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Optical, structural and electrical properties of zinc sulphide vacuum evaporated thin film

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The II-VI group semiconductors are of great importance due to their applications in various opto-electronic devices. Among these semiconductors, zinc sulphide film is the most suitable for its utility in opto-electronic devices. ZnS film has been prepared on glass substrates by using vacuum evaporation method. The optical properties, especially refractive index by transmission spectra of these films have been studied in the wavelength range 400-850 nm using Manifaciers envelope method. The ZnS film has a direct band gap of 3.50 eV. The wurtzite structure of ZnS film has been confirmed by X-ray diffraction analysis. The electrical properties of ZnS especially dark conductivity and photoconductivity at different temperatures have also been studied.

Keywords: Zinc sulphide, Vacuum evaporated thin film, Refractive index, Conductivity

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1 Introduction

Zinc sulphide (ZnS) is II-VI group semiconductor with a large direct band gap in the near UV region. The wide band gap of the material makes it suitable for use in blue light emitting diodes[3] (LEDs) and other opto-electronic devices such as electro-luminescent display[4], cathodoluminescent displays and multilayer dielectric filters[5,6]. The thin films of ZnS are usually prepared by different techniques such as sputtering, chemical bath[1], MOCVD techniques[2], vacuum evaporated techniques etc. The optical, structural and electrical properties of ZnS vacuum evaporated films have been studied in the present paper.

2 Experimental Details

In the present study, thin films of ZnS have been prepared by vacuum deposition technique[7]. For samples preparation, zinc sulphide powder of 99.99 % purity was evaporated at about 115°C from a deep narrow mouthed molybdenum boat. The deposition was made on to highly cleaned glass substrates held at 200°C in a vacuum of 10^{-5} torr. The substrates were cleaned in aqua-regia, washed in distilled water and isopropyl alcohol (IPA). It was separated from the ZnS molybdenum boat by a stainless steel heat shield. Keeping the substrate at an elevated temperature of about 250°C helped to eject any sulphur atoms deposited due to thermal decomposition of ZnS during evaporation. The ZnS thin films deposited on substrate were characterized by using spectrophotometer, X-ray diffraction and electrometer.

2.1 Characterization of samples

Optical properties—Transmission spectra of vacuum evaporated ZnS films were recorded at room temperature with the help of Hitachi Spectrophotometer (Model U-3400) in the wavelength range 187-2600 nm. The optical constants like refractive index of vacuum evaporated thin films of zinc sulphide have been determined from transmission spectra by using Manifacier's envelope method[10] which shows interference patterns. The transmission spectra of ZnS films have been recorded in the range 400 – 850 nm. The refractive index (n) has been determined from transmission spectra (Fig. 1) by using the formula[8,9].

$$n = [\, N + (\, N^2 + n_0^2\, n_1^2\,)^{1/2}\,]^{1/2} \qquad \ldots(1)$$

where n_0 and n_1 are the refractive index of air and substrate, respectively. The number N is given by the following equation:

$$N = [(n_0^2 + n_1^2)/2] + 2\, n_0\, n_1\, [(T_{max} - T_{min})/(T_{max} . T_{min})] \quad \ldots(2)$$

where T_{max} and T_{min} are the upper extreme point and lower extreme point at a particular wavelength, respectively.

The extinction coefficient (k) is given by an expression:

$$k = (- \lambda /4 \pi t) \ln P \qquad \ldots(3)$$

where t is the thickness of the film and P is given by the following equation:

$$P = C_1/C_2 \, [1- (T_{max} / T_{min})] / [1+ (T_{max} / T_{min})] \qquad \ldots(4)$$

where, $C_1 = (n + n_0) (n + n_1)$

$C_2 = (n - n_0) (n_1 - n)$

where n is the refractive index of the film at a particular wavelength, n_1 the refractive index of the substrates and n_0 is the refractive index of the air as given earlier.

Structural properties—The X-ray diffraction pattern of ZnS films is also reported in the present work with the help of a Philip X-ray diffractometer by using CuKα radiation (λ = 1.54045 Å). The d values as obtained from the spectra were compared with the standard ASTM data to confirm the structure of ZnS film.

Electrical properties—The dark conductivity and photoconductivity of the semiconducting ZnS film were measured in a metallic cryostat under a vacuum of 10^{-5} torr. These measurements were carried out by evaporating aluminium contacts across 0.08 cm keeping wide gap of the surface of the films. The measurements were made at 10V and the direct current was measured with a programmable digital electrometer (Keithley mode 610). To ensure that the properties of these films were not unduly affected by moisture absorption, the films were annealed in vacuum at 57°C and the measurements were made in a vacuum of 10^{-3} torr. The temperature was measured using a calibrated copper constantan thermocouple.

3 Results and Discussion

Fig.1 shows the transmission spectra of vacuum evaporated ZnS thin film. The values of T_{max} and T_{min} were determined at different wavelengths and then values of N and n were calculated by substituting T_{max} and T_{min} in a standard equation. The data so obtained

Table 1—Variation of refractive index (n) for vacuum evaporated ZnS thin films

S. No.	Λ (nm)	T_{max} (%)	T_{min} (%)	N	n
1	550	50.83	42.50	2.781	2.437
2	600	74.16	57.50	2.767	2.432
3	650	87.50	65.83	2.757	2.428
4	700	94.16	69.16	2.748	2.425
5	750	98.33	72.50	2.716	2.412
6	800	1.00	73.33	2.712	2.411
7	850	1.00	74.16	2.670	2.394

λ= Wavelength, N= Number, n = Refractive index, T_{max} = upper extreme point,
T_{min} = lower extreme point

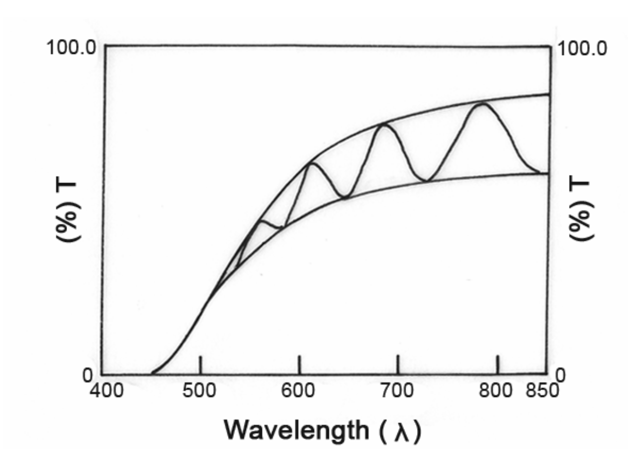

Fig. 1—Transmission spectra of vacuum evaporated ZnS thin film

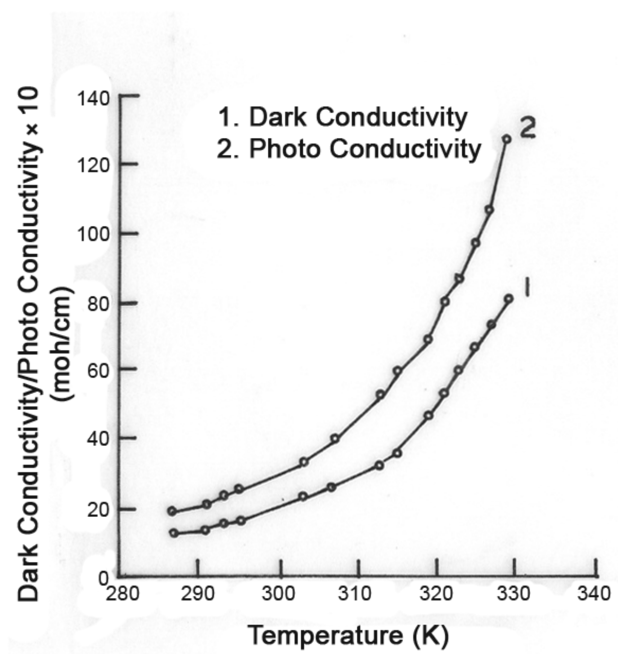

Fig. 2—Variation of refractive index with wavelength of vacuum evaporated ZnS thin film

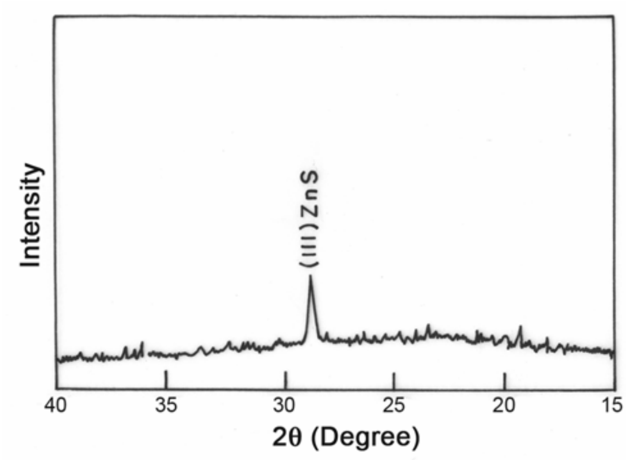

Fig. 3—XRD patterns of vacuum evaporated ZnS thin film

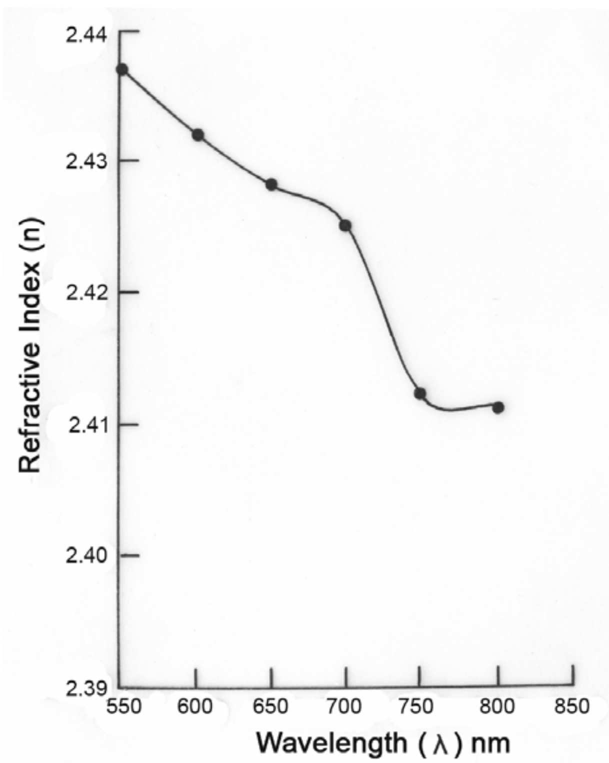

Fig. 4—Variation of dark conductivity and photoconductivity with temperature of ZnS thin film

is reported in Table 1. It is observed that as the wavelength (λ) increases, refractive index (*n*) decreases and there is no change beyond the wavelength 750 nm and the trend is shown in Fig.2. It shows, in general, good transparency exhibiting an interference pattern. The structural properties are reported by X-ray diffraction technique Fig.3.

The dark conductivity and photoconductivity of the vacuum evaporated ZnS film at different temperatures were determined and the data are presented in Table 2. Both the conductivities increase in general with temperature. The values of dark conductivity as well as photoconductivity are plotted versus temperature and shown in Fig.4. The thickness of ZnS film is found to be 0.49 micron which has been determined by using a Hitachi spectrophotometer (Model U-3400).

Table 2—Variation of dark conductivity (σ_d) and Photoconductivity (σ_{ph}) with temperature of ZnS vacuum evaporated thin film

S. No.	T (nA)	I_d (nA)	I_{ph} ($\Omega^{-1}cm^{-1}$)	$\sigma_{ph} \times 10^{-6}$ ($\Omega^{-1}cm^{1}$)	$\sigma_d \times 10^{-6}$
1	287	0.38	0.58	19.230	12.602
2	291	0.41	0.64	21.220	13.596
3	293	0.47	0.75	24.870	15.586
4	295	0.49	0.85	28.180	16.250
5	303	0.70	1.00	33.160	23.210
6	307	0.80	1.20	39.790	26.530
7	313	1.00	1.60	53.060	33.163
8	315	1.10	1.80	59.690	36.479
9	319	1.40	2.10	69.640	46.428
10	321	1.60	2.40	79.590	53.061
11	323	1.80	2.60	86.220	59.693
12	325	2.00	2.90	96.170	66.326
13	327	2.20	3.20	106.120	72.959
14	329	2.40	3.50	126.070	79.591

T= Temperature, I_d = Dark current, I_{ph} = Photo current, σ_d = Dark conductivity,
σ_{ph} =Photoconductivity, W= 13 cm, l= 0.08cm, t = 0.49 micron

4 Conclusions

The ZnS films prepared on glass substrates by using vacuum evaporation method show wurtzite structure. The ZnS film has a direct band gap and was found to be 3.50 eV which makes it a good material for optoelectronic devices.

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