

# OPTOSTRUCTURAL AND ELECTRICAL STUDIES ON ELECTRODEPOSITED ZIRCONIUM SULPHOSELENIDE (ZrS<sub>0.5</sub>Se<sub>0.5</sub>)<sub>2</sub> THIN FILMS

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## ABSTRACT

Zirconium sulphoselenide thin films were obtained onto the thoroughly cleaned conducting glass substrate (stainless steel and FTO) using electrodeposition technique at room temperature. The deposition mechanism and growth of the films were studied by cyclic voltammetry. The X-ray diffraction analysis shows that the films are polycrystalline with hexagonal crystal structure. SEM study shows that the total substrate surface is well covered by densely packed spherical shaped grains. Stoichiometry of the film was studied by EDS technique. Optical absorption study shows the presence of direct transition having band gap energy 1.63 eV. Zirconium sulphoselenide is n-type semiconductor having activation energy, 0.058 eV in low temperature region and 0.168 eV in high temperature region.

**Keywords:** Electrodeposition; Electrical conductivity; Chemical compositional analysis.

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## INTRODUCTION

Transition metal semiconducting thin film materials which is based on sulphide, selenides and tellurides, form a technologically important class of materials due to their widespread utility in various electronic, optoelectronic and solar energy conversion devices<sup>1-5</sup>. The progressive research is going on in the search of photoelectrochemical (PEC) solar cells for low cost energy conversion<sup>6,7</sup>. For a PEC solar cell, the prime requirement for good solar energy conversion is that the photoanode/ photocathode should have a bandgap close to the maximum in the visible spectrum to utilize the solar spectrum efficiently; second, the semiconductor electrodes must be stable against photocathodic/photoanodic reactions<sup>8</sup>. The structure and electronic properties of the solid solutions (Zr<sub>x</sub>Ti<sub>1-x</sub>)<sub>1+y</sub>S<sub>2</sub> have been studied by David et al.<sup>9</sup> Optical transmission in ZrS<sub>3-x</sub>Se<sub>x</sub> single crystals was reported by Provencher et al.<sup>10</sup>. Electrodeposition and chemical bath depositions<sup>11,12</sup> are the alternative methods that are particularly adapted for the deposition of chalcogenide materials. Therefore we decided to deposit zirconium sulphoselenide thin films by electrodeposition and to study their properties. In this study, we have prepared zirconium sulphoselenide thin films by electrodeposition from an aqueous bath containing zirconyl nitrate, sodium thiosulphate and selenium dioxide as a precursor. The influence of growth conditions such as deposition potential, and concentration of the constituents of the bath was optimized initially. The zirconium sulphoselenide thin films deposited at optimized preparative parameters were characterized by optical absorption studies, X-ray diffraction, EDS, SEM and their conductivity studies were carried out at different temperature.

## EXPERIMENTAL

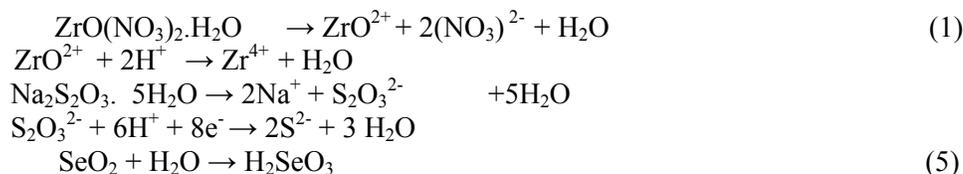
Combinatorial thin films of zirconium sulphoselenide are grown by using electrodeposition technique on stainless steel (SS) and fluorine doped tin oxide (F:SnO<sub>2</sub> or FTO) coated conducting glass substrates. The precursors zirconyl nitrate (0.2 M ZrO(NO<sub>3</sub>)<sub>2</sub>), sodium thiosulphate (0.1 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> 5H<sub>2</sub>O) and selenium dioxide (0.1M SeO<sub>2</sub>) were used respectively as Zr<sup>4+</sup>, S<sup>2-</sup> and Se<sup>2-</sup> ion sources. At the pH 2.5 and

deposition potential of -0.845V/SCE, it is observed that highly reflecting uniform adhesive thin films are formed on the substrate support after 25 min.

Electrochemical studies were carried out by using potentiostat (Princeton Perkin-Elmer, Applied Research Versastat-II; Model 250/270) in the three electrode configuration. The reference electrode was a saturated calomel electrode. Graphite was used as an anode. Stainless steel and FTO coated glass substrates were used as working electrode. Optical absorption was performed on the sample in the wavelength range of 350 to 850 nm with Hitachi-330 UV-VIS-NIR spectrophotometer. The energy gap, absorption coefficient and type of optical transitions of as grown thin film were determined from this measurement. The XRD pattern was obtained for the combinatorial thin film, using Philips X-ray diffractometer PW-1710 for Cu-K $\alpha$  radiation ( $\lambda = 1.5405 \text{ \AA}$ ). SEM micrograph and energy dispersive X-ray analysis were recorded on JEOL-JSM 6360 model. Electrical measurement was performed using two-probe press contact method in the temperature range 300-500 K for heating cycles. The thermo emf was recorded in the temperature range of 300-500 K. Silver contacts were employed for ohmic contact purpose.

### RESULTS AND DISCUSSION

The combinatorial thin film formation of zirconium sulphoselenide occurs as a result of the various chemical reactions taking place in deposition bath. The ionic species of zirconium, sulphide and selenide are produced by the following reaction equilibria in aqueous acidic bath,



On the substrate surface  $\text{H}_2\text{SeO}_3$  reduces to selenium ion<sup>13</sup>.



The successive combination of  $\text{Zr}^{4+}$ ,  $\text{S}^{2-}$  and  $\text{Se}^{2-}$  results in formation of combinatorial thin film zirconium sulphoselenide on the substrate support:



#### *Cyclic voltammetry studies*

Cyclic voltammetry was used to monitor the electrochemical reactions in electrolytic bath containing 0.2 M  $\text{ZrO}(\text{NO}_3)_2$  and 0.1M  $\text{SeO}_2$  to find the suitable deposition potential range for  $\text{ZrSe}_2$  thin film. Fig. 1(a) shows the cyclic voltammograms (CV) on stainless steel substrate recorded from a bath containing 0.2 M  $\text{ZrO}(\text{NO}_3)_2$  and 0.1M  $\text{SeO}_2$ . At -0.830 V/SCE reduction potential;  $\text{ZrSe}_2$  thin films are homogeneous, uniform & well adherent to substrate support. Fig 1(b) shows the cyclic voltammograms (CV) on stainless steel substrate recorded from a bath containing 0.2 M  $\text{ZrO}(\text{NO}_3)_2$  and 0.1 M  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  to find suitable deposition potential for  $\text{ZrS}_2$  thin films. The reduction peak at about -0.865 V/SCE confirms the formation of stable  $\text{ZrS}_2$  thin films on the substrate support.

For the combinatorial zirconium sulphoselenide thin films cyclic voltammograms (CV) was recorded [Fig. 1(c)] on stainless steel substrate from a bath containing 0.2 M  $\text{ZrO}(\text{NO}_3)_2$ , 0.1 M  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  and 0.1M  $\text{SeO}_2$ . Fig. 1(c) indicates that at reduction potential at -0.845 V/SCE, nucleation and growth of combinatorial zirconium sulphoselenide thin film is takes place on the substrate support.

### **Optical absorption studies**

The optical absorption of the thin films has been studied in the wavelength range 350–850 nm, without accounting for reflection and transmission losses. The nature of the transition involved (direct or indirect) during the absorption process was determined by studying the dependence of the absorption coefficient  $\alpha$ , on photon energy  $h\nu$  as,

$$\alpha = A(h\nu - E_g)^n / h\nu$$

where  $E_g$  is the band gap,  $\alpha$  the absorption coefficient,  $\nu$  the frequency,  $A$  is constant. This equation gives the band gap ( $E_g$ ) when straight portion of  $(ah\nu)^2$  against  $h\nu$  plot is extrapolated to the point at  $\alpha = 0$ . The plots of  $(ah\nu)^2$  versus  $h\nu$  shown in Fig. 2 is almost linear at higher wavelength and the optical absorption coefficient is of the order of  $10^4 \text{ cm}^{-1}$  supporting the allowed direct band transition of the material having direct band gap energy value 1.63 eV.

### **X-ray diffraction studies**

XRD patterns of the electrodeposited zirconium sulphoselenide thin films prepared at optimized preparative condition are shown in Fig. 3. The presence of sharp peaks in the XRD pattern confirming the polycrystalline nature of the combinatorial thin film of zirconium sulphoselenide, which shows there are five diffraction peaks of (003), (110), (023), (121) and (114) planes belonging to the hexagonal crystal structure. The observed 'd' values are compared with JCPDS data<sup>15</sup> to determine the crystal structure. Observed 'd' values have been found to be in good agreement with standard 'd' values as shown in Table 1. The crystallites size is deduced using the well known Scherrer's formula<sup>16</sup>,

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

Where  $D$  is the crystallite size,  $\beta$  is the broadening of diffraction line measured at half of its maximum intensity in radians (FWHM) and  $\lambda$  is the X-ray wavelength (1.5405 Å). The calculated crystallite size for zirconium sulphoselenide thin film is 35 nm along the (003) plane

### **SEM / EDS studies**

The surface morphology of the electrodeposited zirconium sulphoselenide thin film was investigated by scanning electron micrograph. Fig. 4 shows the SEM image of as deposited zirconium sulphoselenide thin film at optimized preparative parameters from aqueous acidic bath. From SEM, it is observed that as deposited thin film is compact, uniform, and pinhole free spherical shaped fine grains well covered on the substrate surface having grain size of the material is 315 nm.

The composition of the films has been estimated from energy dispersive X-ray analysis (EDS). Fig. 5 shows the EDS pattern of zirconium sulphoselenide thin film. The EDS spectrum shows the presence of Zr, Se, and S in the film. The atomic percentage for Zr, S and Se obtained from the EDS analysis is 32.18, 31.76 and 36.06 respectively. It is found that deposited film is slightly rich in selenium.

### **Electrical / TEP studies**

Electrical behaviour was studied by using two-point probe technique, varying the temperature range 300 K to 500 K, under constant voltage (5 volt). Fig. 6 shows variation of  $\ln \square$  versus reciprocal of the temperature for the as deposited combinatorial thin film of zirconium sulphoselenide, showing two linear regions are noted with a knee point, one is low temperature and other is high temperature region. Activation energy was calculated by taking slopes of linear plots in the low temperature region and high temperature region.

The temperature dependence of thermo electric power measurement was studied and shown in Fig. 7. The temperature difference between two ends of the sample causes transport of the carriers from the hot to cold end and thus creates an electric field which gives thermal voltage. This thermally generated voltage

is directly proportional to the temperature difference across ends of the semiconductor. From the polarity of generated thermo voltage one can determine whether, the electrons or the holes make the dominant contribution to the conduction mechanism. In our case, film shows negative polarity of the generated voltage which indicates the material is n-type semiconductor.

### CONCLUSIONS

From the above studies, it is concluded that mixed zirconium sulphoselenide thin films were successfully deposited by electrodeposition technique. As deposited zirconium sulphoselenide thin films are polycrystalline with hexagonal crystal structure having band gap energy 1.63 eV. The SEM micrograph shows well adherent and uniform film surface without cracks and pinholes showing mechanical stability of the film. EDAX analysis shows stiochiometry as expected theoretically. The thermoelectric power measurement shows electrons are dominant carriers.

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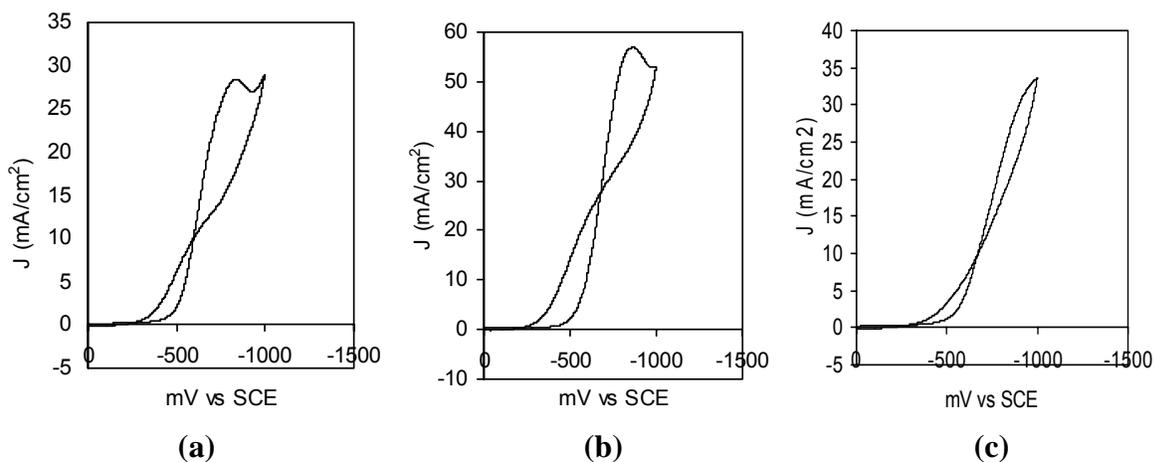
(Received: 7 May 2009

Accepted: 17 May 2009

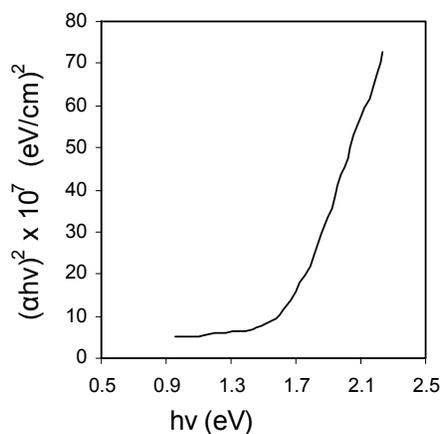
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**Table-1:** Comparison of observed 'd' values with standard 'd' values for zirconium sulphoselenide thin films on stainless steel substrate.

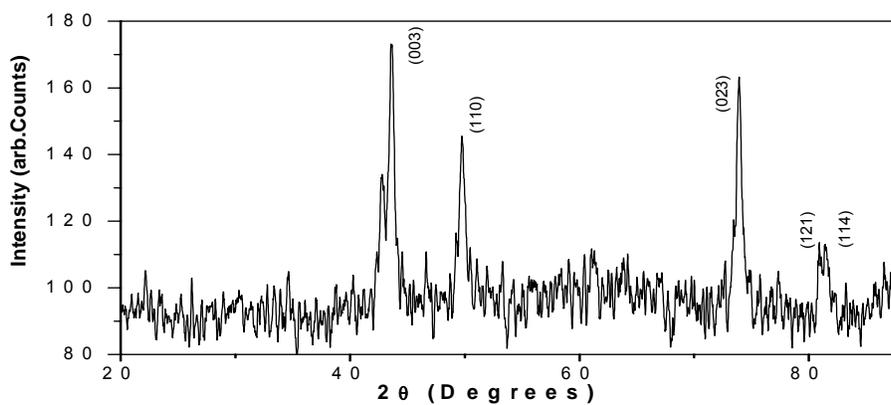
Sr. No.	Standard value (Å <sup>0</sup> )	'd.' Observed value ( Å <sup>0</sup> )	'd.' ( h k l) Planes
1	2.004	2.167	003
2	1.857	1.823	110
3	1.254	1.250	023
4	1.191	1.187	121
5	1.168	1.164	114



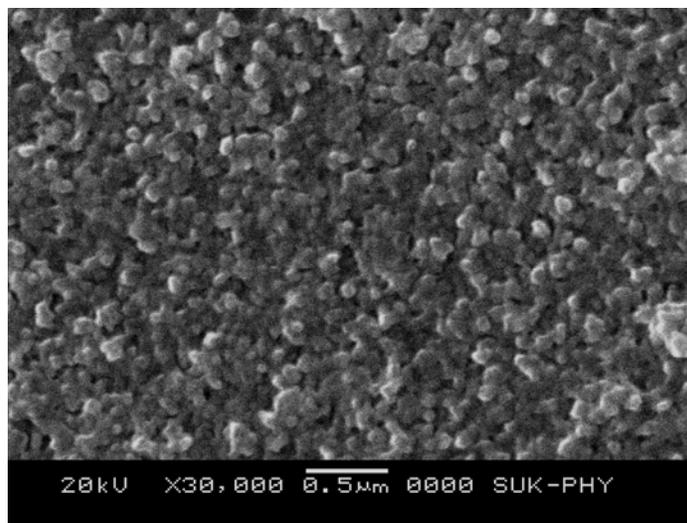
**Fig-1:** (a) Cyclic voltammograms (CV) on stainless steel substrate recorded from a bath containing 0.2 M  $ZrO(NO_3)_2$  + 0.1M  $SeO_2$  (b) 0.2 M  $ZrO(NO_3)_2$  + 0.1 M  $Na_2S_2O_3 \cdot 5H_2O$  (c) 0.2 M  $ZrO(NO_3)_2$  + 0.1M  $SeO_2$  + 0.1 M  $Na_2S_2O_3 \cdot 5H_2O$



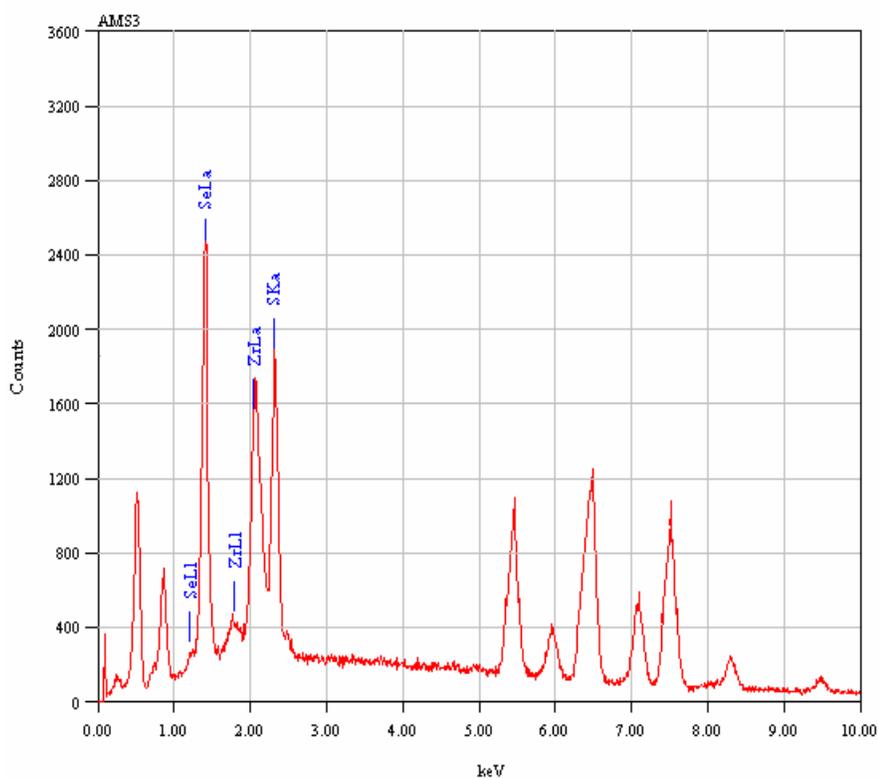
**Fig-2:** Plot of  $(\alpha hv)^2$  Versus  $h\nu$  for zirconium sulphoselenide thin film.



**Fig.3:** XRD pattern of as deposited zirconium sulphoselenide thin film.



**Fig.4:** SEM image of as deposited zirconium sulphoselenide thin film.



**Fig.-5:** EDS pattern of zirconium sulphoselenide thin film deposited on stainless-steel substrate

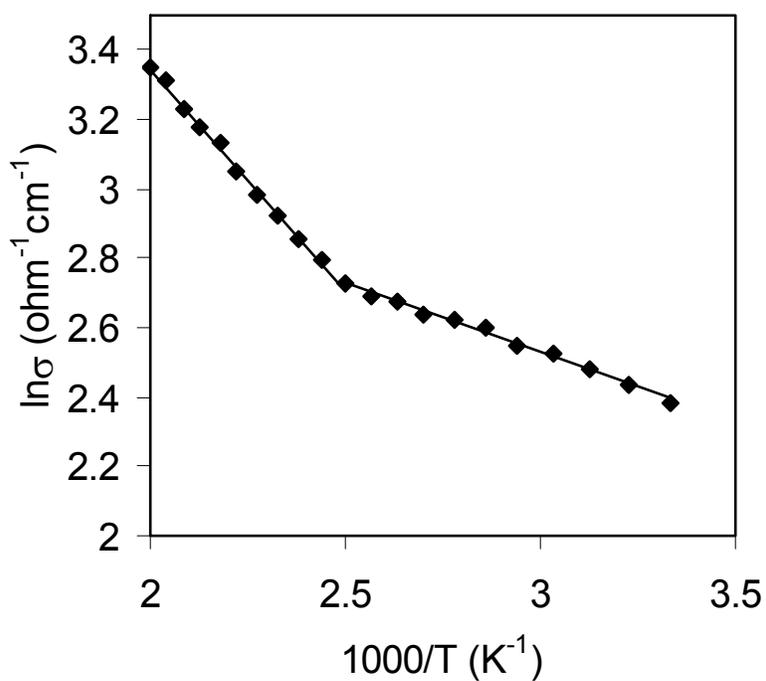


Fig.-6: Plot of  $\ln \sigma$  versus  $1000 / T$  for zirconium sulphoselenide thin film

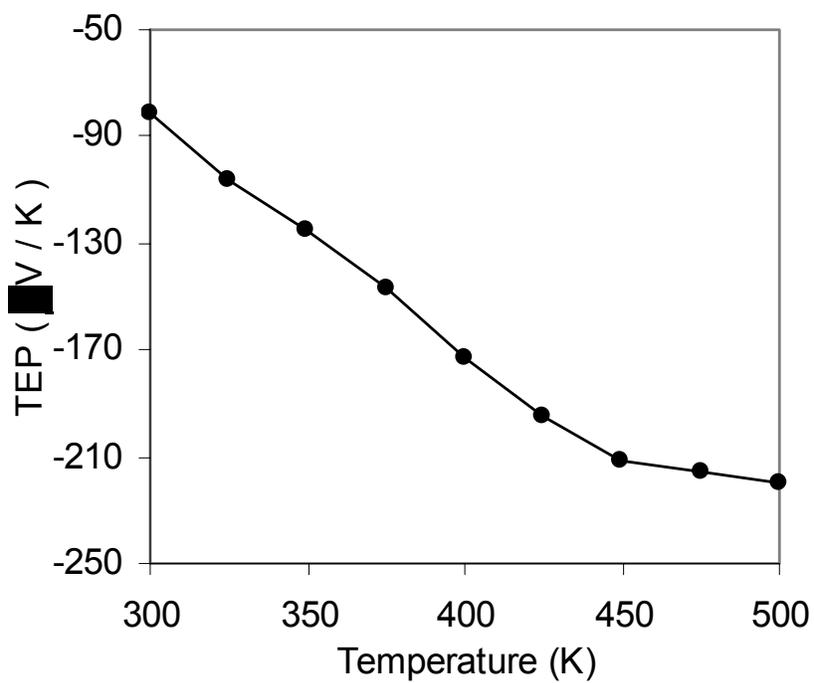


Fig.-7: Temperature dependence of the thermoelectric power of zirconium sulphoselenide thin film