Properties of pulse plated ZnS films

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Abstract

Zinc sulphide thin films were deposited by the pulse plating technique at a duty cycle of 20% and different deposition current densities in the range 50–300 mA cm^{-2}. X-ray diffraction studies indicated the films to be polycrystalline with wurtzite structure. Direct optical band gap in the range of 3.6–4.0 eV was obtained for the films deposited at different deposition current densities. AES studies indicated a Zn/S ratio of 1.02–1.04. The room temperature resistivity values varied in the range of 3.5–17 Ω cm as the deposition current density decreases. Photoluminescence emission peak was observed at 388 nm at room temperature for an excitation of 325 nm.
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1. Introduction

Zinc sulphide (ZnS) is an important II–VI semiconducting material with a wide direct band gap of 3.65 eV in the bulk [1]. It has potential applications in optoelectronic devices such as blue light emitting diodes [2], electroluminescent devices and photovoltaic cells [3]. In thin film solar cells based on CuGaIn (S,Se)$_2$ absorbers, a CdS buffer layer is generally required in order to obtain high conversion efficiency. However, there are toxic hazards with respect to the production and use of the CdS layer. Therefore research in developing Cd-free buffer layers has been encouraged. This has lead to the investigation of ZnS as a buffer layer in ZnO/ZnS/CuInS$_2$ devices [4]. ZnS has a wider energy band gap than CdS, which results in the transmission of more high energy photons to the junction, and to the enhancement of the blue response of the photovoltaic cells. Several techniques such as thermal evaporation [5], molecular beam epitaxy [6], metal-organic vapor phase epitaxy [7], chemical vapor deposition [8], spray pyrolysis [9], and chemical bath deposition (CBD) [10] have been used to produce ZnS thin films. Though there exist an earlier report on pulse deposited ZnS films, only duty cycles greater than 50% were used and the concentration of the precursors was varied

[11]. To our knowledge this is the first report on the pulse deposition of ZnS films at different deposition current densities.

2. Experimental techniques

Generally in electrodeposition technique for producing a metal or compound, a driving force (i.e., the free energy) in the form of a potential or current is applied to the electrode. Either of these can be used as a variable as in the case of continuous electrodeposition. But modern electronics allows one to make use of these parameters as a function of time. This permits a number of possible ways of varying the conditions.

Four variable parameters are of primary importance in pulse plating. They are:

1) Peak current density, i_p
2) Average current density, i_a
3) ON time and
4) OFF time

The sum of the ON and OFF times constitute one pulse cycle. The duty cycle is defined as follows:

$$\text{Duty Cycle} = \frac{\text{ON time}}{\text{ON time} + \text{OFF time}} \times 100\% \qquad (1)$$

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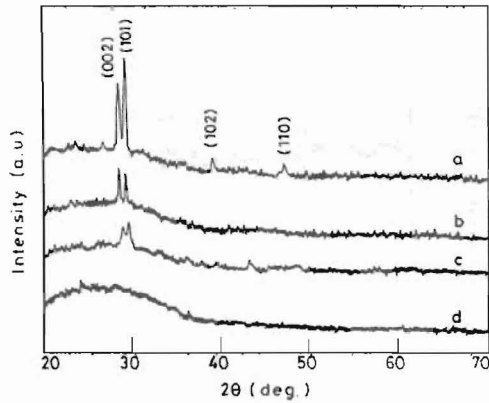*E-mail address:* muraliramkrish@gmail.com (K.R. Murali).

Fig. 1. X-ray diffraction pattern of ZnS films deposited at different current densities: (a) 300 mA cm^{-2}; (b) 250 mA cm^{-2}; (c) 150 mA cm^{-2}; (d) 50 mA cm^{-2}.

A duty cycle of 100% corresponds to conventional plating because OFF time is zero.

In practice, pulse plating usually involves a duty cycle of 5% or greater. The average current density(I_a) under pulse plating conditions is defined as

$$I_a = \text{peak current density} \times \text{duty cycle} \\ = i_p \times \text{duty cycle} \tag{2}$$

During the ON time the concentration of the metal ions to be deposited is reduced within a certain distance from the cathode surface. This so-called diffusion layer pulsates with the same frequency as the applied pulse current. Its thickness is also related to i_p but reaches a limiting value governed primarily by the diffusion coefficient of the metal ions. During the OFF time the concentration of the metal ions build up again by diffusion from the bulk electrolyte and will reach the equilibrium concentration of the bulk electrolyte if enough time is allowed.

These variables results in two important characteristic features of pulse plating which make it useful for alloy plating as well as property changes as mentioned earlier. They are:

(i) Very high instantaneous current densities and hence very high negative potentials can be reached. The high over potential causes a shift in the ratio of the rates of reactions with different kinetics. This high over potential associated with the high pulse current density greatly influences the nucleation rate because a high energy is available for the formation of new nuclei.

The second characteristics feature is the influence of the OFF time during which important adsorption and desorption phenomena as well as recrystallization of the deposit occur.

ZnS films were deposited by the pulse plating technique at a duty cycle of 20%. The substrates used were conducting glass and titanium. The substrates were cleaned prior to deposition. Titanium substrates were etched in HF solution for a short period and then washed thoroughly to remove traces of acid. The conducting glass substrates were dipped in dilute HCl for about 10 min and then washed thoroughly to remove traces of acid. Both

substrates were finally washed with trichloroethylene and then kept in a dessicator prior to deposition. The deposition precursors were AR grade Zinc sulphate and sodium thiosulphate. 20 ml of 0.25 M zinc sulphate and 15 ml of 0.30 M sodium thiosulphate were used. The cleaned substrates were used as the cathode and graphite was used as anode. The duty cycle was fixed at 20% and the deposition current density was varied in the range of 50–300 mA cm^{-2}. The deposition temperature was maintained as room temperature. The total deposition time was kept constant as 60 min in all the cases. Thickness of the films estimated by Mitutoyo surface profilometer was in the range of 1.5–2.5 μm as the deposition current density increased from 50 to 300 mA cm^{-2}. The films were characterized by X-ray diffraction studies using PANalytical X-ray diffractometer and CuKα radiation. Optical absorption studies were made on the films using UV–VIS–NIR Hitachi U3400 spectrophotometer. EDAX studies were made in a JOEL SEM attached with EDAX set up. AFM studies were made by Molecular Imaging system. For electrical measurements, gold dot was evaporated on the top surface of the film and the cross plane resistivity was measured by the two probe resistivity method.

3. Results and discussion

Fig. 1 shows the XRD patterns of the ZnS films prepared by pulse plating technique at different current densities. All the diffraction peaks in Fig. 2a are attributed to phase-pure wurtzite ZnS (JCPDS card 12-688). It is also clearly seen that the intensity of the diffraction peaks increases with deposition current density, which indicates that the crystallinity is improved. The ZnS film deposited at 50 mA cm^{-2} is amorphous. As the deposition current density was increased to 150 mA cm^{-2}, two diffraction peaks corresponding to (002) and (101) were detected. When deposition current density was further increased these two peaks became well separated and for a deposition current density of 300 mA cm^{-2} two more additional peaks corresponding to (102) and (110) were observed.

EDAX studies on the ZnS films deposited at a deposition current density of 300 mA cm^{-2} indicated a composition of Zn = 51%, S = 49%.

Optical absorption measurements were made at room temperature using unpolarized radiation. Absorbance spectra of the films were recorded as a function of wavelength in the range 250–800 nm. The
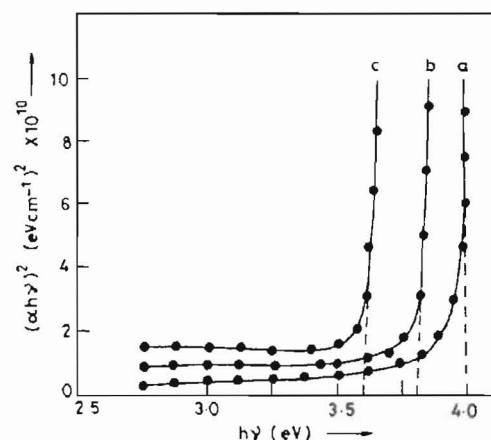

Fig. 2. $(\alpha h\nu)^2$ vs $h\nu$ plot of ZnS films deposited at different current densities: (a) 50 mA cm^{-2}; (b) 150 mA cm^{-2}; (c) 300 mA cm^{-2}.
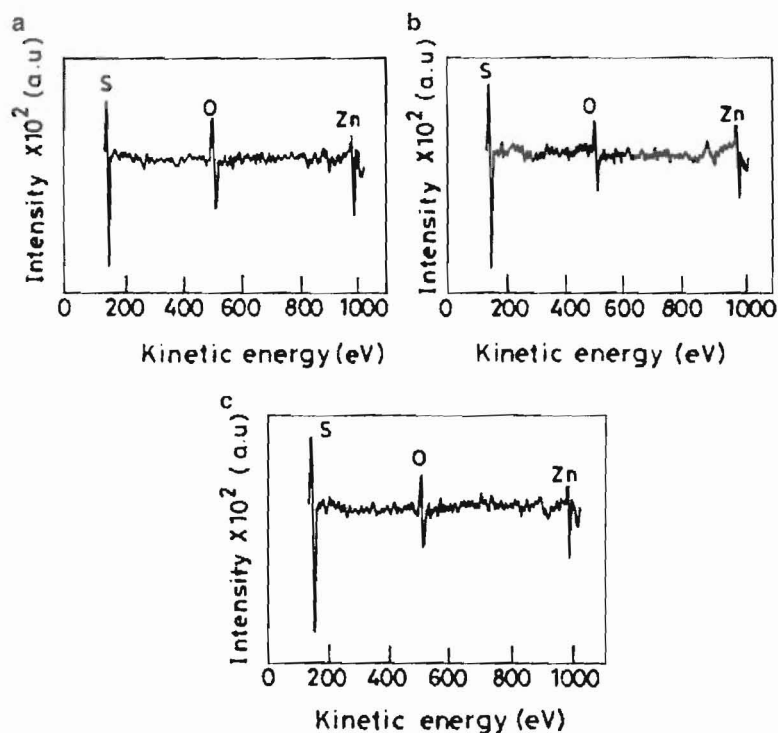
Fig. 3. AES spectra of ZnS films deposited at different current densities: (a) 50 mA cm^{-2}; (b) 150 mA cm^{-2}; (c) 300 mA cm^{-2}.

substrate absorption, if any was corrected by introducing an uncoated clean conducting glass substrate of the same size in the reference beam. Absorption coefficient (α) at various wavelengths was calculated using the equation [12].

$$\alpha = 2.303 A/t$$

Where A is the absorbance value at a particular wavelength and t is the thickness of the semiconductor film. The band gap of the films was determined by plotting a graph between $(\alpha h\nu)^2$ vs $h\nu$. Extrapolation of the straight line to the $h\nu$ axis gives the band gap of the film. Fig. 2 shows the plot of $(\alpha h\nu)^2$ vs $h\nu$ for the films deposited at different current densities. The absorption coefficient (α) was found to be of the order of 10^4 cm^{-1}. It can be observed from the figure that the band gap increases with decrease of current density due to quantum size effects. These values are similar to the values reported earlier [13].

Electrical resistivity measurements were made on the films deposited at different deposition current densities. Gold was vacuum deposited on the sides of the top surface of the films and the in plane resistivity of the films was measured using two probe technique. It is observed that the films deposited at lower current densities possessed a higher resistivity compared to the films deposited at higher current densities. This may be due to the improved crystallinity as well as the larger grain size for the films deposited at higher current densities. The resistivity values varied in the range of 3.5–17 Ω cm These values are higher than those reported for spray pyrolysed films [14].

The Auger spectra of the ZnS films deposited at different current densities are shown in Fig. 3. The Zn/S ratio varies in the range of 1.02–1.04 for the films deposited at different current densities, which is better than the value reported (Zn/S=1.1) in [11], where thin film of zinc sulphide is prepared by the pulsed electrochemical deposition at higher duty cycles and by potentiostatic 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 photoluminescence (PL) spectrum of ZnS thin films deposited at two different current densities under the excitation with a wavelength of 325 nm. In both cases peak is observed at $\lambda \approx 388$ corresponding to the lower energy than that of the energy band gap of ZnS obtained from $(\alpha h\nu)^2$ versus $h\nu$ plot. This peak shifting may be attributed due to donor–acceptor band transition where excess Zn acts as donor and some impurity or defects present at the surface and
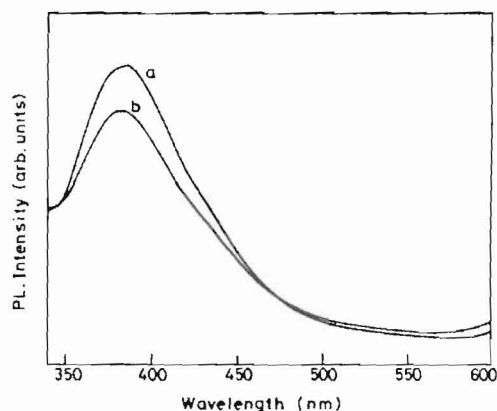

Fig. 4. PL spectra of ZnS films deposited at different current densities: (a) 50 mA cm^{-2}; (b) 300 mA cm^{-2}.

interface of the film acts as acceptor [15]. It is observed that the peak intensity is lower for the film deposited at a higher current density. This result can be explained in terms of surface defect states. On increasing the deposition current density, the grain growth results in smoothening of the surface and consequently a reduction in surface defect states and gives low intense peak [16].

4. Conclusion

This study demonstrates that single phase ZnS films can be easily deposited by the pulse deposition technique. The XRD results indicate that the structures of the ZnS films are wurtzite. Based on the optical transmission measurements, the band gaps of the ZnS films are in the range of 3.6–4.0 eV.

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