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Growth, Electrical, and Optical Study of ZnS:Mn Thin Films

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In this study, ZnS and Mn-incorporated (at 2%, 4%, and 6%) ZnS films were deposited onto glass substrates by ultrasonic spray pyrolysis technique, and the effect of Mn incorporation on the electrical and optical properties of ZnS films was investigated. In order to determine the electrical characterization, the resistivity measurements of the films were performed by four-probe technique. The optical studies such as transmittance, reflectance and band gap energies of the films were carried out by the UV-Vis transmission.

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1. Introduction

Zinc sulfide (ZnS) is one of the typical II–VI semiconductor compounds with band gap energy of 3.65 eV at room temperature. ZnS is an important material having various optoelectronic device applications such as blue light-emitting diodes, electroluminescent devices, electro-optic modulators and window layers in photovoltaic cells, sensors and lasers [1–3]. ZnS films have been deposited by a large variety of techniques such as spray pyrolysis, rf magnetron sputtering, molecular beam epitaxy (MBE), sol–gel, and chemical bath deposition (CBD) [4, 5]. Among these methods, spray pyrolysis is well suited for the preparation of these films because of its simple and inexpensive experimental arrangement, vacuumless, ease of adding various doping materials, high growth rate, and mass deposition capability for homogeneous large area coatings, which are desirable for industrial and photovoltaic solar cell applications [6, 7].

In this study, ZnS:Mn thin films were deposited onto glass substrates by using ultrasonic spray pyrolysis technique and the influence of Mn doping on the electrical and optical properties of undoped ZnS thin films was reported.

2. Experimental

Undoped and Mn-doped zinc sulphide (at 2%, 4% and 6%) thin films were grown onto microscope glass substrates by the ultrasonic spray pyrolysis (USP) technique at a substrate temperature of $350 \pm 5\,^{\circ}\mathrm{C}$. The spraying solution was prepared by mixing the appropriate volumes of zinc chloride (0.1 M), thiourea (0.1 M) and manganese chloride (0.1 M) dissolved in distilled water. The total solution (150 cm^3) was sprayed during 20 min, and the solution flow rate was controlled by a flowmeter and kept at 7.5 $\mathrm{cm}^3\ \mathrm{min}^{-1}$. Compressed purified air was used as the carrier gas with a pressure of 10^5 Pa. The substrates were heated by an electrical heater, and the substrate temperature was controlled using an iron–constantan thermocouple.

TABLE I

The thickness, electrical resistivities and conductivities for ZnS:Mn thin films.

Sample	Sample code	Thickness of the films [nm]	Electrical resistivity [Ω cm]	Electrical conductivity $[\Omega\ \mathrm{cm}]^{-1}$
ZnS	ZM0	120	4.07×10^5	2.46×10^{-6}
ZnS:Mn (2%)	ZM2	118	1.05×10^5	9.55×10^{-6}
ZnS:Mn (4%)	ZM4	116	4.89×10^5	2.05×10^{-6}
ZnS:Mn (6%)	ZM6	116	4.26×10^4	2.35×10^{-5}

The thickness of the films were measured by Filmetrics F20 Thin Film Thickness Measurement System and presented in Table I. The electrical resistivity measurements were carried out at room temperature in dark by using Lucas Lab Pro 4-440N Four-Point Resistivity System. Optical transmittance, absorbance and reflectance spectra for the films were recorded by a Shimadzu UV--2550 (double beam, 190–900 nm) spectrophotometer.

3. Result and discussion

3.1. Electrical characterization

To characterize the electrical properties of the films, resistivity measurements were carried out. Four-probe method has been employed to measure the electrical resistivity of the films, and the electrical resistivity and conductivity values listed in Table I. The electrical resistivities of all films are high, and Mn doping has not an important effect on the electrical properties of the undoped ZnS films, except for ZM6 films which show electrical resistivity one order of magnitude lower than the undoped ZnS films. The decreasing of resistivity with the Mn doping (6 at.%) may be attributed to some physical variations such as crystal structure, carrier concentration and mobility.

To determine the electrical conductivity type of ZnS:Mn films, hot-probe technique was conducted and it was seen that the films show *n*-type conductivity.

3.2. Optical characterization

To have a knowledge on the optical properties of the undoped and Mn doped ZnS films, the transmittance, absorbance and reflectance spectra for all the films were recorded and some optical parameters such as band gap energy (E_g) and band tail (E_0) were analyzed by using these spectra.

The variation of the transmittance spectra with wavelength for the ZnS:Mn thin films in the range of 300–900 nm are presented in Fig. 1a, measured at room temperature in air. Also, transmission values at different wavelength listed in Table II. As seen in Fig. 1a and Table II, the optical transmissions of all the films decreased with reduction in wavelength and were about 40% in the visible region (at > 450 nm) for undoped films. Also, it can be clearly seen that the light transmission decreases remarkably as Mn doping level increases. This effect of the Mn doping on the transmission of the ZnS films may be due to the structural effects. Also, some physical effects such as surface irregularity and defect density may be cause to reduction in the transmission.

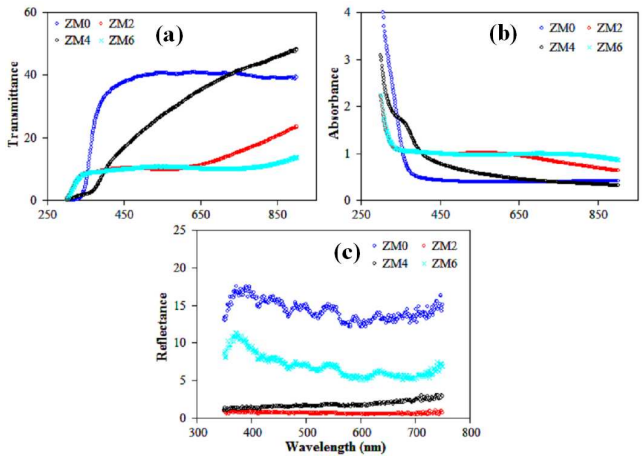

Fig. 1. (a) Transmittance, (b) absorbance and (c) reflectance spectra for the ZnS:Mn thin films.

TABLE II

The optical parameters for ZnS:Mn thin films for different wavelength.

Sample code	λ = 400 nm			λ = 550 nm			λ = 700 nm		
	A	T [%]	R [%]	A	T [%]	R [%]	A	T [%]	R [%]
ZM0	0.48	33.12	16.42	0.39	40.61	14.51	0.39	40.42	13.15
ZM2	1.02	9.63	0.84	1.01	9.88	0.64	0.88	13.07	0.44
ZM4	1.03	9.34	1.50	0.57	27.06	1.75	0.41	38.51	2.43
ZM6	1.03	9.34	9.34	0.97	10.79	6.83	1.00	9.97	5.46

Figure 1b and c shows the variation of absorbance (A) and reflectance (R) with wavelength (λ) for the undoped and Mn doped ZnS films. Also, these values at different wavelength are listed in Table II. From Fig. 1b and this table, it is seen that the absorbance values decreases with the increase in the wavelength, while increases with the increase of the Mn doping. The sharp decreases in absorbance at the wavelength $\lambda < 400$ nm is due to the onset of interband transitions at the fundamental edge.

As seen in Fig. 1c, it is evident that the reflectivity of the undoped ZnS films decreases as a function of the Mn doping. Such decrease in the reflectivity with the increase of the Mn doping may be explained by the decrease of the film density.

The optical band gap, E_g, of the films can be determined from the absorption spectra using the formula $(\alpha h\nu)^2 = A(h\nu - E_g)$ for allowed direct transitions, where α is the absorption coefficient, A is a constant, h is the Planck constant, ν is the frequency of the incident photon [8]. The curves of $(\alpha h\nu)^2$ versus $h\nu$ for all the films are shown in Fig. 2. The values of E_g are evaluated by extrapolation of the linear part to be between 3.75 and 3.90 eV which are listed in Table III. It is obviously seen from this table that the optical band gap of undoped ZnS films remarkably increases with increase of the Mn doping concentration.

TABLE III

The optical band gap energies (E_g) and Urbach parameters (E_0) for ZnS:Mn thin films.

Sample code	Band gap [eV]	Urbach energy [meV]
ZM0	3.75	657
ZM2	3.90	446
ZM4	3.86	587
ZM6	3.90	444

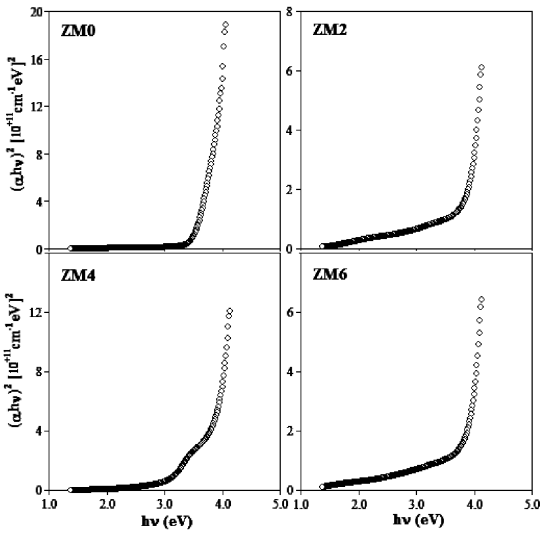

Fig. 2. The $(\alpha h\nu)^2$ versus photon energy ($h\nu$) for the ZnS:Mn thin films.

As known, the effect of impurity or disorder and any other defects in semiconductors leads to local electric fields that affect the band tails near the band edge. The absorption coefficient $\alpha : (h\nu)$ in the low energy range follows the exponential law given by Pankove's formula [9]

$$\alpha(h\nu) = \alpha_0 \exp(h\nu/E_0) \quad \text{for} \quad h\nu < E_g\,, \tag{1}$$

where α_0 is a constant and E_0, called the Urbach energy, has been interpreted as the width of the localized states in the band gap, having dimensions of energy and describing the effects of all possible defects contributing to band tailing. From the slopes of the linear relationship between $\ln\alpha$ and $h\nu$ in the tail region, the empirical parameter E_0 for all the films was estimated, and these results are given in Table III. It is seen from this table that E_0 value decreases for doped films as compared to ZnS films. These results indicate that all the films have localized states which result from the density of defects at the grain boundaries and donor levels.

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