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Preparation of layered semiconductor (MoSe_2) by electrosynthesis

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Abstract

Molybdenum dichalcogenides are semiconductors, which can act as efficient electrodes in the realization of photo-electrochemical solar cells. Among molybdenum dichalcogenides (MoS_2 , MoSe_2 and MoTe_2), MoSe_2 has led to the best solid state cells with efficiencies exceeding 6%. The main advantage of these MoSe_2 semiconductor is the prevention of electrolyte corrosion, because of the phototransitions involving non-bonding d–d orbital of the Mo atoms. MoSe_2 thin films have been electrodeposited cathodically on tin oxide (SnO_2)-coated conducting glass substrates from an ammoniacal solution of H_2MoO_4 and SeO_2 under potentiostatic condition. The electrode potential was fixed at $-0.9 V_{\text{SCE}}$ and the pH was maintained at 9.3 ± 0.1 . The bath temperature was maintained at 40°C . X-ray diffraction analysis showed the presence of highly textured MoSe_2 films with polycrystalline nature. The optical absorption spectra show that the material has an indirect band-gap value of 1.17 eV. Atomic force microscope (AFM) study was used to find the surface roughness of the film and surface morphology studies by scanning electron microscope (SEM) show that the films are smooth, uniform and pin-hole-free useful for device fabrication. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

Recent investigations have shown that the layer-type semiconducting group VI transition metal dichalcogenides (MoS_2 , MoSe_2 and WSe_2), which absorb visible and near-IR light, are particularly interesting materials for photoelectrochemistry solar energy conversion. The most efficient system up to now turned out to be MoSe_2 [1]. Recent applications include intercalation compounds and long-life photoelectrochemical (PEC) solar cells. Some studies on PEC with MoSe_2 have been

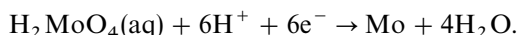
carried out on single crystals. However, polycrystalline electrodes are economically desirable for solar cell applications, where large-area substrates are necessary. Hence, this study has been directed towards obtaining molybdenum diselenide in thin-film form. The usual thin film preparation techniques, such as sputtering, thermal evaporation, etc., are cost intensive and sometimes present special problems for the preparation of transition metal chalcogenide films [2]. The present paper reports a simple electrodeposition technique for depositing molybdenum diselenide film cathodically on a conducting tin oxide-coated glass substrate.

Theoretically, it is possible to deposit Mo from aqueous solution according to the following

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reaction:



But experimentally it is not as easy as described in theory. The free energy of formation of the anion MoO_4^{2-} is $-218.8 \text{ kcal mol}^{-1}$ which indicates its high thermodynamic stability. In general, metals cannot be deposited from aqueous solutions if their electrode potentials are more negative than the hydrogen discharge potential, as in the case for molybdenum. The molybdate ion is stabilized by its inner orbital hybridization in which the 4d orbitals are hybridized with 5s and p orbitals. The energy required for breaking such hybridization exceeds the energy necessary for the cathodic discharge of hydrogen. Therefore, it has not been possible to deposit pure molybdenum by electrolysis of an aqueous solution. However, many workers have succeeded in codepositing Mo together with iron group metals [3–12]. The electrodeposition of Mo in the presence of other metal ions is also referred to as induced codeposition. The concept of “induced codeposition” was the guiding principle to determine whether Mo can be codeposited with Se. The present work clearly shows that the presence of selenium leads to an induced codeposition of molybdenum leading to MoSe_2 formation.

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 selenides in the fabrication of a photoelectrochemical solar cell, in which the charge transfer reaction at the semiconductor — electrolyte interface is responsible for the generation of photocurrent/photovoltage [13]. The characterization of films was carried out in detail using X-ray diffraction analysis, optical studies, SEM and AFM studies.

2. Experimental details

2.1. Electrodeposition of molybdenum diselenide films

The cyclic voltammetry (CV) experiments were prepared using an electrochemical analyzer (EG

& G Versostat II Model 270) which was useful for fixing deposition potentials. A three-electrode system was adopted to deposit MoSe_2 thin films. Typically, a 50 ml glass beaker was used to contain the solution. Magnetic stirrer cum heater set-up was used to deposit the films by stirring the bath as well as raising the temperature. A saturated calomel electrode was immersed into the bath very near to the cathode. This 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).

The electrolysis cell consisted of a tin oxide-coated glass substrate on which MoSe_2 is to be deposited which acts as the cathode and the graphite electrode as the counter electrode/anode. An ammoniacal solution consisting of a mixture of $\text{H}_2\text{MoO}_4 + \text{SeO}_2$ was used as electrolyte. The electrolyte was prepared by mixing an ammoniacal solution of molybdic acid whose pH is 10.3. The pH of SeO_2 dissolved in water is 6.1. The final pH of the mixture ($\text{H}_2\text{MoO}_4 + \text{NH}_3 + \text{SeO}_2 + \text{H}_2\text{O}$) was 9.3. The deposition of films was carried out at a temperature of 40°C for different intervals of time (8, 10 and 12 min) and different electrolyte ($\text{H}_2\text{MoO}_4 + \text{SeO}_2$) concentrations. The film thickness varies between 0.8 to $1.2 \mu\text{m}$. To prepare electrolyte solutions having relative concentrations of SeO_2 and H_2MoO_4 , the following two basic solutions were first prepared: solution A containing 8.52 g of H_2MoO_4 in 100 ml of 1.47 N ammoniacal solution (9.42 ml) and solution B containing 12 mg of SeO_2 in 100 ml of water. Different volumes of these two basic solutions were mixed to give different electrolysis solutions.

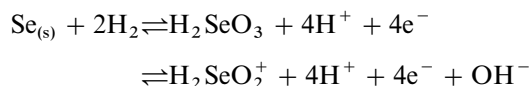
X-ray diffraction studies were carried out using RIGAKU (USA) VERSION 2.5 X-ray diffractometer with CuK_α radiation to study the structural characteristics of the films. Optical absorption spectra were recorded from 300 to 1500 nm at

300 K using a Cary – 14 Spectrophotometer. Surface morphology of the film was carried out using JEOL JSM 840A scanning electron microscope (SEM) and atomic force microscope (AFM) studies were carried out using Nanoscope® E Scanning Probe Microscopy 3138 J to find the surface roughness.

3. Results and discussions

3.1. Electrochemistry of molybdenum diselenide films

The electrode potentials as Se and Mo using their electrode reactions can be as [14]



Electrode potential (V)

$$= 0.50(E^\circ) + \frac{RT}{4F} \ln \left(\frac{a_{\text{HSeO}_2^+}}{a_{\text{Se}}} \right) + \frac{3RT}{4F} \ln C_{\text{H}^+}$$

$$= 0.50 + 0.0148 \ln \left(\frac{a_{\text{HSeO}_2^+}}{a_{\text{Se}}} \right) - 0.0443 pH$$



Electrode potential (V)

$$= -1.29 + \frac{RT}{6F} \ln \left(\frac{a_{\text{MoO}_4^{2-}}}{a_{\text{Mo}}} \right).$$

All the potentials are expressed with reference to the saturated calomel electrode (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 ions. The symbols $\text{Mo}_{(s)}$, $\text{Se}_{(s)}$ 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 selenium is far more positive than that for molybdenum deposition. Further, to obtain simultaneous deposition of Mo and Se, the electrolyte concentration should be adjusted so as to bring the electrode potentials of both the deposits closer. It is desirable 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, approaching the Se deposition potential. The deposition of Se will be diffusion controlled due to a very low concentration of SeO_2 (and consequently of the HSeO_2^+). Based on these electrode reactions, a higher concentration of 0.5 M of Mo and very low concentration of 1.0 mM of Se have been taken in the bath for the deposition of MoSe_2 film.

3.2. X-ray diffraction studies

X-ray diffraction pattern of the electrodeposited MoSe_2 films is shown in Fig. 1. The observed 'd' values are compared with ASTM standard values to determine the crystal structure. The sharp peaks reveal the polycrystalline nature of the as-deposited MoSe_2 films. The structural features fit into the hexagonal structure of the films with lattice parameter values $a = b = 0.3291$ nm and $c = 1.2917$ nm. These values are in very good agreement with the standard values of $a = b = 0.3285$ nm and $c = 1.292$ nm. The crystallite size was calculated from the measurement of full-width at half-maximum (FWHM) in different X-ray peaks, values are in the range of 75–90 nm. All the peaks show nearly the same intensity values confirming the random orientation of the planes in the film. Annealing of the films was done in air at different temperatures from 100 to 250°C. There is a small increase in the peak intensities of the MoSe_2 films when heated up to about 200°C. This

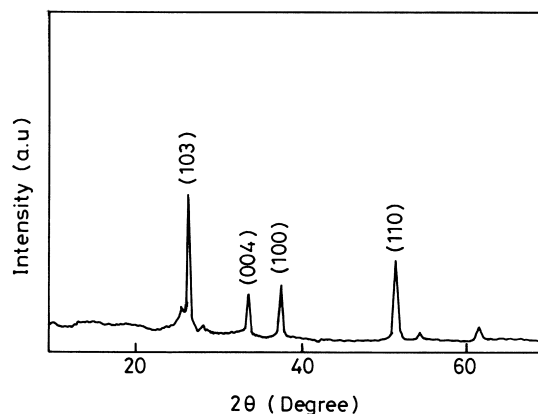


Fig. 1. XRD pattern of the MoSe_2 thin film.

reveals that the as-deposited films are well crystallized and heating in air produces a slight realignment in orientation. On heating above 200°C the films are peeled off from the substrate.

3.3. Optical studies

The transition metal chalcogenides are usually indirect band-gap semiconductors. The present study reports optical absorption measurements near the fundamental edge, with the object of estimating the band gap of electrolytically obtained MoSe₂ films. For optical absorption studies, the films were deposited on transparent tin oxide-coated conducting glass substrates. Optical absorption spectrum was taken for MoSe₂ thin film using an identical tin oxide-coated glass plate as reference and the values of optical absorption coefficient (α) were not corrected for the reflectance from the film surface.

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. 2. The intersection point gives the indirect band gap of the material and was found to be 1.17 eV. It is in good agreement with the reported value of 1.14 eV for the electrodeposited film [13].

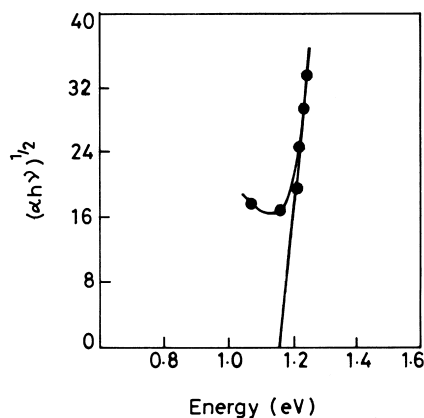


Fig. 2. Plots of $(\alpha h\nu)^{1/2}$ with photo energy for MoSe₂ thin film.



Fig. 3. SEM photograph of electrodeposited MoSe₂ thin film.

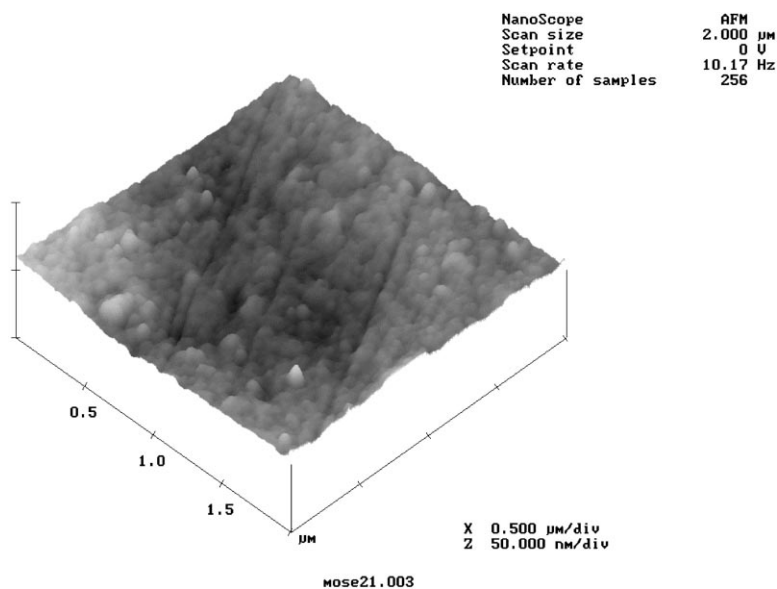


Fig. 4. Atomic force micrograph of MoSe₂ film.

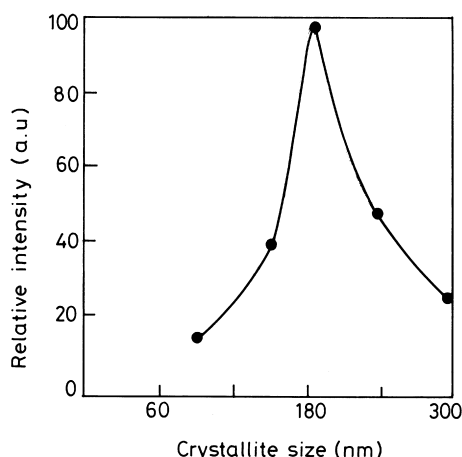


Fig. 5. Distribution of crystallites.

3.4. SEM and AFM studies

The surface morphology of the as-deposited films was studied using scanning electron microscope analysis. The surface is uniform with individual and interconnected grains as shown in Fig. 3. The scanned area is $25\ \mu\text{m} \times 20\ \mu\text{m}$ which shows closely packed grains that are uniformly spread over the substrate without any pinholes. The grain size varies in the range of 200–300 nm. The micrograph of the surface obtained by AFM shows the good adhesion of the films to the substrate. It shows that the films are uniform and pin-hole-free as seen from Fig. 4 which is the two-dimensional presentation of the MoSe_2 film surface. The grain size is found to be in the range of 75–300 nm as shown in Fig. 5. This is in good agreement with the grain size values observed from the SEM studies.

4. Conclusions

Using electrodeposition technique MoSe_2 films were successfully deposited on tin oxide-coated conducting glass substrates. SEM photograph shows that the films are uniform and pin-hole-free. Stoichiometric films were deposited at an opti-

mized deposition potential of $-0.9\ V_{\text{SCE}}$ keeping the bath pH at 9.3 ± 0.1 and temperature at $40^\circ\text{C} \pm 1^\circ\text{C}$. XRD pattern shows that the films are polycrystalline in nature and possess hexagonal structure. X-ray diffraction studies show the crystalline nature of the as-deposited films. The indirect band-gap value of 1.17 eV confirms the formation of stoichiometric MoSe_2 films. The surface morphology by SEM study confirms the uniform surface of the electrodeposited films rendering them useful for photoelectrochemical device fabrication and surface roughness of the film is found from AFM.

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