Engineering Science Conference 2011
(UMIES 2011), Kuala Lumpur, 12-14 July 2011
OF MALAYA
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Synthesis and Characterization of $MoTe_2$ Thin Films for Photoelectro-chemical Cell Applications

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Abstract *- Thin films of transition metal chalcogenides, molybdenum ditelluride ($MoTe_2$) have been electrodeposited cathodically on indium tin oxide-coated conducting glass substrates from ammonaical solution of H_2MoO_4 and TeO_2. These $MoTe_2$ thin films are useful as photovoltaic cell and photoelectro-chemical (PEC) solar cell. The electrode potential was varied while the bath temperature was maintained at 40±1 ºC and deposition time of 30 minutes. X-ray diffraction analysis showed the presence of highly textured $MoTe_2$ films with polycrystalline nature. Compositional analysis by EDX gives their stoichiometric relationships. Scanning electron microscope (SEM) was used to study surface morphology and shows that the films are smooth, uniform and useful for device fabrication. The optical absorption spectra showed that the material has an indirect band-gap value of 1.91-2.04 eV with different electrode potential. Besides, the film exhibited p-type semiconductor behavior.*

Keywords: Molybdenum ditelluride; Thin films; Electrodepositon; Solar cell

1. INTRODUCTION

Recently there has been a growing interest in layered semiconducting compounds consisting of group VI transition metal dichalcogenides MX_2 (M = Mo, W, Cd, Ni etc. and X = S, Se, Te) [1-3]. Among these works not many have been devoted to $MoTe_2$. Only a systematical study of the electrical properties of $MoTe_2$ powders and then single crystals has been done [4-6]. Molybdenum dichalcogenides are semiconductors with layered type structure, which can act as efficient electrodes in the realization of photo electrochemical solar cells [7]. The usual thin film preparatory techniques, such as sputtering, thermal evaporation etc, is cost intensive and sometimes present special problems for the preparation of transition metal chalcogenide films [2].

As the development of thin films processing technique improved, the intention to lower the cost and complexity of the process also increased. Furthermore, electrodeposition method is relatively lower cost, less time consuming, and environmental friendly because it produce no contamination to the surrounding. Hence, no vacuum facility needed. Films deposits obtained by electrodeposition show distinct advantage like improved deposit distribution, minimzed edge effect, pin hole free deposit, less hydrogen uptake, uniform thickness, better adhesion, and low impurity content compared to conventional methods [2].

The present paper reports an electrodeposition technique for depositing molybdenum ditelluride film cathodically on a conducting indium tin oxide (ITO) coated glass substrate. There is generally a difference between the properties of thin films and of single crystals of a material. The former is strongly dependent on the preparatory technique used. Therefore it is imperative to characterize different films of molybdenum ditellurides in the fabrication of photo electrochemical solar cell, in which the charge transfer reaction at the semiconductor electrolyte interface is responsible for the generation of photocurrent/ photovoltage [2]. The characterization of films were carried out in detail using X-ray diffraction analysis, optical studies and SEM /EDX studies.

2. EXPERIMENTAL

The Princeton Applied Research Potentiostat (VersaSTAT 3 model 400) driven Electrochemical Analysis System software (VersaStudio) was used to control the electrodeposition process and to monitor the current and voltage profiles. The cyclic voltammetry (CV) experiments were useful for fixing deposition potentials. A three-electrode system was adopted to deposit $MoTe_2$ thin films. Magnetic stirrer cum heater set-up was used to deposit the films by stirring the bath as well as raising the temperature. The electrolysis cell consists of an indium tin oxide (ITO) coated glass substrate on which $MoTe_2$ is to be deposited which acts as the working electrode (cathode) and the graphite electrode as the counter electrode (anode). While the saturated calomel electrode (SCE) with Ag/AgCl reference system as reference electrode. The mixture solution consisting of $H_2MoO_4 + NH_3 + TeO_2 + H_2SO_4 + H_2O$ was used as electrolyte. To prepare electrolyte solutions having relative concentrations of 0.5M H_2MoO_4 and 1.5mM TeO_2, the following two basic solutions were first prepared: solution A containing 42.6 g H_2MoO_4 (85 %, Merck) in 500 ml of NH_3 (25 %, Merck) solution (47.1 ml) and solution B containing 0.1197 g TeO_2 (99+ %, Sigma Aldrich) in 500 ml of 2.66 ml H_2SO_4 (95-97 %, Merck) and water. All the solutions were prepared by using analytical grade reagents and distilled water. The equal volumes of these two basic solutions were mixed to give the electrolyte. The experiment will be carried out at temperature of 40±1 °C for deposition time of 30 minutes by varying the desired deposition potentials obtained from the cyclic voltammetry test.

Film thickness measurement was carried out by using weight gain method. The ITO coated conducting glass substrates before and after the depositions of films were

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measured, the weight gain of the thin film can be calculated immediately.

X-ray diffraction (XRD) measurements were carried out on PAN analytical XPERT PROMPD PW 3040/60 diffractometer using monochromatic CuK_α radiation (λ = 1.5405 Å). The d_{hkl} spacing was given directly by the graphical program. Structural information of the as-grown films was obtained in the range of 2θ angles from 10º – 90º. The crystallographic properties such as the crystal system, inter planar distance, '*d*' spacing values and (*h k l*) planes of the binary transition metal chalcogenide were analyzed.

The optical absorption spectrum will be taken using Shimadzu 1700 UV-Vis Spectrophotometer in the wavelength region of 200 – 1100 nm to study their optical properties. From this absorption spectrum the band gap energy of the $MoTe_2$ thin films will be calculated and to confirm their band gap nature. The uncoated ITO glass substrate was put across the reference path whereas the film-coated ITO glass substrate was placed across the sample radiation pathway.

From Scanning Electron Microscope (SEM) analysis, surface of thin films will be studied to determine the grain's condition and the present of pin-hole free morphology. The compositional study of $MoTe_2$ thin film is conducted using the Energy Dispersive X-ray Spectroscopy (EDX) analysis to confirm their composition from the prepared aqueous solutions. This study is done only to the thin film deposited with potential voltage of -1.0 V with deposition time of 30 minutes and V = -0.9 V (t =35 minutes).

ZENTECH A3302-01 Test Leads LCR Meter with an inbuilt function generator of a frequency of 1000 Hz was used for the measurement of space–charge capacitance to obtain Mott-Schottky plots. Mott-Schottky plot was used to study the semiconducting nature of these materials. Mott-Schottky plot will enable us to calculate the conversion efficiency of these materials, type of conductivity, energy gap, conduction and valence band edge, flat band potential etc. parameters. Mott-Schottky plots have been drawn (in the dark condition) to evaluate the semiconductor parameters. The value of flat band potential (V_{fb}) will be obtained using the relation: The positive slope of the Mott-Schottky plot will conclude the n-type conductivity of $MoTe_2$ films, while negative slope will shows p-type conductivity. The intercept of the linear plot will be taken as the electrode potential of the semiconductor at which the bond bending is zero.

3. RESULTS AND DISCUSSION

3.1. Cyclic Voltametry Studies

Cyclic voltammetry (CV) test was carried out between two potential limits (-1.00 V to 1.00 V) for the mixture solutions prepared to probe the prospective potentials for deposition of the thin films. Figure 1 shows the cyclic voltammogram of the electrode in the H_2MoO_4 + TeO_2 mixture solution.

The forward scan initially increases linearly and came to a constant at approximately -0.5 V until a sharp current rise at – 0.1 V suggesting a reduction process. The current change is associated with the reduction of molybdenum and telluride

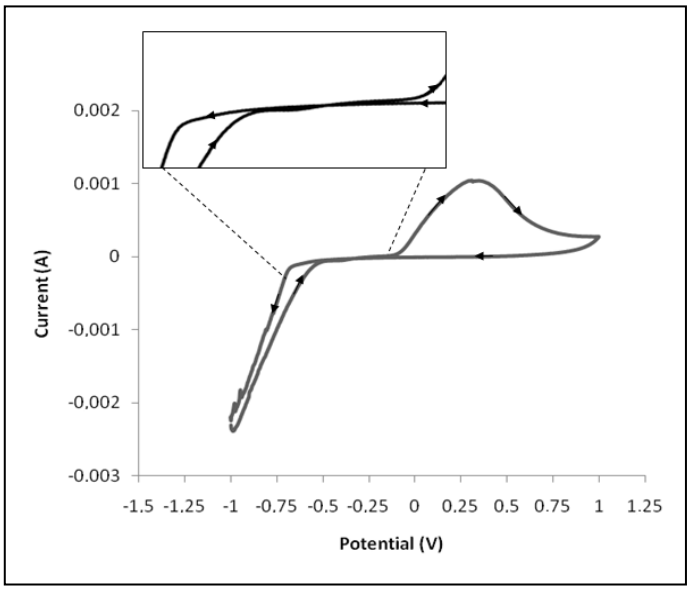

Figure 1: Cyclic voltammogram of $MoTe_2$

ions to form solid molybdenum telluride, $MoTe_2$ compound on the substrate. The deposition of molybdenum telluride on the substrate continued until all the equilibrium potential is achieved at an interception between the forward and reverse scan at approximately – 0.3 V versus Ag/AgCl. However, the dissolution of $MoTe_2$ is less compared to the amount of $MoTe_2$ deposited during the forwards scan. From the results obtained through CV, the deposition was carried out at different selected potentials, namely -0.6, -0.7, -0.8, -0.9 and -1.0 V for 30 minutes to determine the best characteristics of the films at different potentials.

3.2. Thicknesses measurement of $MoTe_2$ thin films

The ITO coated conducting glass substrates were cleaned thoroughly and dried and its weight was measured before deposition. After the deposition process immediately the weight gain is measured. The thickness of $MoTe_2$ thin film is calculated by using the relation between mass and volume in the density calculation, where density is equal to the value of mass over the volume as in Equation 1 [2].

$$\text{Thickness (cm)} = \frac{\text{Mass (g)}}{\text{Density (g/cm}^3\text{)} \times \text{Area(cm}^2\text{)}} \quad (1)$$

The density of $MoTe_2$ film was data gives the value of 7.68 g/cm^3 and the area of the substrate is ≈4.5 cm^2 (3 cm x 1.5 cm). The value of thickness for various deposition potentials is illustrated in Figure 2.

The deposition time and bath temperature were set at 30 minutes and at 40±1 ºC respectively to suppress the effect of time and temperatures on the deposition of the thin film. From Figure 2, it shows that the thickness of the $MoTe_2$ thin film decrease from 1.1574 µm at potential voltage -1.0 V to 0.7812 µm at -0.6 V. It can be concluded that the thickness of $MoTe_2$ decrease with the increasing of potential voltages and the deposition of films were more favor at more negative potential voltage.

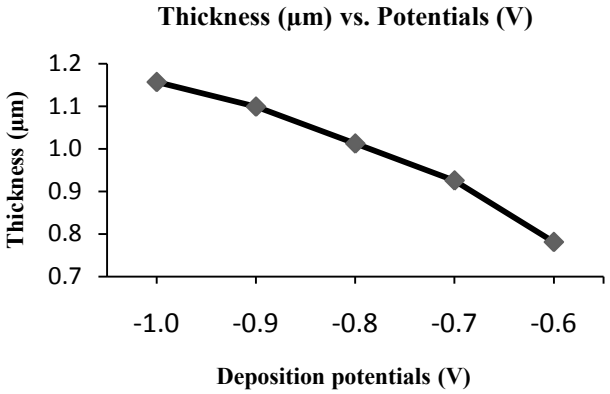

Figure 2: Thickness of thin films vs. potentials.

3.3. X-ray Diffraction Studies

The samples have been analyzed by X-ray diffraction (XRD). The *d* spacing of $MoTe_2$ thin film and the peaks for $MoTe_2$ thin films deposited with various potential voltages.were compared to the standard [8] and shown in Table 1 and Figure 3. The *d* spacing values of $MoTe_2$ thin film at various potential voltages were same as observed value at -1.0 V. The structural features of $MoTe_2$ thin film in the XRD plot is fit to the hexagonal structure with lattice parameter values of a=b=3.5190 and c=13.9640 which is in good agreement as reported; a=b=3.52 and c=13.96 [9].

Table 1: Comparison of *d* spacing for $MoTe_2$ thin film potential voltage of -1.0 V (t = 30 minutes) with standard.

Angle (2θ)	(*h k l*)	*d* spacing (Å) of JCPDS	*d* spacing (Å) of observed value
15.808	(1 0 1)	5.6016	5.6022
26.469	(0 1 1)	3.3647	3.3649
33.253	(-2 0 3)	2.6921	2.6987
43.469	(-1 1 5)	2.0802	2.0806
50.428	(1 1 6)	1.8082	1.7988

XRD pattern shown in Figure 3 revealed that the films exhibit polycrystalline nature due to the sharp peaks on the XRD patterns. The $MoTe_2$ peaks appear significantly with higher intensities by the decreased of potential voltage which indicated that the films growth on plane (1 0 1), (0 1 1), (-2 0 3), (-1 1 5) and (1 1 6). Stainless Steel substrate are identified at the planes (1 1 1), (2 0 0), and (2 2 0) with standard [10].

XRD pattern exhibits lower intensity for the peak of $MoTe_2$ phase (2θ = 43.469°) with the increasing of potential voltage due to the presence of the peak for stainless steel (2θ = 43.583°). Meanwhile the peak for stainless steel shrunk and disappeared gradually indicating that the growth of film at (-1 1 5) plane surmounted the stainless steel phase at (1 1 1) plane with decreasing potential voltages. Furthermore, the peak of $MoTe_2$ phase corresponds to (1 1 6) plane appeared gradually with the peaks of stainless steel at 2θ = 50.40°while decreasing the potential voltage. This indicated that the growth of MoTe correspond to (1 1 6) plane at -0.9 V and -1.0 V.

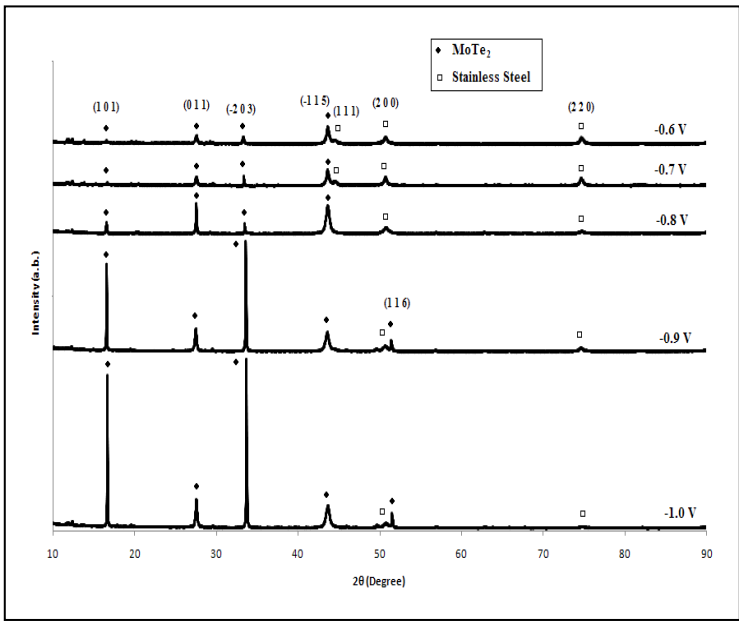

Figure 3: XRD plot of $MoTe_2$ for different potential voltages.

3.4 Compositional Studies

The compositional studies of $MoTe_2$ thin film is conducted using the EDX analysis. This study is done only to the thin film deposited with potential voltage -1.0 V (t = 30 minutes) and potential voltage -0.9 V (t = 35 minutes). Theoretically, the weight percentage of molybdenum in the $MoTe_2$ thin film is 33.3% and 66.7% for tellurium corresponding to its empirical formula. The composition of the elements found on the $MoTe_2$ thin film is presented in Table 2.

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 used 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.

Table 2: The weight percentage (wt. %) of $MoTe_2$ with deposition potentials -1.0 V (t = 30 minutes) and -0.9 V (t =35 minutes).

Elements	**(wt. %) for -1.0 V and 30 min.**	**(wt. %) for -0.9 V and 35 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

3.5 Surface Morphological Studies

The surface morphology of the $MoTe_2$ thin films was analyzed by scanning electron microscope (SEM). The thin films deposited on the ITO-coated glass substrate with only the minimum and maximum value of potential voltage (-0.6 V and -1.0 V) have been studied as shown in Figure 4(a) and Figure 4(b) with magnifications of 3000 X.

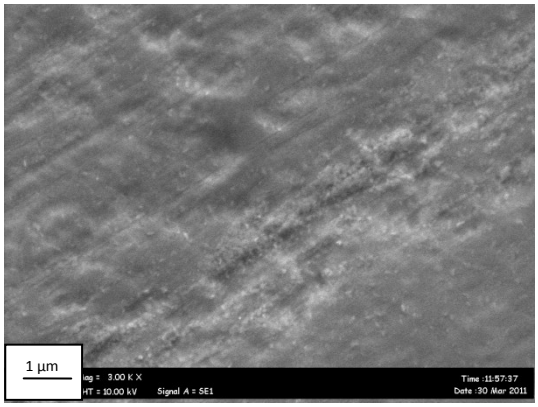

Figure 4(a): SEM Micrograph of $MoTe_2$ thin film deposited at potential voltage of -0.6 V.

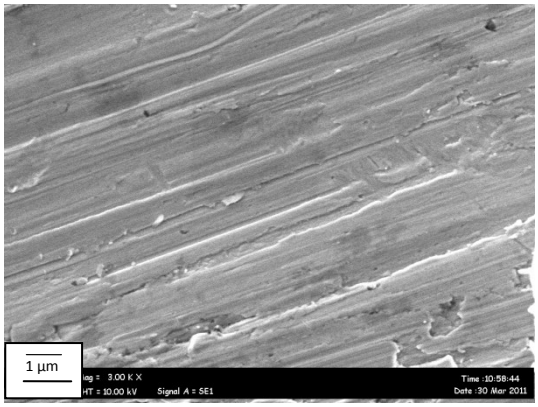

Figure 4(b): SEM Micrograph of $MoTe_2$ thin film deposited at potential voltage of -1.0 V.

The film deposited at -1.0 V is more uniform and continuous compared to the film deposited at -0.6 V. As discussed earlier, the thickness of the thin films decreased with the increasing of potential voltages, therefore thicker film can be observed in Figure 4(b) than in Figure 4(a). The micrographs revealed that the layered structures appeared on both of the films.

3.6 Optical Studies

The transition metal dichalcogenides possessed usually indirect band gap semiconductor in nature [2]. Optical studies of the molybdenum ditelluride thin films deposited on ITO-coated glass substrates were carried out using an identical blank ITO-coated glass substrate as a reference to compute the band gap energy value of the deposited thin films. A graph of $(\alpha hv)^2$ vs. hv is drawn and the linear portion of the graph is extrapolated to the energy axis until the intercepts of the linear part of these plots on the energy axis at $\alpha=0$. The value will gives the band gaps of these compounds.

The result obtained from UV-Vis Spectrophotometer is the K alpha average absorbance (K*α) value for each wavelength and the value of hv is calculated using Equation 2, where h is the Planck's constant (6.636×10^{-34} J), c is the velocity of light (3.0×10^8 ms^{-1}) and λ is the wavelength (nm).

$$E = hv = \frac{hc}{\lambda} \quad (2)$$

The films show good absorption in the visible region. A pronounced absorption edge is evident in the vicinity of 500 – 1000 nm for all the films with different potential voltages. The value of K alpha average absorbance (K*α) value for each wavelength and the value of hv is calculated and shown in Table 3 and the optical band energy values were extrapolated as shown in Figure 5.

Table 3: Value of $(\alpha hv)^2$ and hv for various potential voltages (t = 30 minutes).

λ (nm)	hv (eV)	$(\alpha hv)^2$ for Thin Films with Various Potential Voltages				
		-0.6 V	-0.7 V	-0.8 V	-0.9 V	-1.0 V
500.0	2.4885	2.8232	19.7665	19.2374	54.2464	60.8665
600.0	2.0738	0.5134	3.3882	3.5924	17.2526	20.1335
700.0	1.7775	0.3023	1.1039	0.6973	7.6407	3.3428
800.0	1.5553	1.2241	4.5212	3.2884	9.2865	7.1081
900.0	1.3825	0.1269	0.2824	0.1391	1.6339	0.5594

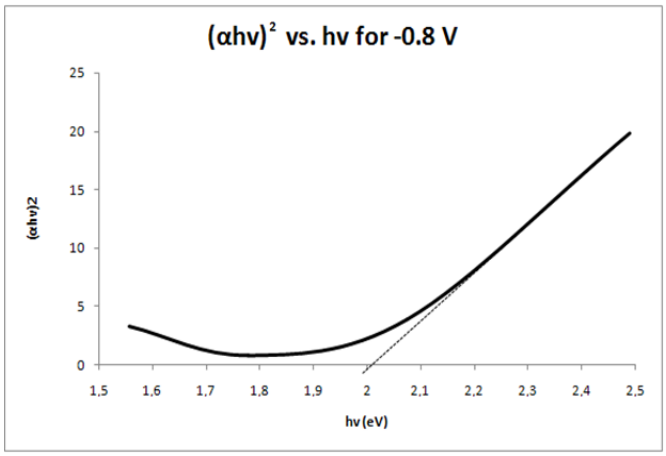

Figure 5: Band gap energy for potential voltage -0.8 V.

The band gap energies of the $MoTe_2$ thin films are determined from the absorption spectrum and they possessed indirect band gap which is in good agreement with the reported value [11] which showed that $MoTe_2$ has indirect band gap. The relation of band gap energies for different potential voltage is illustrated in Figure 6.

The band gap energy (E_g) of the $MoTe_2$ thin film exhibited non-linear increase with the increasing of potential voltage. This result is positive to the theory that the smaller the band gap, the less energy needed to move electrons from the valence band to the conduction band and semiconductor

is a material with a small but non zero band gap, lies in between metal conductor and insulator materials.

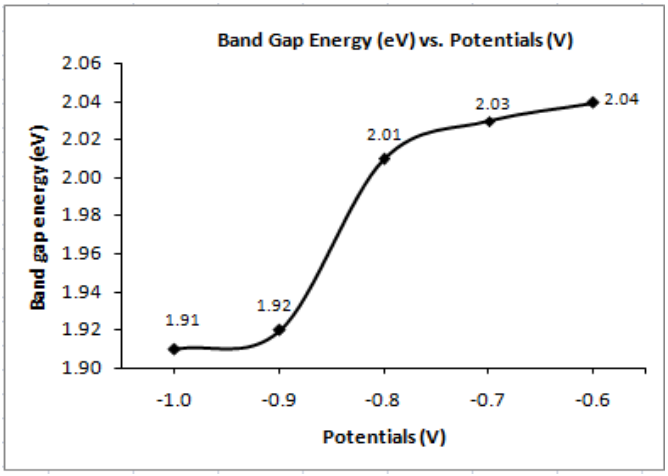

Figure 6: Band gap energy vs. deposition potentials for $MoTe_2$ thin films.

3.7 Mott-Schottky Plot

Mott-Schottky relationship expresses the potential dependence of the electrode under depletion; where band bending in semiconductor due to the applied potential condition. The plot may be fitted with a straight line according to Equation 2. The negative slope of the Mott-Schottky plot reconfirms the p-type conductivity of $MoTe_2$ according to the reported value [5]. This flat band potential is equal to 1.00 V_{SCE}. The interception 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 [2]. In p-type semiconductor the accumulation occurs at potential greater than the flat band potential.

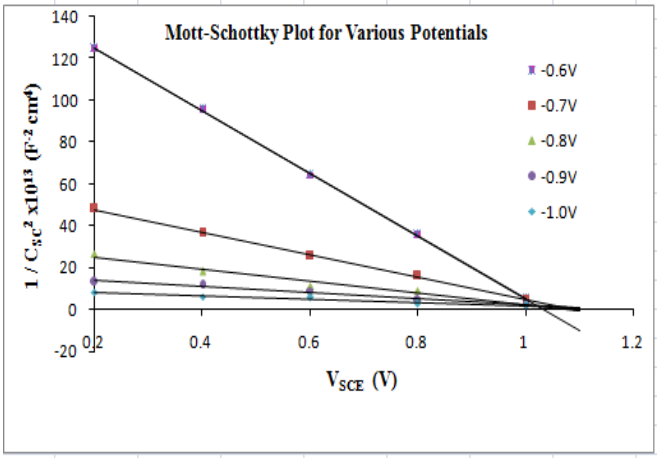

Figure 7: Mott-Schottky plot for deposition potentials of -0.6 V, -0.7 V, -0.8 V, -0.9 V, and -1.0 V.

4. CONCLUSION

By applying the electrodeposition technique, molybdenum ditelluride thin films were successfully deposited on ITO-coated glass substrates with varies potential voltage. The best film was deposited at an optimized deposition potential of -1.0 V, keeping the bath at temperature 40±1 °C. Besides, the thickness of thin films is in the range of 0.78-1.18 µm. XRD studies confirmed that the present of polycrystalline in nature and possessed hexagonal structure with lattice parameters values $a = b = 3.519$ nm and $c = 13.964$ nm. The data from UV–Vis-NIR Spectrophotometric measurements revealed that the optical band gap values of the thin films decreased with lower potential voltage. SEM analysis showed that the distribution of the $MoTe_2$ thin films is more uniform and continuous for lower potential voltage value. From the Mott-Schottky plot, the semiconductor parameters were found and the film was found to be p-type.

ACKNOWLEDGMENTS

This work is funded by the short term grant of University Technical Malaysia Melaka [Project No: PJP/2009/FKP (18A) S608].

REFERENCES

1. L.M. Peter and R.L. Wang, *Channel flow cell elctrodeposition of CdTe for solar cells.* Electrochemistry Communications, 1999. **1**: p. 554-558.
2. T.Joseph Sahaya Anand, *Synthesis and characterization of MoS_2 films for PEC cells.* Sains Malaysiana, 2009. **38**: p. 85-89.
3. Z. Zainal, N.Saravanan and H.L. Mien, *Electrodeposition of nickel selenide thin films in the presence of triethanolamine as a complexing agent.* Materials Science: Materials In Electronics, 2005. **16**: p. 111- 117.
4. J.C. Berne`de, C.A., L. Assmann and M. Spiesser, *X-ray photoelectron spectroscopy study of $MoTe_2$ single crystals and thin films.* Applied Surface Science 2003. **219**: p. 238-248.
5. A. Conan, A.B., A. Amrouche and M. Spiesser, *Semiconducting properties and band structure of $MoTe_2$ single crystals.* J. Physic, 1984. **45**: p. 459-465.
6. M. Kettaf, A.C., A. Bonnet and J. C. Bernede, *Electrical Properties Of Molybdenum DitelluridеI Thin Films.* Physical Chemical Solids, 1990. **51**(4): p. 333-341.
7. T. Joseph Sahaya Anand, C. Sanjeeviraja and M. Jaychandran, *Preparation of layered semiconductor ($MoSe_2$) by electrosynthesis.* Vacuum, 2001. **60**(4): p. 431-435.
8. *Joint Committee of Powder Diffraction Standards (JCPDS), File No. 01-071-0117.*
9. N.L. Heda, A.D., Ambica Marwal, Yamini Sharma, S. K. Srivastava, Gulzar Ahmed, Rajesh Jain, B. L. Ahuja, Journal of Physics and Chemistry of Solids, 2010. **71**: p. 187-193.
10. *Joint Committee of Powder Diffraction Standards (JCPDS), File No. 00-033-0397.*
11. S. K. Srivastava, N.G. and J.C.Bernede, *Growth of textured nonstoichiometric $MoTe_2$ films from Mo/Te layers and their use as precursor in the synthesis of $MoTe_{2-x}S_x$ films.* Solid State Communications 2004. **132**: p. 601-606.

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