# Structural and Optical Properties of Electrodeposited $MoS_2$ Thin Films for Photoelectrochemical (PEC) / Solar Cell Applications

S. Shariza, Z. M. Rosli & T. Joseph Sahaya Anand*

Faculty of Manufacturing Engineering,
Universiti Teknikal Malaysia Melaka,
Durian Tunggal, 76109 Melaka, Malaysia
Phone: +606-3316489, Fax: +606-3316411
*Email: anand@utem.edu.my

*Abstract* – **Thin films of transition metal chalcogenides (TMC), specifically molybdenum sulphide, $MoS_2$ been prepared by electrodeposition technique on from an aqueous bath of high purity molybdenum and sulphide materials. These materials are useful as high temperature lubricants in the cryogenic rockets and other applications such as in photoelectrochemical (PEC) / solar cells. The films deposited onto stainless steel and indium-tin-oxide (ITO) glass substrates were adherent to the substrate. The obtained films were characterized for their structural and optical properties by XRD, SEM, UV-Vis spectroscopy and Mott-Schottky analysis. X-ray diffraction (XRD) studies confirmed the polycrystalline structure of these films. Scanning electron microscopy (SEM) showed that the films are continuous and uniform. The optical absorption spectrum by UV-Vis spectrophotometer of the films gave an indirect bandgap energy of 1.7 eV. Other semiconducting parameters of the films were obtained by the Mott-Schottky plot.**

*Keywords* – **Transition metal chalcogenides, PEC / solar cells, Mott-Schottky plot, high temperature lubricants, ITO glass substrates.**

## INTRODUCTION

Solar energy is one of the most convenient non-conventional energy resources to be considered for the power requirements of the 21st century. In recent years, transition metal chalcogenide (TMC) compounds have been actively investigated for photoelectrochemical (PEC) and solar cell applications [1, 3, 4, 8, 13]. Apart from being an excellent material for PEC and solar cells, these materials are also useful as high temperature lubricants in cryogenic rockets [2].

The main advantages of such semiconductor is that they meet the requirements in order to function as a lubricant and efficient photoelectrode, (i) they exhibit intercrystalline slip and they adhere to the substrate well [2], and (ii) their inherently resistive nature to photocorrosion [3], because the photo transitions involve non bonding d-d orbitals of Mo atoms [4].

There has been a growing interest in semiconducting compounds consisting of group VIA transition metal dichalcogenides $MX_2$ (M = Mo, W and X = S, Se & Te) [5]. In the group of molybdenum dichalcogenides, molybdenum sulphoselenide ($MoS_xSe_{2-x}$) is a diamagnetic semiconductor with modulated structure consisting of X – Mo – X (X = S, Se) layers with strong in-plane bonding and a very weak Vander Waals bonding between the layers [6].

These characteristics have made TMC the compounds that have attracted much attention as solar energy materials for efficient conversion of light energy into electrical energy [7]. Among the many semiconducting materials investigated as electrodes in PEC / solar cells, TMCs have attracted considerable attention because they are cheap and abundant, available in both, n-and p-type forms, have energy band gaps well suited to solar energy conversion, and an extremely good stability when in contact with various aqueous and non-aqueous electrolytes [6].

The synthesis of TMCs are considered as attractive semiconducting processes as they are not susceptible to photocomposition as are many other materials whose band gaps are in the region of maximum solar energy efficiency. Solar energy conversion efficiencies up to 7 % using a liquid junction cell based on a $MoS_xSe_{2-x}$ polycrystalline thin film as the active electrode have been achieved [9].

Studies on PEC with TMC such as $ZrSe_2$, CdSeTe, and $Bi_2S_3$, have been carried out on single crystals systems [10-12]. However, polycrystalline electrodes are economically desirable for solar cell applications, where large-area substrates are necessary. Interest in the use of PEC / solar cells for low-cost energy conversion has led to an extensive research in the search for thin film polycrystalline materials [13]. Hence, this study has been directed towards obtaining molybdenum sulphide, $MoS_2$ in thin-film form.

The usual thin film preparation techniques, such as selenization [14], sputtering [15], solid state reaction, sulphurization, and electrolytic reduction are cost intensive and sometimes present special problems for the preparation of transition metal chalcogenide films [13].

Therefore, the present work has adopted the electrodeposition technique at potentiostatic mode for depositing molybdenum sulphide film cathodically on both ITO–coated conducting glass substrates as well as stainless steel substrates.

The aim of this work is to prepare a stoichiometric $MoS_2$ compound in thin film form by electrodeposition from high purity electrolytic materials. The crystallographic structure, chemical composition, optical and semiconducting parameters have been studied by X-ray diffraction (XRD), scanning electron microscope (SEM), optical absorption, and Mott-Schottky analysis respectively.

## EXPERIMENTAL METHOD

*Electrodeposition of molybdenum sulphide thin films*

The electrodeposition of $MoS_2$ thin films was carried out using a Princeton Applied Research Model VersaSTAT 3 Potentiostat. The deposition potential of this transition metal chalcogenide $MoS_2$ thin film was first derived from cyclic voltammetry technique followed by synthesis of the chalcogenides by electrodeposition route.

A three – electrode cell system was adopted for the deposition of the film as shown in Fig.1. The electrolysis cell consisted of (i) an ITO-coated glass substrate or stainless steel substrate as the working electrode (WE) on which the $MoS_2$ thin film is to be deposited; (ii) graphite as the counter electrode (CE); and (iii) a saturated calomel electrode (SCE) as the reference electrode. The SCE measures the potential of the working electrode. The electrode spacing should be carefully adjusted to obtain good quality results. Both working and counter electrodes are kept as close as 1 cm to each other and the two surfaces facing each other were kept parallel, so that released ions will be attracted and deposited exactly perpendicular to the cathode surface. The reference electrode tip is placed very close to the cathode surface so that the exact potential at the surface will be monitored unaffected by the solution resistance (internal resistance of the cell).

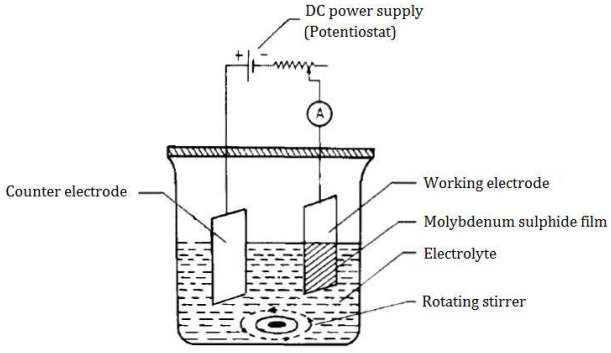


Fig. 1. Electrolysis cell setup for $MoS_2$ thin film deposition.

An ammoniacal solution consisting of a mixture of molybdic acid and sodium thiosulphate pentahydrate ($H_2MoO_4$ + $Na_2S_2O_3.5H_2O$) was used as electrolyte. The deposition of films was carried out at a temperature of 40 °C ± 5 °C for 30 minutes. To prepare electrolyte solutions having relative concentrations of $Na_2S_2O_3.5H_2O$ and $H_2MoO_4$, the following two basic solutions were first prepared: solution A containing $H_2MoO_4$ in ammonia and solution B containing $Na_2S_2O_3.5H_2O$ in water. These two basic solutions were mixed to obtain the electrolysis solutions.

*X-ray diffraction studies*

The X-ray diffractograms of the thin film was obtained on a PANalytical XPERT PROMPD PW 3040/60 diffractometer using monochromatic $CuK_\alpha$ radiation ($\lambda$ = 1.5405 Å). Structural information of the as-grown films was obtained in the range of 2θ angles from 10º – 90º. The binary transition metal chalcogenide's crystallographic properties were analyzed. This study will confirm the presence of sulphide phases present in the film stoichiometry.

*Optical studies*

The optical absorption spectrum studies were carried out in the wavelength range 200 to 1100 nm at room temperature using a Shimadzu 1700 UV-Vis Spectrophotometer. Optical studies were carried out using an identical ITO glass substrate as reference.

*Scanning Electron Microscope Analysis*

The surface morphological studies were conducted on a JSM 6400 JOEL scanning electron microscope (SEM). This study will reveal the uniformity of the surface area of the electrodeposited thin film.

*Mott-Schottky Analysis*

The type of conductivity of the films was found by using Mott-Schottky plots which were carried out using EDUTECH EDU – 9100B LCR – 7 bridge with a built-in function generator of a frequency of 1 kHz. From these studies the semiconductor parameters of the films are also calculated.

## RESULTS AND DISCUSSION

*Electrodeposition of molybdenum sulphide thin films*

Cyclic voltammetry (CV) test was carried out before the deposition process. It was done between two potential limits (-1.00 *V* to 1.00 *V*) for the solutions prepared to probe the prospective potentials for deposition of the thin films. The solutions are those of the mixture of ammoniacal molybdic acid and sodium thiosulphate pentahydrate, $H_2MoO_4$ + $Na_2S_2O_3.5H_2O$ for the deposition of $MoS_2$. The Electrochemical Analysis System Software (PAR Versa Studio 2.0) was used to control the deposition process and to monitor the current and voltage profiles.

The cyclic voltammetry measurements of $MoS_2$ deposition as shown in Fig. 2, showed that the forward scan initially dropped and remained constant until a

current drop at -0.8 *V* suggesting a reduction process (See inset figure).

The current change is associated with the reduction of molybdenum and sulphide ions to form solid molybdenum sulphide, $MoS_2$ compound on the substrate. The deposition of molybdenum sulphide on the substrate continued until all the equilibrium potential is achieved at an interception between the forward and reverse scan at approximately 0.1 *V* versus Ag/AgCl.

*X-Ray Diffraction Studies*

X-ray diffraction pattern of the electrodeposited $MoS_2$ thin film on stainless steel substrate is shown in Fig. 3.

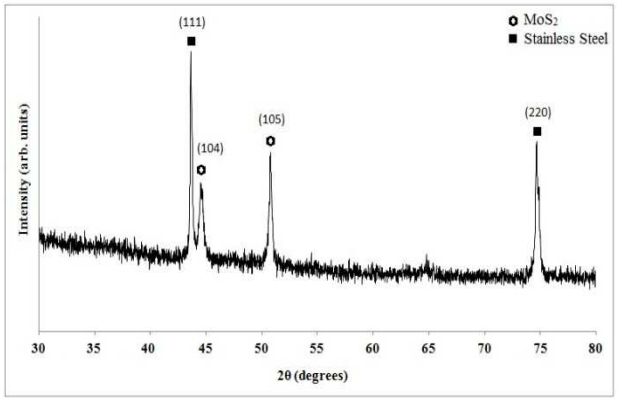


Fig. 3. X-ray diffraction pattern for $MoS_2$ thin film.

Different XRD peaks, marked in the figure, have been indexed with the help of the JCPDS file and the respective XRD data values are summarized in Table 1.

Peaks belonging to $MoS_2$ and stainless steel substrate are detected and identified as (104) and (105) planes of $MoS_2$; and (111) and (220) planes of the stainless steel substrate. The sharp peaks reveal the polycrystalline nature of the as-deposited $MoS_2$ films. The structural features fit into the hexagonal structure of the films with lattice parameter values $a = b = 0.315$ nm and $c = 1.23$ nm.

The crystallite size was calculated from the measurement of full-width at half-maximum (FWHM) in different X-ray peaks and values are in the range of 54 – 90 nm.

Table 1 : Comparison of experimental '*d* ' values with JCPDS data for $MoS_2$ thin film

| Angle (2θ) | $'d'_{JCPDS}$ (Å) | $'d'_{exp}$ (Å) | ( *h k l* ) |
|---|---|---|---|
| 43.72 | 2.075 | 2.074 | ( 1 1 1 ) |
| 44.50 | 2.040 | 2.034 | ( 1 0 4 ) |
| 50.73 | 1.820 | 1.798 | ( 1 0 5 ) |
| 74.67 | 1.270 | 1.270 | ( 2 2 0 ) |

*Optical studies*

The transition metal chalcogenides are usually indirect band gap semiconductors [9]. The optical absorption spectrum was taken for $MoS_2$ thin film using an identical ITO-coated glass plate as reference.

The absorption behaviour of the film was studied in the region 200 – 1100 nm. The films show good absorption in the visible region. A pronounced absorption edge is evident in the vicinity of 700 – 800 nm for the films. From this absorption spectrum the band gap energy of the molybdenum sulphide, $MoS_2$ thin films are calculated and they show that they possess indirect band gap.

A graph of $(\alpha h\nu)^{1/2}$ vs. $h\nu$ is drawn and the linear portion of the graph is extrapolated to the energy axis as shown in Fig. 4. The intersection point gives the indirect

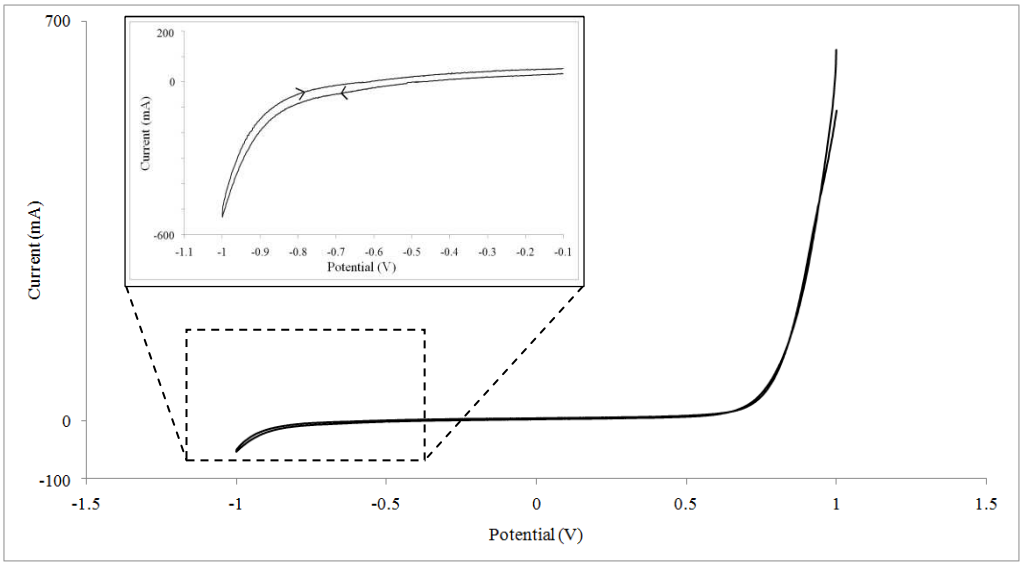


Fig. 2. Cyclic voltammogram for $MoS_2$ thin film deposition in ammoniacal $H_2MoO_4 + Na_2S_2O_3.5H_2O$ solution.

band gap of the material and was found to be 1.70 eV. It is in good agreement with the reported value of 1.78 eV for the electrodeposited film [8].

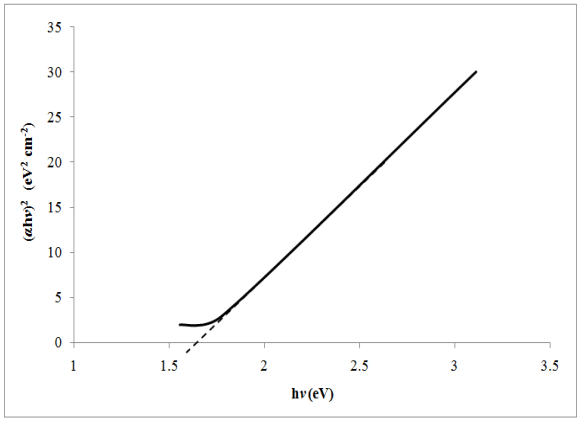


Fig. 4. Plot of $(\alpha h\nu)^{½}$ vs. $h\nu$ for $MoS_2$ thin film.

*Scanning Electron Microscope Analysis*

The surface morphology of the $MoS_2$ thin film was determined by scanning electron microscope (SEM) analysis. From SEM analysis, it is found the surface appears to be comparatively granular with irregularly shaped grains. The SEM micrograph of the $MoS_2$ thin film deposited on indium-tin-oxide (ITO) glass substrates is shown in Fig. 5.

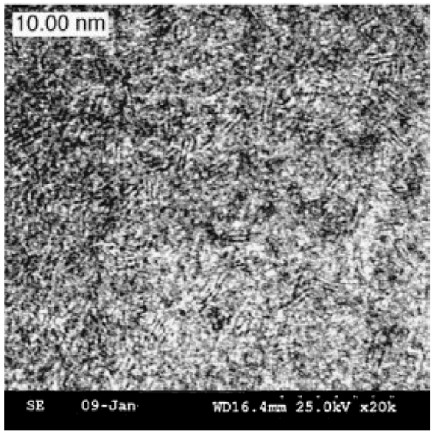


Fig. 5. SEM photograph of electrodeposited $MoSe_2$ thin film.

The average grain size of the microcrystallites (grain size) was calculated from the intercept method using the SEM picture as given by the formula:

$$\text{Average grain size} = 1.5\, l / mn.$$

whereby, $m$ is the magnification of the micrograph, $l$ is the length of the line drawn on the micrograph, $n$ is the number of grains crossed by the line and 1.5 is the parameter assuming spherical grains.

It is seen that the grains exhibit an average size of 0.28 μm. This reveals that the closely packed grains provide a pin-hole free morphology leading improvement in the special contact between the grains.

It shows that the electrodeposited films can provide device quality $MoS_2$ films for use in PEC / solar cells. Knowledge of the grain size and distribution is essential, as the most important parameters of PEC / solar cells such as the series and shunt resistances are governed by the grain size.

*Mott-Schottky Analysis*

Mott-Schottky plots have been drawn (in the dark condition) to evaluate the semiconductor parameters. An EDUTECH EDU 9100 B LCR – 7 bridge with an inbuilt function generator of a frequency of 1 kHz was used for the measurement of space–charge capacitance to obtain Mott-Schottky plots drawn using the capacitance data at a frequency of 1 kHz for the system n-$MoS_2$ | $K_2SO_4$, KI, $I_2$, $H_2SO_4$ | graphite.

The value of flat band potential ($V_{FB}$) was obtained using the relation:

$$1 / C_{SC}^{\,2} = (V - V_{FB} - k_BT/e)\, 2 / \varepsilon\varepsilon_0 eN_D$$

where $\varepsilon_0$ is the dielectric constant of free space, $\varepsilon$ is the dielectric constant of $MoS_2$ (6.52), e is the electronic charge and $N_D$ is the doping density which is calculated from the slope of the graph. T is the temperature of the operation, $k_B$ is the Boltzmann's constant and $C_{SC}$ is the space charge capacitance.

The positive slope of the Mott-Schottky plot reconfirms the n-type conductivity of $MoS_2$ films as shown in Fig. 6.

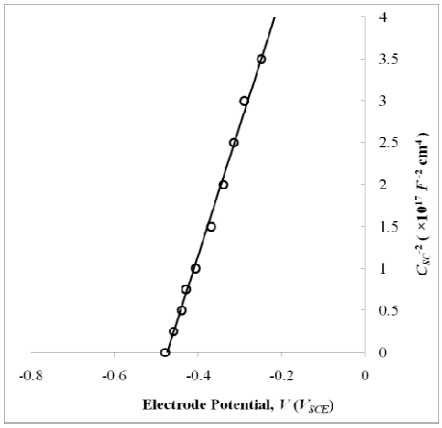


Fig. 6. Mott-Schottky plot of $MoS_2$ thin film.

The intercept of the linear plot ($1/C_{SC}^{\,2} = 0$) was taken as the electrode potential of the semiconductor at which the bond bending is zero. This potential is the flat band potential and is equal to – 0.46 $V_{SCE}$. The depletion layer width (W) was calculated from the relation:

$$W = \{(2\, \varepsilon\varepsilon_0 V_b) / eN_D)\}^{\,1/2}$$

where $V_b$ is the built in voltage or the band bending. The semiconductor material parameters of $MoS_2$ thin films from the Mott-Schottky plots are given in Table 2.

Table 2 : Semiconductor parameters for $MoS_2$ thin film

| Semiconductor parameters | Results |
|---|---|
| Type of semiconductor | n – type |
| Flat band potential ($V_{FB}$) | $-0.46 \pm 0.02\ V_{SCE}$ |
| Doping density ($N_D$) | $3.44 \pm 0.05 \times 10^{19}\ cm^{-3}$ |
| Depletion layer width (W) | $1.53 \pm 0.02$ Å |
| Density of states in Conduction Band ($N_c$) | $1.19 \times 10^{24} \pm 0.05\ m^{-3}$ |
| Band bending ($V_b$) | $0.15 \pm 0.02 V_{SCE}$ |
| Conduction band edge ($E_c$) | $-0.60 \pm 0.02$ eV |
| Valance band edge ($E_v$) | $1.05 \pm 0.03$ eV |
| Fermi level of the semiconductor below conduction band | $-0.13 \pm 0.02$ eV |
| Energy gap ($E_g$) | $1.70 \pm 0.02$ eV |

## CONCLUSION

Using electrodeposition technique, $MoS_2$ thin films were successfully deposited on indium-tin-oxide, ITO-coated glass substrates and stainless steel substrates. Stoichiometric films were deposited at an optimized deposition potential of -1.0 $V_{SCE}$ keeping the bath at temperature 40 ± 5 °C. The XRD pattern shows that the thin films are polycrystalline in nature and possess hexagonal structure with lattice parameters values $a = b =$ 0.315 nm and $c = 1.23$ nm. The indirect band gap value of 1.70 eV confirms the formation of stoichiometric $MoS_2$ films. SEM photograph shows that the films are continuous and pin-hole-free with closely packed grains. From Mott-Schottky plot, the semiconductor parameters are found. From the optical studies, the indirect energy gap value is calculated to be 1.70. It is clear that from the above studies, the electrodeposited film can provide device quality films for use in photoelectrochemical cell applications.

## ACKNOWLEDGEMENT

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