Preparation and Characterization of Spray Pyrolysed ZnS Thin Films and the Effect of Chlorine Doping

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Abstract. Employing low cost spray pyrolysis technique, ZnS thin films were prepared, using different precursors and by varying sulfur concentration. Effect of chlorine doping was studied on all the samples. Characterization of the sprayed ZnS thin films was done using XRD, UV-Vis-NIR spectrophotometer and fluorimeter. ZnS thin films prepared using zinc chloride precursor showed better crystallinity. An obvious variation in band gap and photoluminescence was observed with variation in sulfur concentration in ZnS samples.

Keywords: Zinc sulfide, Spray pyrolysis, photoluminescence
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INTRODUCTION

Zinc sulfide (ZnS) is an important wide band gap [3.65eV] binary semiconductor material. Bulk and thin film forms of this material have been receiving ever increasing attention owing to different potential uses. ZnS is highly suitable as window layer in heterojunction solar cells due to its wide band gap, low window absorption losses and hence improved short circuit current of the cell.

Chemical spray pyrolysis [CSP] which is inexpensive, simple and useful for depositing large area uniform and homogeneous layers, was used in the present work for preparing ZnS thin films. In this technique, usually aqueous solution is sprayed directly onto the substrate at high temperature and the details about spray parameters are given elsewhere [1].

EXPERIMENTAL

Two precursors were used to prepare ZnS thin films; the first one containing zinc acetate and thiourea while the second one containing zinc chloride and thiourea[2]. The solution was sprayed on to the substrate kept at 440^0 C, at a spray rate of 5 ml/min. Volume of the solution sprayed was 50 ml. Zinc to sulfur ratio was varied from 1: 0.25 to 1: 6. Structural analysis was done using Rigaku X-Ray diffractometer. Absorption studies were done using JASCO V-570 Spectrophotometer.

RESULTS AND DISCUSSIONS

There was a clear variation in the crystallinity of films containing chlorine. Acetate based ZnS films were amorphous while chloride based films were crystalline [Figure 1] having hexagonal wurtzite structure with lattice parameters a=3.82Å and c=24.96Å (JCPDS card no.72-0163). Since chloride based films were crystalline, ratio variation was tried to monitor the variation in crystallinity [Figure 2].

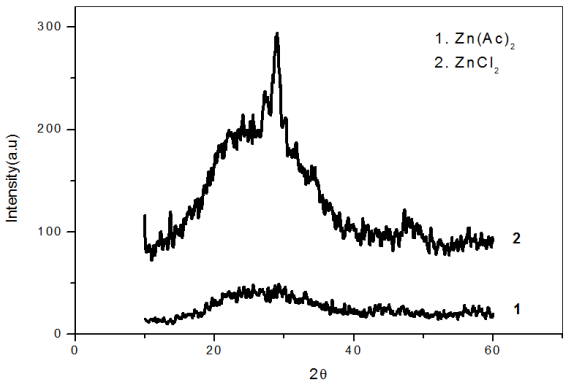

FIGURE 1. Comparison of XRD patterns of ZnS thin films prepared from zinc acetate and zinc chloride precursors

In the X-Ray Diffraction pattern, the peak at $2\theta=29.15^0$ corresponding to (103) plane, confirmed the

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crystallinity of ZnS [JCPDS card number 72-0163]. The films were better crystalline for Zn: S = 1:4. From the XRD Analysis [Figure 2] it was also found that the crystallinity and orientation are dependent on sulfur concentration.

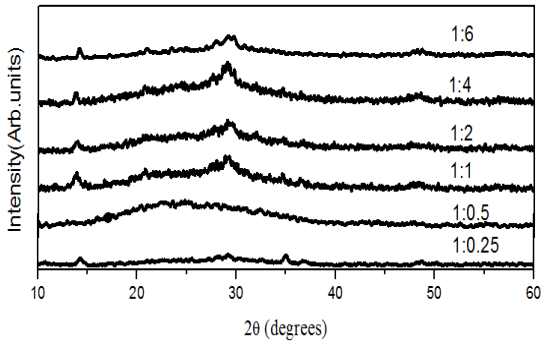

FIGURE 2. The variation in crystallinity of ZnS thin films for different Zn: S ratios.

The variation in band gap of ZnS thin films with varying sulfur concentration is clearly visible in the absorption spectra [Figure 3].

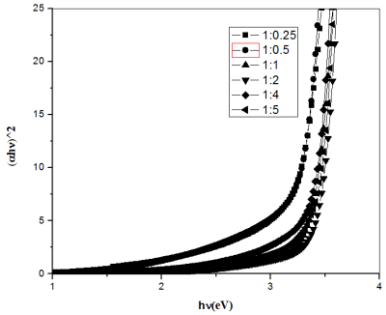

FIGURE 3.The variation in band gap of chloride based ZnS thin films with sulfur concentration.

The band gap varied from 3.2 eV to 3.5 eV with variation of sulfur concentration.

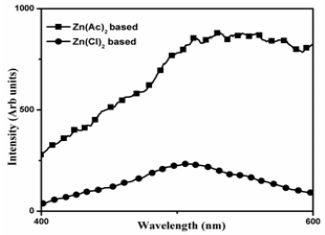

FIGURE 4. PL spectra of ZnS thin films prepared using $Zn(Ac)_2$ and $ZnCl_2$ precursors

Photoluminescence [PL] studies were also conducted on these samples.From the Photoluminescence spectra [Figure 4] it is quite obvious that the emission from $ZnCl_2$ based films are well defined in comparison with that from $Zn(Ac)_2$. Broadening and/or increase in FWHM of PL spectra are an indication of loss of crystallinity of the films.

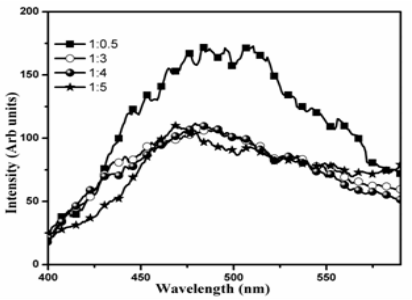

FIGURE 5. The variation in PL from chloride based ZnS films with sulfur concentration.

It could also be observed that among the various Zn:S ratios tried out, $ZnCl_2$ based films with Zn:S=1:4, exhibited PL emission around 490nm with the least FWHM [Figure 5]. This emission has been reported to be due to a transition between sulphur vacancies (V_s) and a self-activated vacancy of zinc (V_{Zn}) acceptor [3]. Also the sulphur deficient samples showed an emission around 430nm which has been reported as V_s-VB (valence band) transition.

CONCLUSION

ZnS films were deposited by CSP technique using automated spray machine. Better crystalline films were obtained from precursors containing chlorine. The band gap varied with variation in sulfur concentration. The PL studies supported the effect of chlorine viz., improvement of crystallinity.

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