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Electrosynthesis and characterisation of n-WSe_2 thin films

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Abstract

Tungsten diselenide (WSe_2) semiconductor thin films were electrodeposited by the galvanostatic route. Polycrystalline n-WSe_2 thin films were deposited on transparent conducting oxide (TCO) coated glass substrates. The variation of growth rate with temperature has been studied. Both the as-deposited and annealed films showed hexagonal structure. The optical absorption studies showed a direct band gap nature of the WSe_2 films. The composition of the film was found by EDAX analysis. The surface morphology of the films were studied by scanning electron microscopy. The type of the semiconductor was found from the Mott–Schottky plot as n-type and confirmed by hot probe technique. The semiconductor parameters like acceptor density and flatband potential were reported from the study of Mott–Schottky plots.

Keywords: WSe_2 thin films electrodeposition; Structural; Mott–Schottky; Characterisation

1. Introduction

Tungsten diselenide (WSe_2) is a promising semiconducting material with its application in many photoelectronic devices [1]. WSe_2 posses a layered structure with the metal (W) atoms bonded covalently between the layers of chalcogen atoms (Se). The chalcogen layers are bonded by weak Van der Waals forces resulting Se–W–Se layers. This arrangement exhibits the anisotrophy of the material. Two types of WSe_2 single crystals are reported as type-I with the *c*-axis of the crystal parallel to the substrate and type-II with *c*-axis perpendicular to the substrate [2,3]. The salient feature of the WSe_2 is highly antiphotocorrosive due to the observation of d–d transition in the crystal lattice, which make it as a strong candidate in the development of high efficiency photoelectrochemical (PEC) solar cells [4]. The band gap is nearer to the optimum value (1.6 eV) required for high efficiency PEC solar cell [5]. Both direct and indirect transitions were reported [6]. A PEC efficiency of 17.1% has been reported by Prasad and Srivastava [7] using n-WSe_2 single crystal. Preparation of this material by the following techniques like selenisation of WO_3, on quartz and metal coated quartz substrates [8], Van der Waals rheotaxy (VdWR) method on Ni_3Se_2 substrate [9], chemical vapour deposition on tungsten foils and then annealing [3] were reported in the literature. But only one report is available [10], which gives a brief account of the electrodeposition mechanism of WSe_2 thin films on titanium substrates. In the present study, the deposition of WSe_2 films on tin oxide coated conducting and transparent substrates have been systematically carried out and the materials properties are presented.

2. Experimental

A stock solution of tungstic acid of 0.25 M was prepared by dissolving H_2WO_4 (AR grade) in an alkaline medium and SeO_2 of 1.8 mM was prepared separately by dissolving SeO_2 (AR grade) in triple distilled water mixed in a ratio of 1:10 by volume and the pH was fixed as 9.0. The transparent conducting oxide (TCO) substrate of about 5 $\Omega\,\square^{-1}$ sheet resistance, cleaned ultrasonically with triple distilled water, was used as cathode on which the films were deposited. The platinum electrode was the counter electrode and a saturated calomel electrode (SCE) was used as the reference electrode. The linear polarisation studies were carried out using EG&G PARC 362 potentiostat. Deposition of the films were carried out for 60 min at a current density of 10 mA cm^{-2} maintaining the bath temperature constant at 70 °C. The growth rate of the WSe_2 films was studied by the gravimetric method, by depositing the films at different temperatures ranging from 50 to 80 °C and at different current densities varying from

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5 to 20 mA cm^{-2}. The films deposited on TCO substrate were annealed at 300 °C in vacuum for 1 h. The structural X-ray analysis was carried out using Philips Xpert instrument for both the as-deposited and the annealed films. The composition of the films were analysed using Philips EDX spectrometer (XL30 ESEM TMP). The optical absorption spectrum for the electrodeposited WSe_2 films were recorded from 400 to 1000 nm using a SHIMADZU UV2410 S spectrophotometer and the band gap was calculated from the absorption curves. The capacitance–voltage measurements were carried out with Vasavi VCLR7 meter at a fixed frequency of 1 kHz using a three electrode cell with 0.2 M, Na_2SO_4 electrolyte. The surfaces of the films were scanned with JEOL JSM 6400 scanning electron microscope.

3. Results and discussion

3.1. Linear polarisation studies

The current–voltage, linear polarisation studies were carried out for W, Se and the binary W–Se systems at room temperature and at 70 °C. Fig. 1, shows the linear polarisation curves on TCO substrate. It is obvious that Se deposits initially and faster than W as the standard deposition potential of Se starts from +0.5 V_{SCE} [10]. Since W is a non reducible metal and Se is highly noble, higher and lower concentration of W and Se were taken in the bath. From Fig. 1, the onset potential for W starts at −1.4 V_{SCE}, and that of Se starts from −0.5 V_{SCE}. At higher voltage beyond −1.5 V_{SCE} hydrogen evolution occurs. When both W–Se are present the polarisation curve is observed in between the polarisation curves observed for the deposition of W and Se. Here the higher negative potential observed for Se deposition is due to the fact that the cathode electrode surface becomes highly resistive with the initially deposited Se layer. When the deposition of W and Se are considered simultaneously, the over potential required for the co-deposition internal resistance (IR) is developed by the initially deposited resistive Se film. This observation shows that the competitive deposition mechanism associated with the reduction of Se and tungsten acquires an extra potential due to which the co-deposition is observed without H_2 evolution in the potential range of −1.2 to −1.4 V_{SCE}, this reaction is accompanied with a current density of 5–20 mA cm^{-2}.

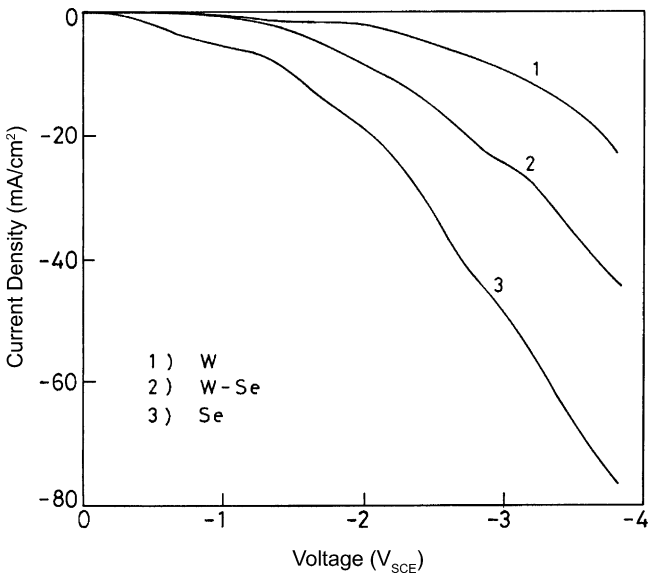

Fig. 1. Linear polarisation curves for W, Se, W–Se systems at 70 °C.

Deposition on TCO substrates were carried out cathodically at 5, 10 and 20 mA cm^{-2}. At low current densities (<5 mA cm^{-2}) the thickness built at the substrate was moderate and at high current density above 20 mA cm^{-2} gas evolution occurred and the film peeled off from the substrate. Well adherent bluish grey films were deposited at a current density of 10 mA cm^{-2}. The temperature of the bath plays an important role in the deposition of WSe_2 films. The films deposited at 70 °C showed maximum thickness of 0.8 μm (Fig. 2) due to the large free energy associated with it as in

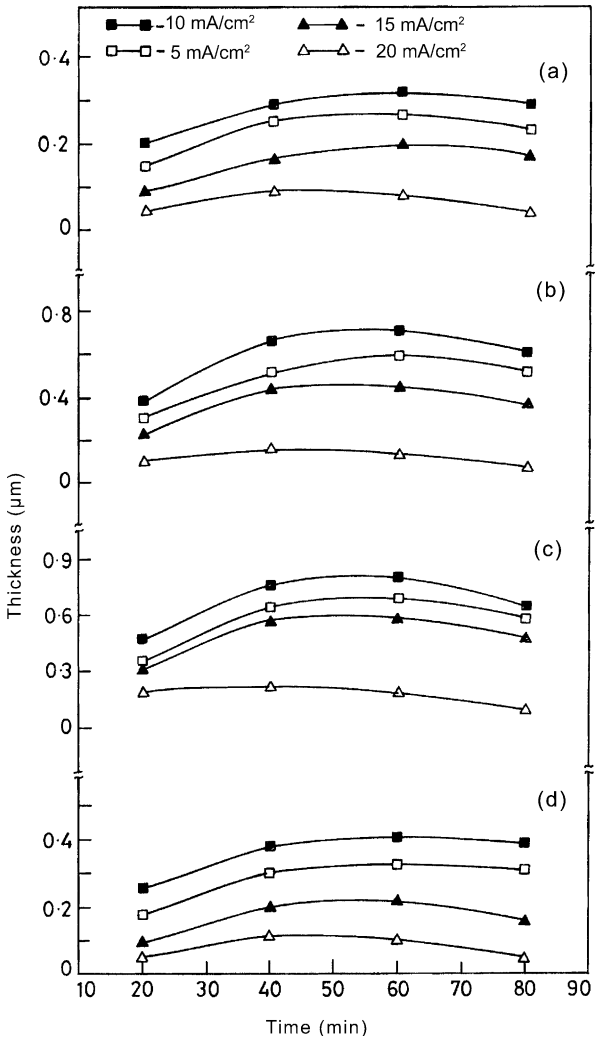

Fig. 2. Growth of WSe_2 thin films at: (a) 50 °C; (b) 60 °C; (c) 70 °C; (d) 80 °C.

the case of electrodeposition of WS_2 thin films [11]. When the temperature of the bath is raised above 70 °C the film growth reduces and very thin films were formed.

3.2. Structural studies

Fig. 3 shows the X-ray diffraction pattern of the as-deposited WSe_2 thin films on TCO substrate and annealed at 300 °C in vacuum. The sharp XRD peaks reveal that the films are polycrystalline. The preferential orientation is along (0 0 4) plane revealing that its *c*-axis is perpendicular to the substrate, revealing texture II type of the deposited WSe_2 films unlike the thin films prepared by Tenne et al. [2] in (0 0 2) plane. The XRD pattern also showed (1 0 0), (1 0 1), (1 0 3) and (2 0 0) Bragg reflections in addition to the peaks that observed for the highly textured films reported by Salitra et al. [8]. The Se peaks at $2\theta = 45.1$ and 52.3° are also observed in the as-deposited film. The annealed films show increased intensities for the (0 0 4), (1 0 2) and (1 0 3) reflections and reduction in the intensities of (1 0 0) and (1 0 1) peaks due to recrystallisation. In all the X-ray patterns the reflections due to TCO substrate also observed due to the small thickness of the film. The observed peaks coincide well with the JCPDF data (38–1388). The lattice parameters are calculated as $a = b = 3.359$ and $c = 12.592$ Å which is well in agreement with the reported values [12]. The crystallite size has been calculated using the Scherrer formula

$$t = \frac{0.97\lambda}{2\beta} \quad (1)$$

where t is the crystallite size, λ the wavelength of the X-rays used and β the full width at half maximum of the Bragg's peak, which ranges about 0.02 μm and increased

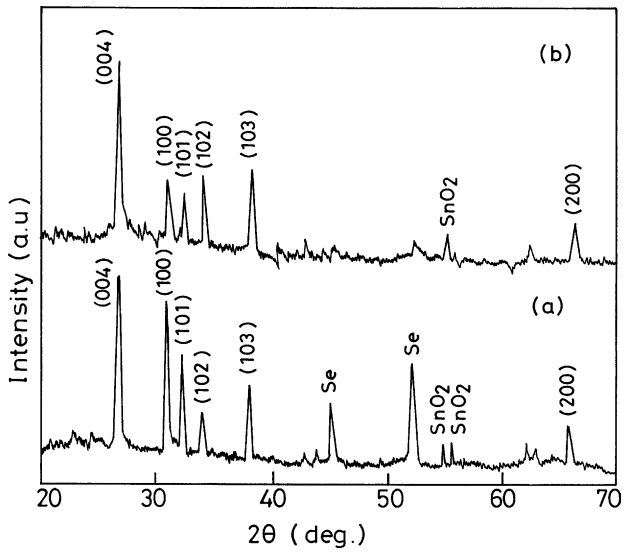

Fig. 3. XRD pattern of WSe_2 thin films at optimised condition: (a) as-deposited; (b) annealed at 300 °C for 1 h.

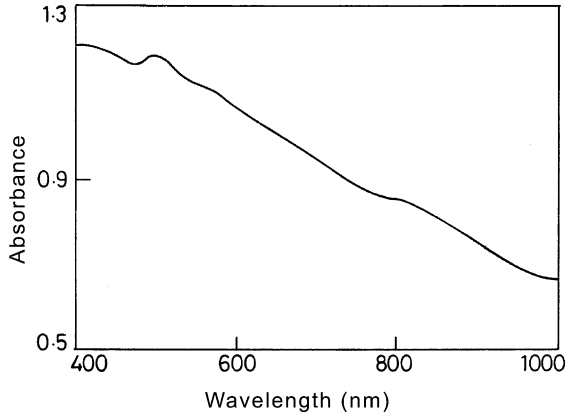

Fig. 4. Absorption spectrum of WSe_2 thin film.

to about 0.15 μm on annealing at 300 °C in vacuum. The composition of the WSe_2 film deposited at optimised condition is recorded in the binding energy range from 0.0 to 9.0 keV. The intense peak at 8.39 and 1.41 keV confirms the elemental presence of W and Se and the ratio of weight percentage of W and Se found to be nearly two.

3.3. Optical studies

The band gap of the film is determined from the classical theory of interband absorption for semiconductors using the relation

$$\alpha = A(E - E_g)^n \quad (2)$$

where α is the absorption coefficient, A is a constant, E the photon energy and E_g the band gap. The value of n is 2 for indirect transition and 1/2 for direct transition. The absorption edge of the film is observed in the range of 600–800 nm from the optical absorption spectrum shown in Fig. 4. The band gap is calculated from extrapolating the linear portion to the energy axis. The allowed direct band gap is calculated as 1.46 eV (Fig. 5), which is in well agreement with the reported values [13].

3.4. Capacitance–voltage studies

The capacitance–voltage measurements were taken in an aqueous Na_2SO_4 (0.2 M) solution and the Mott–Schottky plots were drawn from which the flatband potential is found to be $-0.46\ V_{SCE}$ (Fig. 6). The flat band potential is found from the following relation [14]

$$\frac{1}{C_{SC}^2} = \frac{2(V - V_{fb} - k_B T/e)}{\varepsilon_o \varepsilon_s N_A e} \quad (3)$$

where ε_o is the permittivity of free space, ε_s the permittivity of the electrode, e the charge of the carriers, N_A the acceptor concentration, T the temperature of the electrolyte, k_B the Boltzmann's constant and C_{SC} the space charge

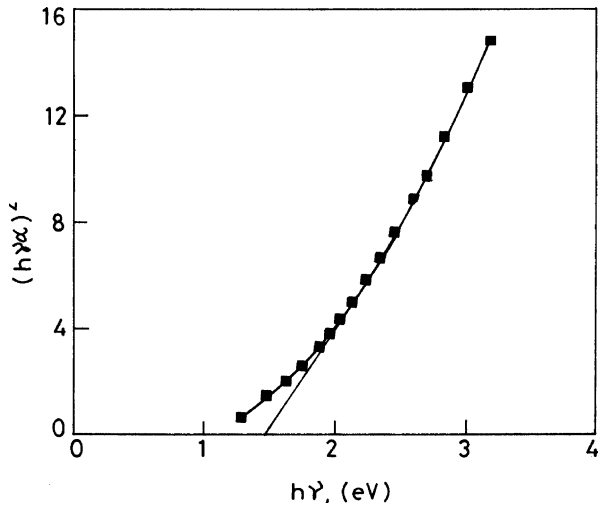

Fig. 5. Photon energy ($h\nu$) vs. $(\alpha h\nu)^2$ curve for WSe_2 thin film.

capacitance. This is in good agreement with the reported value of Cabrera and Abruna [15] and with 1 N $Ce^{4+/3+}$ in 0.1 N H_2SO_4 redox couple [16]. The conductivity type of the deposited WSe_2 films determined as n-type from the slope of the Mott–Schottky plot which is also confirmed by the hot probe method. The donor density is found as $4.25371 \times 10^{19}\,cm^{-3}$, which is slightly higher than the values reported by Cabrera and Abruna [15], which may be due to the impurities in the donor level.

The scanning electron micrographs of the film is shown in Fig. 7(a). The films are found to be pinhole free and no cracks are found on the surface of the film. The film deposited on the TCO substrate shows a granular growth. Annealing the film increases the grain size, as shown in Fig. 7(b).

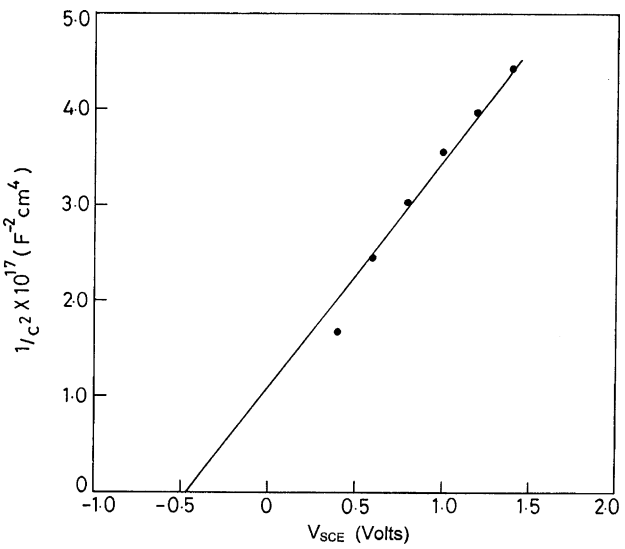

Fig. 6. Capacitance–voltage (V_{SCE}) plot for WSe_2 thin film in 0.2 M, Na_2SO_4 electrolyte.

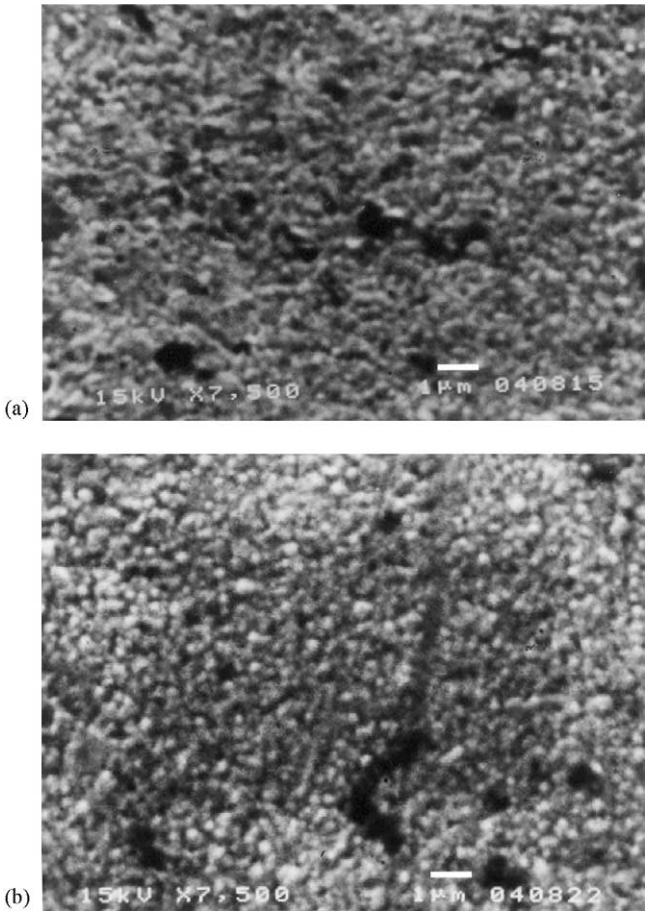

Fig. 7. Scanning electron micrographs of WSe_2 thin films: (a) as prepared film; (b) film annealed at 300 °C for 1 h.

4. Conclusion

WSe_2 films are galvanostatically deposited on TCO substrates. Well adherent pinhole free films with bluish grey in colour are deposited with $10\,mA\,cm^{-2}$, keeping the bath temperature constant at 70 °C. The films showed preferential orientation along (0 0 4) plane which is the desired orientation for obtaining high PEC efficiency. It can be concluded that under the optimised deposition conditions, n-type semiconducting WSe_2 films are deposited with the required materials properties useful for developing PEC devices.

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