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Pulsed electrodeposition and characterization of molybdenum diselenide thin film

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Abstract

Molybdenum dichalcogenides are semiconductors with layered type structure, which can act as efficient electrodes in the realization of photoelectrochemical solar cells. The main advantage of this molybdenum diselenide ($MoSe_2$) semiconductor is the prevention of electrolyte corrosion because of the phototransitions involving non-bonding d–d orbital of the Mo atoms. Polycrystalline molybdenum diselenide thin films are prepared by pulsed electrodeposition on conducting glass and titanium substrates in galvanostatic mode from an ammoniacal solution of H_2MoO_4 and SeO_2. The growth kinetics of the film was studied and the deposition parameters such as electrolyte bath concentration, bath temperature, time of deposition, deposition current, pH of the electrolyte and duty cycle of the current are optimized. X-ray diffraction analysis of the as deposited and annealed films showed the presence of highly textured $MoSe_2$ films with polycrystalline nature. EDAX spectrum of the surface composition confirms the nearly stoichiometric $MoSe_2$ nature of the film. Surface morphology studies by scanning electron microscope (SEM) shows that the films are pinhole free and of device quality nature. The optical absorption spectra show an indirect band gap value of 1.16 eV. Conductivity measurements were carried out at different temperatures and electrical constants such as activation energy, trapped energy state and barrier height were calculated.

Keywords: A: Semiconductors; B: Chemical synthesis; C: X-ray diffraction; D: Electrical properties

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1. Introduction

Interest in the use of photoelectrochemical (PEC) solar cells for low-cost energy conversion has lead to an extensive research in the search for novel and suitable thin film semiconductor materials [1,2]. Recent investigations have shown that the layered type semiconducting group VI transition metal dichalcogenides ($MoSe_2$, WSe_2 and MoS_2), which absorb visible and near-IR light are particularly interesting materials for photoelectrochemical solar energy conversion. The most efficient system till date turned out to be $MoSe_2$ [3]. Recent applications include intercalation compounds and long-life PEC solar cells. Some studies on PEC with $MoSe_2$ have been carried out on single crystals. However, polycrystalline electrodes are economically desirable for solar cell applications, where large area semiconductor substrates are necessary. Hence, this study has been directed towards obtaining molybdenum diselenide in thin film form. Many workers have succeeded in co-depositing Mo together with iron group metals [4–14]. Molybdenum diselenide thin films have been deposited under potentiostatic route [15] and soft selenization technique by Sanjeeviraja et al. [16]. Layered compounds such as tungsten diselenide (WSe_2) have been prepared through galvanostatic route by Jebaraj Devadasan et al. [17], tin disulphide (SnS_2) using the spray pyrolysis technique by Amalraj et al. [18], tin sulphide (SnS) using brush plating technique by Jayachandran et al. [19] and using electrodeposition technique by Subramanian et al. [20]. Tungsten diselenide films have been pulsed electrodeposited on titanium and SnO_2: F-coated glass substrates under galvanostatic condition by Mary Delphine et al. [21].

The electrodeposition of Mo in the presence of other metal ion is also known as induced co-deposition. The concept of induced co-deposition was the guiding principle to determine whether Mo can be co-deposited with Se. The usual thin film preparation techniques, such as sputtering, thermal evaporation etc., are cost intensive and sometimes present specific problems for the preparation of transition metal chalcogenide films [22].

In this report, an attempt is made to prepare $MoSe_2$ films through pulsed electrodeposition technique on conducting glass and titanium substrates which enables the film to be used for characterization studies like structural, surface composition, surface morphology, optical and electrical.

2. Experimental details

Thin films of $MoSe_2$ were cathodically pulsed electrodeposited on conducting transparent oxide (CTO) coated glass substrates and on titanium substrates under galvanostatic mode using PC based pulse console potentiostat/galvanostat developed indigenously at Central Electrochemical Research Institute (CECRI), Karaikudi, India. The pulse duty cycle is defined as the ratio of ON time to ON + OFF time. The on times were 1, 2, 3, 4 and 5 s with corresponding OFF time fixed as 1, 3, 7, 16 and 45 s which correspond to a duty cycle of 50, 40, 30, 20 and 10%, respectively. The CTO or titanium substrates were used as the cathode in the three-electrode cell with platinum as the counter electrode and saturated calomel electrode (SCE) as the reference electrode. An ammoniacal solution consisting of a mixture of $H_2MoO_4 + SeO_2$ was used as electrolyte. The electrolyte was prepared by mixing an ammoniacal solution of molybdic acid of molarity 0.40 M of molybdic acid whose pH was 10.3 and SeO_2 dissolved in water to make a molarity of 0.50 mM with pH as 6.1. The final pH of the electrolyte containing $H_2MoO_4 + NH_3 + SeO_2 + H_2O$ was 9.3. The chemicals used are all G.R. grade E-Merck. Before deposition, the substrates were thoroughly cleaned with triple distilled water and acetone to degrease the surface. The distance between the working electrode and the platinum counter electrode was kept constant as 1 cm during the deposition. From the visual observation during pulse plating of $MoSe_2$ it was observed that at first a brownish coating, possibly few monolayers of Se was formed, which slowly changed to grayish black confirming the formation of molybdenum selenide. These pulse plated $MoSe_2$ films were found to be well adherent, uniform and pinhole free. Detailed growth kinetics was studied by changing the two dominant deposition parameters like molarities of the solution and bath temperature.

The structural properties of the pulsed electrodeposited $MoSe_2$ films were studied using Philips Analytical PW1710 diffractometer with Cu Kα radiation (λ = 1.5418 Å). The surface morphology of the film was studied by taking scanning electron micrographs (SEM) using a Flex Scan E53F JEOL Scanning Electron Microscope. JEOL FINE COAT ION SPUTTER JFC-1100 sputtering unit was used to give a thin gold coating on the surface of $MoSe_2$ films. The composition of the film was analyzed by using EDAX spectrometer XL 30 ESEMTMP. The optical absorption spectrum was taken in the range of 400–1100 nm using a Shimadzu-UV 410S spectrophotometer. The electrical conductivity measurements were carried out using Keithley 2000 electrometer in the temperature range from 303 to 623 K.

3. Results and discussion

3.1. Electrochemistry of molybdenum diselenide formation

Generally, metals cannot be easily deposited from aqueous solutions if their electrode potentials are more negative than the hydrogen discharge potential, as in the present case for molybdenum. Using aqueous solutions, some metals, like molybdenum, whose electrode redox potentials are more negative than the hydrogen evolution potential, cannot be easily deposited at the cathode. The redox reaction associated with the deposition of Mo can be represented as [23]:

$$H_2MoO_4(aq) + 6H^+ + 6e^- \Leftrightarrow Mo + 4H_2O$$

which is pH dependent. But the anion $MoO_4{}^{2-}$, produced at the intermediate stage, is associated with a very high value of the energy of formation (−218.8 kcal mol), which shows that this anion is thermodynamically more stable, and cannot be easily separated into Mo and O ions.

In addition, the $MoO_4{}^{2-}$ ion is strongly bound and stabilized by the presence of inner orbital hybridization in which the 4d orbitals are hybridized with 5s and p orbitals [25]. Under such conditions, the potential (energy) needed for breaking such a strong hybridization bond far exceeds the cathodic potential required for the discharge of hydrogen. Hence, it will not be that much easy to deposit pure metallic molybdenum by cathodic deposition from an aqueous solution under normal bath conditions and deposition reaction mechanism. It may be made possible by the critical control of bath composition, conditions and the reaction mechanism initially observed at the bare electrode surface.

The electrode potentials of Se and Mo for their respective redox reactions can be written as [26]:

$$SeO_2 + H_2O \Leftrightarrow H_2SeO_3$$

$$
\begin{aligned}
&H_2SeO_3 + 4H^+ + 4e^- = HSeO_2^+ + 4H^+ + 4e^- + OH^- \\
&\quad = Se_{(s)} + 3H_2O \\
&\quad = E(H_2SeO_3) + (RT/4F)\ln\,(a_{HSeO_2^+})/(a_{Se}) + (3RT/4F)\ln C_{H^+} \\
&\quad = 0.50V_{SCE} + 0.0148\ln\,[(a_{HSeO_{2+}})/(a_{Se})] - 0.0443\mathrm{pH}
\end{aligned}
$$

$$
\begin{aligned}
&Mo_{(s)} + 8(OH)^- \Leftrightarrow MoO_4^{2-} + 4H_2O + 6e^- \\
&\quad = -1.29V_{SCE} + (RT/6F)\ln\,[(a_{MoO_4^{2-}})/(a_{Mo})] \\
&\quad = -1.29V_{SCE}
\end{aligned}
$$

Here, E is the equilibrium potential expressed with reference to SCE.

The quantity '*a*' refers to the activities of the ions present in the solution and in the deposit; $C_H{}^+$ is the concentration of the hydrogen ion. The symbols $Mo_{(s)}$ and $Se_{(s)}$ denote the species in the solid deposit. From the equilibrium electrode potentials of Se and Mo, it can be seen that the equilibrium electrode potential for the deposition of selenium is far more positive than that for molybdenum deposition. Further, to obtain simultaneous deposition of Mo and Se, the respective electrolyte concentration should be adjusted high or low so as to bring the electrode potentials of both the deposits as closer as possible. Therefore, it is theoretically recommended to use a high concentration of Mo and a low concentration for the nobler component Se, so that the deposition potential of Mo shifts towards a positive value and the Se deposition potential gets shifted to a negative value. Hence, the deposition of Se will become diffusion controlled due to the very low concentration of SeO_2 (consequently of the $HSeO_2{}^+$). Based on these electrode reactions, a very low concentration of 0.5 mM of SeO_2 has been taken in the bath for the deposition of $MoSe_2$ film.

3.2. Growth kinetics study

A detailed growth kinetics study was carried out by changing the composition of the electrolyte and bath temperatures. The film thickness was slowly built up at the initial stages linearly and finally saturated to a maximum of about 1–2 μm for about 15–60 min keeping the bath temperatures as 30, 40 and 50 °C, respectively, for different molarities of molybdic acid. Fig. 1 shows the growth kinetics of $MoSe_2$ films deposited at 30 °C for ammoniacal molybdic acid of different molarities 0.40, 0.47 and 0.55 M, keeping the concentration of SeO_2 constant as 0.5 mM. For 0.55 M concentration of molybdic acid, the growth of the film is very slow as time of deposition increases and the film thickness increases marginally up to 75 min. For 0.47 M concentration of molybdic acid, the film deposition thickness is linear up to 15 min and reaches a value of 0.49 μm after which the thickness built up is nearly constant. For 0.40 M concentration, the film growth is found to be fast and linear up to about 30 min and the thickness reached was about 1.5 μm. The growth rate is highly reduced in the deposition range of 30–75 min. The films deposited at 40 and 50 °C also showed almost the same growth trend and for 0.40 M concentrations only a maximum thickness of about 1.7 and 1.73 μm was obtained, respectively. From these observations, we can conclude that $MoSe_2$ films of uniform and maximum thickness were formed under the following optimized pulse plating conditions: 30 °C, 30 min of deposition duration, molybdic acid concentration of 0.40 M and SeO_2 concentration of 0.50 mM. After 30 min, the growth of thickness of the film became slow and attained saturation. For other higher concentrations more than 0.55 M of H_2MoO_4, the thickness was very much lower than that of the previous concentration. If the concentration

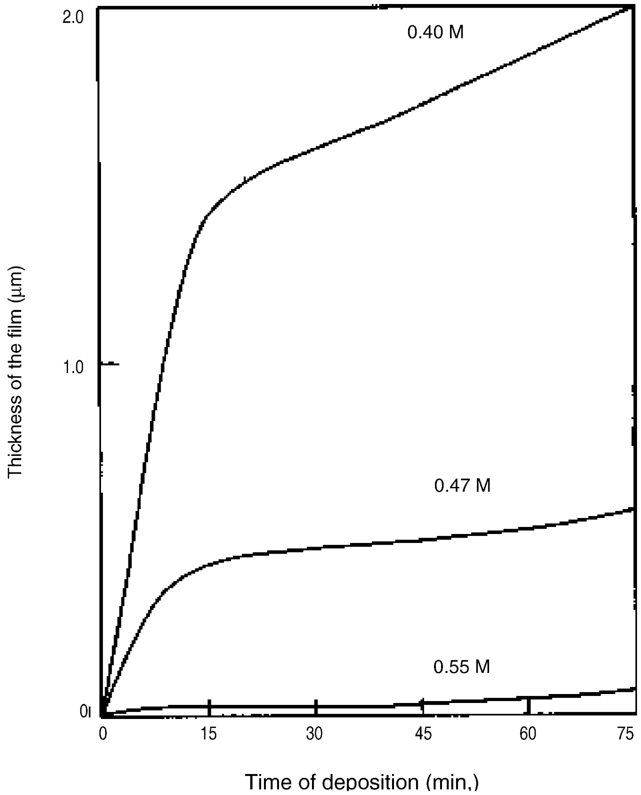

Fig. 1. Growth kinetics of $MoSe_2$ film at: (a) 30 °C, (b) 40 °C, (c) 50 °C bath temperature.

of the solution was lower than 0.40 M, the thickness was not sufficiently built on the substrate. For other higher temperatures, the thickness of the film was less while compared to 30 °C as the bath temperature. By keeping the concentration of the electrolyte solution H_2MoO_4 as 0.40 M, the concentration of SeO_2 as 0.50 mM and the bath temperature constant at 30 °C, the duty cycle was varied as 10, 20, 30, 40 and 50% and growth kinetics was studied and the thickness variations are shown in Fig. 2. Thickness of the film is found increasing for all duty cycles up to 60 min. The maximum thickness is obtained for the duty cycle of 30%. The optimized pulsed electrodeposition parameters are tabulated in Table 1.

3.3. Structural and surface morphological characterization

The X-ray diffraction patterns (XRD) of the pulsed electrodeposited $MoSe_2$ films with concentration of H_2MoO_4 as 0.40, 0.47 and 0.55 M keeping the concentration of SeO_2 constant at 0.5 mM and duty cycle 30% were recorded. The Bragg peak heights for (*h k l*) are found continuously increasing as the concentration of Mo is decreased from 0.55 to 0.40 M of H_2MoO_4. By varying the duty cycle of the pulsed electrodeposited $MoSe_2$ films, the structural study was carried out. The XRD spectra were taken for the pulsed electrodeposited films under optimized conditions (pH 9.3, concentration of H_2MoO_4 and SeO_2 as 0.40 M and 0.50 mM, respectively, temperature 30 °C and time of deposition 30 min) for various duty cycles of 10, 20, 30, 40 and 50%. Films deposited with duty cycle 30% show very sharp and intense

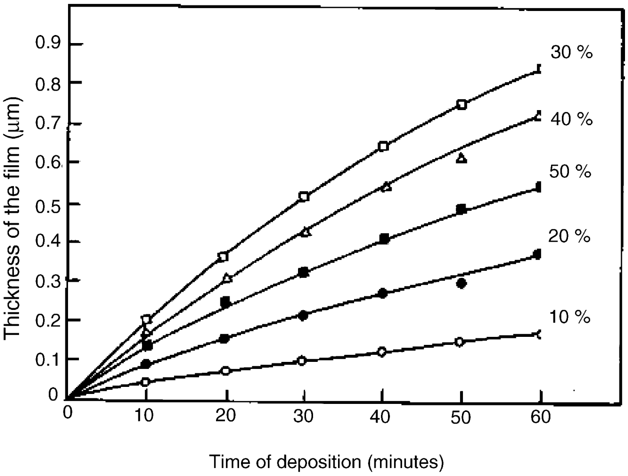

Fig. 2. Growth kinetics of $MoSe_2$ film for different duty cycles.

Table 1
Optimized parameters for the pulsed deposition of $MoSe_2$ film

Parameter	Optimized value
H_2MoO_4 solution concentration (M)	0.40
SeO_2 solution concentration (nM)	0.50
pH	9.3
Bath temperature (°C)	30
Deposition time (min)	30
Current density (mA/cm^2)	2.5
Duty cycle (%)	30

peaks indicating the highly crystalline nature with nearly stoichiometric composition of $MoSe_2$. The observed *d*-values are compared with JCPDS [27] values to determine the crystal structure. The *d*-values obtained are tabulated along with JCPDS data in Table 2. The peak corresponding to $2\theta = 40.1^\circ$ is for titanium substrate. When the concentration of H_2MoO_4 is decreased further, the Bragg peaks corresponding to $MoSe_2$ are reduced and other peaks pertaining to Se are found appearing.

Table 2
Comparison of experimental *d*-values with JCPDS data

2θ degree	*d*-JCPDS	*d*-observed	*h k l*
35.35	2.605	2.5371	1 0 2
38.46	2.373	2.3388	1 0 3
41.09	2.153	2.1949	0 0 6
53.07	1.717	1.7243	1 0 6
59.24	1.591	1.5584	1 1 2
70.76	1.351	1.3303	2 0 3

The sharp peaks reveal the polycrystalline nature of the as deposited $MoSe_2$ films. The structural features fit into hexagonal one with lattice parameter values of $a = b = 0.329$ nm and $c = 1.212$ nm. These values are in good agreement with the standard values of $a = b = 0.3285$ nm and $c = 1.294$ nm [24]. This shows that the $MoSe_2$ film is of single-phase nature obtained in the pulsed electrodeposition technique. The crystallite size was calculated from the full-width at half-maximum (FWHM) measurement for the prominent X-ray diffraction peaks, and the values are in the range of 8–15 nm. Annealing of the 30% duty cycle films was done in vacuum at four different temperatures 100, 150, 200 and 250 °C for 60 min. The XRD patterns for the as prepared $MoSe_2$ film and the annealed films obtained are shown in Fig. 3a–e, respectively. Annealing at 150 °C shows sharp intense peaks, which reveals that the films annealed at this temperature are more suitable for device fabrication. A significant increase in the XRD peak intensities is observed for the $MoSe_2$ films at 250 °C when compared to the peaks at 100 °C. This reveals that the as deposited films were well crystallized and heating in vacuum produces more realignment in orientation leading to improved crystallinity. But while heating at and above 250 °C the films start peeling off from the substrates. From these XRD diffractograms, it can be observed that the films are in the stoichiometric ($MoSe_2$) and single phase.

The EDAX was recorded in the binding energy region of 0–30 keV for the film deposited on titanium substrate and is shown in Fig. 4. The spectrum peak reveals the presence of Mo and Se at 1.6 and 2.3 keV, respectively, which confirms the presence of Mo and Se in the film. The ratio of the weight percentage of Se and Mo is 2, which is the required stoichiometric ratio of single-phase molybdenum diselenide films pulse plated at the optimized deposition condition as given in Table 1.

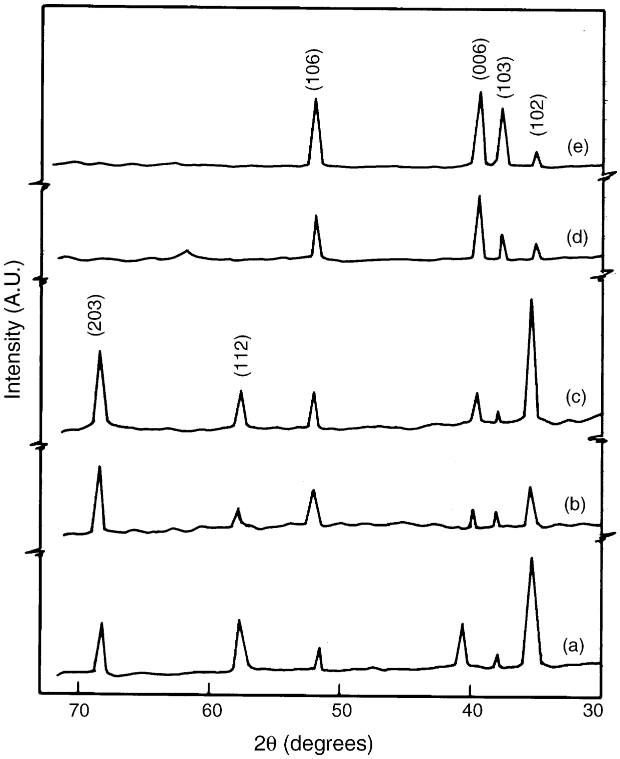

Fig. 3. XRD pattern of $MoSe_2$ (a) as deposited (b) annealed at 100 °C, (c) 150 °C, (d) 200 °C and (e) 250 °C.

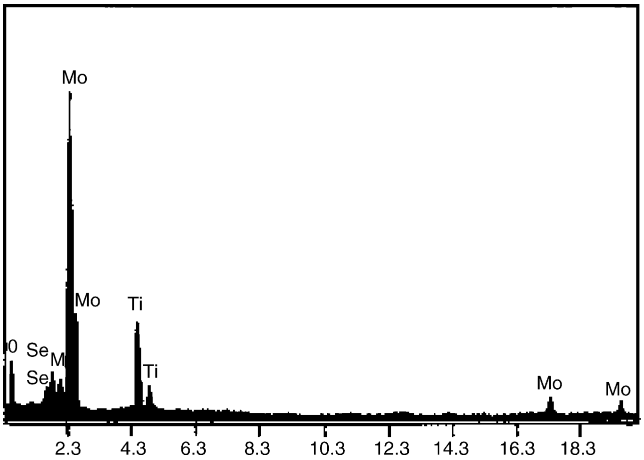

Fig. 4. EDAX spectrum of $MoSe_2$ film.

The SEM micrograph shows well adherent, smooth and uniform film surface without cracks and pinholes. Fig. 5a shows the surface morphology of the $MoSe_2$ thin film prepared under optimized conditions, which exhibits spherical grains of uniform size of about 0.23 μm spread all over the surface. SEM photograph of vacuum annealed sample prepared as above is shown in Fig. 5b. It also shows a smooth surface with grains spread over the surface after coalescence.

3.4. Optical studies

For optical absorption studies $MoSe_2$ deposited on CTO glass plates were used. The optical band gap of $MoSe_2$ films of 0.7 μm thick was estimated from the absorption spectrum taken in the wavelength range of 400–1100 nm, which is shown in Fig. 6. The optical band gap of the $MoSe_2$ films was determined by plotting the relevant portion of the data as $(\alpha h\nu)^{1/2}$ versus $h\nu$ where the absorption coefficient 'α' was determined from $I = I_0 \exp(-\alpha t)$ by substituting t which is the measured film thickness. A graph (insert of Fig. 6) was drawn by taking $(\alpha h\nu)^{1/2}$ along the Y-axis and $h\nu$ in eV along the X-axis. The graph obtained looks like a part of a parabola. The linear portion is extrapolated and it cuts the X-axis at 1.16 eV, which corresponds to the band gap of $MoSe_2$ film. It is in close agreement with the earlier reported value of 1.14 eV for the electrodeposited film [25].

3.5. Electrical properties

Using two-point probe technique the electrical resistivity of the film was studied by varying the temperature of the film from 303 to 623 K, while doing so the resistivity was found decreasing from 4.5×10^4 to $0.1 \times 10^4\ \Omega$ cm. The temperature dependence of the electrical resistivity when the temperature is varied from 303 to 623 K is shown in Fig. 7. By plotting $\ln(\sigma)$ versus $(1/T)$, the activation energy was calculated using the relation:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right)$$

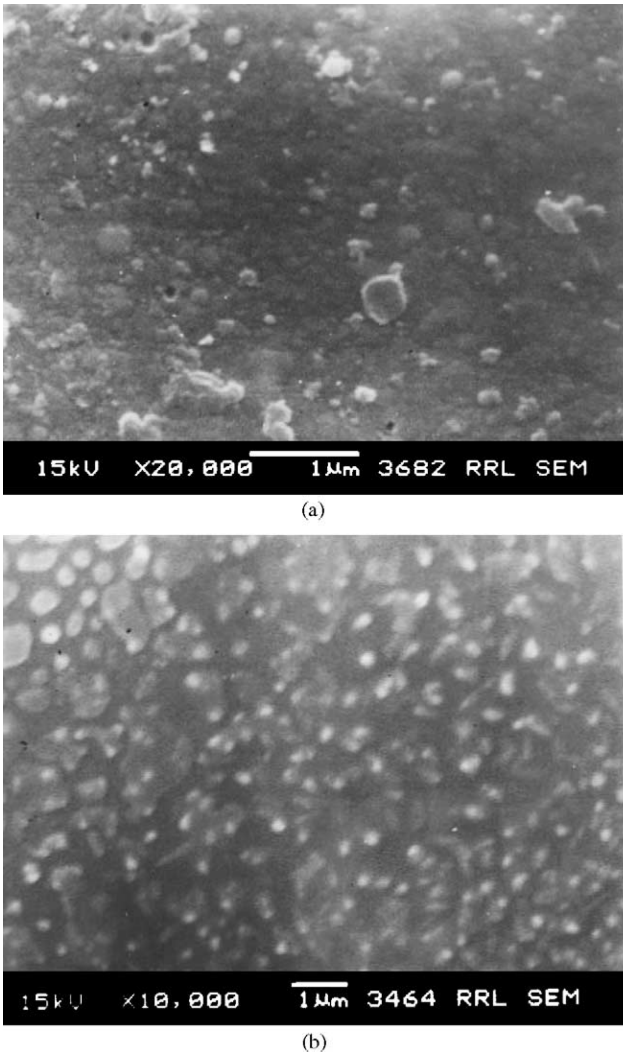

Fig. 5. SEM photograph of $MoSe_2$ film (a) as deposited and (b) annealed at 150 °C.

The electrical conductivity variation with temperature was studied for films deposited at different duty cycles. The calculated activation energies (E_a) are in fair agreement with the earlier reported value of 0.57 eV calculated in the temperature range 500–550 K [28,29]. From the plot of the $\ln(\sigma T^{-1})$ versus $1/T$, the trapped energy state (e_τ) was calculated using the relation:

$$\sigma \propto T \exp \frac{-(E_g/2 + e_\tau)}{kT}, \quad \text{if } N^* > N$$

By taking $\ln(\sigma T^{1/2})$ versus $1/T$, the barrier height φ_B was calculated using the following relation:

$$\sigma \propto T^{-1/2} \exp\left(-\frac{\varphi_B}{kT}\right), \quad \text{if } N^* < N$$

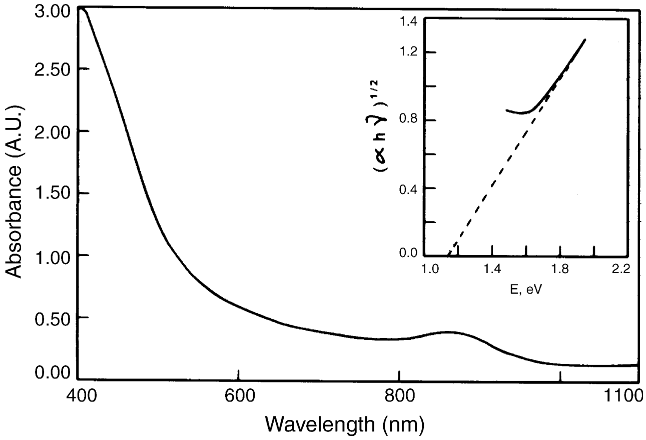

Fig. 6. UV–vis–NIR absorption spectrum of $MoSe_2$ thin film (insert shows the plot of $(\alpha h\nu)^{1/2}$ vs. $h\nu$ plot).

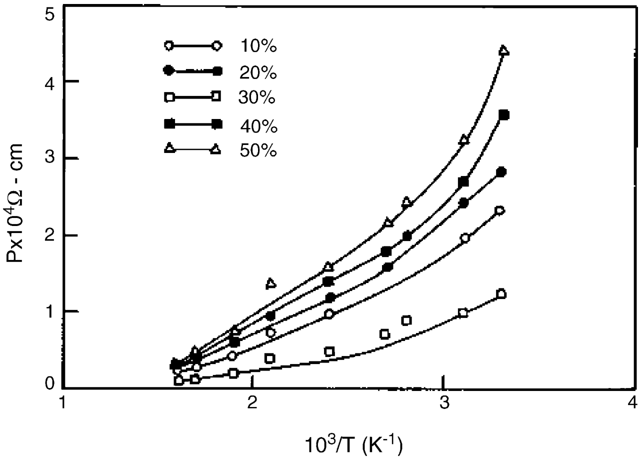

Fig. 7. Plot of ρ vs. $1/T$ plot.

Table 3

Electrical parameters of $MoSe_2$ for different duty cycles

Duty cycle (%)	Activation energy, E_a (eV)	Trapped energy state, e_τ (eV)	Barrier height, φ_B (eV)
10	0.86	0.365	0.123
20	0.71	0.201	0.130
30	0.86	0.365	0.162
40	0.71	0.201	0.110
50	0.71	0.201	0.110
10	0.86	0.365	0.123

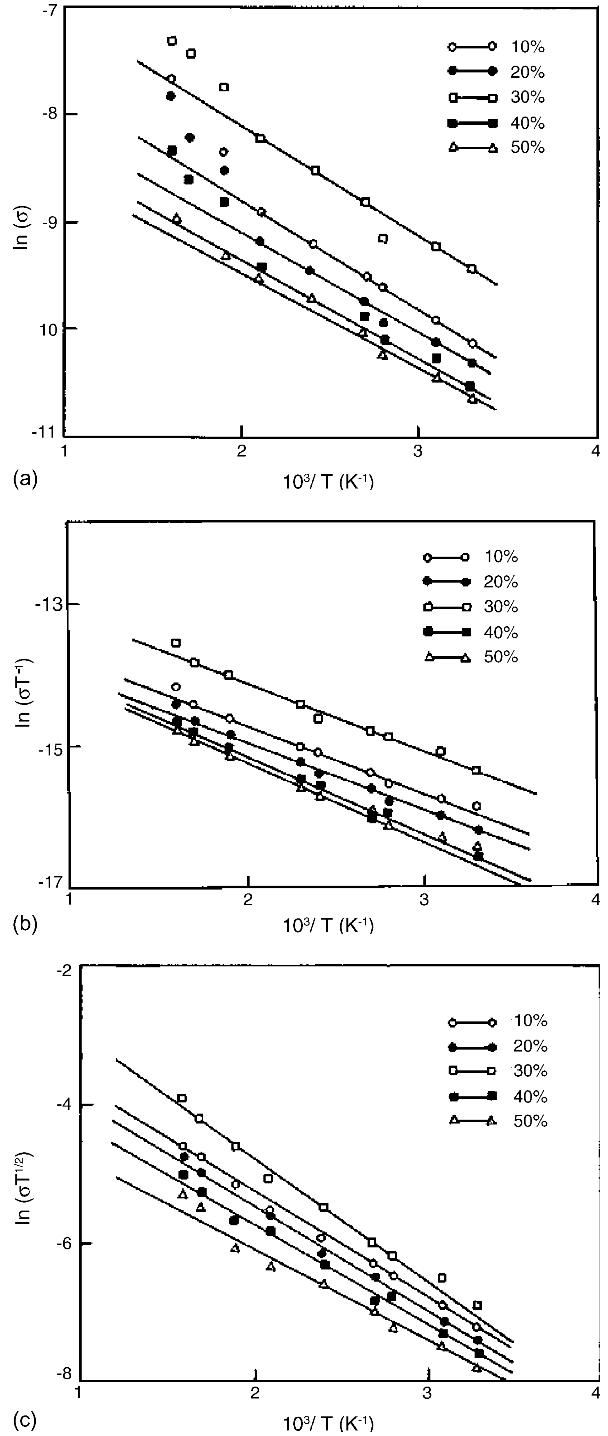

Fig. 8. Plot of: (a) ln σ vs. $1/T$, (b) $\ln(\sigma T^{-1})$ vs. $1/T$, (c) $\ln(\sigma T^{1/2})$ vs. $1/T$.

where N being the acceptor concentration and N^* exists for which the grains are only partially depleted ($2W < d$, d being the grain size); W is the width of the depletion region, k the Boltzmann constant and T is the absolute temperature in Kelvin unit.

The E_a, e_τ and φ_B values are given in Table 3. All the corresponding plots are shown in Fig. 8a–c. The barrier height values calculated for the pulsed electrodeposited $MoSe_2$ films are in close agreement with the earlier reported values range of 0.167–0.185 eV observed at 780 K [4].

4. Conclusions

Polycrystalline $MoSe_2$ thin films are prepared by pulsed electrodeposition technique on conducting glass and on titanium substrates. Films prepared using the optimized deposition parameters show preferential orientation along (1 0 2). Annealing treatment of the film in vacuum shows an improvement in the polycrystalline nature of the film with a smoothened surface. These $MoSe_2$ films are in single phase. EDAX results confirm the presence of Mo and Se in 1:2 ratio, which shows the stoichiometric nature composition of the films deposited at the optimized condition. The SEM micrographs show the device quality nature of the surface without any pinholes. From optical studies, the indirect band gap value was found as 1.16 eV, which is comparable with the reported value. From electrical conductivity measurements, the electrical constants like the activation energy, trapped energy state and barrier height were calculated and the values are tabulated in Table 3. It reveals that the pulsed electrodeposited $MoSe_2$ films, prepared under the optimized conditions, show semiconductor nature and can be effectively used for the fabrication of efficient PEC solar cells.

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