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Electrochemical Synthesis and Characterisation of $ZrSe_2$ Thin Films

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Polycrystalline $ZrSe_2$ thin films have been electrodeposited on stainless steel and fluorine-doped tin oxide (FTO) coated conducting glass substrate from an aqueous acidic bath using zirconyl nitrate as a zirconium ion source and selenium dioxide as a selenium ion source. The deposited films have been characterized by using optical absorption, X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive x-ray analysis (EDAX). X- ray diffraction (XRD), studies reveals that films are polycrystalline with hexagonal crystal structure. Surface morphology studies by scanning electron microscopy (SEM) shows that the grains are uniformly distributed over the entire surface of substrate. EDAX studies indicate that the zirconium diselenide films are stiochiometric. $ZrSe_2$ is n-type semiconductor and room temperature electrical conductivity is 16.34 $ohm^{-1}cm^{-1}$. The optical absorption study shows direct transition having band gap energy 1.65 eV.

Keywords: Thin Films; Electrodeposition; Optical properties: X-ray diffraction

1. INTRODUCTION

In last few years, there is considerable interest in the preparation and characterisation of chalcogenide thin films because of their potential applications in various fields of science and technology [1-7]. The extensive research is going on in the search of photoelectrochemical (PEC) solar cells for low cost energy conversion [8,9]. Zirconium diselenide belongs to the group IV^B transition metal dichalcogenide and is semiconducting with layered structure. The electronic properties of ZrS_2 and $ZrSe_2$ have been reviewed and found to be crystallize in hexagonal CdI_2 layer structure with space group D^3_{3d} by Wilson and Yoffe [10]. Photoelectrochemical study of zirconium dichalcogenide reported by Agarwal et al. [11]. Lee et al. [12] shows that $ZrSe_2$ is a semiconductor with an indirect band gap of 1.2 eV. The band structure of $ZrSe_2$ have been calculated using the semi-

empirical tight binding linear combination of atomic orbitals shows that these materials are semiconductor with energy gaps of 1.37 eV [13,14]. Electrochemical characteristics of $ZrSe_2$ in a secondary lithium battery were reported by Onuki et al. [15]. Negative resistance in $ZrSe_2$ were reported by Bartwal et al. [16].

The present manuscript describes synthesis of $ZrSe_2$ thin films by electrodeposition technique, using zirconyl nitrate as source of Zr^{4+} ion and selenium dioxide as source of Se^{2-} ions. The preparative parameters such as deposition potential, concentration of precursors, pH of the plating bath have been optimized at initial stages of deposition. The optical, electrical, structural, morphological and compositional analysis have been studied and reported here.

2. EXPERIMENTAL PART

The $ZrSe_2$ thin films were electrodeposited on stainless steel (SS) and fluorine doped tin oxide (F:SnO_2 or FTO) coated conducting glass substrates from aqueous electrolytic bath containing 0.1 M $ZrO(NO_3)_2$ and 0.1M SeO_2. All the chemicals used were pure Analytical Grade (Supplied by S. D. Fine Chemicals. Mumbai, India). The pH of electrolytic bath was maintained to 2. The films were deposited at potential -0.830 V with respect to saturated calomel electrode (SCE) as a reference electrode. Graphite plate was used as an anode & stainless steel and FTO coated glass substrate were used as working electrode. The uniform and well adherent thin films have been deposited at room temperature for deposition period of 30 min. Before using the stainless steel as substrate supports, they were first mirror polished by fine grade polish paper, washed with liquid detergent, followed by drying in the alcohol vapour. Then the substrates were etched in 3% HCl for 10 min. and further ultrasonically cleaned. FTO coated glass substrates were boiled in chromic acid for 20 min. and ultrasonically cleaned with double distilled water and dried in hot alcoholic vapour.

Electrochemical studies and film deposition were made using a potentiostat (Princeton Perkin-Elmer, Applied Research Verrsatat- II; Model 250/270). The deposited films were characterized for their structural properties using Philips X –ray diffractometer PW-1710 (λ =1.5405 A^0) for Cu-Kα radiation in the diffraction angle range of 30-90°. The electrical conductivity measurements were carried out using two probe method. The area of the film was defined and silver paste was applied to ensure good electrical contact to the film. The working temperature was recorded using a Chromel-Alumel thermocouple. The potential drop across the film was measured with the help of Meco 801 digital multimeter and current passed through the sample was noted with a sensitive 4 digit picoammeter (Scientific equipment, Roorkee DPM 111).The measurement was carried out by keeping the film system in a light tight box.

Thermoelectric power measurement was carried out under the condition of maximum temperature difference and minimum contact resistance. The thermoelectric voltage was measured with digital Testronix micro voltmeter. The microstructure was studied by using a scanning electron microscope (SEM) (JEOL Model-6360) attached with an energy dispersive X-ray analysis (EDAX) to measure quantitative composition of the sample. Optical absorption study of the film deposited on

FTO coated glass substrate was carried out in the wavelength range of 350-850 nm using Systronic Model-119 spectrophotometer.

3. RESULTS AND DISCUSSION

Zirconium diselenide thin films have been formed according to the following overall reactions:

$$ZrO(NO_3)_2.H_2O \longrightarrow ZrO^{2+} + 2(NO_3)^{2-} + H_2O \quad (1)$$

$$ZrO^{2+} + 2H^{+} \longrightarrow Zr^{4+} + H_2O \quad (2)$$

$$SeO_2 + H_2O \longrightarrow H_2SeO_3 \quad (3)$$

On the substrate surface H_2SeO_3 reduces to selenium ion [17].

$$H_2SeO_3 + 4H^{+} + 6e^{-} \longrightarrow Se^{2-} + 3\,H_2O \quad (4)$$

The successive combination of Zr^{4+} and Se^{2-} results in $ZrSe_2$ thin film formation as per equilibria,

$$Zr^{4+} + 2\,Se^{2-} \longrightarrow ZrSe_2 \quad (5)$$

3.1 Cyclic voltammetry studies.

To understood the reduction and growth of $ZrSe_2$ thin films, electrochemical technique Cyclic voltammetry was used. From Fig. 1(a) shows cyclic voltammogram of 0.2 M $ZrO(NO_3)_2$ on stainless steel substrate. It is observed that during the cathodic scan, visible silver gray films have been appeared on the surface of the working electrode at a potential of about -0.895 V/SCE indicates reduction of elemental Zr takes place at this particular reduction potential. The formation of reddish elemental Se layer was observed at a constant potential of -0.53 V/SCE, a cyclic voltommogram of 0.1M SeO_2 is shown in Fig 1 (b).

The cyclic voltammogram measured for the electrolytic bath of 0.2 M $ZrO(NO_3)_2$ + 0.1M SeO_2 is shown in Fig 1.(c), it is clearly indicate that the cathodic current increases sharply from -0.600 V upto -0.860 V/SCE, which belongs to simultaneous reduction of both zirconium and selenium ions. At -0.830 V/SCE reduction potential, films are homogeneous, uniform & well adherent to substrate support.

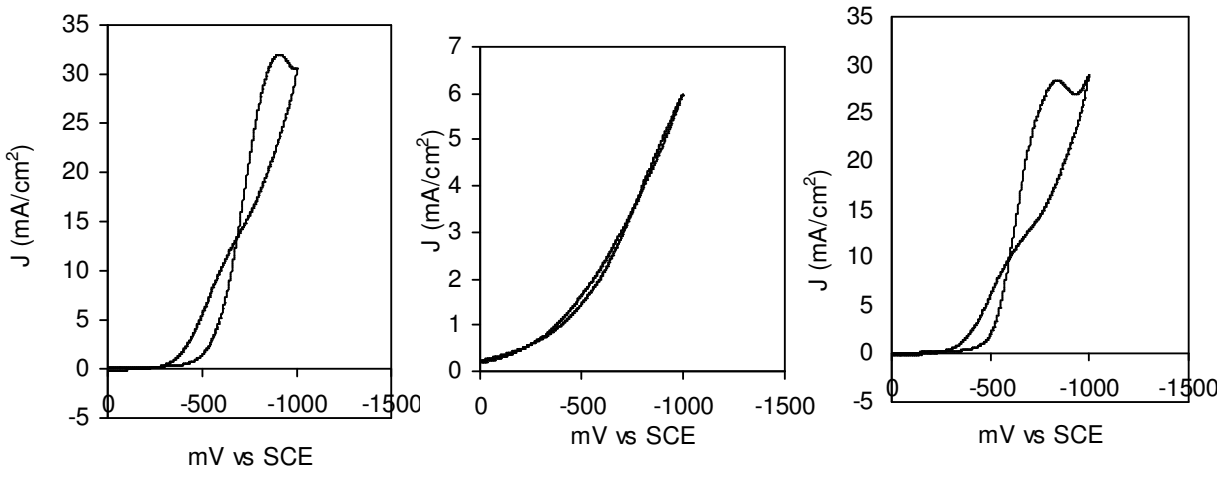

Figure 1. Cyclic Voltammogram on stainless-steel substrate in the solution containing (a) 0.2 M $ZrO(NO_3)_2$; (b) 0.1 M SeO_2 and (c) 0.2 M $ZrO(NO_3)_2$ + 0.1 M SeO_2

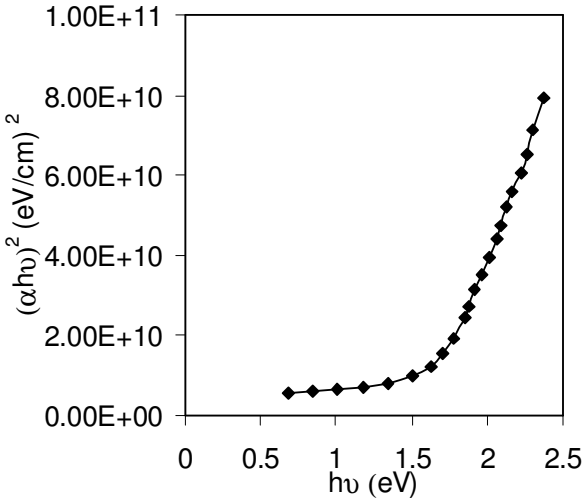

Figure 2. Plot of $(\alpha h\nu)^2$ Versus hν for $ZrSe_2$ thin film deposited at room temperature.

3.2 Optical absorption studies

The optical absorption spectrum of the $ZrSe_2$ thin film deposited on FTO coated glass substrate was recorded in the wavelength range 350 nm to 850 nm. The absorption data are further analysed for near–edge optical absorption of semiconductor using a classical relation,

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

Where n= ½ for direct allowed transition. The absorption coefficient (α) is found to be high in the order of 10^4 cm^{-1} confirming the direct allowed transition. Fig. 2 shows plot $(\alpha h\nu)^2$ versus hν is linear at higher energies indicates direct type of transition. The straight line portion is extrapolated to the energy axis at α= 0, which gives the band gap energy (E_g) of $ZrSe_2$ to be 1.65 eV.

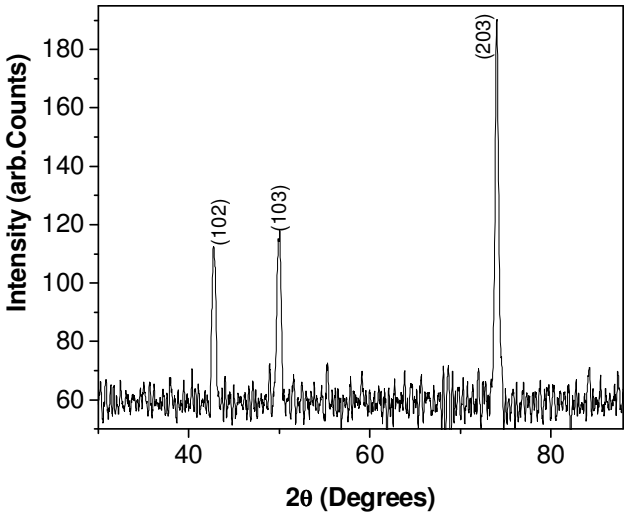

Figure 3. XRD pattern of as deposited $ZrSe_2$ thin film at room temperature.

Table 1. Comparison of observed 'd' values with standard 'd' values for Zirconium diselenide thin films on stainless steel substrate.

Sr. No.	Standard 'd.' value ($Å^0$)	Observed 'd.' value ($Å^0$)	(h k l) Planes
1	2.240	2.197	102
2	1.740	1.748	103
3	1.280	1.280	203

3.3 X- ray diffraction studies

Fig. 3 shows typical XRD pattern of the as deposited $ZrSe_2$ thin films on the stainless-steel substrate at optimized preparative parameters. The sharp peaks reveal the polycrystalline nature with hexagonal crystal structure. The observed 'd' values are compared with JCPDS data [18] 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 crystallite size was calculated from the full-width at half- maximum (FWHM) measurement for the prominent X-ray diffraction peaks using Scherrer formula,

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

Where D is the crystallite size, λ is the wavelength of the X-ray radiation used, β is the full width at half maximum and θ is Bragg angle. The crystallite size calculated for more intense peak (203) is 28 nm.

3.4 SEM/ EDS studies

Fig. 4 shows the typical SEM micrograph of $ZrSe_2$ thin film deposited at room temperature on stainless- steel substrates. The micrograph reveals that the material shows compact, pinhole free with large number of spherical grains uniformly distributed over the entire surface of the substrate. The average grain size of the material is 340 nm.

Fig. 5 shows a typical EDAX pattern for as deposited $ZrSe_2$ thin film under the acceleration voltage of 15 keV. The quantitative elemental analysis was carried out only for Zr and Se; the average atomic percentage for these elements is 33.58 and 66.42 respectively, showing that film is exactly stiochiometric.

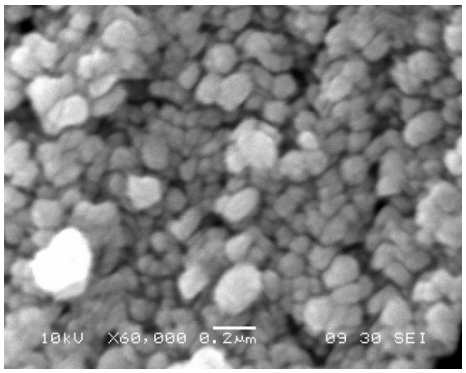

Figure 4. SEM image of as deposited $ZrSe_2$ thin film at room temperature.

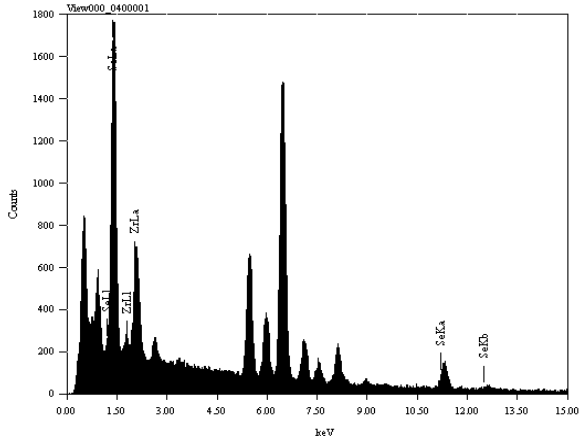

Figure 5. EDAX analysis of as deposited $ZrSe_2$ thin film on stainless-steel substrate

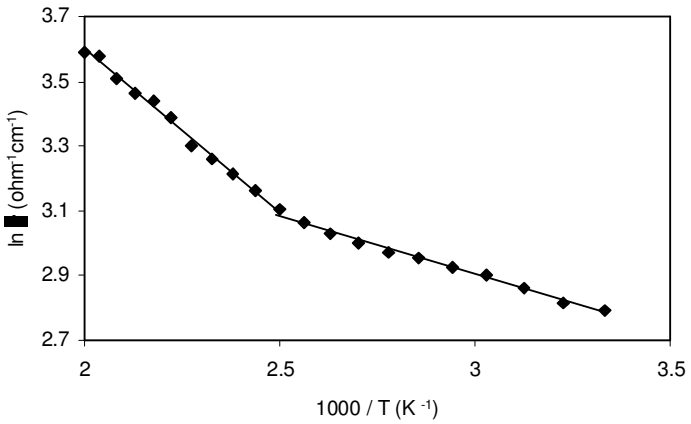

Figure 6. Plot of ln σ versus 1000 / T for $ZrSe_2$ thin film

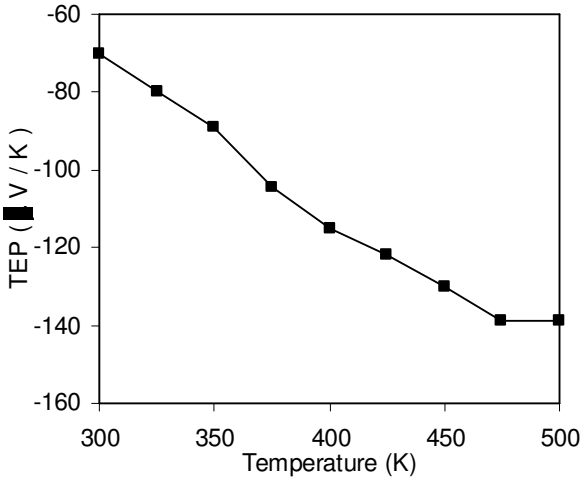

Figure 7. Temperature dependence of the thermoelectric power of $ZrSe_2$ thin film.

3.5 Electrical / TEP studies

Electrical conductivity of the film was studied using two-point probe technique by varying the temperature range 300 K to 500K, under constant voltage (5 volt). The activation energy is calculated from the relation

$$\sigma = \sigma_o \, e^{(-Ea/\kappa T)}$$

Where E_a is activation energy, κ is Boltzmann constant and σ_0 is the pre exponential factor. The plot of $\ln \sigma$ versus 1000 / T for as deposited $ZrSe_2$ thin films are shown in figure 6 and two linear regions are noted with a knee point one below 400 K, where the conductivity varies slowly with 1 / T and other above 400 K, where the conductivity varies abruptly with temperature. From the slopes of linear plots, activation energy for conduction was calculated for two temperature region. The activation energy for low temperature region is 0.031 eV and in high temperature region is 0.088 eV. The thermoelectric power of $ZrSe_2$ thin film is negative and increases with increasing temperature. The negative sign stems from a dominance of n-type charge carriers. The temperature dependence of the thermoelectric power of as deposited $ZrSe_2$ film is shown in Fig. 7

4. CONCLUSIONS

$ZrSe_2$ semiconducting thin films were successfully deposited by electrodeposion technique from aqueous acidic bath. As deposited $ZrSe_2$ thin films are polycrystalline with hexagonal crystal structure having band gap energy 1.65 eV. EDAX analysis shows 1: 2 stiochiometry as expected theoretically. The SEM micrograph shows the device quality nature of the surface without any pinholes. The thermoelectric power measurement shows electrons are dominant carriers.

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