Available online at www.scholarsresearchlibrary.com

Scholars Research Library

Archives of Physics Research, 2014, 5 (2):14-22
(http://scholarsresearchlibrary.com/archive.html)

Archives of Physics Research
Scholars Research Library
ISSN : 0976-0970
CODEN (USA): APRRC7

Pulse Electrodeposition and Characterization of $Mo_x W_{1-x} Se_2$ Thin Films

S. Mary Delphine[2] and C. Sanjeeviraja[1]

[1]Department of Physics Alagappa University,
[2]Department of Physics, Holy Cross College, Nagercoil, India

---

ABSTRACT

The layer type Structure compounds MX_2 (M=Mo, W: X=S, Te, Se) have aroused much attention in the last ten years because of their Possible application as photovoltaic and photoelectrocatalytic solar energy converters. Mo_xW_{1-x} Se_2 coated glass substrates from an ammoniacal solution of H_2WO_4, He MoO_4 and SeO_2 under galvanostatic conditions. The growth kinetics of the film was studied and the deposition parameters such as duty cycle electrolyte bath concentration, bath temperature, time of deposition, deposition current, pH of the electrolyte, were optimized X- ray analysis showed the presence of highly textured Mo_x W_{1-x} Se_2 film with hexagonal structure.The optical absorption spectra show that the material has an indirect band gap. The electrical conductivity measurements were carried and the semiconductor parameters such as the activation energy, trapped energy state and the barrier height were evaluated.

Keywords: Photovoltaic, Photoelectrocatalytic, $Mo_x W_{1-x} Se_2$, Electrodepostition, Solar Energy Converters

---

INTRODUCTION

Several Studies have been carried out on the electrical properties of the queasy two dimensional crystals of the transition metal dichacogenides by various workers [1-3]. Thin films of SnS were cathodocally electrodeposited on conducting glass substrates from aqueous solution containing $SmCl_2$ and $Na_2S_2O_3$ by Subramanium et,al [4]. Deposited film has been characterized with X-ray diffractograms, microstructure analysis, chemical analysis optical and electrical measurements. Brush plating technique has been adopted for the preparation of layered compound semiconductor as the first time B. Subramanium et.al[5] . To coat tin selenide (SnS) thin films on tin oxide coated conducting substrates and the characterization was also carried out. Thin films of tin disulphide (SnS_2) on glass substrates is prepared using spray pyroysis technique by Amalraj et.al [6] and the films are characterized, Joseph Sahaya Anand et.al [7] have electrodeposited thin films of molybdenum solution of H_2 MoO_4 and SeO_2 under potentiostatic conditions, and the characterizations were done. Sanjeeviraja et.at [8] have prepared molybdemum diselenide by soft selenization technique from high purity milybedenum foil and selenium granules and calculated the semiconductor parameters of the film like doping density,band bending valence band edge etc. Jebaraj Devadasan etal [9] have electrodepositat tungsten diselenide (WSe_2) thin films by galvanstatic toute and done the characterizstion. Pulsed electrodeposition and characterization of Wse2 thin films was also reported by Mary Delphine et.al [10]. Studies have been made on mixed systems also. Thus the electrical Properties of the (Mo / W) Te_2 and (Mo/W) Se_2

Systems [11], the (Mo/W)(Se / Te_2) systems [12] have been studied. Agarwal and Wani [13] reported the temperature dependence of resisivity technique. Hofmanan at al [14] syntheses sigles cryyals of $Mo_x W_{1-x} Se_2$ (0< x

>) with metal powders (H.C Strack purity m4 N) and selenium pellets (Aldrich m6N). The stoichiometric mixtures were sealed in evacuated (10-16 Torr) Silica tubes. The qurtz ampoules had dimensions of 25- 28mm in diameter and 100-180 mm in length. Before the heat treatment the quartz tubes were etched with a mixture of concentrated H_2SO_4 Hf and water in the ratio Hf. H_2SO_4: H_2O =1:3:1 for 20 minutes washed with bidistilled H_2O several times dried at 100^{o}C for one day and finally flame polished under vacuum with an oxyhydrogen.For the compound preparation the samples were heated slowly (50^{o}C/h) up to 500^{o}C in a horizondal furnace and kept for two days.After this reaction step a fine black power was formed which was then heated up to 1000^o C for 6 days. This treatment leads tp a magnification of grain size of the power; a recrystallization took place and gray shiny platelets were obtained. Agarwall et. al [15] have grown layered crystals of Mo_x $W_{1-x}Se_2$ (0<x>1) by a direct transport technique.

The present paper reports a simple pulses electro deposition technique for depositions Mo_x W_{1-x} Se_2 (X=1/4,1/2,/3/4) film cathodically on F: SnO_2 glass and titanium substrates. These films are characterized by XRD , EDAX ,SEM, optical and its conductivity studies are carried out at different temperatures.

MATERIALS AND METHODS

2. Experimental details

The electroysis cell consisted of (i) a titanium or FL SnO2 coated glass substrated on which Mo_x W_{1-x} Se_2 film was to be deposited and which acts as the cathode (ii) graphite as the counter electrode/anode and(iii) an ammoniacal solution of H_2MoO_4 + H_2WO_4 + SeO_2 as an electroyte. The electrolyte was prepared by mixing the first ammoniacal solution A of molybadic acid 0.40 M and aqueous solution of SeO_2 0.50 mM was taken in the volume ratio 1: 10 and tungstic acid 0.35 M and SeO_2 o.50mM taken in the volume ratio 1:6 as the second solution B. To prepare Mo_x W_{1-x} Se_2 (x = 0.25,0.50 0.75) thin films of the two electroylyte solutions A and B are mixed in these volume ratios 1: 3, 1: 1and 3: 1 respectively. The chemicals used were all AR grade E Merck. The distance between the working electrode and the graphite counter electrode was kept constant as 1 cm apart. The electroysis was carried out at different bath temperature such as 50,60 and 60^{o}C with current densities of 5 mA/cm^2 to 15 mA/cm^2 under galvanostatic route using pulse cansole . The deposition times are changed from 15 minutes to 75 minutes in steps of 15 minutes. The growth kinetics was carried out and is shown in Fig. 1(a) ,(b) and (c).

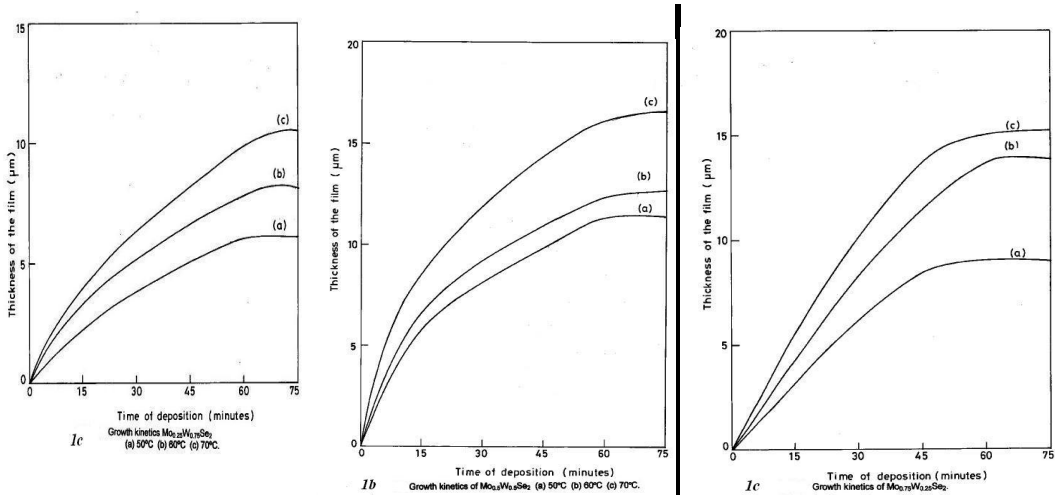


Fig 1a **Fig 1b** **Fig 1c**

Fig. 1.Growth kinetics of $Mo_xW_{1-x}Se_2$ thin films at (a) 50°C (b) 60°C and (c) 70°C.

From the graphs it was found that as the time of depostion increases the film thickness increases linearly and then attained saturation after 75 minutes due to a resistance developed on the electrode, the film thickness of $Mo_{0.25}W_{0.75}$ Se_2, $Mo_{0.5}$ $W_{0.5}$ Se_2 and Mo $_{0.75}$ $W_{0.25}Se_2$ was maximum about 11.5 ,18 and 15.3 µm respectively. Initially for all compositions Mo_xW_{1-x} Se_2 (X= 0.25,0.50 and 0.75) as the time of deposition increases the thickness of the film deposited on the substrate increases linerly around 45 minutes of deposition and for the near stoichiomatric ratio

$Mo_{0.5}W_{0.5}Se_2$ only when the temperature of the electrolyte was at 60°C.After 75 minutes of pulses deposition of the film thickness attains saturation for a film thickness of 1.5µm under optimized condition. For all other compostions and for all other temperature of depositions the film thickness has not reached saturation even after this time of deposition. The deposited film layers have a composition of $Mo_xW_{1-x}Se_2$. The films are found to be shiny silvery in colour. The optimized pulsed electrdeposited parameters for the near stochimetic ternary solution $Mo_{0.5}W_{0.5}Se_2$ are shown in Table.1

Table.1 Optimized parameters for the pulsed electrodeposition of $Mo_{0.5}W_{0.5}Se_2$ films

Parameter	Optimized value
Composition of bath H_2MoO_4	$Mo_{0.5}W_{0.5}Se_2$
H_2WO_4	0.35M
SeO_2	0.50mM
pH	6.5
Bath temperature	60°C
Current density	$10mAcm^{-2}$
Time of deposition	75 minutes
Duty cycle	30%

The Optimzed pulsed electrodepostedl films are characterized by XRD Philps Analytical PW 1710 Diffractometer for the structureal studies. The surface compositional analysis was carried out using EdAXZAF Philps EDX spectrometer (Xl30 ESEM TMP). The Surface morphology of the film was studied using scanning electron micrographs with JEOL JSM 6400 after sputtering with a thin gold coating on the surface. The band gap of the material was evaluated by taking optical obsorption spectrum in the UV-Vis NIR region using Hitachi V 3400 UV-Vis NIR spectrophotometer. Two Probe electrical conductivity measurements were carried out using keitley 2000 electrometer in the temperature range of 303 to 623 K.

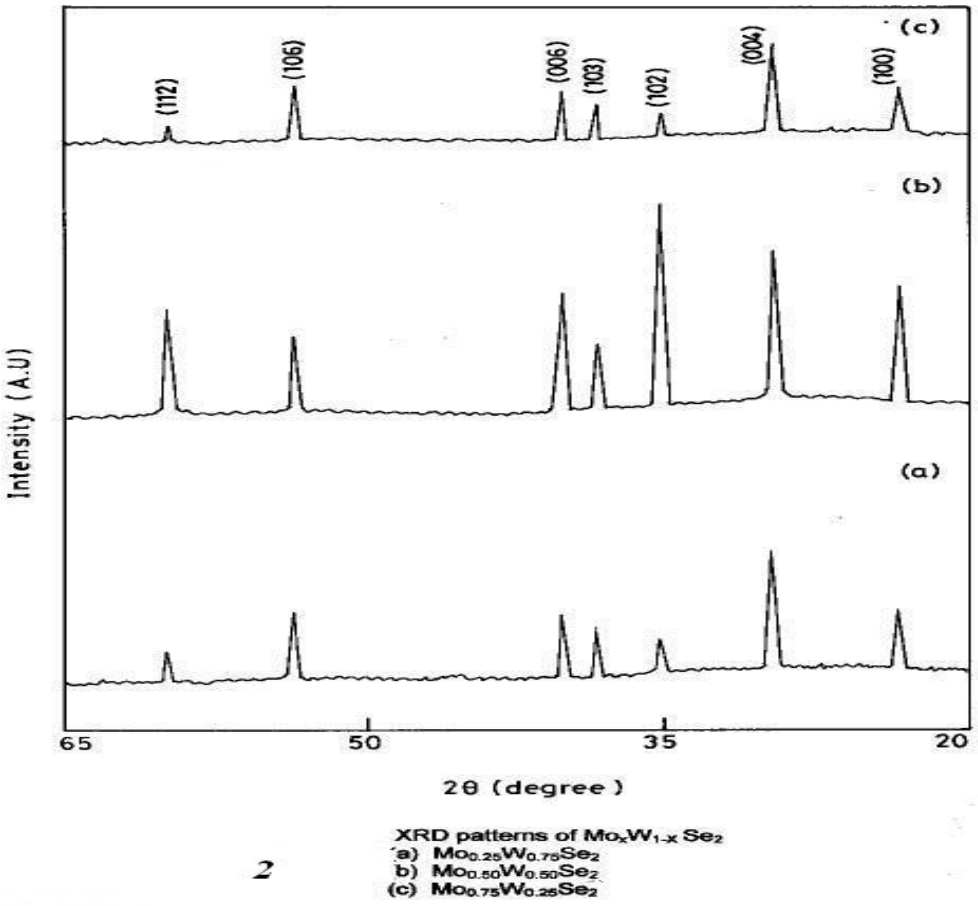


Fig. 2. XRD patterns of $Mo_xW_{1-x}Se_2$ thin films at (a)x=0.25,(b)x=0.5 and(c)x=0.75.

RESULTS AND DISCUSSION

3.1 Structural Characterization.

X-ray diffraction patterns (XRD) of pulsed electrodeposited films $Mo_xW_{1-x}Se_2$ (X=1/4,1/2 and 3/4) prepared under the optimized conditions were shown in Fig 2, (a) ,(b) and (c) .

The XRD peaks are corresponding to hexagonal structure[7]. The d -Values evaluated for the dominant peaks having hexagonal structure with the JCPDS data for $MoSe_2$, WSe_2 are compared with $Mo_{0.5}W_{0.5}Se_2$ of pulse electodeposited films are presented in Table.2.

Table 2

WSe_2	$MoSe_2$	$Mo_{0.5}W_{0.5}Se_2$	h k l
d-JCPDS	d-JCPDS	d-obs	--------
--------	--------	3.7978	--------
2.8451	--------	3.0105	0 0 4
2.6043	2.605	2.5468	1 0 2
2.3777	2.373	2.2455	1 0 3
2.1630	2.153	2.2065	0 0 6
1.7222	1.717	1.7292	1 0 6
1.5537	1.591	1.5606	1 1 2

the lattice parameters are calculated as a = b = 3.21 A° and c = 12.592A°. From the lattice parameters and using Vegards law , the compostition of the film has been confirmed. The average grain size of these films varies in the range of 0.029 A° to 0.17 A°. The observed peaks coincide well with the JCPDS data (38-1388) and (29-914). The composition of the $Mo_xW_{1-x}Se_2$ (x = 0.25,0.50 and 0.75) films deposited at optimized condition is recorded of the binding energy range from 0.0 KeV to 20.0 keV. The intense peak at 2.23 KeV,1.85 KeV and 1.70 KeV confirms the elemental presence of Mo, W and Se and in the weight percentage of 0.02638, 0.3870 and 0.0128 for $Mo_{0.25}W_{0.75}Se_2$ and 0.4077, 0.2803 and 0.0158 for $Mo_{0.5}W_{0.5}Se_2$ and 0.3055, 0.2530 and 0.0185 for $Mo_{0.75}W_{0.25}Se_2$ respectively and are shown in Fig 3 (a), (b) and (c).

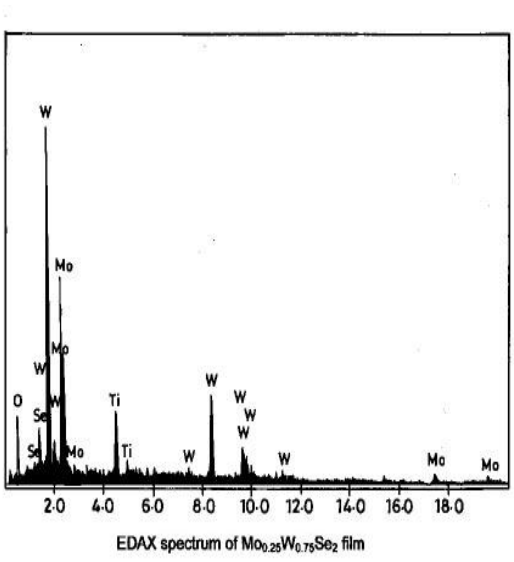


Fig 3a

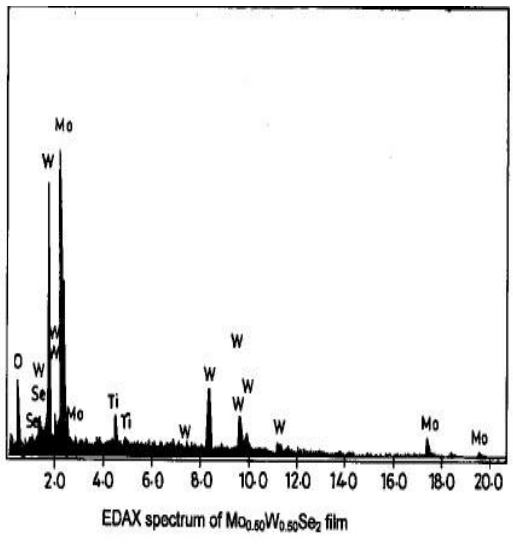


Fig 3b

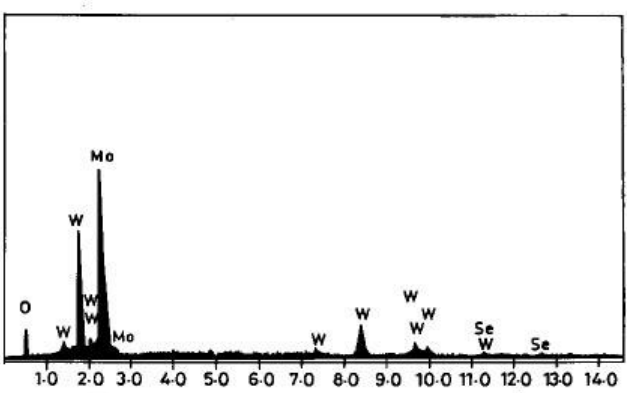


Fig. 4.20. EDAX spectrum of $Mo_{0.75}W_{0.25}Se_2$ film

Fig 3c

Fig. 3. EDAX Spectrum of (a)$Mo_{0.25}W_{0.75}Se_2$,(b)$Mo_{0.50}W_{0.50}Se_2$ and (c) $Mo_{0.75}W_{0.25}Se_2$.

A graph was drawn by taking solution compostion along the X- axis and the film compostion along the Y axis.The graphs show the film composition is little high for x = 0.25, 0.5 and little less for x = 0.75 in the case of pulse electrodeposited $Mo_xW_{1-x}Se_2$.

The SEM micrographs (Fig 4)show the surface morphology of the $Mo_{0.5}W_{0.5}Se_2$ thin film which exhibts granular shaped grain of uniform size spread all over the surface.

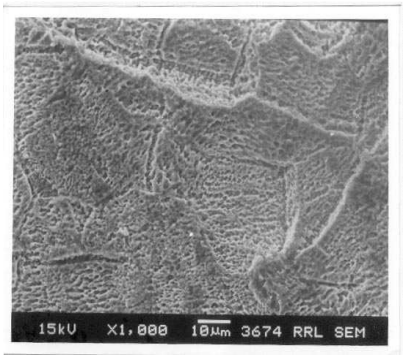


Fig 4a

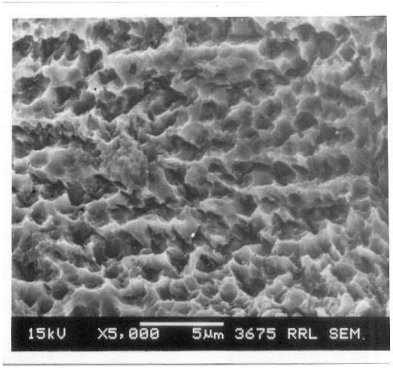


Fig 4b

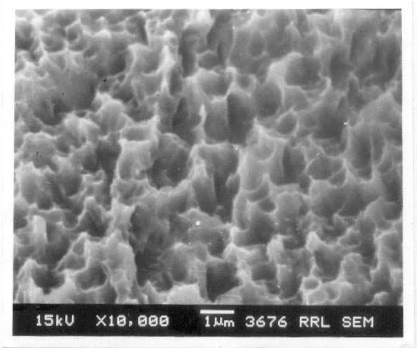


Fig 4c

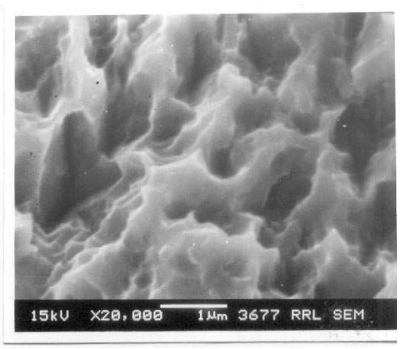


Fig 4d

Fig. 4.SEM of $Mo_{0.5}W_{0.5}Se_2$ thin films

3.2 Optical studies

The band gap of the film is determined from the classical of inter band absorption semiconductors using the relation $\alpha = A (E-E_g)^n$

Where α is the absorption coefficient, A is a constant, E the incident photon energy and E_g the band gap expressed in eV. The Vaule of refractive index n is 2 for indirect transition. The absorption edge of the film is observed in the range of 400 nm to 600 nm. The optical obsorption spectra are shown in Fig. 5(a), (b) and (c) for $Mo_x W_{1-x} Se_2$ (x = 0.25, 0.50, 0.75) respectively .

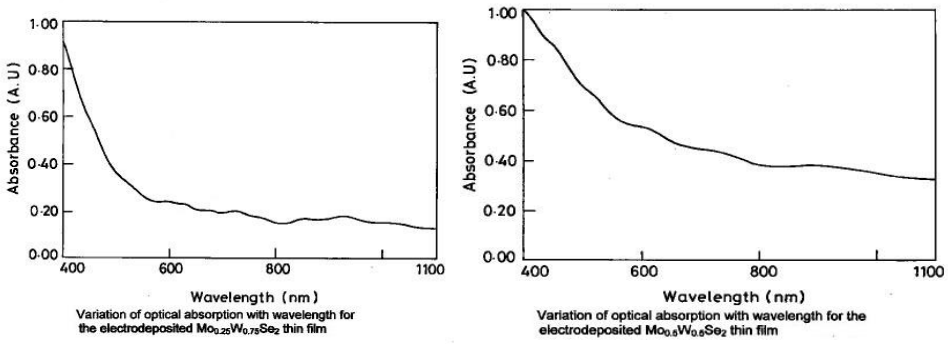


Fig 5a **Fig 5b**

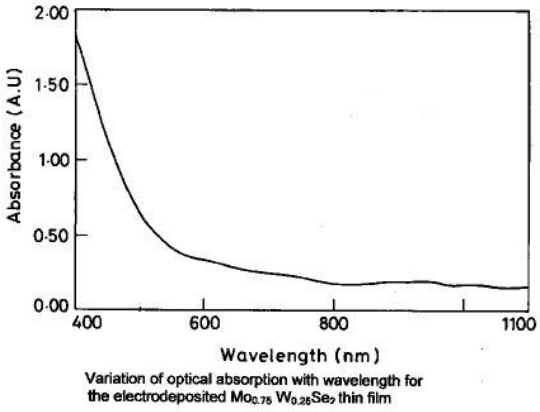


Fig 5c

Fig. 5.Absorption Spectrum of (a) $Mo_{0.25}W_{0.75}Se_2$,(b)$Mo_{0.50}W_{0.50}Se_2$,and (c) $Mo_{0.75}W_{0.25}Se_2$ thin films.

The band gap is calculated from the extrapolation of the linear portion of the graph between $(\alpha h\gamma)^{1/2}$ versus hγ to cut the energy axis. The allowed indirect band gap is observed as 1.30 eV, 1.14 eV and 1.15 eV for x = 0.25, 0.50, 0.75 respectively and are shown in fig 6(a) , (b) and (c).

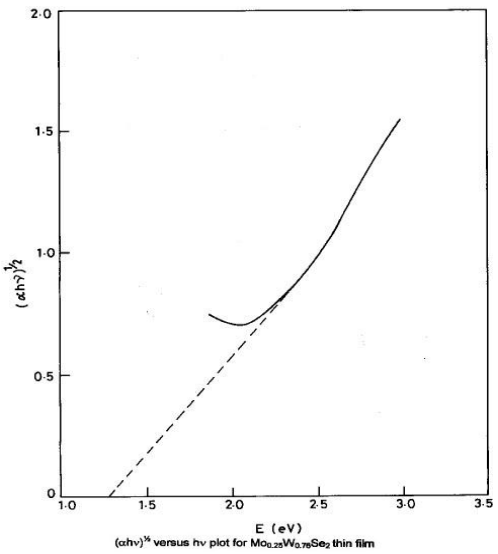


Fig 6a

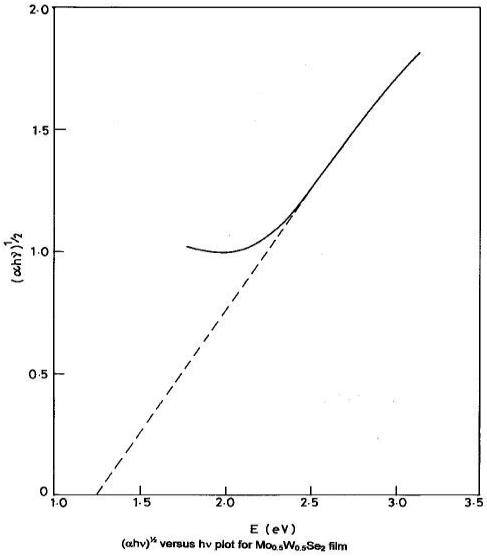


Fig 6b

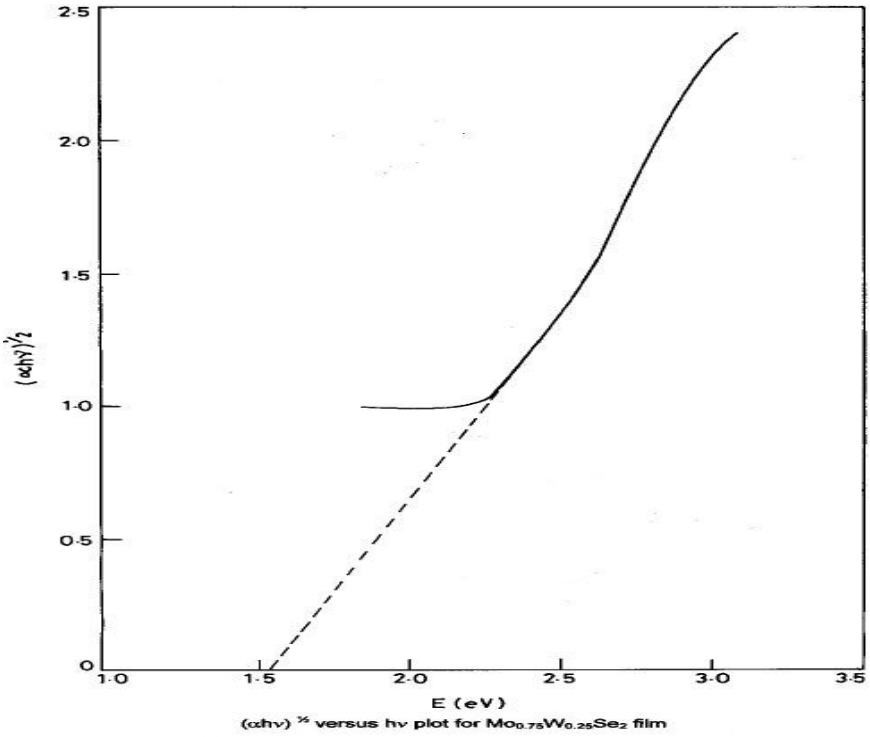
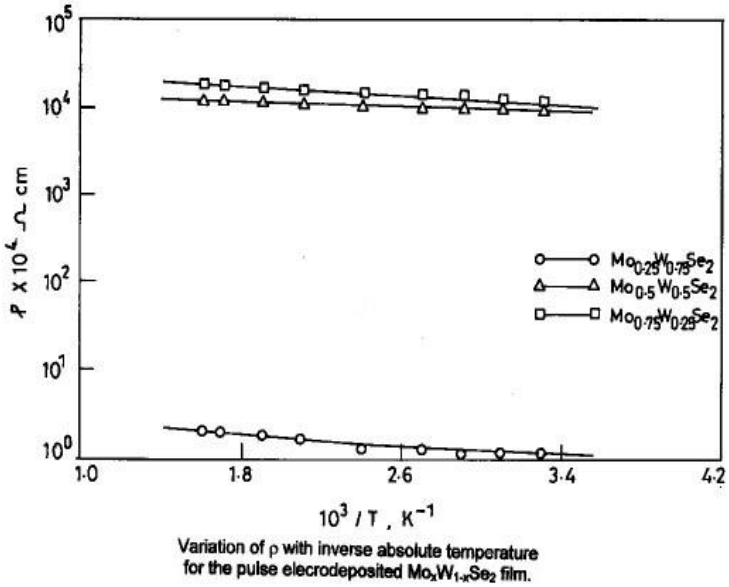


Fig 6c

Fig. 6. $(\alpha h\nu)^{1/2}$ versus hν curves for $Mo_xW_{1-X}Se_2$ thin films at (a)x=0.25,(b)x=0.5 and(c)x=0.75.

3.3 Electrical Properties

The film deposited on titanium substrate was used for the electracial conductivity measurments. Using two point probe technique the temperature dependence of the electrical resistance between 303 K and 623 K for Mo_x W_{1-x} Se_2 (x = 0.25,0.50 0.75) films. The variation of electric resistivity ρ with 1/T is shown in Fig 7.



Variation of ρ with inverse absolute temperature for the pulse elecrodeposited $Mo_xW_{1-x}Se_2$ film.

Fig. 7.Variation of ρ with inverse absolute temperature for $Mo_xW_{1-X}Se_2$ thin films at (a) x=0.25,(b) x=0.5 and (c) x=0.75.

It is clear from Fig 7 that the conductivity increases with the increase of temperature, which is the characterstic of impurity conduction.The increase in conductivity is due to the decrease in mobility caused by scattering of charge carried from the ionized impurity centers. From this as the temperature increases the electricall resistivity was found to decrease. By drawing plots lnσ versus 1/T,the activation energy E_a, the trapped energy state e_τ and barrier height φ_B calculated using the following relations[9].

$\sigma = \sigma_o \exp(-E_a/kT)$
$\sigma \alpha T \exp[(-E_g/2)/kT]$ when N* > N
$\sigma \alpha T^{1/2} \exp(-\varphi_B/kT)$ when N* < N

Where N being the acceptor concentration
N* exists for which the grains are only partially depleted (2W < d,d being the grain size)
W - width of the depletion regions
T - absolute temperature in Kelvin unit

For films deposited at different composition are tabulated in Table. 3 The activation energy calculated was in agreement with the earlier reported value 0.57 eV and the barrier height is 0.15 eV, which is again comparable with the reported value [10]

Table 3 Electrical parameters of the $Mo_xW_{1-x}Se$ (x = 0.25, 0.50, 0.75) films.

Composition	Activiation Energy E_a in eV	Trapped Energy State e_τ in eV	Barrier Height in φ_B eV
$Mo_{0.25}W_{0.75}Se_2$	0.10	0.11	0.86
$Mo_{0.5}W_{0.5}Se_2$	0.07	0.13	0.91
$Mo_{0.75}W_{0.25}Se_2$	0.06	0.67	1.18

CONCLUSION

Using pulse eletrodeposition technique under galvanostatic conditions thin films of $Mo_x W_{1-x} Se_2$ were successfully deposited on conduction glass and titanium substrates.The X-ray diffractrogrames reveal that the films are polycrystalline in nature and possess hexagonal structure. No peaks are observed for the elemental Mo and Se.This shows that the films are in single phase nature in crystalline form . EDAX results confirm the presence of elemental Mo,W and Se atomic weight percentages.From the optical studies the indirect band gap values for $Mo_xW_{1-x}Se_2$ (x = 0.25, 0.50, 0.75) was found as 1.30 eV,1.25 eV,1.53 eV respectively.From electrical conductivity measurements

electrical constants activation energy, trapped energy state and barrier height were calculated. The SEM micrograph shows the device quality nature of the surface without pinholes and the semiconductor parameter of this $Mo_{0.5}W_{0.5}Se_2$ film can be used for the fabrication of PEC solar cells.

REFERENCES

[1] J.A. Wilson and A.D Yoffe, *Adv. Phys*., **1969**, 18,193.
[2] L.H. Brlxner, *J. Electrochem. Soc*., **1963**, 110,289.
[3] R. R. Mansfiles and A. Salam, Proc Phys. Soc B **1953**, 66,377.
[4] B. Subramanian, C.Sanjjeeviraja,M.Jayachandran, *Material Chemistry and physics* **2001**, 71, 40.
[5] B. Subramanian, C.Sanjjeeviraja,M.Jayachandran,*Journal of Crystal Growth* **2002**, 234,421.
[6] L.Amalaraj, C.Sanjjeeviraja,M.Jayachandran, *Journal of Crystal Growth* **2002**, 234, 683.
[7] T.Joseph Sahaya Anand, C.Sanjjeeviraja,M.Jayachandran,Vacuum **2001**,)60,431.
[8] C. Sanjjeeviraja, T. Joseph Sahaya Anand, M. Jayachandran, Proc.Intl.Workshop & Charact.Tech.Imp.Single Crystal National Physical Laboratory, New. Delhi, Feb.26 – 28,2001.S.K Gupta, S.K.Halder and G. Bhagavannarayanan (Eds).
[9] J.Jebaraj Devadasan, C.Sanjjeeviraja,M.Jayachandran, *Material Chemistry and physics* **2002**,77,397.
[10] S.Mary Delphine,M.Jayachandran, C.Sanjjeeviraja, *Material Chemistry and physics* **2003**,81,78.
[11] E.Revolinsky and D.Beerntsen, *J. appl. Phys*. **1964**, 35,2086.
[12] J.A.Champion,Brit., *J. appl. Phys*. **1965**,16,1035.
[13] M.K.Agarwal and P.A.Wani, *Phys. Stat. Sol*. C2,**1980**,0631.
[14] W.K.Hofmann,H.J.Lewerenz and C.Pettenkofer,*Solar Energy Material* **1988**, 17,165.
[15] M.K.Agarwal,P.D.Patel and O.Vijayan, *Phys. Stat. Sol* **1983**, 78,103.
[16] C.C.Lu,C.Y.Luan,J.D.meindl:*IEEE Trans*,Ed **1981**, 28,818.
[17] J.Pouzet,J.C.Bernede and A.Ouadah, *Phys. Stat. Sol*.(a) **1993**,139,471.