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CHARACTERISTICS OF BRUSH PLATED ZnS FILMS

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Zinc sulphide(ZnS) thin films were deposited by the brush electrodeposition technique at 80°C and at different deposition current densities in the range of 80 – 200 mA cm^{-2}.The films were polycrystalline with peaks corresponding to single phase cubic ZnS. Films with direct band gap in the range of 3.79–3.93 eV were obtained. The grain size increased from 20 – 70 nm as the deposition current density increased. The films exhibited resistivity in the range of 100 – 1000 ohm cm. The photooutput obtained with photoelectrochemical cells employing these films was higher than the previous report.

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1. Introduction

Zinc sulfide belongs to the II–VI family of semiconducting material receiving ever-increasing attention due to its wide variety of applications. Owing to wide band gap value of 3.7 eV, it can be used for fabrication of optoelectronic devices such as blue light-emitting diodes, electroluminescent devices, electro-optic modulator, optical coating, n-window layers for thin film heterojunction solar cells, photoconductor and especially photovoltaic devices [1-3]. Thin films of ZnS doped with transition-metal element or rare-earth element has also been used as effective phosphor material [4]. In the area of optics, ZnS can be used as reflectors [5] and dielectric filters [6] because of its high refractive index and its high transmittance in visible range. ZnS has also been investigated as a buffer layer in ZnO/ZnS/$CuInS_2$ devices [7]. Several techniques have been used to produce ZnS thin film such as thermal evaporation [8], spray pyrolysis [9], molecular beam epitaxy [10], sputtering [11], chemical bath deposition (CBD) [12 – 15]. In this work, the brush plating technique was employed for the deposition of ZnS films at different current densities.

2.Experimental

Thin ZnS films were deposited by the brush plating technique employing different densities in the range of 80 mAcm^{-2} - 200 mA cm^{-2} on titanium and conducting glass substrates. Deposition at lower current densities resulted in thin films (<0.5µm). Higher current densities resulted in large grained films and the film thickness did not increase further. The precursors were 0.1M$ZnSO_4$ and 0.2M$Na_2S_2O_3$. Higher concentrations of $Na_2S_2O_3$ resulted in preferential deposition of sulphur. The deposition temperature,deposition time were kept constant at 80 °C and 20 min respectively. The details of the brush plating technique are given elsewhere[16]. The films were characterized by X-ray diffraction technique using a PANalytical X-ray diffractometer with Cu Kα radiation. Optical absorption studies were made using a U 3400 UV–vis–NIR Hitachi spectrophotometer. Thickness of the films was measured by Mitutoyo surface profilometer and it was found to be in the range of 0.8 –1.3μm as the deposition current density increased. Photoluminescence measurements were made at room temperature using a Hitachi 650–10S Photoluminescence spectrometer. The excitation wavelength was 325 nm. Photoelectrochemical measurements were made in 1Mploysulphide (1MNaOH, 1MNa2S, 1MS) electrolyte using a 250W tungsten halogen lamp.

3. Results and discussion

X-ray diffractograms of films prepared at different deposition current densities are shown in Fig. 1. The sample is amorphous at the lowest deposition current density. The overall intensity of the reflections increased when the deposition current density increased without the appearance of any new reflections. Thus, no other phases were formed, but only the crystallinity of the formed phase was improved. Phase identification revealed that only cubic ZnS (JCPDS card 77–2100) is formed. The crystallite size was measured using Debye Scherrer's formula [17]

$$L = 0.9\lambda/\beta \cos \theta$$

where λ is the wavelength ofCuK_radiation and β is theFWHM value. The crystallite size increased from 20 to 70 nm as the deposition current density increased.

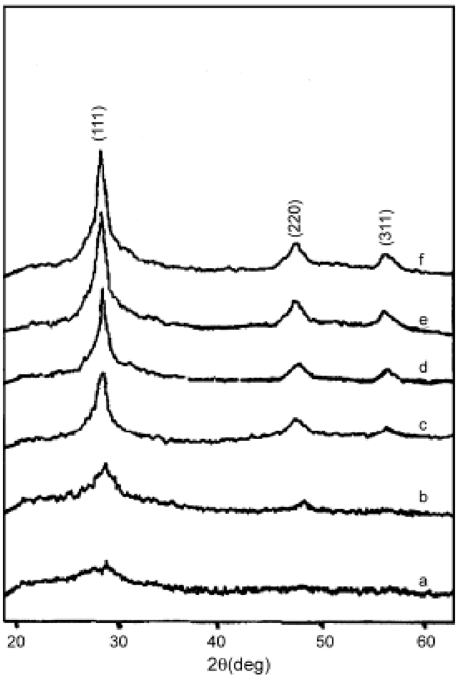

Fig.1. X-ray diffraction pattern of ZnS films deposited at different current densities (a) 80 mA cm^{-2} (b) 100 mA cm^{-2} (c) 150 mA cm^{-2} (d) 175 mA cm^{-2} (e) 200 mA cm^{-2}

The dislocation density (δ) was determined using the relation [18]

$$\delta = 15\beta \cos \theta/4aD \tag{2}$$

where β is the full width at half maximum and D is the crystallite size. The variation of dislocation density with substrate temperature is also indicated in Table-I. It was observed that the dislocation density decreased with the increase of deposition temperature. This might be due to the improvement in crystallinity.

Table. I. Variation of lattice parameters and dislocation density with substrate temperature.

Deposition Current density(mA cm^{-2})	Grain size(nm)	Dislocation density (x 10^{14} lines m^{-1})
80	20	1.87
50	45	1.24
70	65	1.08
80	70	0.98

The optical properties of ZnS thin films were determined from transmission measurements in the range of 290–800 nm.The absorption coefficient (α) was analyzed using the following expression for near-edge optical absorption of semiconductors:

$$\alpha h\nu = K(h\nu - E_g)^{n/2}$$

where K is the constant, E_g the separation between the valance and conduction bands and n is a constant that is equal to 1, for direct band gap semiconductors. The band gap values were determined from the intercept of the straight-line portion of the $(\alpha h\nu)^2$ against the $h\nu$ graph on the $h\nu$-axis (Fig. 2). The band gap value was calculated in the range of 3.79–3.93 eV. The band gap values are higher than bulk value because of quantum confinement of ZnS nanocrystals. It is consistent with the literature [19]. The quantum size effect of confinement of electrons in size reduced systems was theoretically predicted and experimentally observed in many cases [20,21].

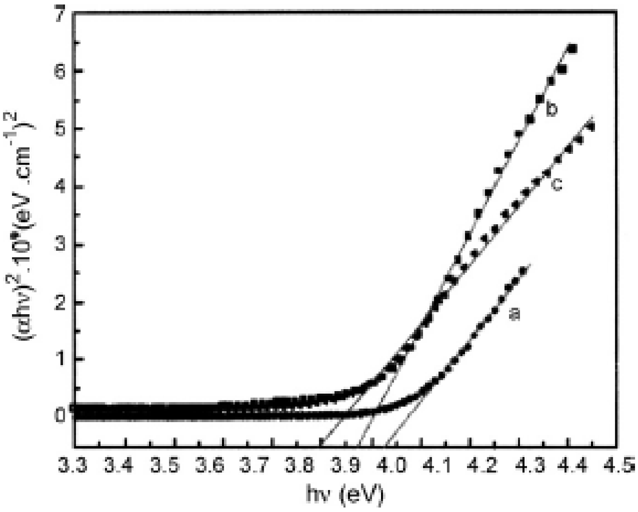

Fig.2. $(\alpha h\nu)^2$ vs hν plot of ZnS films deposited at different current densities (a) 80 mA cm^{-2} (b) 150 mA cm^{-2} (c) 200 mA cm^{-2}

Hall measurements were made on the films adopting the procedure reported earlier [22]. In this method the ZnS layer is mechanically transferred from the conducting substrate onto a non-conductive epoxy resin without the formation of cracks [23]. The electrical properties of the ZnS layers were examined at room temperature by resistivity and Hall measurements using Van der Pauw method. Vacuum evaporated Indium served as the ohmic contact. The value of the resistivity determined from Van der Pauw method varied from 1000 to 100 ohm cm as the deposition current density increased. Hall measurements also indicated the films to be n-type. The carrier density, mobility and resistivity of the films of different substrate temperature are shown in Table-II. The resistivity values are lower than earlier reports[24,25].

Fig. 3 shows the PL spectra of the ZnS film deposited at a temperature of 80 ◦C. The excitation wavelength was 325 nm. Films deposited at lower current densities did not exhibit any luminescence. The spectra consist of two peaks. In general, both Schottky and Frenkel defects exist in all solids, but there is always a tendency for one type of defect to be dominant, since their formation energies are usually unequal [26]. It is known that Schottky defects are dominant in cubic ZnS [27]. Therefore, the blue emission of the peak around 420 nm could be ascribed to S^{2-} vacancies. The green emission of the peak around 480 nm may be assigned to the emission from the impurity either of the precursors $ZnSO_4$ or sodium thiosulphate, which were incorporated during the deposition process [28].

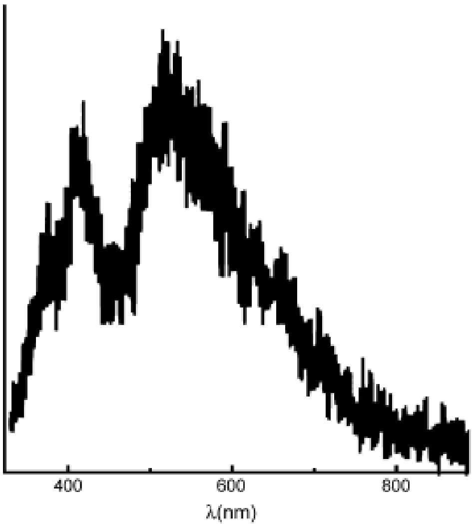

Fig. 3. PL emission spectra of ZnS films deposited at a current density of 200 mA cm^{-2}.

Table 2. Resistivity, Mobility and carrier density of ZnS films deposited at different

Deposition Current density(mA cm^{-2})	Current densities		Carrier density (cm^{-3})
	Resistivity (ohm cm)	Mobility (cm^{2}V^{-1}s^{-1})	
80	1000	4.0	1.4 x 10^{15}
125	750	5.8	1.45 x 10^{15}
150	457	7.3	1.87 x 10^{15}
200	100	9.7	6.44 x 10^{15}

Photoelectrochemical measurements were made on the films deposited at different current densities. The as deposited films exhibited photoactivity. Fig.4 shows the load characteristics of the films deposited at different current densities. It is observed that the photo-output increases with increase of deposition current density.

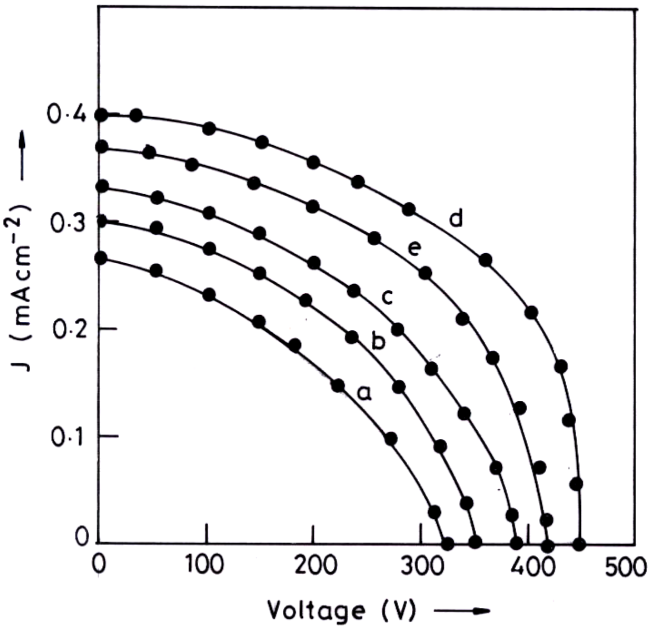

Fig.4. Load characteristics of ZnS films deposited at different current densities (a) 80 mA cm^{-2} (b) 125 mA cm^{-2} (c) 150 mA cm^{-2} (d) 200 mA cm^{-2} (e) 175 mA cm^{-2}

The PEC output for the electrodes obtained by this technique are higher than those reported earlier[29]. This may due to the fact that the films obtained by this technique are possess lower resistivity compared to the earlier samples.

4. Conclusions

The results of this investigation clearly demonstrates that ZnS films can be easily deposited by the brush plating technique. Fulms with resistivities in the range of 100 – 1000 ohm cm cane be obtained. Films with grain size in the range 20 – 70 nm can be obtained. Films exhibit Photoluminescence and photoelectrochemical cells with higher outputs than previous reports can be obtained.

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