Electrodeposited Molybdenum Chalcogenide (MoX_2) Thin Films for Photovoltaic Applications

Possible alternate material for Photovotaic Applications

S. Shariza, Lim Mei Ying, T. Joseph Sahaya Anand
Department of Engineering Materials, Faculty of Manufacturing Engineering,
Universiti Teknikal Malaysia Melaka,
Durian Tunggal, 76100 Melaka, Malaysia
Email: anand@utem.edu.my

***Abstract*—Thin films of molybdenum chalcogenides (MoX_2, X=S, Se and Te) have been electrosynthesized on indium-tin-oxide; (ITO)-coated glass and stainless steel substrates. The films were characterized for their structural, morphological and compositional characteristics. Their optical and semiconducting parameters were also analyzed in order to determine the suitability of the thin films for photoelectrochemical (PEC) / solar cell applications. Structural analysis via X-ray diffraction (XRD) reveals that the films are polycrystalline in nature. Scanning electron microscope (SEM) studies reveals the films were adherent to the substrate. Compositional analysis via energy dispersive X-ray (EDX) technique confirms the presence of Mo, S, Se and Te elements in the film stoichiometry. The optical studies show that the films are of direct bandgap. Results on the semiconductor parameters analysis of the films showed that the nature of the Mott-Schottky plots indicates that the films obtained are of n-type material. For all films, the semiconductor parameter value falls in the range of many other transition metal chalcogenides and this has proven that MoX_2 thin films is capable as a solar / PEC cell material**

Keywords-Molybdenum chalcogenide, Thin Films, Electrodeposition, Direct bandgap, Mott-Schottky plots.

I. INTRODUCTION

Molybdenum chalcogenides (MoX_2, X=S, Se and Te), one of the many transition metal chalcogenides (TMCs) are semiconductors, which can be used as an efficient photovoltaic material. These materials have become the subject of remarkable and wide spreading technological interest [1]. The application of these materials in photoconverters, sensors as well as photoluminescent devices is becoming an important and growing area of technology [2-3]. The high production cost of solar energy materials constitutes a serious drawback for the commercialization of photovoltaic cells [4]. The economical advantages of these materials rely upon the lower level of purification needed, the low cost of synthesis and the possibility of manufacturing photovoltaic devices in thin film form, owing to their high absorption coefficients, thus allowing a considerable reduction of material consumption. For many applications, thin layers of TMC materials on substrates are normally required. The preparation of thin film materials opens the opportunity of observing the evolution of physical properties of the materials with sizes [5]. The reduction of sizes, in terms of thickness of the thin film provide the possibility of observing novel behaviour such as size dependent structural, electrical and optical properties [6]. In this report, the electrodeposition technique at potentiostatic mode for depositing molybdenum chalcogenide thin films cathodically on ITO–coated conducting glass substrates as well as stainless steel substrates is presented. The various aspects of thin films like growth mechanism, characterization and some of its properties are discussed.

II. EXPERIMENTAL DETAILS

A. Electrodeposition of molybdenum sulphide thin films

The precursors molybdic acid (H_2MoO_4), sodium thiosulphate pentahydrate ($Na_2S_2O_3.5H_2O$), selenium dioxide (SeO_2) and tellurium dioxide (TeO_2) of analytical grade were used as Mo^{4+}, S^{2-}, Se^{2-} and Te^{2+} ion sources, respectively. ITO glass and stainless steel substrates of dimension 15 × 25 × 1 mm size were cleaned before film deposition. ITO glass were dipped into diluted hydrochloric acid, rinsed with double distilled water then cleaned in hot air while stainless steel substrates were mirror polished and finally cleaned in an ultrasonic cleaner. This treatment increases the adhesion of the electrodeposits to the substrate and allows thicker deposition without peeling.

To prepare the electrolyte solutions having relative concentrations of 0.5M H_2MoO_4, 0.5M SeO_2, 0.5M $Na_2S_2O_3.5H_2O$ and 1.5mM TeO_2, the following solutions were first prepared: solution A containing H_2MoO_4 in ammonia, solution B containing $Na_2S_2O_3.5H_2O$, solution C containing SeO_2 in distilled water and solution D containing TeO_2 (99+%, Sigma Aldrich) dissolved in sulphuric acid (95-97%, Merck). These solutions were mixed in proportional amounts as the precursor electrolyte.

For the synthesis of MoS_2, $MoSe_2$ and $MoTe_2$, the electrolyte mixture ratio between the precursor solutions of H_2MoO_4 with $Na_2S_2O_3.5H_2O$ or SeO_2 or TeO_2 (where applicable) was selected to be 1:2 following its stoichiometry. The pH of the reactive mixture is maintained at ~pH 10 by

adding drops of NaOH to the mixture. After mixing for 5 min under stirring and heating to reach a reaction temperature of 40±1 °C, the mixture is ready for synthesis of the films at 30 minutes deposition time.

The electrodeposition of the molybdenum chalcogenide, MoX_2 thin films was carried out using a Princeton Applied Research Model VersaSTAT 3 Potentiostat. The deposition potential of the molybdenum chalcogenide thin film was first derived from cyclic voltammetry (CV) technique followed by synthesis of the film by electrodeposition technique. A three – electrode cell system was adopted for the cyclic voltammetry analysis and deposition of the films. The electrolysis cell consisted of (i) an ITO-coated glass substrate or stainless steel substrate as the working electrode (WE) on which the thin film is to be deposited; (ii) graphite as the counter electrode (CE); and (iii) a saturated calomel electrode (SCE) with Ag/AgCl reference system as the reference electrode [7]. The SCE measures the potential of the working electrode. The electrode spacing should be carefully adjusted to obtain good 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).".

B. Characterization of Electrodeposited Thin Films

Structural and morphological film characterization for MoX_2 (X=S, Se and Te) samples were determined by X-ray diffraction (XRD) and scanning election microscopy (SEM) analysis by using PANalytical ZPERT PROMPD PW 3040/60 diffractometer (for 2θ range from 20 to 80° with CuK_α radiation) and SEM ZEIZZ EVO 50 scanning microscope, respectively and its composition analysis with energy dispersive X-ray (EDX) analysis. Optical properties for determination of energy band gap of the films and semiconductor properties of the films related to its possible application in the photoelectrochemical (PEC) / solar cell were studied using UV-VIS spectrophotometer and Mott-Schottky plot analysis, respectively.

III. RESULTS AND DISCUSSION

A. Structural Characterization

The structural characterization via XRD measurement is a diffractogram, showing phases present (peak positions), phase concentrations (peak heights), amorphous content (background hump) and crystallite size / strain (peak widths) [8]. X-ray diffraction patterns of the electrodeposited MoX_2 (X=S, Se and Te) thin films on stainless steel substrates (JCPDS Card No. 33-397) are shown in Fig. 1. The sharp peaks reveal the crystalline nature of the deposited MoX_2 (X=S, Se and Te) films. The preferred orientation is attributed to the enhancement in surface diffusion of the absorbed species resulting in crystalline peaks of MoX_2 thin films. The observed '*d*' values are compared with JCPDS standard values to determine the crystal structure.

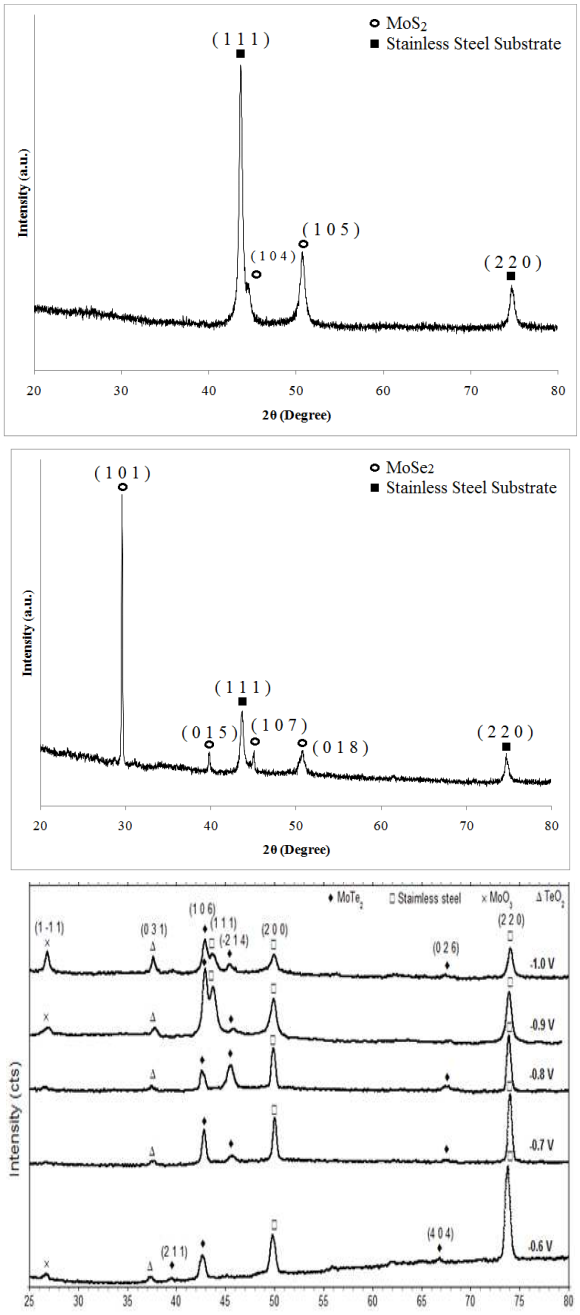

Fig. 1. XRD diffractograms for MoS_2, $MoSe_2$ and $MoTe_2$ thin films

The structural features fit into the hexagonal structure of the MoS_2 films with lattice parameter values $a = b = 0.3150$ nm and $c = 1.2300$ nm which is in good agreement with the standard JCPDS values [9]. The diffractogram structural features fit also showed rhombohedral structure of the $MoSe_2$ films with lattice parameter values $a = b = 0.3292$ nm and $c = 1.9392$ nm in good agreement with the standard JCPDS values [10] while $MoTe_2$ films showed monoclinic crystal structure with lattice parameter values $a = 0.633$; $b = 0.347$ and $c = 1.380$ nm in agreement with the standard values JCPDS values [11].

According to the Debye–Scherrer approach [12], the interplanar distances*'d'* corresponding to different (*h k l*) planes were calculated from the X-ray diffractograms. 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 for MoS_2 films, 45 – 65 nm for $MoSe_2$ films and 11-53 nm for $MoTe_2$ films.

B. Morphological Characterization

The surface morphology of MoX_2 (X=S, Se and Te) thin films deposited on stainless steel substrates is shown in Fig. 2. The structure of the films starts to crack into grains (flakes) although still adhering to the substrate. The cracking in thin films is attributed to drying shrinkage in this case of hydrous films. It has been reported that films having thickness greater than 0.2 mm are prone to cracking [13].

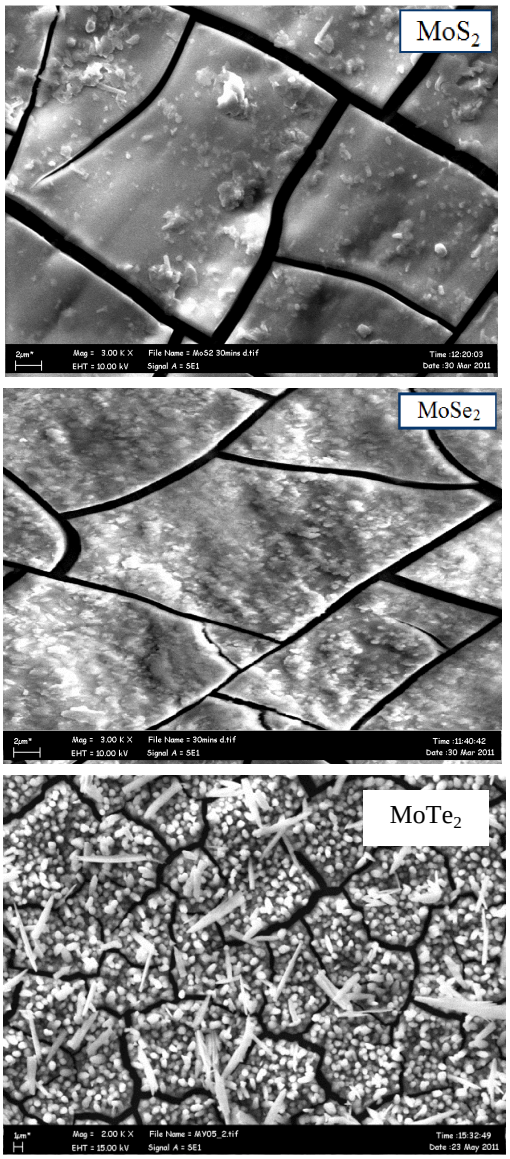

Fig. 2. SEM photographs for MoS_2, $MoSe_2$ and $MoTe_2$ thin films

C. Compositional Characterization

Fig. 3 shows the EDX patterns for MoX_2 (X=S, and Se) thin films. Referring to the spectra, strong peaks for Mo, S, Se and Te were identified. It is confirmed that MoX_2 (X=S and Se) thin films have been formed through the electrodeposition process. The overlapping peaks for Mo and S elements has been identified as a limitation of the EDX technique due to the corresponding X-rays generated by emission from different energy-level shells (K, L and M). Although elements C and O do not play any role in the synthesis of the films, their peaks can be observed in the spectrum. This is due to the particular advantage of EDX whereby it possesses the capability for detection of low atomic number elements such as carbon and oxygen, which are ubiquitous in our environment. Furthermore, inclusion of oxygen is observed for all the films because it is found to be unavoidable for chemically deposited films as testified [14, 15]. This is true and accepted for all films svnthesized.

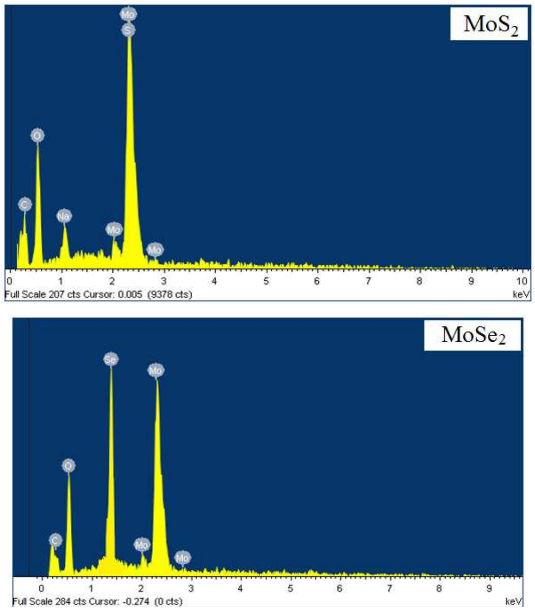

Fig. 3. EDX patterns for MoS_2 and $MoSe_2$ thin films

The compositional studies of $MoTe_2$ thin film theoretically calculated as 33.3% and 66.7% for tellurium corresponding to its empirical formula. But the composition of the elements found by using EDX doesn't match this stoichiometry due to presence of other elements as presented in Table 1.

Table 1: The weight percentage (wt. %) of $MoTe_2$ with deposition potentials -1.0 V (t = 30 minutes) and -0.9 V (t =30 minutes).

Elements	**(wt. %) for -1.0 V and 30 min.**	**(wt. %) for -0.9 V and 30 min.**
Tellurium	64.84	61.89
Molybdenum	13.11	16.79
Silicon	10.83	2.94
Oxygen	9.60	13.15
Sulfur	1.62	2.34
Carbon	-	2.89

The EDX analysis for $MoTe_2$ thin film showed the presence of other elements such as silicon, sulphide, oxygen, and carbon. The silicon is presence due to the use of ITO coated conductive glass substrate. The presence of oxygen is expected to come from the surrounding atmosphere and the oxidation of Mo / Te. The presence of sulphide and carbon are assumed as the contaminants during the experiment regarding the handling and procedures. These contaminants and other materials can be removed by annealing and the growth of thicker film.

D. Optical Properties of Electrodeposited Thin Film

The films show good absorption in the visible region. From this absorption spectrum the band gap energy of the molybdenum disulfide thin films are calculated. From the transmittance spectrum obtained, the corresponding bandgap energy of the thin films was studied.

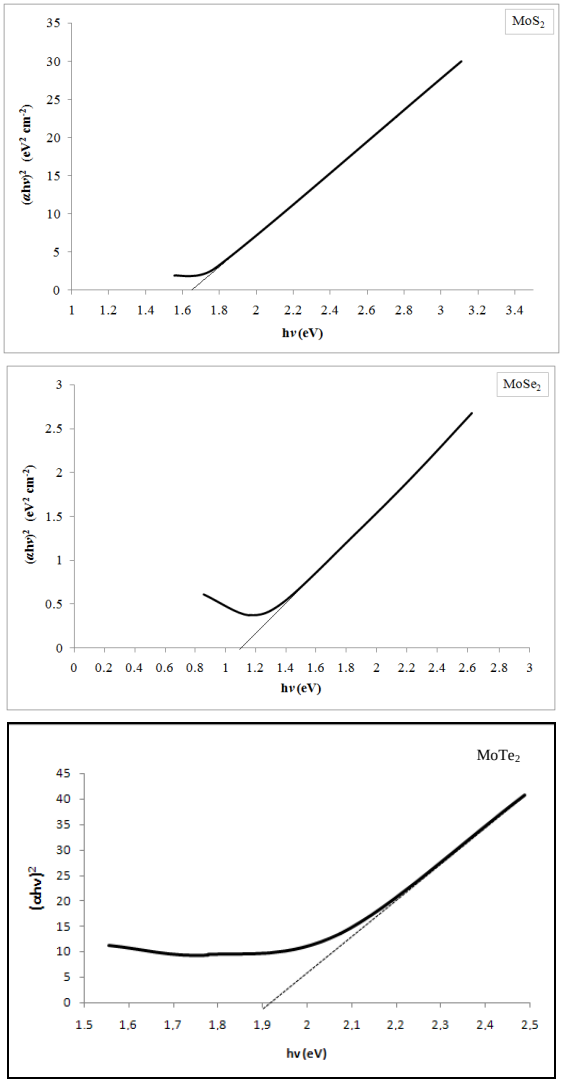

Fig. 4. $(\alpha h\nu)^2$ vs. $h\nu$ plots of MoS_2, $MoSe_2$ and $MoTe_2$ thin films

The optical transitions in transition metal chalcogenides films are found to be direct and allowed type [16]. Hence, a graph of $(\alpha h\nu)^2$ vs. $h\nu$ is drawn and the optical bandgap energy has been estimated by extrapolating the straight line portion to cut the energy axis. Fig. 4 shows the $(\alpha h\nu)^2$ vs. $h\nu$ plots of MoX_2 (X=S, Se and Te) thin films. The intersection of the plots at energy axis showed bandgap energy of 1.12 eV for MoS_2 films, 1.64 eV for $MoSe_2$ films and 1.92 eV for $MoTe_2$ films.

E. Semiconductor Parameters of Electrodeposited Thin Films

A tabulation of the potential – capacitance behaviour data of MoX_2 (X=S, Se and Te) thin films for the system n-MoX_2 | polyiodide | graphite electrode is done by plotting the inverse of the square of the capacitance versus the applied potential to the films. In the Mott-Schottky graphs of $1/C^2$ sc versus V_{SCE}, the voltage axis intercepts give the flat band potentials V_{FB}.

In terms of experimental voltages, the Mott Schottky equation is defined as:

$$\frac{1}{C^2} = \frac{2\,(V - V_{FB} - k_B T / e)}{\varepsilon\,\varepsilon_0\, e\, N} \quad \text{..... (1)}$$

where C is the space charge capacitance, k_B is the Boltzmann's constant (1.38 x 10^{-23} J/K), T is the temperature of the operation (300 K), e is the electronic charge (1.603 x 10^{-19} C), ε is the dielectric constant of the film material, ε_o is the dielectric constant of free space (8.854 x 10^{-12} F / m) and N is the carrier concentration which is calculated from the slope of the graph.

Table 2. Summary of the results obtained from the Mott–Schottky plots for MoX_2 films

Semiconductor parameters	**MoS_2**	**$MoSe_2$**	**$MoTe_2$**
Type of semiconductor	n	n	n
Flat band potential (V_{FB}) (V)	-0.48	-0.28	-0.61
Dielectric constant (ε)	27.4	33.5	23.2
Doping density (N)× 10^{29} (m^{-3})	0.48	0.72	0.37
Depletion layer width (W) (Å)	1.95	1.24	2.12
Density of states in Conduction Band (N_c)× 10^{13} (m^{-3})	4.196	4.196	4.196
Band bending (V_b) (V)	0.775	0.575	0.915
Energy gap (E_g) (eV)	1.64	1.12	1.92

Another important parameter to be deduced is the depletion layer width (W) and the band bending (V_b) that can be calculated from the relation:

$$V_b = V_{F,redox} - V_{FB}$$

$$W = \left(\frac{2\,\varepsilon\,\varepsilon_0\,V_b}{e\,N}\right)^{1/2} \quad \text{..... (2)}$$

where V_b is the built in voltage or the band bending and $V_{F,redox}$ is the redox potential of the $2I^- / I_2$ redox couple. An expression for the density of states, N_c can be written as:

$$N_c = \frac{2}{h^3} (2 \pi m_e^* k T)^{3/2} \quad \text{..... (3)}$$

where h is the Planck's constant (4.136×10^{-15} eV s) m_e is the effective electron mass in the conduction band and taken as $\approx 0.5\ m_e$ for molybdenum chalcogenides [17]. The semiconductor material parameters of MoX_2 (X=S, Se and Te) thin films from the Mott-Schottky plots are given in Table 2.

IV. CONCLUSION

Results proved that MoX_2 (X=S, Se and Te) thin films were successfully deposited on ITO-coated glass and stainless steel substrates. XRD analysis of the films proved polycrystalline MoX_2 thin films with while EDX pattern confirmed that mixed combinatorial films of MoX_2 (X=S, Se and Te) thin films have been formed through the electrodeposition process. Optical studies show the direct optical bandgap energy of the film in good range for a photovoltaic material. Results on the semiconductor parameters of the films revealed it is of n-type material and all semiconductor values come in the range of suitable photovoltaic material and this has proven that MoX_2 (X=S, Se and Te) thin films are capable for photoelectrochemical applications.

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