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Optical characteristics of undoped and Mn doped ZnS films

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Undoped and Mn doped ZnS films were prepared in the temperature range 250–350°C by the spray pyrolysis technique. As the deposition temperature increased, the optical transmittance and the intensity of blue emission in the ZnS film were enhanced due to the decrease in the Zn/S ratio. By adding the manganese ion up to 7 at.% in the mixed solution, the orange-yellow emission of the films was enhanced. But the concentration quenching effect resulted in the decrease of the emission at higher concentration of the manganese ion.

1. Introduction

Nowadays, large-area display devices are considered as a promising idea to motivate the research for the flat panel display. A systematic study of the luminescence of ZnS : Mn layers has been continued to investigate for the phenomenon of electroluminescence. The IIb-VIb compound such as zinc sulfide is used as a host matrix for the luminescent devices because of the wide band gap (≈3.7 eV), good quality of the optical transmittance, and low scattering in the visible and infrared region [1]. Luminescent centers incorporated into the host matrix as the dopants should have the deep energy levels and high driving voltage stability. The transition elements, rare-earth elements, and fluorides were reported as the activators. Among them, the Mn^{2+} ion with similar ionic radius and same charge with Zn^{2+} ion can be the efficient luminescent center of ZnS films.

The Spray pyrolysis technique involves a thermally stimulated chemical reaction between clusters of the liquid/vapor atoms of different chemical species [2]. Since Foex [3] obtained conducting transparent oxides from the $SiCl_4$ solution, various thin films and bulky powders have been achieved. In this work, the undoped and Mn doped ZnS films were prepared from the solution of zinc chloride, thiourea, and manganese chloride tetrahydrate by spray pyrolysis technique. The structural, compositional, and optical characteristics of the films were investigated as a function of the deposition temperature and content of the manganese ion.

2. Experiment

ZnS and Mn doped ZnS films were prepared from a mixed solution of 0.7 M zinc chloride and thiourea ethylalcohol. Mn doping was processed by adding the manganese tetrahydrate in the mixed solution with a concentration range from 0 to 20 at.%. A few drops of hydrochloric acid were added to the solution to dissolve some precipitates resulting from the decrease of pH on adding manganese chloride to the mixed solution [2]. The mixed solution was sprayed through the Pyrex glass nozzle and carried to the substrate by nitrogen as a carrier gas at a fixed flow rate of 10 *l*/min as shown in Fig. 1. The single crystal (100) silicon and corning glass were used as substrates. The substrate temperature was varied from 250 to 350°C. The thickness of the film was about 4000 Å.

The films were subjected to the structural analysis by X-ray diffractometer (Philips PW 1710). The quantitative compositions of the films were analyzed by energy dispersive spectroscopy (EDS, S-2700, Hitachi). Transmission (%) of the films was obtained in the range of 400–8000 cm^{-1} from the measured absorption data of IR spectra by Fourier transform infrared spectroscopy (FT/IR-300E, Jasco, Japan). Transmittance of the films was characterized in the wavelength range from 200 to 800 nm by UV-VIS-NIR spectrophotometer (UV-VIS-NIR recording spectrophotometer, UV-3100, Shimadzu). The room temperature photoluminescence spectra were measured by spectrofluormeter with excitation wavelength of 320 nm monochromatic light from 150 W Xenon lamp.

3. Results and discussion

The cubic phase sphalerite structure was obtained in the ZnS films deposited at 250–350°C. As shown in Table I, The compositional analysis of ZnS films by EDS showed that there was higher chlorine concentration in the film deposited at 250°C than the others. The ZnS film deposited at 250°C contained about 6 at.% chlorine, but the ZnS film deposited at 350°C contained only about 0.15 at.% chlorine. It was considered that high concentration of chlorine was remained in the film prepared at low substrate temperature because of surface cooling effect resulted in insufficient thermal decomposition of $ZnCl_2$ and intermediate compounds [2, 4, 5]. Fig. 2 shows the IR spectra of ZnS films deposited at 250–350°C in the range of 1300–5000 cm^{-1}. Three absorption peaks were observed in 1500–1900,

TABLE I Compositional analysis of ZnS films deposited at 250°C, 300°C and 350°C characterized by EDS

Deposition Temperature	Zn (at.%)	S (at.%)	Cl (at.%)	Zn/S
250°C	51.01	43.13	5.86	54.19
300°C	52.70	44.69	2.61	54.11
350°C	52.74	47.11	0.15	52.82

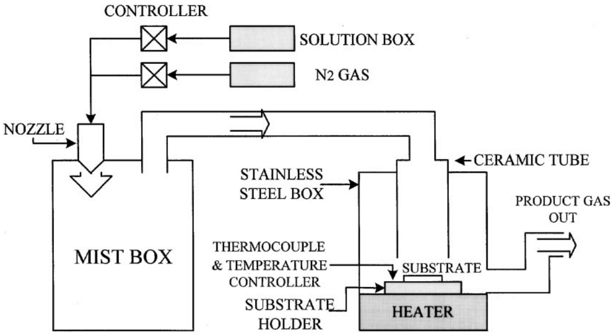


Figure 1 Schematic diagram of setup for spray pyrolysis.

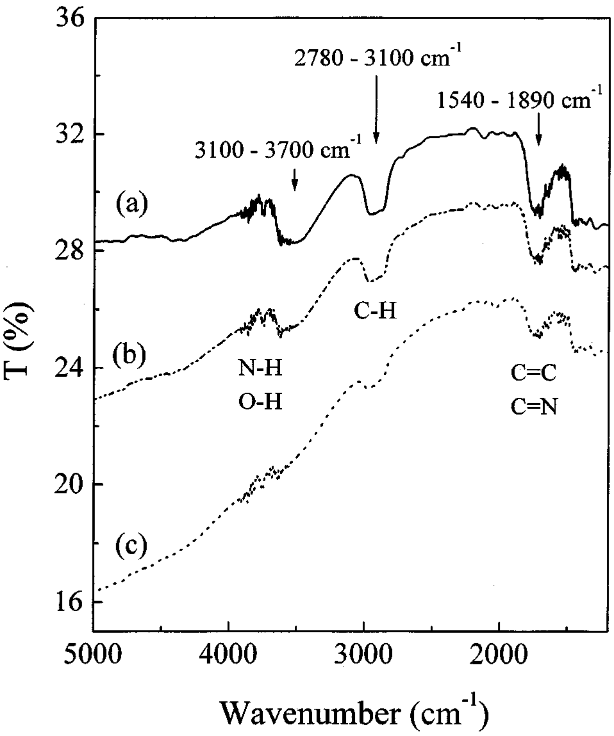
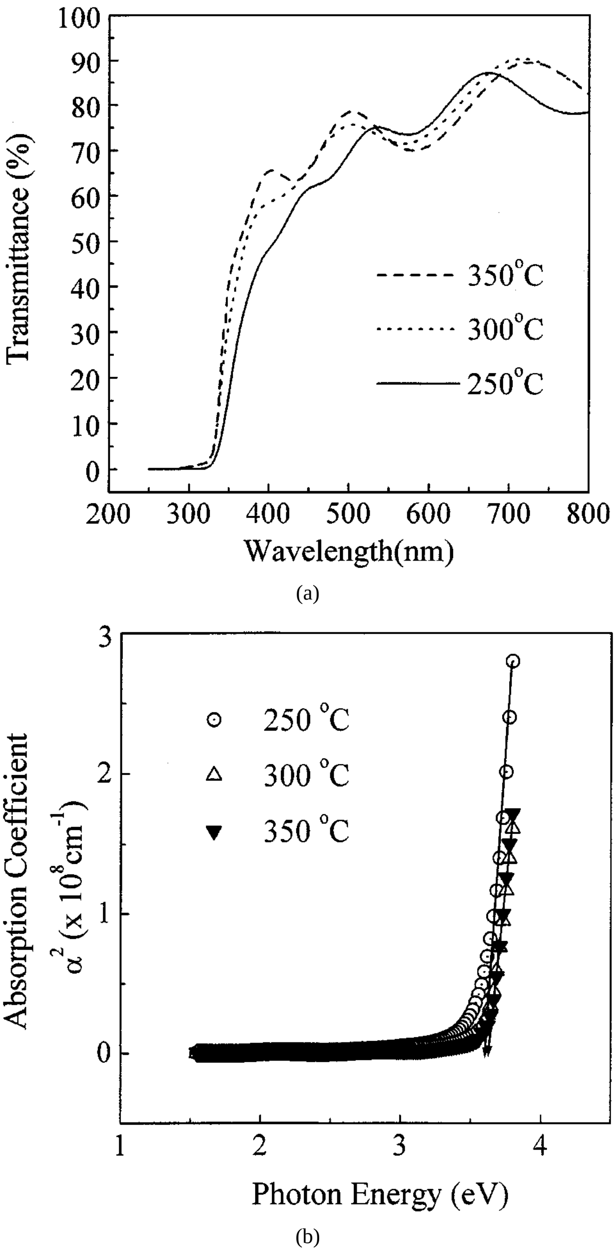


Figure 2 IR spectra of ZnS films deposited at 250°C, 300°C and 350°C.

2700–3100 and 3100–3700 cm^{-1} and their intensities were reduced with an increase of deposition temperature. The peaks in the range of 1450–1950 cm^{-1} corresponded to an absorption by the vibrations of C=C and C=N bond, and the peak in the range of 2700–3100 cm^{-1} was from an absorption by the mainly hydrogen stretching vibration with the other elements. In the range of 2850–3000 cm^{-1}, C-H vibration in aliphatic groups caused absorption, and in 3100–3700 cm^{-1}, absorption from stretching vibration of the O-H or N-H bond was observed [5]. Thiourea (CH_4N_2S) includes C-N bonds and the intermediate compounds such as $C_6H_9N_{11}HSCN$, $C_6H_9N_{11}$, C_6H_6N and $C_6H_3N_9$ have C-C and C=C bond. HSCN (isothiocyanic acid) has double bonds like C=S or C=N [2, 4]. As the deposition temperature increased, the decomposition of the organic salt and aliphatic intermediate compounds was accelerated, and the intensities of absorption peaks were reduced.

The optical transmittance spectra and absorption coefficients of the undoped ZnS films are shown in Fig. 3. The transmittance in the visible region was greater than 60%. The transmittance of the undoped ZnS films enhanced with an increase of deposition temperature because of the reduced diffuse scattering due to an increase of grain size [2] and improvement in the stoichiometry of the films [6]. Table I shows the composition of ZnS films deposited at 250–350°C characterized by EDS. As the deposition temperature increased, the stoichiometry of the films was improved and the chlorine contents in the films were decreased. The grain size of the films was increased with an increase of deposition



(a)

(b)

Figure 3 (a) Transmittances and (b) absorption coefficients of ZnS films deposited at various temperatures.

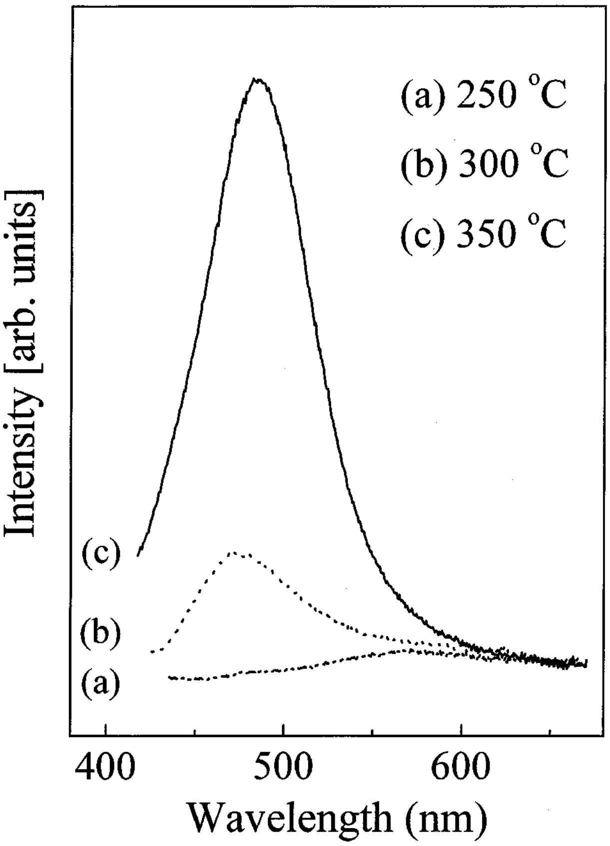


Figure 4 Room temperature emission spectra of ZnS films deposited at 250°C, 300°C and 350°C.

temperatures, as mentioned above. Relative low transmittance of the film deposited at 250°C could be resulted from the chemical species remaining in the films which was unreacted or partially decomposed due to low substrate temperature [7]. Fig. 3b shows the photon energy dependence of the absorption coefficients of the ZnS films. These absorption coefficients were calculated by the method reported by Tarey *et al.* [8], who assumed reflection was neglected in the ultra violet region. It was reported that direct optical transition from band to band would proceed when the absorption coefficient, α^2 showed linear dependence on the photon energy, hν [6, 9–12]. By extrapolating the linear region to the abscissa, the optical transition gap, Eg can be estimated. The obtained Eg value was about 3.6 eV which corresponded to ZnS, and independent on the deposition temperature.

Fig. 4 shows the emission spectra of ZnS films with excitation wavelength of 320 nm. The excitation band near 320 nm corresponds to the energy value of 3.8 eV and this matches with the band to band transition of the host material, ZnS [13]. The ZnS films deposited at 300 and 350°C emitted blue luminescence due to two subbands centered at 470 nm and 497 nm. Samelson *et al.* [14] reported that the subbands in the blue emission region were originated from the recombination of electron with trapped hole at $V_{Zn'}$ and $V_{Zn''}$ [14–17]. It was observed that the integrated intensity and peak width of the blue emission were increased with an increase of substrate temperature. It was reported that the increase of the emission peak width was resulted from the optical transition in which many phonons are generated in addition to an electronic transition on the dopant ion. And such processes are indicative of strong coupling between the ion and the environment [18]. Therefore, it can be proposed that an increase in the deposition temperature increased the optical and electronic transitions and the blue emission of the films was enhanced.

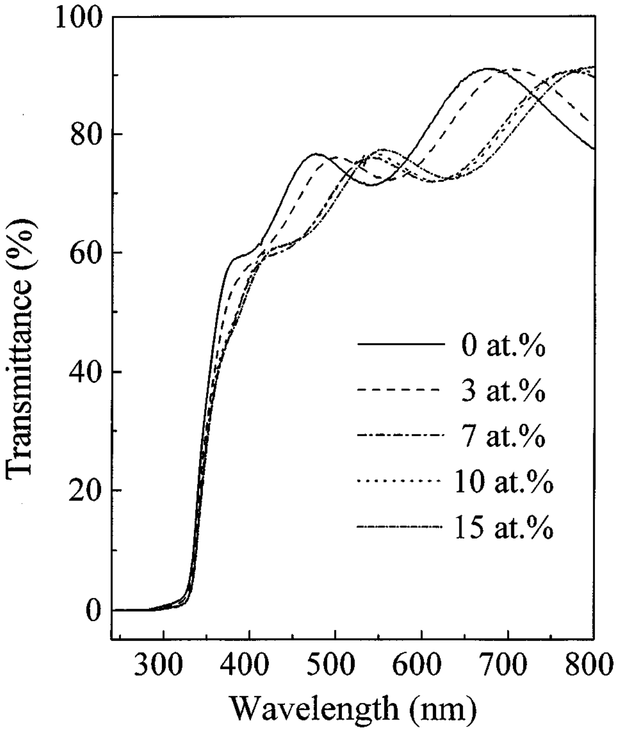


Figure 5 Transmittances of Mn doped ZnS films deposited at 350°C with contents of manganese ion.

Fig. 5 shows the optical transmittance of the Mn doped ZnS films deposited at 350°C. The transmittance in the visible region was greater than 60%. Doping of the manganese ion in the mixed solution resulted in the nonstoichiometric composition of the films and the transmittance was gradually reduced with an increase of concentration of the manganese ions [7, 19]. The calculated absorption coefficients were not significantly changed.

Emission spectra of the Mn doped ZnS films deposited at 350°C are presented in Fig. 6. The concentration of the manganese ion in the mixed solution was varied from 0 to 20 at.%. The blue band luminescence was emitted at 470 and 497 nm and orange-yellow emission was observed at 590 nm. In the blue band luminescence, subband emissions centered at 470 nm were weaker than those at 497 nm and disappeared in specimens prepared from the mixed solution added the manganese ion higher than 10 at.%. On the other hands, the orange-yellow emission of the films was enhanced by adding the manganese ion in the mixed solution up to 7 at.%, and then decreased. The manganese ions could be substituted for the zinc sites and acted as the luminescence centers for orange-yellow emission. Excitation centered at 320 nm activated efficiently blue emission through the ZnS host excitation, and then electrons and holes formed by the host excitation recombined at the localized Mn centers transferring excitation energy to the Mn centers. From this gained

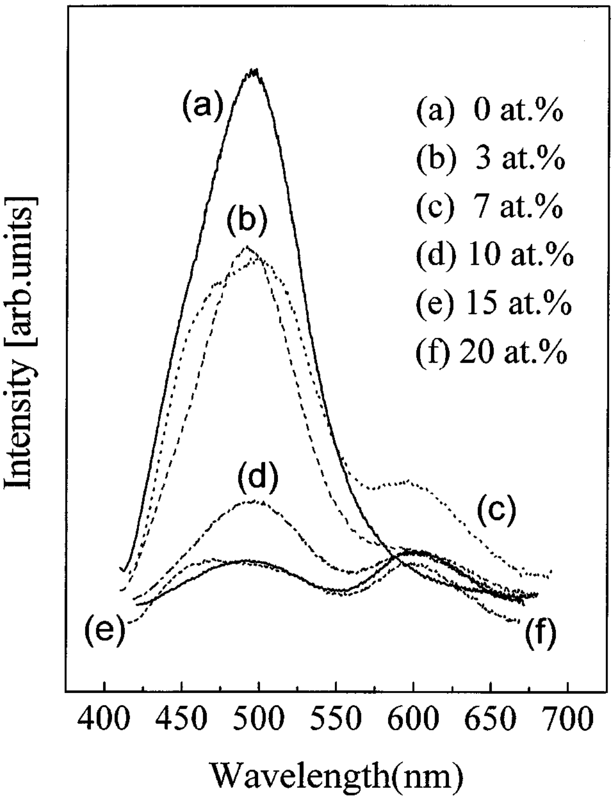


Figure 6 Room temperature emission spectra of Mn doped ZnS films deposited at 350°C with contents of manganese ion.

energy, excitation and recombination process of the Mn centers resulted in orange-yellow emission [13, 18]. It was reported that the concentration quenching effect was observed with an increase of the manganese content in the ZnS films [18, 20] and the concentration quenching effect occurred in the 0.45 wt.% Mn doped ZnS film prepared by evaporation method [21]. In this work, the manganese content in the ZnS film prepared from the mixed solution doped with 7 at.% of Mn was 0.49 wt.% by EDS analysis. Therefore, the decrease of orange-yellow emission of the ZnS film prepared from the mixed solution doped with higher than 7 at.% of Mn was attributed to the concentration quenching effect. Red emission tails observed in films might be related to the formation of the Mn pairs or the localized phase transition [20].

4. Conclusion

With an excitation wavelength of 320 nm, the undoped and Mn doped ZnS films showed blue, and blue and orange-yellow emission, respectively. The blue emission of the ZnS films increased with an increase of deposition temperature. In the Mn doped ZnS films, the blue emission decreased with an increase of the Mn content while the orange-yellow emission enhanced by adding the manganese ions in the mixed solution up to 7 at.% and then decreased.

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