International Journal of Chemistry Studies
www.chemistryjournal.in
ISSN: 2581-348X
Received: 24-05-2022, Accepted: 09-06-2022, Published: 25-06-2022
Volume 6, Issue 1, 2022, Page No. 83-86

Synthesis of zirconium disulphide thin films and its optical and electrical study

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Abstract
Zirconium Disulphide 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 substrate surface is well covered by densely packed spherical shaped grains. Stiochiometry of the film was studied by EDS technique. Optical absorption study shows the presence of direct transition having band gap energy 1.8 eV. Zirconium Disulphide is n-type semiconductor having activation energy, 0.0071 eV in low temperature region and 0.212 eV in high temperature region.

Keywords: Electrodeposition, Electrical conductivity, Elemental analysis

Introduction
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 [1-5]. The progressive research is going on in the search of photoelectrochemical (PEC) solar cells for low cost energy conversion [6, 7]. 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 [8].The structure and electronic properties of the solid solutions $(Zr_xTi_{1-x})_{1+y}S_2$ have been studied by David *et al* [9]. Optical transmission in $ZrS_{3-x}Se_x$ single crystals was reported by Provencher *et al* [10]. Electrodeposition and chemical bath depositions are the alternative methods that are particularly adapted for the deposition of chalcogenide materials. Therefore we decided to deposit zirconium sulphide thin films by electrodeposition and to study their properties. In this study, we have prepared zirconium sulphide thin films by electrodeposition from an aqueous bath containing zirconyl nitrate, and sodium thiosulphate 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 sulphide 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.

Experimental
Zirconium disulphide thin films was carried out by using electrodeposition technique on stainless steel (SS) and fluorine doped tin oxide ($F:SnO_2$ or FTO) coated conducting glass substrates. The precursors zirconyl nitrate (0.2 M $ZrO(NO_3)_2$ and sodium thiosulphate (0.1 M $Na_2S_2O_3$ $5H_2O$) were used respectively as Zr^{4+}, and S^{2-} ion sources. The electrolytic bath was prepared by mixing 12 mL 0.2 M $ZrO(NO_3)_2$ and 14 mL 0.1 M $Na_2S_2O_3$ $5H_2O$ solution. The final pH of the electrolytic bath containing 0.2 M $ZrO(NO_3)_2$and 0.1 M $Na_2S_2O_35H_2O$ was 1.75. During the deposition the distance between working electrode (stainless steel (ss) and FTO coated glass substrate) and counter electrode (graphite plate) was kept constant as 1 cm. The electrodeposited ZrS_2thin films were found to be pin hole free, uniform and well adherent to substrate support
at deposition potential of -0.865V/SCE, it is observed that highly reflecting uniform adhesive thin films are formed on the substrate support after 35 min. 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-Kα radiation (λ =1.5405 A^0). 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 Zirconium Disulphide thin films occur as a result of the various chemical reactions taking place in deposition bath. The ionic species of zirconium, and sulphide are produced by the following reaction equilibria in aqueous acidic bath,

$ZrO(NO_3)_2.H_2O \rightarrow ZrO^{2+} + 2(NO_3)^{2-} + H_2O$ (1)
$ZrO^{2+} + 2H^+ \rightarrow Zr^{4+} + H_2O$ (2)
$Na_2S_2O_3.\ 5H_2O \rightarrow 2Na^+ + S_2O_3^{2-} + 5H_2O$ (3)
$S_2O_3^{2-} + 6H^+ + 8e^- \rightarrow 2S^{2-} + 3\ H_2O$ (4)

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

$Zr^{4+} + S^{2--} \rightarrow ZrS_2$ (5)

Cyclic voltammetry studies
Cyclic voltammetry is used to study the electrochemical reactions in electrolytic bath containing 0.2 M ZrO $(NO_3)_2$ and 0.1M $Na_2S_2O_3$. $5H_2O$ to find the suitable deposition potential range for ZrS_2 thin film. The cyclic voltammograms (CV) on stainless steel substrate recorded from a bath containing 0.2 M $ZrO(NO_3)_2$ and 0.1 M $Na_2S_2O_3$ $5H_2O$ to find suitable deposition potential for ZrS_2 thin films. The reduction peak at about -0.865 V/SCE confirms the formation of stable ZrS_2 thin films on the substrate support.

Optical absorption studies
Absorption study of the thin films has been studied in the wavelength range 350–850 nm. The nature of the transition involved (direct or indirect) during the absorption process was determined by studying the dependence of the absorption coefficient α, on photon energy h*v* [11] as,

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

where E_g is the band gap, α the absorption coefficient, v the frequency, A is constant. This equation gives the band gap (Eg) when straight portion of $(ahv)^2$ against h*v* plot is extrapolated to the point at $\alpha = 0$. The plots of $(ahv)^2$ versus hv is almost linear at higher wavelength and the optical absorption coefficient is of the order of 10^4 cm^{-1} supporting the allowed direct band transition of the material having direct band gap energy value 1.8eV.

SEM / EDS studies
The SEM micrograph as deposited zirconium disulphide thin film at room temperature shows the homogeneous film growth without cracks or holes. Fig. 1 shows the SEM image of as deposited zirconium disulphide 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 compositional analysis of the films has been estimated from energy dispersive X-ray analysis (EDS). Fig. 2shows the EDS pattern of as deposited zirconium disulphide thin film. The atomic percentage for Zr and S obtained from the EDS analysis is 38.46 % zirconium and 61.54 % sulpher respectively, that the Zr and S ratio is almost 1:2 expected for ZrS_2

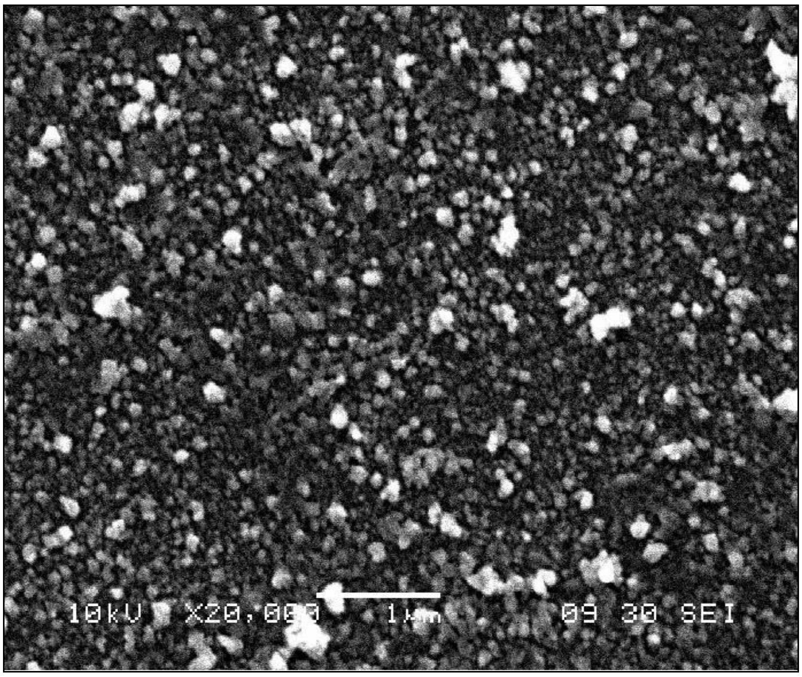

Fig 1: SEM image of as deposited zirconium disulphide thin film.

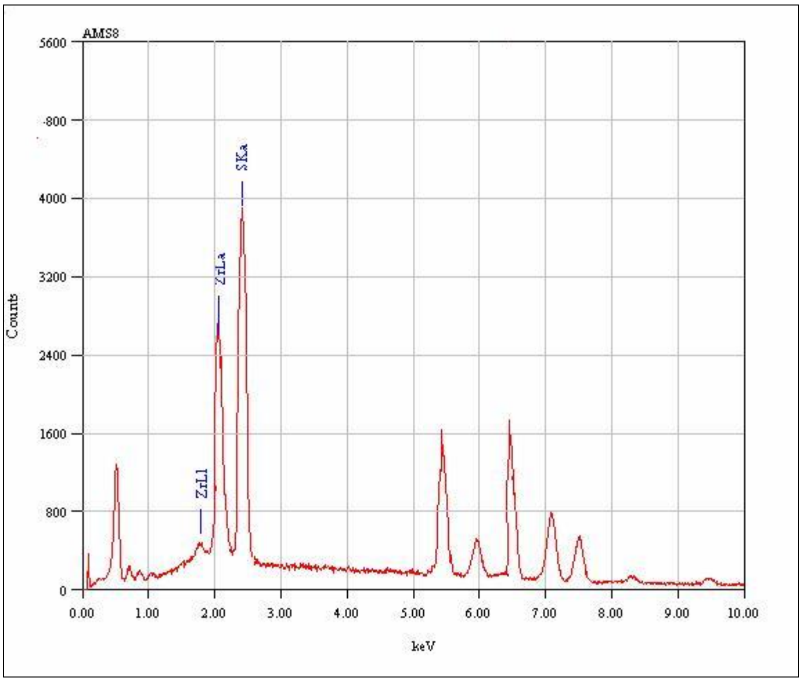

Fig 2: EDS pattern of as deposited zirconium disulphide thin film.

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. 3 shows variation of ln versus reciprocal of the temperature for the as deposited combinatorial thin film of zirconium disulphide, 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. 4 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

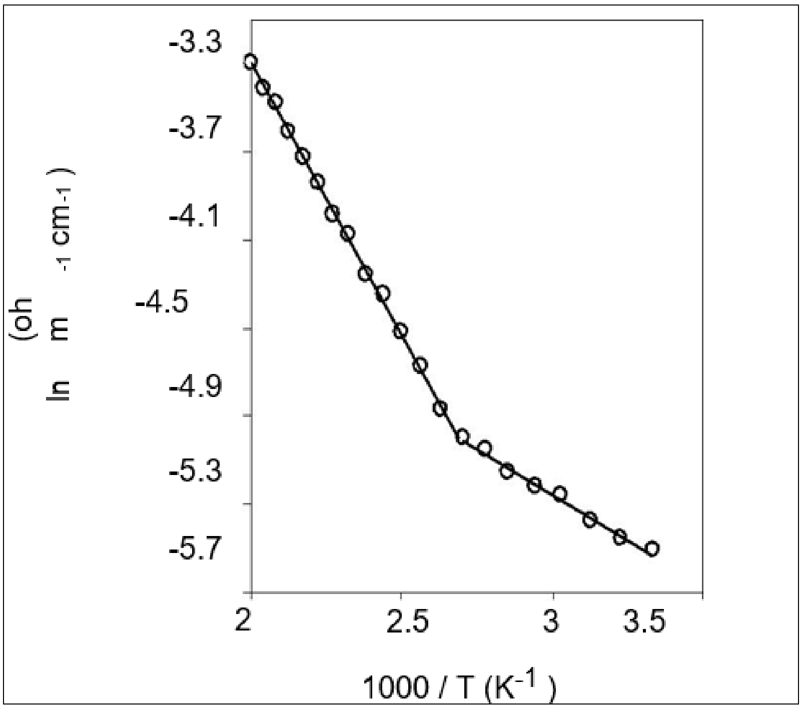

Fig 3: Plot of ln σ versus 1000/T of as deposited ZrS_2 thin film

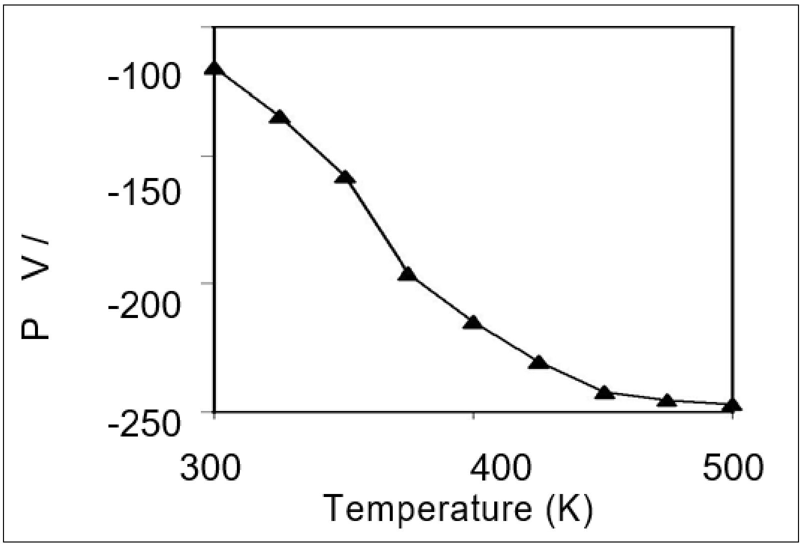

Fig 4: Temperature dependence of the thermoelectric power of ZrS_2 thin film.

Conclusions

Polycrystalline n-type ZrS_2 semiconducting thin films are successfully prepared by electrodeposition technique on stainless-steel and FTO coated conducting glass substrate from aqueous acidic bath. The X-ray diffractograms reveal that the films are polycrystalline in nature and possess hexagonal crystal structure. The optical absorption study shows direct type of transition having band gap energy 1.8 eV.SEM micrograph shows densely packed spherical grains having average grain size of the material is found to be 340 nm. The compositional analysis of the as deposited thin film is carried out by EDS technique, showing the film is stiochiometric. Temperature dependence of electrical conductivity indicates that films are semiconducting having activation energy for low temperature region is 0.071 eV and in high temperature region is 0.212 eV. The thermoelectric power measurement shows n-type conduction.

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