films could be prepared at room temperature. So materials in thick film form can be studied without affecting their temperature sensitive properties.
- Properties of bulk materials were obtainable through the thick films.
- Band gap energy of $Zn_xCd_{1-x}S$ is controllable function of composition.
- Band gap values of $Zn_xCd_{1-x}S$ go on increasing from 2.41 to 3.72 eV with increase in concentration of Zn.
- The absorption edges go on shifting towards shorter wavelength side with increasing Zn content in the composition.

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