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Study on (Mo/W) Se_2 Layered Compound Semi Conductors Useful for Photoeletrochemical Solar Cells

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Abstract: Molybdenum / Tungsten dichalcogenides constitute a well- defined family of compounds which crystallize in a layer type structure. These compounds have tailoring properties to use them as storage electrodes in the rechargeable photoelectrochemical solar energy storage cells. These compounds find a wide range of applications in the field of catalysis and as a lubricant at high temperatures and pressures. Amongst IV – VI semiconducting compounds, (Mo/W) Se_2 layered compound dichalcogenides exhibit a hexagonal structure. The basic structural unit of such a compound is a sandwich of three planes, one of transition metal atoms between two of halogen atoms. These sandwich type are only loosely bound together through weak Van der Waals (vdw) forces, and therefore, extremely anisotropic physical properties result. The material properties of the layered semiconductors molybdenum diselenide($MoSe_2$), tungsten diselenide(WSe_2) and molybdenum tungsten diselenide($Mo_xW_{1-x}Se_2$) are prepared by different methods and are presented in this review.

Keywords: Dichalcogenide, semiconducting thin film, molybdenum diselenide, tungsten diselenide, molybdenum tungsten diselenide.

Introduction

As worldwide energy demand increases, conventional energy resources, such as fossil fuels, will be exhausted in the not – too – distant future. Therefore, we must develop and use alternate energy resources, especially our only long – term natural resource, the sun. The solar cell is considered a major candidate for obtaining energy from the sun, since it can convert directly to electricity with high conversion efficiency, can provide nearly permanent power at low operating cost, and is virtually free of pollution. Solar cells at present furnish the most important long duration power supply for satellites and space vehicles. Recently, research and development of low cast, flat panel solar cells, thin film devices, concentrator systems and many innovative concepts have increased. The main objectives of all technological developments are to develop energy sources which may be long lasting, pollutions free, easily available and cost effective [1-9], for application in photovoltaic and PEC solar cells, semiconductor thin films like CdSe, CdS, CdHgTe, GaAs, $CuInSe_2$, CuInS, CdTe, $SrTiO_3$, SnO_2, In_2O_3, TiO_2, SnSe, SnS, SnSSe, $MoSe_2$,WSe_2 have been elaborately studied [7,10 & 11]. The general survey

for this review article has been made from the literature available upto 2005 related to solar cells. The present article will help research workers in selecting preparative and crystal growth methods and stimulate further research work on the properties of molybdenum tungsten dichalcogenides.

Methods of preparations

There are several methods for preparing thin films. Some of them are vacuum evoperation, sputtering, hot wall epitaxy, spray pyrolysis, chemical vapour deposition, solution growth, electrodeposition, electroless deposition, brush plating, screen printing, pulse electrodeposition etc. Discussion about the various methods of film preparation was given by Chopra [10], Maissel and Glang [12] and Behrndt [13],chemical deposition technique like electrodeposition, chemical vapour deposition, brush plating are particularly used for preparing large area semiconducting devices and are low in cost. A simple and brief discussion about the various methods of film preparation was discussed here in [15]. Crystals with isoelectric group VI mixed cations of composition $Mo_x W_{1-x} Se_2$ were grown by the reaction of the constituent elements. Single crystals were prepared by chemical vapour transport (CVT) [14], direct vapour transport [15, 16] Molybdenum/Tungsten dichalcogenides constitute structurally and chemically a well defined family of compounds having a general formula MX_2 (M = Mo, W; X = S, Te, Se). The methods of preparation of molybdenum/tungsten dichalcogenides are discussed below.

Among molybdenum chalcogenides $MoSe_2$ has led to the best solid state cells with efficiencies exceeding 6%, in particular due to surprisingly large short circuit currents of $33mAcm^{-2}$ [17, 18]. Unfortunately the low open circuit voltage still keeps the efficiency low, but Molecular Beam Epitaxy (MBE) is a new field, where atomically smooth and abrupt interfaces can be fabricated. But there is hetero epitaxial systems is limited by surface dangling bonds, surface states, surface symmetry, ability to smoothen the surface, the lattice mismatch between the two materials. In addition, the difference in the thermal expansion coefficients between epilayer and substrate result in appreciable thermal stresses at the interface. Van der Waals epitaxy (VDWE), a method recently developed by Koma [16,17] gives a new route to hetero epitaxy about most of the constraints mentioned above, VDWE is the growth of several 2D metal chalcogenide material one upon the other, where the layers are bound together by weak Van der Waals forces. Many metal dichalcogenides have two-dimensional materials with structures characterized by chalcogen – metal – chalcogen layers held together by Van der Waals forces. Most interesting one for the photoelectrochemical solar cell application is the energy band structure of molybdenum and tungsten dichalcogenides, which are compounds with a trigonal prismatic crystal symmetry. Their upper energy band, derived from the transition metal d-states, is split into two bands, a lower d_{z^2} occupied energy band and a higher unoccupied 2 band derived by d_{xy} and $d_{z^2-y^2}$ states, separated by an hybridization indirect band gap ranging from 1-2 eV [5-7]. This gives to these compounds the characteristics of a semiconductor not only appropriate for the absorption of the solar spectrum, but also with favourable optical transitions between nonbonding electronic orbital which would not affect the original bonds of the semiconductor, thus enhancing its stability against photodecomposition. In fact, in all the semiconducting electrodes where the absorption of a photon with energy larger than the band gap corresponds to the breaking of an electronic band (like in the p→s photo transition of CdS and CdSe) the missing electron at the electrode surface can catalyze the anodic dissolution reaction of the semiconductor or the anodic formation of an insulating area, unless a fast charge-transfer reaction can restore this band. The binary compounds $Mo_xW_{1-x}Se_2$ (x = 0,1) have been known for several years not only for their properties as solid lubricants [8], but also for their unusual physical properties as materials with two dimensional layered crystal structures [9,10]. The basic structural unit of such a compound is a sandwich of three planes, one of transition metal atoms, between two of chalcogen atoms. Within a plane each Mo, W atom is surrounded by six Se atoms.

The conceptional difference between a conventional hetero interface and an interface fabricated via the Van der Waals epitaxy growth good reason for hope to achieve efficiencies well above 10% after these first attempts.This hope is also based on the better performance of electrochemical cells based on $MoSe_2$ exceeding the 10% efficiency limit [19].

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

Parameter	Optimized value
Composition of bath H_2MoO_4 = 0.40 M	$Mo_{0.5}W_{0.5}Se_2$
H_2WO_4	0.35 M
SeO_2	0.50 mM
PH	6.5
Bath temperature	60°C
Current density	10 $mAcm^{-2}$
Time of deposition	75 minutes
Duty cycle	30 %

Experimental details:

The electrolysis cell consisted of (i) a titanium or F: SnO_2 coated glass substrates on which $Mo_xW_{1-x}Se_2$ 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 electrolyte. The electrolyte was prepared by mixing the first ammoniacal solution A of molybdic acid 0.40 M and aqueous solution of SeO_2 , 0.50 mM taken in the volume ratio 1:10 and tungstic acid 0.35 M and SeO_2 0.50 mM taken in the volume ratio 1:6 as the second solution B. To prepare $Mo_xW_{1-x}Se_2$ (x = 0.25, 0.50 and 0.75) thin films the two electrolyte solutions A and B are mixed in these volume ratios 1:3, 1:1, 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 1cm.The electrolysis was carried out at different bath temperature such as 50, 60 and 70°C with current densities between 5mA/cm^2 and 15mA/cm^2 under galvanostatic route using pulse console. The deposition times are changed from 15 minutes to 75 minutes in steps of 15 minutes. The growth kinetics method was used to optimize the deposition parameters.The optimized pulse electrodeposition parameters of $Mo_{0.5}W_{0.5}Se_2$ was given in Table – 1.

Result and discussion.

Surface characterization.

X-ray diffraction patterns (XRD) of pulse electrodeposited films $Mo_xW_{1-x}Se_2$ (x = 0.25, 0.50 and 0.75) prepared under the optimized conditions taken using Philips Analytical PW 1710 diffractometer were shown in Fig.1. (a), (b) and (c).

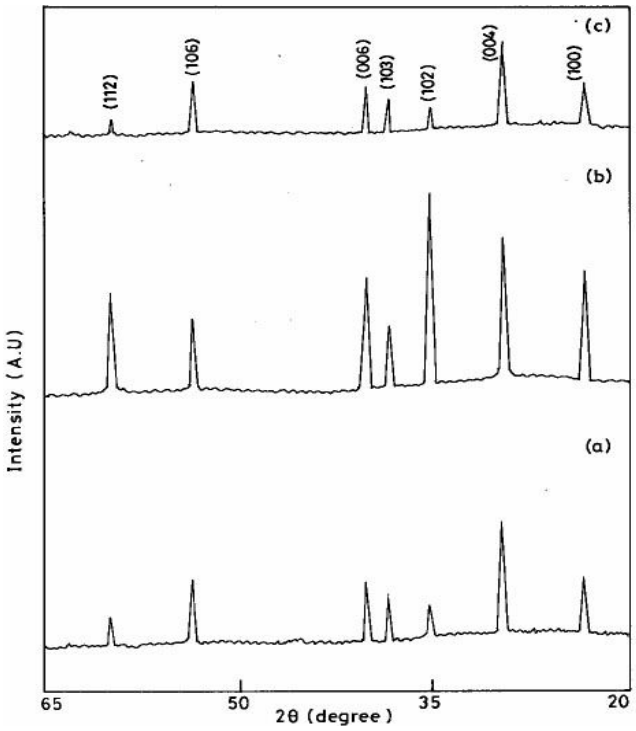

Fig. 1. XRD Patterns of $Mo_xW_{1-x}Se_2$

(a) $Mo_{0.25}W_{0.75}Se_2$

(b) $Mo_{0.50}W_{0.50}Se_2$

(c) $Mo_{0.75}W_{0.25}Se_2$

Table.2. JCPDS data.

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	2.3455	1 0 3
2.1630	2.153	2.2065	0 0 6
1.7222	1.717	1.792	1 0 6
1.5537	1.591	1.5606	1 1 2

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 $Mo_{0.5}W_{0.5}Se_2$ pulse electrodeposited films are presented in Table.2.

The lattice parameters evaluated for $MoSe_2$ and WSe_2 thin films prepared using pulse electrodeposition technique under optimized condition are already reported by the same author as a = b = 3 29 Å and c = 11.12 Å and a = b = 3.29 Å and c = 12.97 Å respectively for hexagonal structure [10,18]. The lattice parameters are calculated as a = b = 3.210 Å and c = 12.592 Å. From the lattice parameters and using Vegards law, the composition of the film has been confirmed. The average grain size of these films varies in the range of 0.029 μm to 0.17 μm. The observed peaks coincide well with the JCPDS data (38 - 1388) and (29 - 914). The composition of the $Mo_{0.5}W_{0.5}Se_2$ film deposited at optimized condition is recorded in the binding energy range from 0.00 keV to 20.00 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 0.4077, 0.2803, 0.0158 for $Mo_{0.5}W_{0.5}Se_2$ is shown in Fig.2.

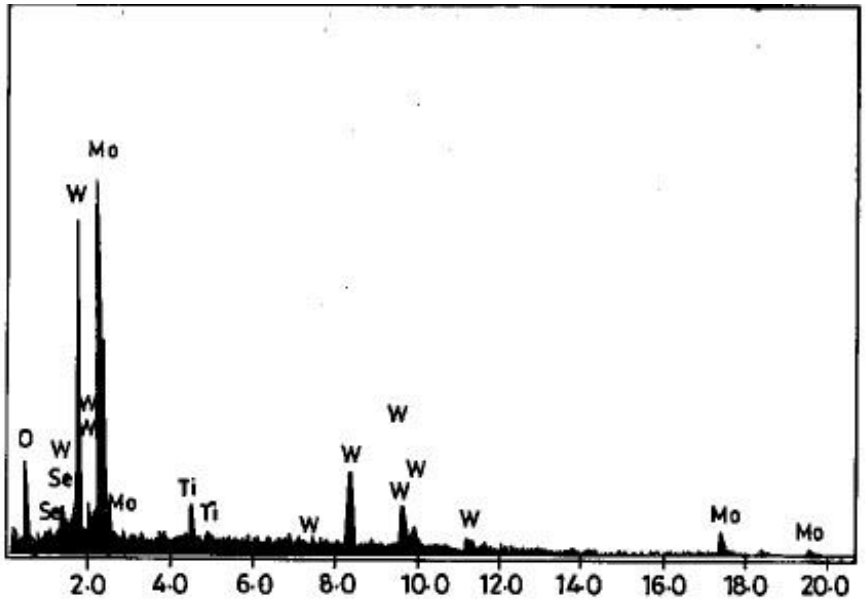

Fig. 2. EDAX spectrum of $Mo_{0.50}W_{0.50}Se_2$ film

SEM Studies on $Mo_xW_{1-x}Se_2$ (x = ½)

The scanning electron micrograph of an asdeposited and annealed $Mo_{0.5}W_{0.5}Se_2$ film annealed in vacuum at 150°C for 1 h deposited on titanium substrate is shown in Fig.3. (a), (b), (c) and (d). The grain size for the asdeposited film is 0.841 μm and for vacuum annealed film is 0.940 μm.

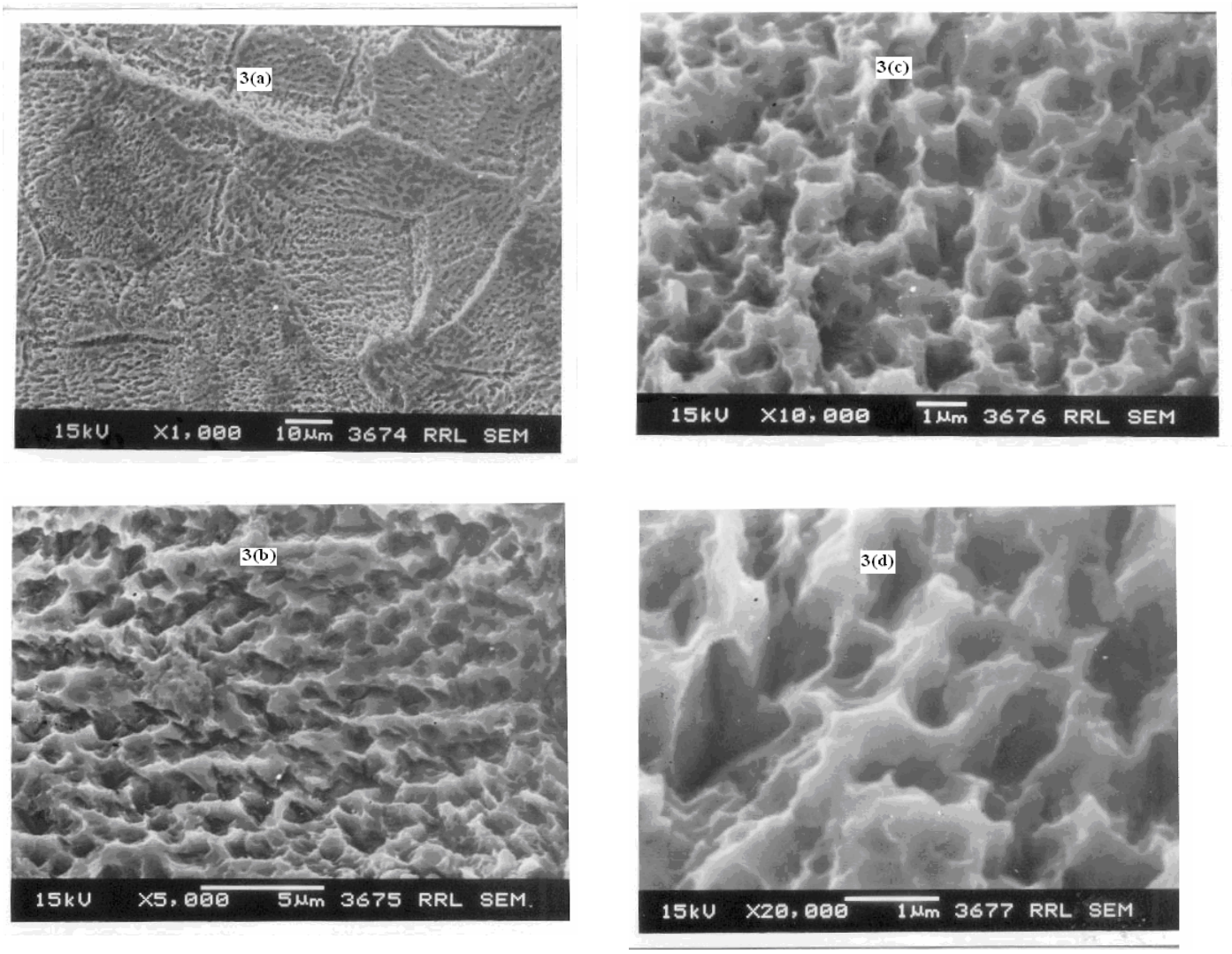

Fig.3. SEM micrograph of $Mo_{0.5}$ $W_{0.5}$ Se_2 film annealed at 150°C in vacuum with magnification (a) × 1000, (b) × 5000, (c) ×10000 and (d) × 20000.

Morphology of Pulse Electrodeposited $Mo_xW_{1-x}Se_2$ thin films

AFM images reveals that these films have a granular morphology. Irregular shaped grains are seen. The AFM data are analyzed by averaging the roughness of an area 5 x 5 μm for different random positions on the sample surface in order to minimize the influence of local topography variation. Figures 5 shows three-dimensional AFM images for an area of 5 x 5 μm for $MoSe_2$, WSe_2 and $Mo_{0.5}W_{0.5}Se_2$ in the asdeposited and annealed in vacuum at 150°C for 1 h respectively with thickness of 1.0 μm.

All these figures show the presence of high hills on the top of a homogeneous granular background surface. The density and the height of the hills increase with the thickness of the deposit. The perturbance scanned by the AFM is a measure of the crystallographic columnar size. It is assumed that the growth mode of molybdenum and tungsten dichalcogenide on tin oxide coated glass substrates by pulse electrodeposition from aqueous solutions is three dimensional without the diffusion of adatoms on the surface [20].

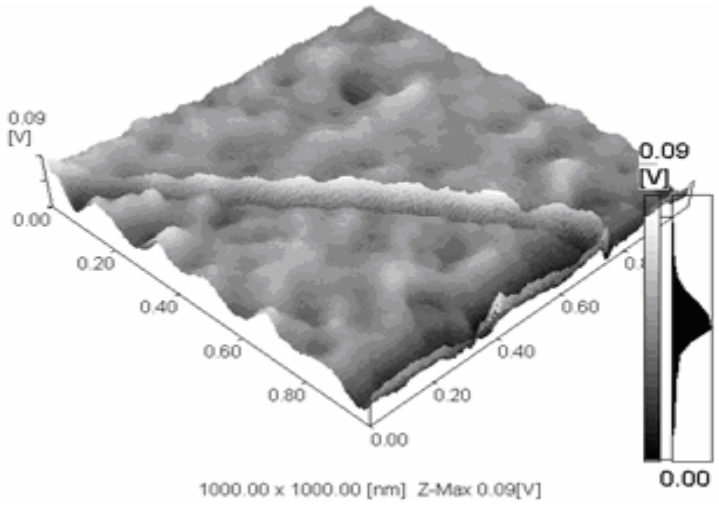

Fig. 4. AFM image of $Mo_{0.5}W_{0.5}Se_2$ Film

Optical study on $Mo_{0.5}W_{0.5}Se_2$ Film:

The absorption spectra taken using spectrophotometer in the wave length region 400 nm to 1100 nm is shown in Fig.5. To calculate the energy band gap value a graph was drawn by taking E along the x-axis and $(\propto h\gamma)^{1/2}$ along the y-axis. The intercept of the straight line portion with the x- axis gives E_g = 1.25 eV. The plot is shown in Fig.6. The variation of the values of 'n' and 'k' for the pulse electrodeposited $Mo_{0.5}W_{0.5}Se_2$ film is shown in Fig.7. The 'n' values vary in the range of 2.75 - 3.92, which shows the same trend as $MoSe_2$ and WSe_2. The increasing trend of 'n' starts at about 400 nm, which coincides with the absorption edge value already reported in the previous section. The 'k' values are very low in the order of about 0.50 x 10^{-5}.

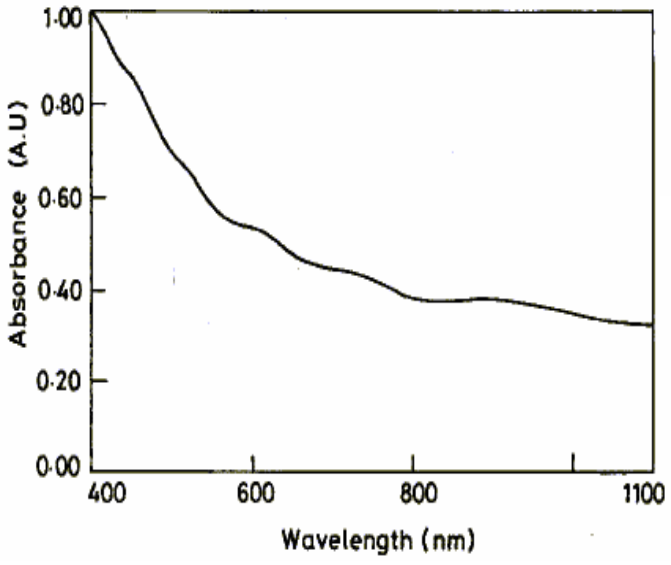

Fig. 5. Variation of optical absorption with wave - length for the electrodeposited $Mo_{0.5}W_{0.5}Se_2$ Film

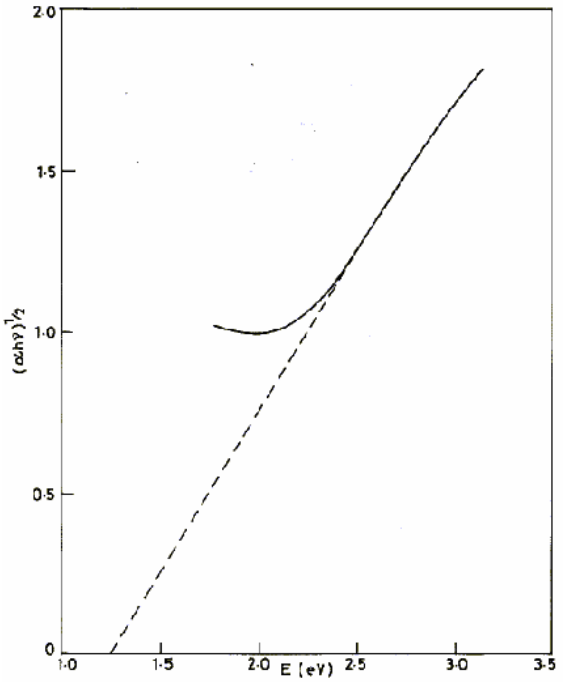

Fig. 6. $(\alpha h\nu)^{1/2}$ versus hν plot for $Mo_{0.5}W_{0.5}Se_2$ Film

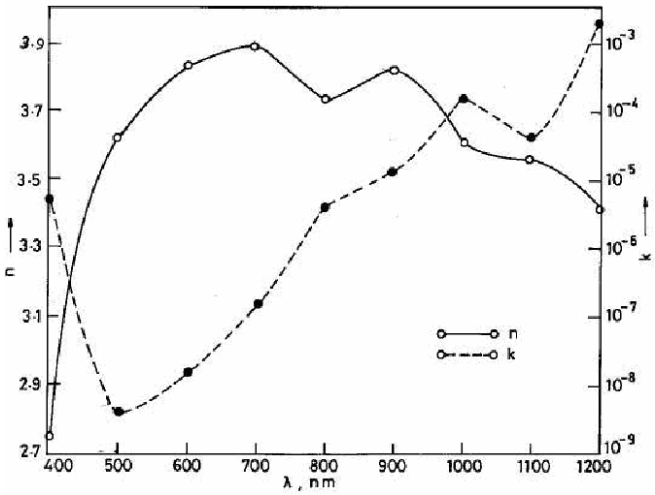

Fig. 7. n and k versus λ for $Mo_{0.5}W_{0.5}Se_2$ Film

Conclusion

A survey on less expensive semiconducting molybdenum diselinide, tungsten diselinide and molybdenum tungsten diselinide was eloberately studied. The materials properties of the films prepared using different deposition techniques are reported .The films prepared are mostly found to be poly crystalline in nature and show p, n type semiconducting nature. The structural, surface morphological and optical studies reveal that device quality semiconducting molybdenum / tungsten dichalcogenides can be prepared using pulse electrodeposition technique and used for PEC solar cells.

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