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NOVEL ROUTE FOR PREPARATION OF ZIRCONIUM DI-SELENIDE THIN FILMS

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ABSTRACT
Thin films of $ZrSe_2$ have been prepared on stainless steel and fluorine doped tin oxide (FTO) coated glass substrates using electrodeposition technique at potentiostatic mode. Double distilled water containing precursors Zr and Se with Ethylene Diamine Tetra- acetic Acid (EDTA) disodium salt as a complexing agent to obtain good quality deposits by controlling the rate of reaction. The preparative parameters such as concentration of bath, deposition time, bath temperature and pH of the bath have been optimized. X-ray diffraction (XRD) study reveals that the deposited $ZrSe_2$ thin film is polycrystalline with hexagonal crystal structure. Optical absorption shows the presence of direct transition and band gap energy is found to be 1.5 eV.

KEY WORDS: Electrodeposition, $ZrSe_2$ thin films, XRD and Band gap.

INTRODUCTION

The thin films of $ZrSe_3$ has a chain like structure belonging to the space group $P2_1lm$ **(Furuseth, 1975)**. The linear chain of metal atoms is parallel to the crystallographic b- axis, which is growth axis. Six chalcogenide atoms (S, Se, or Te) are surrounded by each metal atom forming distorted trigonal prisms. The crystal growth in the form of layer runs parallel to the b-axis and each chain in the layer is displaced from the neighbouring chain by half of the unit cell along the b-axis.

Electrical properties of $ZrSe_3$ single crystal along the chain axis have been carried out in the temperature range from 200 – 400 K (Ikari, 1983). The $ZrSe_3$ exhibits a rather layer–like semiconducting behavior (Patel, 1993). $ZrSe_3$ exhibits direct as well as indirect band transition with band gap energy 1.47 and 1.17 eV is studied. Optical transmission in ZrS_xSe_{3-x} single crystals through temperature modulated reflectivity was reported (Provencher, 1988). The anisotropy ratio decreases with increase in temperature in the 303-403 K has been studied (Kaushik, 2005).

Raman scattering for ZrS_3 was reported as a function of hydrostatic pressure. Thermo reflectance spectra of $ZrSxSe3_{-x}$ single crystal have been measured at 50K. (Devilee, 1982).

The metallic chalcogenides have applications in photovoltaic and photoelectrochemical solar cells. Among them, disulphide and diselenide of zirconium present some interesting switching and memory effects (Jandl, 1981). Zirconium diselenide thin films have applications in solid state solar cells. Thin films of $ZrSe_3$, $ZrS_{3-x}Se_x$ were deposited by gas phase processes. The semiconducting nature of ZrS_3 and $ZrSe_3$ is studied from resistance vs. temperature measurement. The detail study of valence band by synchrotron radiation photoemission spectroscopy had demonstrated the existence of paired anion ligand in zirconium trichalcogenide. The growth, optical and electrical properties of $ZrSe_3$ thin films prepared by chemical vapor deposition was reported. Electrochemical characteristics of $ZrSe_2$ in a secondary lithium battery and the conduction band structure of ZrS_2 and $ZrSe_2$ were reported.

This paper discusses synthesis of ZrSe2 thin films by simple and low cost electrodeposition technique. Studies have been made by using XRD and optical absorption techniques respectively.

Experimental Details

Thin films of $ZrSe_2$ were electrodeposited onto the stainless steel and fluorine doped tin oxide (FTO) coated glass substrates of area 1 cm^2 from a bath containing precursors of Zr and Se. The substrates of stainless steel were mirror polished by polish paper and cleaned with laboline (a non-ionic liquid detergent/surfactant) and finally with ultrasonic cleaner. An inert polished graphite plate was used as a counter electrode. The molarity of $ZrSO_4$ and SeO_2 were kept constant at 0.01 M. Ethylene diamine tetra-acetic acid [EDTA] disodium salt of 0.01 M was used as a complexing agent to maintain uniform deposition rate and to improve the quality of deposits. The deposition was carried out from a stirred solution (25 ml) under potentiostatic mode using saturated calomel electrode (SCE) as a reference electrode. The X-ray diffraction patterns for $ZrSe_2$ thin films deposited onto stainless steel and FTO coated substrates were recorded by Philips X-ray diffractometer model 1710 with Cr-Kα radiation in the span of angle between 10^0 and 100^0. The

optical absorption studies were carried out in the wavelength range 350 – 1350 nm. By UV-VIS-IR spectrophotometer model Hitachi –330 (Japan).

RESULTS AND DISCUSSION

The films of $ZrSe_2$ have been deposited at potentiostatic mode at 420 mV / SCE. The Fig.1 shows the variation I_{sc} and V_{oc} with deposition time, from the graph it is observed that I_{sc} and V_{oc} increases with increase in deposition time, attains maximum values for film deposited at 40 minutes and further increase in deposition time both I_{sc} and V_{oc} decreases this indicates that the formation of good quality and nearly stoichiometric compound at 40 minutes. The lower values of I_{sc} and V_{oc} may be originated due to deviation from stoichiometry and high surface recombination of photogenerated carrier by the surface state and which is good agreement with reported result (Deshmukh, 2005).

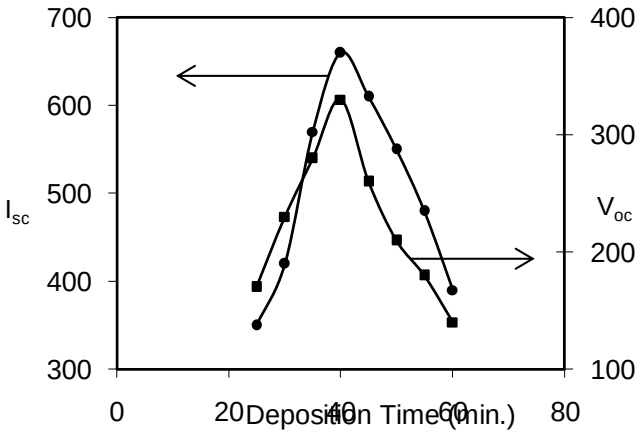

Figure 1. The variation I_{sc} and V_{oc} with deposition time for the $ZrSe_2$ thin films.

The decrease in I_{sc} and V_{oc} with increase in deposition time may be attributed to the non-optimized thickness and transition between defect levels. The PEC cell with configuration $ZrSe_2$ / 0.1 M polysuphide / graphite is used to check the type of conductivity exhibited by $ZrSe_2$ thin films. The polarity of dark voltage is negative towards $ZrSe_2$ photoelectrode and positive towards the graphite electrode for all samples showing n – type semiconducting behavior. From the graph it is observed that I_{sc} and V_{oc} increases with increase in bath temperature and attains maximum values for the film deposited at 50^oC, indicating probably a better formation of stiochiometric semiconducting compound, further increase in bath temperature, decreases the values of I_{sc} and V_{oc}. The lower values of I_{sc} and V_{oc} may be attributed to non-stoichiometric growth of $ZrSe_2$ thin films due to insufficient thermal energy provided during the deposition (Nikale, 2004).

The X-ray diffraction pattern of $ZrSe_2$ thin film deposited at optimized preparative parameters is displayed in Fig.2. The presence of large number of peaks indicates that the film is polycrystalline in nature. The XRD pattern fairly matches with the peak position (2θ) of standard X-ray powder diffraction data (ASTM data file No.3-1189). The indexing of the pattern was therefore done by assuming the hexagonal structure. The Comparison of experimental d-values with standard d-values (ASTM data) for $ZrSe_2$ thin film is tabulated in Table 1.

Table1: Comparison of experimental d-values with ASTM data for $ZrSe_2$ thin film:

Sr. No.	Standard ‘d’ value (A^o)	Observed ‘d’ value (A^o)	(h k l) planes
1.	2.89	2.882	(101)
3.	1.59	1.602	(201)
5.	1.39	1.402	(104)
6.	1.39	1.386	(113)

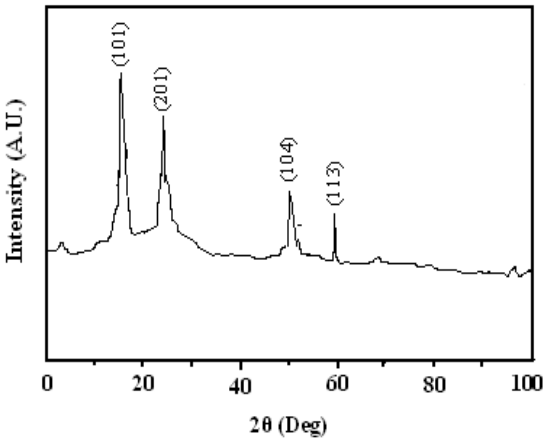

Figure2. The XRD spectra for $ZrSe_2$ thin film deposited at optimized preparative parameters.

The optical absorption of the films has been studied in the range 350 – 1350 nm. The variation of optical density with wavelength is analyzed to find out the nature of transition involved and the optical bandgap. Fig. 3 shows the room temperature optical emission spectra of the sample deposited at optimized preparative parameters. The transmittance was corrected for the absorption of the $F:SnO_2$/ glass substrate. The transmission spectra show a large decrease in the transmission in 800 – 1150 nm. wavelength range. The optical bandgap and absorption coefficient in the region of the fundamental band edges have been determined at various photon energy from the transmission spectra using the relation,

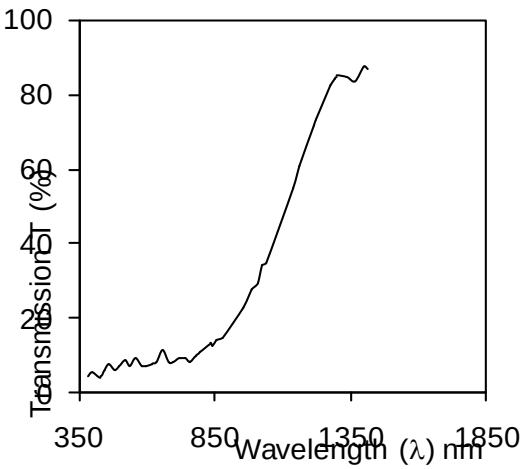

Figure 3. Transmission spectra of $ZrSe_2$ thin film deposited at optimized preparative parameters.

Where t is the thickness (0.83 μm) of the film and 'T' is the observed trasmittance (since the films are highly absorbing and thick, the reflection is ignored). The value of absorption coefficient is of the order of 10^4 cm^{-1} that supports the direct band gap nature in $ZrSe_2$ thin film. The result has been replotted according the direct transition.

$\alpha = B (h\upsilon - Eg)^{1/2} / h\upsilon$ ----------(1)

It is linear indicating the presence of direct transition. The straight portion is extrapolated to energy axis at $\alpha = 0$, which gives the band, gap energy of $ZrSe_2$ to be 1.5 eV.

CONCLUSIONS

Preparation of semiconducting $ZrSe_2$ thin films onto stainless steel and FTO coated glass substrate is feasible by electrodeposition technique. In order to prepare good quality deposits optimization of preparative parameters by PEC technique is suitable. The XRD study reveals that the deposited $ZrSe_2$ thin film is polycrystalline with hexagonal crystal structure. The material involves direct transition with band gap energy 1.5 eV.

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