

Brush plated ZnS films and their properties

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Abstract

Zinc sulphide thin films were deposited by the brush plating technique using AR grade zinc sulphate and sodium thiosulphate on titanium and conducting glass substrates at a current density of 80 mA cm^{-2} and at different deposition temperatures in the range $30\text{--}80^\circ\text{C}$. The films exhibited cubic structure. Band gap of the films were in the range of $3.79\text{--}3.93 \text{ eV}$. Auger spectra of the ZnS films deposited at different current densities indicated that the Zn/S ratio varies in the range of $1.02\text{--}1.04$. Room temperature PL spectrum of the films deposited at 80°C indicated two emission peaks at 420 and 480 nm for an excitation of 325 nm . Resistivity of the film varied from $200\text{--}769 \Omega \text{ cm}$ as the deposition temperature increased. © 2007 Elsevier B.V. All rights reserved.

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1. Introduction

ZnS thin films with a wide direct band gap and n-type conductivity are promising candidates for optoelectronic device applications, such as electroluminescent devices and photovoltaic cells. ZnS can also be used for light emitting diodes in the blue ultraviolet region because of its wide band gap. Deposition of these films by RF sputtering [1], chemical vapour deposition [2], spray pyrolysis [3], atomic layer deposition [4] and chemical bath deposition (CBD) [5–8], electrodeposition [9] are well known. In this work, the brush plating technique has been employed for the first time to deposit ZnS films. In the brush plating technique, only 5 ml of precursor mixture is necessary for preparation of the films compared to larger volumes of solution required for deposition of the films by conventional electrodeposition. Moreover, films of $1.5\text{--}2.0 \mu\text{m}$ thickness can easily be obtained in 20 min , by the brush plating compared to nearly 60 min by the conventional electrodeposition technique.

2. Experimental

Thin ZnS films were deposited by the brush plating technique employing a constant current density of 80 mA cm^{-2} on titanium and conducting glass sub-

strates. Deposition at lower current densities resulted in thin films ($<0.5 \mu\text{m}$). Higher current densities resulted in large grained films and the film thickness did not increase further. The precursors were 0.1 M ZnSO_4 and $0.2 \text{ M Na}_2\text{S}_2\text{O}_3$. Higher concentrations of $\text{Na}_2\text{S}_2\text{O}_3$ resulted in preferential deposition of sulphur increasing the sulphur concentrations greater than 80% . The deposition temperature was varied in the range of $30\text{--}80^\circ\text{C}$. The deposition time was varied in the range $10\text{--}30 \text{ min}$. The details of the brush plating technique are given elsewhere [10]. The films were characterized by X-ray diffraction technique using a PANalytical X-ray diffractometer with $\text{Cu K}\alpha$ radiation. Optical absorption studies were made using a U 3400 UV-vis-NIR Hitachi spectrophotometer. EDAX measurements were made using a 35CF JOEL SEM fixed with EDAX attachment. Thickness of the films was measured by Mitutoyo surface profilometer and it was found to be in the range of $1.5\text{--}2.0 \mu\text{m}$ as the deposition temperature increased from 30 to 80°C . 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 1 M polysulphide (1 M NaOH , $1 \text{ M Na}_2\text{S}$, 1 M S) electrolyte using a 250 W tungsten halogen lamp.

3. Results and discussion

X-ray diffractograms of films prepared at different deposition temperatures are shown in Fig. 1. The sample is amorphous at the lowest deposition temperature (30°C). The overall intensity of the reflections increased when the deposition temperature increased without the appearance of any new reflections. Thus, no other phases were formed, but only the crystallinity of the formed phase was improved. Above 60°C , a well-crystallized

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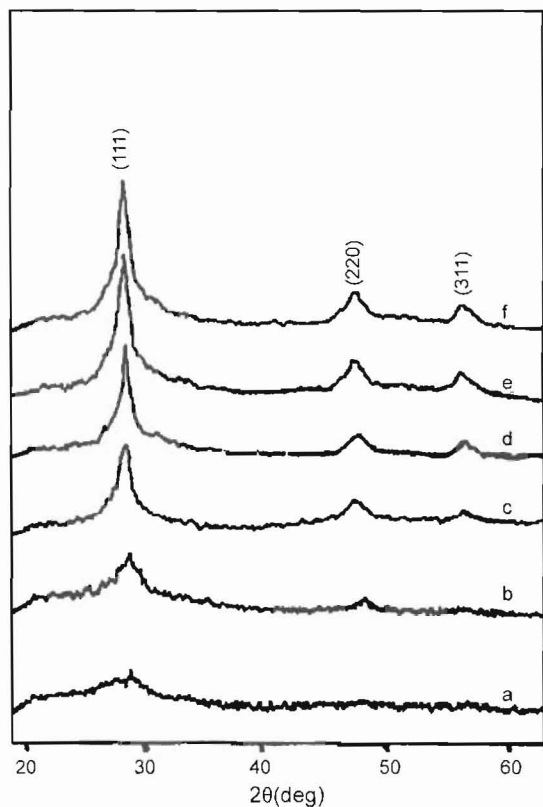


Fig. 1. X-ray diffraction pattern of ZnS films deposited by the brush plating technique for 10 min at different temperatures (a) 30 °C, (b) 40 °C, (c) 50 °C, (d) 60 °C, (e) 70 °C and (f) 80 °C.

film was obtained. Phase identification revealed that only cubic ZnS (JCPDS card 77–2100) is formed. Thus, the preparation conditions of a certain technique not only greatly affects the number of phases formed but also their microstructural characteristics, such as crystallinity. The crystallite size was measured using Debye Scherrer's formula [11]

$$L = \frac{0.9\lambda}{\beta \cos \theta}$$

where λ is the wavelength of Cu $K\alpha$ radiation and β is the FWHM value. The crystallite size increased from 15 to 50 nm as the deposition temperature increased from 30 to 80 °C. The optical properties of ZnS thin films were determined from transmission measurements in the range of 290–800 nm. Fig. 2 shows the transmission spectra of the ZnS films deposited at different temperatures. 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

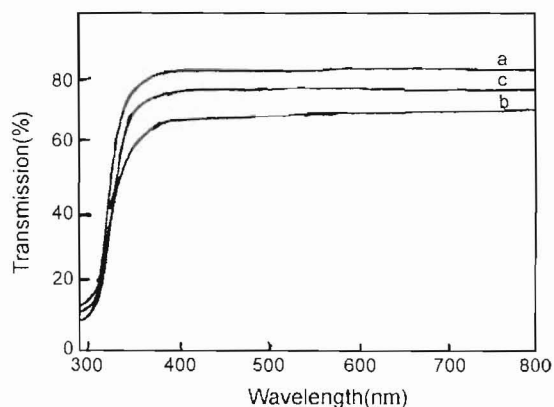


Fig. 2. Transmission spectra of ZnS films deposited at different temperatures for 10 min (a) 30 °C, (b) 60 °C and (c) 80 °C.

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 [12]. The quantum size effect of confinement of electrons in size-reduced systems was theoretically predicted and experimentally observed in many cases [13–15].

The Auger spectra of the ZnS films deposited at different current densities is shown in Fig. 3. The Zn/S ratio varies in the range of 1.02–1.04 for the films deposited at different temperatures, which is better than the value reported (Zn/S = 1.1) in [16], where thin film of zinc sulphide was prepared by the pulsed electrochemical deposition. On the other hand, excess elemental S is absent in the film, and hence S should be possibly present in the film mainly in the form of ZnS. The oxygen may be incorporated into the film either from the atmosphere or from the aqueous medium of the bath solution. The source for carbon contamination may be due to the exposure of the samples to atmospheric air. Fig. 4 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 temperatures did

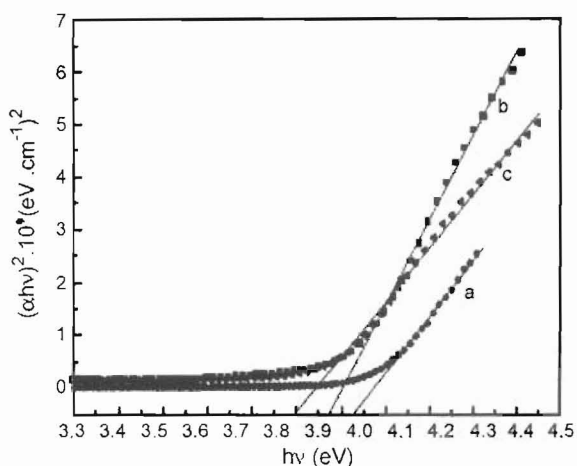


Fig. 3. $(\alpha h\nu)^2$ vs. $h\nu$ plot of ZnS films deposited at different temperatures for 10 min (a) 30 °C, (b) 60 °C and (c) 80 °C.

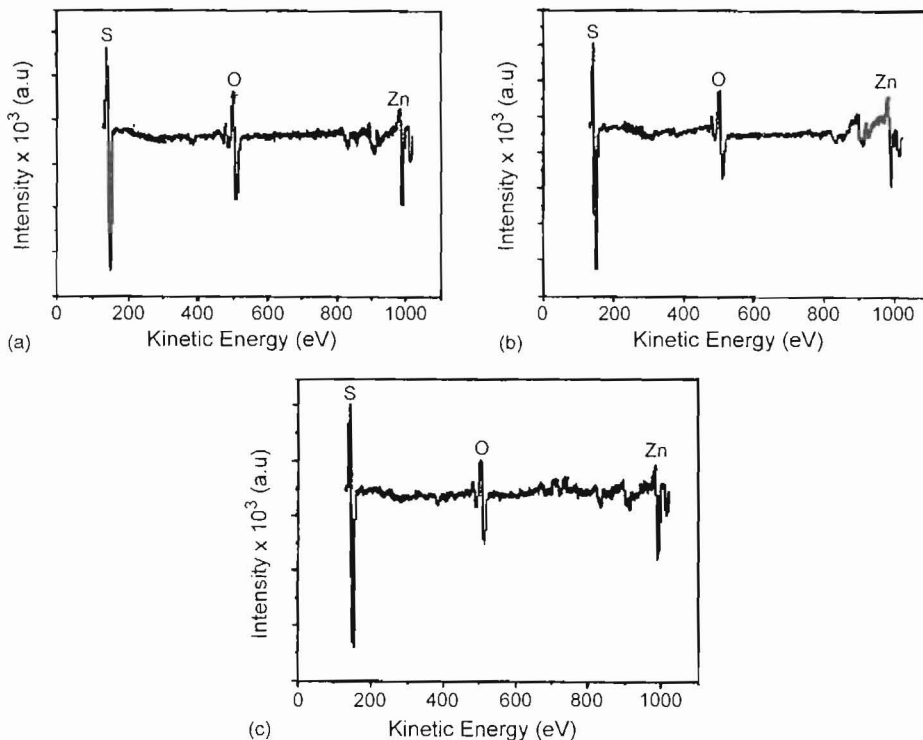


Fig. 4. AES spectra of ZnS films deposited at different temperatures (a) 30 °C, (b) 50 °C and (c) 80 °C.

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 [17]. It is known that Schottky defects are dominant in cubic ZnS

[18]. 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 [19].

Current–voltage characteristics (Fig. 5) was measured at room temperature by applying voltage in the range of 0–50 V. For this purpose, gold was evaporated on the top of the titanium substrate and over this gold film, zinc sulphide film was brush

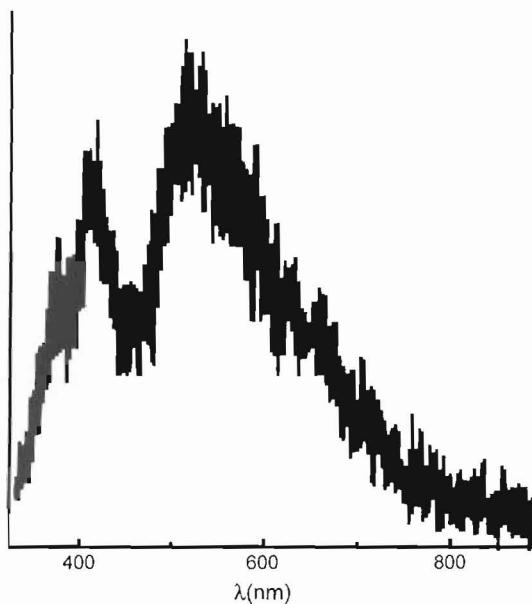


Fig. 5. PL spectra of the ZnS film ($\lambda_{exc} = 325$ nm) deposited at a temperature of 80 °C.

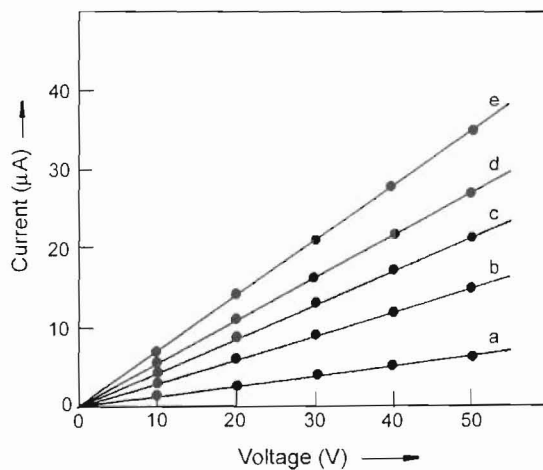


Fig. 6. I–V characteristics of the ZnS films deposited at different temperatures (a) 30 °C, (b) 40 °C, (c) 50 °C, (d) 70 °C and (e) 80 °C.

plated. Gold was evaporated on top of the zinc sulphide film to serve as the top contact. All the films exhibited linear behaviour. The slope of the line yielded the resistance of the film. From this data, resistivity of the films was calculated. Resistivity of the film varied from 200–769 Ω cm as the deposition temperature increased. The value of the resistivity is lower than the previous reports (Fig. 6) [20,21].

4. Conclusion

The results of this investigation demonstrate that thin n-type ZnS films with resistivity values around 200–769 Ω cm and exhibiting luminescence at 420 nm possessing a cubic structure can be easily deposited by the brush plating technique. The resistivity of the films is lower than the reported values. This technique can be scaled up for large area films to be useful for display devices.

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