Study of Structure, Composition and Optical Properties of ZnS_{0.5}Se_{0.5} Films as a Function of Sintering Temperature

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Thin films of ZnS_{0.5}Se_{0.5} have been prepared on glass substrate by screen printing method followed by sintering process using ZnS, ZnSe, ZnCl₂, H₂O and ethylene glycol as a binder. To deposit good quality films, optimum conditions have been determined. The structure, composition and optical properties of these films have been investigated as a function of sintering temperature. The layers grown below 400°C shows secondary phases of ZnS, ZnSe and ZnCl₂ in conjunction with a ZnS_{0.5}Se_{0.5} phase. At growth temperatures above 400°C, all the secondary phases start to disappear favouring the formation of ZnS_{0.5}Se_{0.5}. Polycrystalline ZnS_{0.5}Se_{0.5} films with a strong (200) orientation were grown at a sintering temperature of 500°C. These layers have the wurtzite crystal structure. The band gap of these films are determined by reflection spectra in the wavelength range (325 – 600) nm using Tauc relation. These films have a direct band gap. The energy band gap was found to be 2.82 eV for ZnS_{0.5}Se_{0.5} film.

Keywords: Zn-S-Se, Band gap, Screen printing, Sintering, Reflection spectra.

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1. Introduction

The II – VI compounds, ZnS (Eg = 3.50eV) and ZnSe (Eg = 2.66 ev) have proved to be useful for the fabrication of a wide range of opto-electronic devices. ZnS_{x}Se_{1-x} is an alloy of these compounds and it is possible to alter the energy band gap, lattice constant and electron affinity by changing the ratio of S to Se in the material. There are reports in the literature that ZnSe (S) can be used as a buffer layer in polycrystalline thin films heterojunction solar cells, as a Cd – free alternative to replace CdS usually used, and also to improve the blue response of the cells [1-3]. Thin films of ZnS_{x}Se_{1-x} have been deposited by a variety of techniques [4-9]. Most of these techniques involve the use of either sophisticated deposition facilities, which increase the fabrication costs or using toxic gases like H₂S and / or H₂Se. In present work screen printing technique followed by sintering has been used to deposit thin films of ZnS_{x}Se_{1-x}. The screen printing technique is simple, inexpensive, viable and attractive means of obtaining films of II-VI semiconductors [10-12]. In this work variations in the structure, composition and optical properties of the grown films with sintering temperature are reported and discussed.
2. Experimental details

For the preparation of ZnS$_{0.5}$Se$_{0.5}$ an appropriate amount of ZnS, ZnSe, ZnCl$_2$. H$_2$O and ethylene glycol as a binder were thoroughly mixed. The compositions of materials were taken as:

\[
\begin{align*}
\text{wt of ZnS} &= 97.446 \times 0.5 \text{ gm} \\
\text{wt of ZnSe} &= 144.330 \times 0.5 \text{ gm} \\
\text{wt of ZnCl}_2 \cdot \text{H}_2\text{O} &= 10\% \text{ wt of } (\text{ZnS + ZnSe})
\end{align*}
\]

If the weights are large, we can reduce the weights in same proportion. These three materials were mixed properly along with the weight of ethylene glycol. The paste thus prepared was screen printed on a glass substrate which has been cleaned properly. The samples thus prepared were dried at 120$^\circ$C for 4h and then sintered by varying temperature range 400 – 500 $^\circ$C for 10 min in air atmosphere to remove the organic materials left. To minimize the diffusion problem, the film was covered with a glass plate of substrate size. The thickness of these prepared films is of the order of a micron

3. Techniques of characterization

The optical reflectance versus wave length traces of all the films were recorded in 325 – 600 nm wavelength range using a double beam spectrophotometer (Hitachi U – 3400). The XRD traces were recorded using Philips X – ray diffractometer using CuK$_\alpha$ radiation.

4. Results and discussion

All the films prepared by this method are smooth, uniform and adherent to substrate surface. The X-ray diffraction spectra of the films prepared at various sintering temperatures showed the presence of different peaks. ZnS$_{0.5}$Se$_{0.5}$ films prepared at temperature $\leq 400$ $^\circ$C indicated various peaks corresponding to ZnS, ZnSe and ZnCl$_2$ in addition to ZnS$_{0.5}$Se$_{0.5}$. The appearance of secondary phases was probably due to the insufficient thermal energy required to form the ternary ZnSSe at such temperatures. With the increase of sintering temperature, the intensity of peaks corresponding to ZnS$_{0.5}$Se$_{0.5}$ phase increased while those due to the presence of secondary phases vanish. This indicated that ZnS, ZnSe and ZnCl$_2$ phases observed at temperatures $\leq 400$ $^\circ$C reacted together at higher temperatures leading to the formation of the ZnS$_{0.5}$Se$_{0.5}$ phase. However for deposition temperatures $\geq 500$ $^\circ$C a ZnO phase was observed in the films in conjunction with ZnS$_{0.5}$Se$_{0.5}$ phase. This might have been due to the formation of oxides during sintering of these films [13].

ZnS$_{0.5}$Se$_{0.5}$ films deposited at substrate temperatures in the range 400 – 500 $^\circ$C was polycrystalline in nature with the appearance of many reflections corresponding to the ZnS$_{0.5}$Se$_{0.5}$ phase. Fig. 1 shows the X-ray diffraction pattern of a ZnS$_{0.5}$Se$_{0.5}$ film formed at 500 $^\circ$C. The diffraction pattern exhibits different peaks that correspond to (112), (200), (103), (110), (102), (101), (002), (100) planes of ZnS$_{0.5}$Se$_{0.5}$. The appearance of these peaks indicates the hexagonal (wurtzite) structure of ZnS$_{0.5}$Se$_{0.5}$ films. In literature ZnS$_x$Se$_{1-x}$ films have been found to grow either in sphalerite or wurtzite or a mixture of both the structures depending on deposition process [9, 14].
Figure 1. X-ray diffraction pattern of ZnS₀.₅ Se₀.₅ sintered film.

In fig.1 all the peaks are indicated and which shows the formation of ZnS₀.₅ Se₀.₅ composite excepting two peaks, which show traces of ZnO, which are also present in this composite due to oxide formation during the sintering of the films.
Fig. 2 shows the relative variation of the full width at half maximum (FWHM) of the (200) and (110) peaks with sintering temperature. The relative FWHM values decreased with increase of sintering temperature. This indicates an improvement in the crystallinity of the films with increasing sintering temperature.

The optical reflectance of the films was studied in the wavelength range 325-600 nm at room temperature. Fig. 3 shows the variation of reflectance with wavelength of a single phase ZnS$_{0.5}$Se$_{0.5}$ film. The optical band gaps of these films were determined with the help of reflection spectra [15]. Almost all the II – VI compounds are direct band gap semiconductors. According to Tauc relation [16], the absorption coefficient for direct band gap material is given by
Figure 3. Reflection spectra of ZnS$_{0.5}$Se$_{0.5}$ sintered film.

\[ a\hbar = A(h\nu - E_g)^n \]

where \( h\nu \) is photon energy, \( A \) is the constant, \( E_g \) is the band gap and \( n \) is equal to \( \frac{1}{2} \) for direct band gap material. To measure energy band gap from reflection spectra a graph between \( (a\hbar)^2 \) vs \( h\nu \) is plotted. Absorption coefficient \( \alpha \) is proportional to the reflection coefficient \( R \) as explained in equation [15] where reflectance falls from \( R_{\text{max}} \) to \( R_{\text{min}} \) due to absorption by the material and \( R \) is the reflectance for any intermediate energy photons. So \( \alpha \) is used in terms of reflectance as \( \ln[h\nu(R_{\text{max}} - R_{\text{min}})/(R_{\text{max}} - R_{\text{min}})] \) and extrapolation of straight line to \( (a\hbar)^2 = 0 \) axis give the value of energy band gap of the film material.
Fig. 4 shows a plot between \( \frac{h\nu \ln(R_{\text{max}} - R_{\text{min}})}{(R - R_{\text{min}})} \) versus \( h\nu \) for sintered ZnS\(_{0.5}\) Se\(_{0.5}\) film. The extrapolation of straight line to \((ah\nu)^2 = 0\) gives the value of direct band gap. From this graph, the value of energy band gap comes out to be 2.82 eV.

**5. Conclusions**

The present study demonstrates that a polycrystalline ZnS\(_x\) Se\(_{1-x}\) films may be prepared using simple & low cost deposition process. The ZnS\(_{0.5}\) Se\(_{0.5}\) films prepared by screen printing technique have the wurtzite crystal structure with a (200) preferred orientation. The films prepared are smooth, uniform and adherent to substrate surface. The optical band gap of film was found to be 2.82 eV. The presence of intense X - ray diffraction peaks confirms the good quality of the films produced. These results show the excellent promise of both the technique as well as the material (Zn-S-Se) for making low cost, cadmium free layers for use in thin film solar cells.

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