ABSTRACTS

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Electrodeposited $MoTe_2$ Thin Films for Photoelectrochemical (PEC) Cell Applications

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Abstract

Thin films of transition metal chalcogenides, molybdenum ditelluride ($MoTe_2$) have been electrodeposited cathodically on both indium tin oxide-coated conducting glass substrates and stainless steel substrates from H_2MoO_4 and TeO_2 solutions. These $MoTe_2$ thin films are useful as photovoltaic cell and photoelectrochemical (PEC) solar cell. The electrode potential was set to -0.9 V while the bath temperature was maintained at 40±1 °C with varies deposition time. 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 continuous, uniform and useful for device fabrication. The optical absorption spectra showed that the material has an indirect band-gap value of 1.92-2.03 eV with different deposition time. The film also exhibited p-type semiconductor behavior.

Keywords: Electrodeposition; Molybdenum ditelluride; Solar cell; indirect band gap; Thin films

1. INTRODUCTION

Interest in the layered semiconducting compounds consisting of group VI transition metal dichalcogenides MX_2 (M = Mo, W, Cd, Ni etc. and X = S, Se, Te) due to the effort of finding new materials for solar energy conversion [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]. 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 [7].

Electrodeposition is a perspective competitor in thin film preparation because of several advantages such as the possibility for large-scale production, minimum waste of components and easy monitoring of the deposition process. This technique is generally less expensive than those prepared by the capital-intensive physical methods. The composition of the electrolytes plays an important role in determining the quality of the films deposited [3].

The present paper reports an electrodeposition technique for depositing molybdenum ditelluride film cathodically on both conducting indium tin oxide (ITO) coated glass substrate and stainless steel substrate. There are generally differences between the properties of thin films and of single crystals counter part of any 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/ photo voltage [7]. The characterizations 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 study the electrodeposition process and to monitor the time, 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 potential of -0.9 V by varying the desired deposition time.

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

X-ray diffraction (XRD) measurements were carried out on PAN analytical XPERT PROMPD diffractometer using goniometer PW 3040/60 and 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 10° – 90°. 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 was 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 was 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 was studied to determine the grain's condition and the present of pin-hole free morphology. The compositional study of $MoTe_2$ thin film was conducted using the Energy Dispersive X-ray Spectroscopy (EDX) analysis to confirm their composition from the prepared aqueous solutions.

ZENTECH A3302-01 Test Leads LCR Meter 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. Mott-Schottky plot was used to study the semiconducting nature of these materials. Mott-Schottky plot was enable us to identify the type of conductivity, energy gap, conduction and valence band edge, flat band potential etc. parameters. The value of flat band potential (V_{fb}) was 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 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 Voltammetry Studies

Cyclic voltammetry (CV) test was carried out between two potential limits (-1.00 V to 1.00 V) for the mixture of 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 ions to form solid molybdenum telluride, $MoTe_2$ compound on the

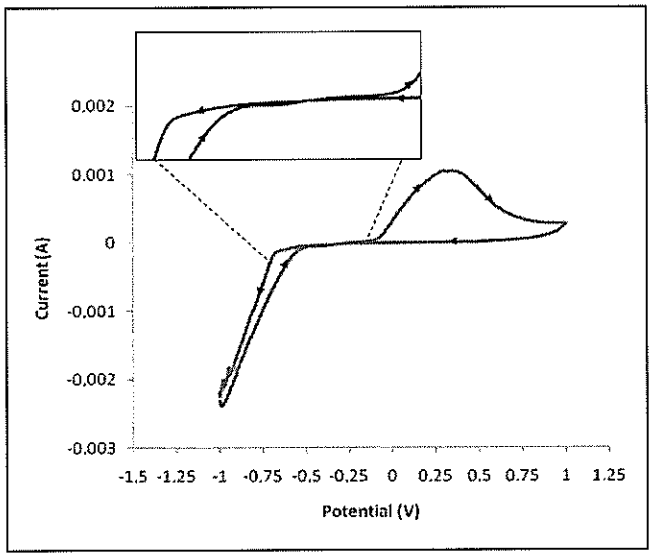

Figure 1: Cyclic voltammogram of $MoTe_2$

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. The CV result showed that the film can be deposited in the potentials range of -0.6 V to -1.0 V. The deposition was carried out at -0.9 V to determine the best characteristics of the films at different deposition times.

3.2 Thicknesses measurement of $MoTe_2$ thin films

The deposition potential and bath temperature were set at -0.9 V and at 40±1 °C respectively to suppress the effect of deposition potential and temperatures on the deposition of the thin film.

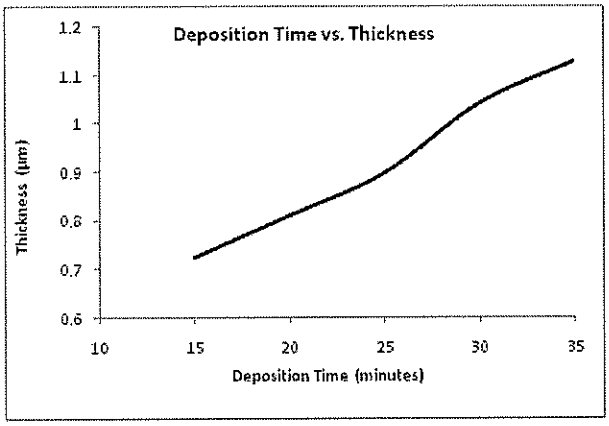

Figure 2: Thickness of thin film vs. time

From Figure 2, it shows that the thickness of the $MoTe_2$ thin films increase from 0.7234 µm at 15 minutes to 1.1285 µm at 35 minutes. It can be concluded that the thickness of $MoTe_2$ increase with the increasing of deposition time.

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 deposition times 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 deposition times were similar as observed value at 30 minutes. 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 Å and c=13.9640 Å which is in good agreement as reported; a=b=3.52 Å and c=13.96 Å [9]. The peaks for stainless steel substrate are identified at the planes (1 1 1), (2 0 0), and (2 2 0) with standard [10].

Table 1: Comparison of *d* spacing for $MoTe_2$ thin film at deposition time of 30 minutes and potential voltage of -0.9 V with standard JCPDS.

Angle (2θ)	(*h k l*)	*d* spacing (Å) of JCPDS	*d* spacing (Å) of observed value
19.660	(1 0 2)	4.51187	4.51283
28.240	(2 0 0)	3.15761	3.13394
33.253	(-2 0 3)	2.69211	2.69151
38.523	(2 1 0)	2.33511	2.33803
43.469	(-1 1 5)	2.08017	2.08429
49.777	(-2 1 5)	1.83032	1.83306

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 at longer deposition time which indicated that the films growth on plane (1 0 2), (2 0 0), (-2 0 3), (2 1 0), (-1 1 5), and (-2 1 5). XRD pattern exhibits lower intensity for the peak of $MoTe_2$ phase (2θ = 43.469°) with the increasing of deposition times 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 increasing deposition times. Furthermore, the peak of $MoTe_2$ phase corresponds to (-2 1 5) plane appeared gradually with the peaks of stainless steel at 2θ = 50.4° at longer time. This indicated that the growth of $MoTe_2$ correspond to (-2 1 5) plane at 30 min. and 35 min.

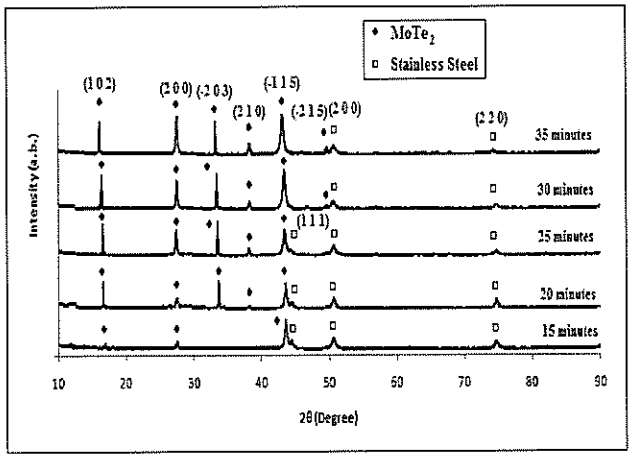

Figure 3: X-ray diffractograms of $MoTe_2$ for different deposition time.

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.

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

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.

3.5 Surface Morphological Studies

The surface morphology of the $MoTe_2$ thin films was analyzed by scanning electron microscope (SEM).

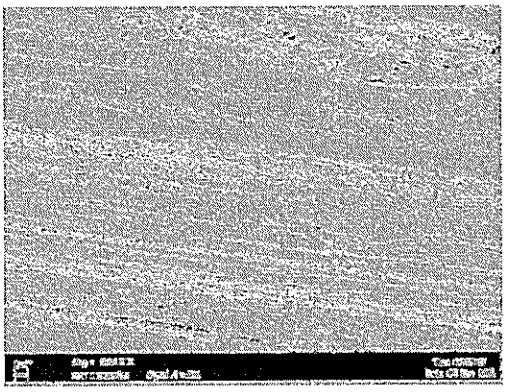

Figure 4: SEM micrograph of $MoTe_2$ thin film deposited for 15 minutes.

The thin films deposited on the stainless steel substrate at deposition time of 15 minutes has been studied as shown in Figure 4 with magnifications of 3000 X.SEM micrograph revealed the uniform and continuous texture of film deposited. The layer structure of the film also can be seen from the micrograph.

3.6 Optical Studies

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 $(\alpha h\nu)^2$ vs. $h\nu$ 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 ($K^*\alpha$) value for each wavelength and the value of $h\nu$ 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).

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

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 ($K^*\alpha$) value for each wavelength and the value of $h\nu$ is calculated and shown in Table 3 and the optical band energy value was extrapolated as shown in Figure 5.

Table 3: Value of $(\alpha h\nu)^2$ and hν for various deposition times (-0.9 V).

λ (nm)	$h\nu$ (eV)	$(\alpha h\nu)^2$ for Thin Films with Various deposition times -0.6 V	-0.7 V	-0.8 V	-0.9 V	-1.0 V
500.0	2.4885	1.9025	4.5236	18.6848	18.4637	40.6482
600.0	2.0738	0.4372	1.1715	4.5171	5.0234	12.2047
700.0	1.7775	0.4985	0.8182	2.1198	1.8493	8.5737
800.0	1.5553	0.7197	1.2715	5.9529	3.4301	10.3017
900.0	1.3825	0,1771	0,2915	0,8229	0,2195	1,4119

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.

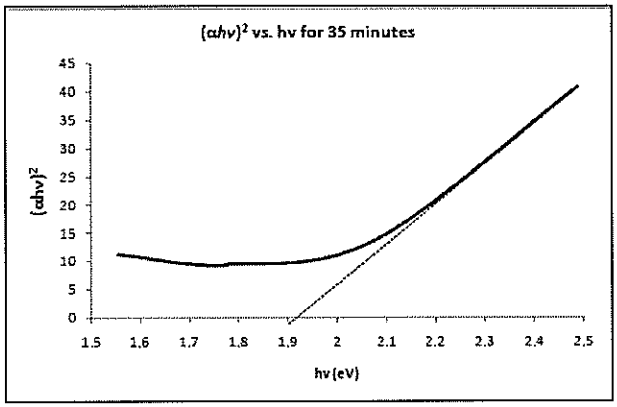

Figure 5: Band gap energy for deposition time of 35 minutes.

The band gap energy (E_g) of the $MoTe_2$ thin film exhibited non-linear decrease with the increasing of deposition times. 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.

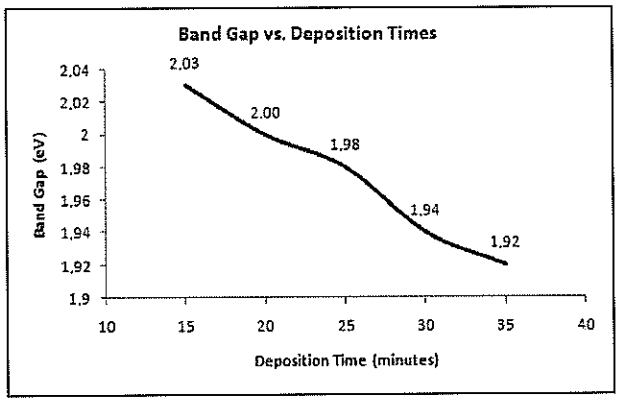

Figure 6: Band gap energy vs. deposition times for $MoTe_2$ thin films.

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.

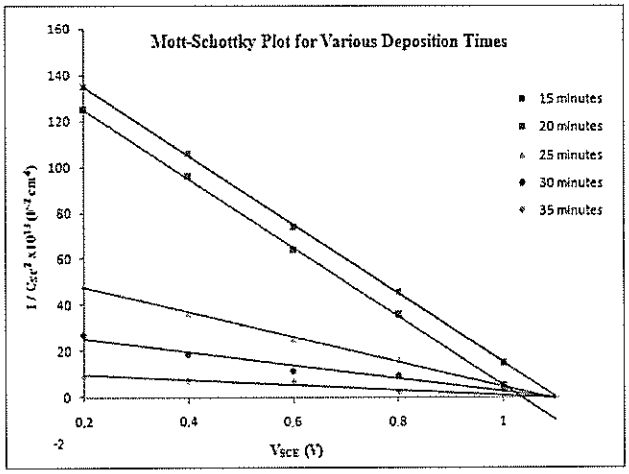

Figure 7: Mott-Schottky plot for deposition potentials of -15 min., 20 min., 25 min., 30 min., and 35 min.

4. CONCLUSION

Using the electrodeposition route for synthesizing the molybdenum ditelluride thin films were successfully deposited on two different substrates with varies deposition time. The stoichiometric quality 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 0.7234 - 1.1285 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 longer deposition time. SEM analysis showed that the distribution of the $MoTe_2$ thin films is uniform and continuous. From the Mott-Schottky plot, the semiconductor parameters were found and the film was found to be p-type semiconductor.

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