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Electrodeposition of p-WS_2 thin film and characterisation

J. Jebaraj Devadasan[a,c], C. Sanjeeviraja[a,*], M. Jayachandran[b]

[a] *Department of Physics, Alagappa University, Karaikudi-630 003, India*
[b] *Electrochemical Materials Science Division, Central Electrochemical Research Institute, Karaikudi-630 006, India*
[c] *Pope's College, Sawyerpuram-628251, India*

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Abstract

Polycrystalline tungsten disulfide (WS_2) thin films are electrodeposited on conducting glass plates in galvanostatic route. The deposited films are characterised structurally by taking X-ray diffraction, and the phase is confirmed as 2H-hexagonal and the preferential orientation is along (0 0 4) plane. The electrodeposited films are of type-II with the Van der Waals face parallel to the substrate. The lattice constants are calculated and reported. The band gap of the material is found from the absorption spectrum and the surface morphology is analysed by scanning electron microscope. The nature of the film is found as p-type from the negative slope of the Mott–Schottky plot and the semiconductor parameters like flatband potential and acceptor density are calculated. The photoelectrochemical solar cell behavior of p-WS_2 film is studied and its output characteristics are presented.

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1. Introduction

In the recent years lot of interest has been shown on transition metal dichalcogenide [TMDC] compounds like MX_2 (M = W, Mo; X = S, Se) as these materials show high efficiency when used in solar cells [1]. The layered semiconductors are of interest in solar energy conversion due to the ingenuous arrangement of structural lattice with cations and anions [2]. WS_2 single crystals and thin films have selective properties, like bandgap in the range of 1–2 eV, high optical absorption, the layered type of arrangement between the cations, all of which make this material an important candidate in the photoelectrochemical conversion and photovoltaics [2]. These films are layered type semiconductors in which chalcogenide–metal–chalcogenide layer is formed and each layer is tied by weak Van der Waals force. The strong covalent bond within the layer and weak Van der Waals force between the layers make this material anisotropic [3–5]. Single crystals of TMDC materials are mostly used in solid state devices and photoelec-

*Corresponding author. Fax: +91-4565-425202.
E-mail address: alagappa@md3.vsnl.net.in (C. Sanjeeviraja).

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trochemical (PEC) solar cells. The maximum efficiency of PEC is reported as 17% using n-type WSe_2 single crystals [6]. Two types of WS_2 single crystals, grown with c-axis parallel ($c_{\parallel}$) to the surface (type-I) and c-axis perpendicular ($c_{\perp}$) to the surface (type-II), are reported by Genut et al. [7]. Layered WS_2 thin films have been prepared by MOCVD technique, on quartz, steel, mica substrates [9], sulpurisation of tungsten foils [8], ion beam sputtering of tungsten on different substrates and then heating at high temperature in the presence of H_2S gas [7]. In this report, an attempt is made to electrodeposit p-WS_2 films on conducting tin oxide (CTO) substrates which enables the films to be used directly for PEC device and the characterisation studies are presented.

2. Experimental procedure

Thin films of WS_2 were cathodically deposited on CTO coated glass substrates (sheet resistance of 10 Ω per square) in galvanostatic mode using a PAR EG&G180 potentiostat. The CTO substrate was used as the cathode in a three electrode cell with platinum as the counter electrode and saturated calomal electrode (SCE) as the reference electrode. The deposition bath was a 1 : 1 mixture of tungstic acid (E-merck) of 0.27 M and Na_2SO_3 (E-merck) of 0.36 M aqueous solution. Before deposition, the substrates were thoroughly cleaned with triple distilled water and acetone to degrease the surface. Films were deposited at different current densities ranging from 20 to 60 mA/cm^2, keeping the temperature of the bath at 40°C, 60°C and 80°C, and the bath pH between at 7.0 and 9.5. The deposited films were rinsed in triple distilled water, dried and stored in the vacuum descicator. The variation of thickness of the film with deposition time was found by gravimetric method for different current densities from 20 to 60 mA/cm^2 for different bath temperatures keeping the pH as 9.2. The films were vacuum annealed at 300°C for 60 min in a vacuum of 10^{-3} Torr.

The structural characterisation of the electrodeposited WS_2 films was studied using JEOL JDX 803A X-ray diffractometer instrument with Cu K_α radiation ($\lambda = 1.5418$ Å). The as-deposited and annealed films were analysed and the results are reported. The composition of the film was analysed by taking EDAX spectrum of the sample using Philips EDX spectrometer (XL30 ESEM TMP). The surface morphology of the film was studied by taking scanning electron micrographs with JEOL JSM 6400 after sputtering with a thin gold coating on the surface. The optical absorption spectrum was taken in the range of 300–900 nm using Shimadzu-UV410S spectrophotometer. The capacitance–voltage measurements were carried out with Vasavi VCLR7 meter at fixed frequency of 1 kHz using a three electrode cell with WS_2 as the cathode, platinum as the anode and SCE as the reference electrode and 0.2 M of Na_2SO_4 as the electrolyte.

3. Results and discussion

Uniform bluish gray WS_2 films with well adherence are deposited. The films deposited at a current density of 30 mA/cm^2 and bath temperature, 40°C and keeping the pH = 9.2 are thick and highly opaque to light. At high current densities i.e. above 50 mA/cm^2, the film deposition was poor. Thick films are obtained at a bath temperature of 40°C where as at higher temperatures gas evolution was observed and hence the films are formed with pin holes. As deposition time increases the thickness of the film builds up and reaches the saturation after 40 min, on further deposition thickness builds up very slowly as the resistivity of the already deposited WS_2 film restricts it [10]. The variation of thickness with deposition time keeping the temperatures as constant is shown in Fig. 1. From the growth kinetics plot, the saturation is reached at 25 min for the bath temperature of 80°C. But for the bath temperature of 40°C, the thickness is linearly increased on the substrate upto the period of 40 min and then reaches the saturation region. The same trend is observed for the bath temperature of 60°C with less thickness when compared with other bath temperatures. If the bath temperature is decreased below 40°C, the thickness is not appreciably built up on the substrate which is not shown in the figure. From these observations,

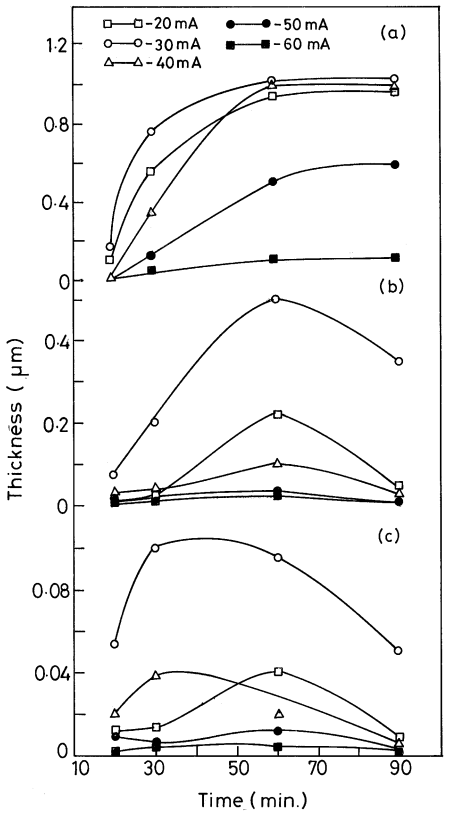

Fig. 1. Growth of WS_2 thin films at bath temperature: (a) 40°C, (b) 60°C, (c) 80°C.

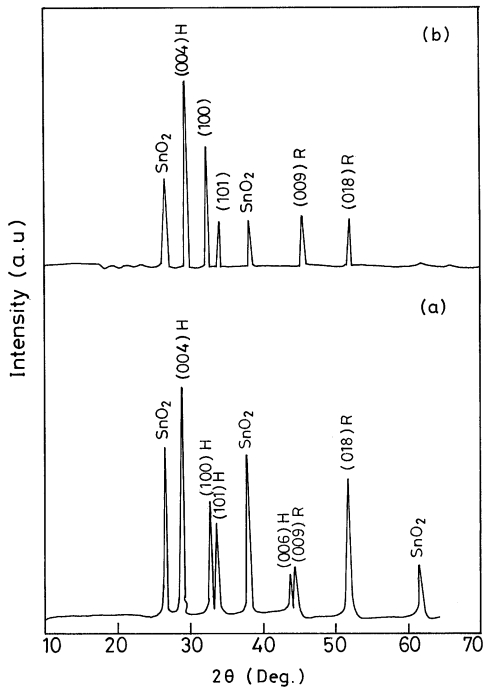

Fig. 2. XRD of electrodeposited WS_2 thin films: (a) as deposited, (b) vacuum annealed at 300°C for an hour.

the optimum bath temperature is fixed at 40°C. When pH of the bath is increased beyond 9.5, films are not deposited on the substrate but for lower pH, i.e. below 8.0, poor thickness with highly transparent nature are formed. Hence the pH of the bath is fixed at 9.2. From the above observations, the optimised deposition parameters are listed as below,

Deposition current density: 30 mA/cm^2
The temperature of the bath: 40°C
The pH of the electrolyte bath: 9.2
Deposition time: 60 min
Thickness of the film: 1.12 μm

The XRD pattern of the as-deposited films and films annealed at 300°C are shown in Fig. 2. It is clear that the films are polycrystalline with hexagonal structure. The preferential orientation of the electrodeposited films, in the present study, is along (0 0 4) plane revealing the *c*-axis perpendicular to the substrate (type-II) [2]. The lattice parameters are calculated as $a = b = 3.22$ Å, $c = 12.42$ Å. The Bragg peaks are in agreement with the standard values (JCPDF : 8-237). In addition to the 2H phase, two peaks of 3R-rhombohedral phase are also observed at $2\theta = 45°$, 51.6° corresponding to (0 0 9) and (0 1 8) planes (JCPDF : 35-651), respectively, with relatively low intensities. Hence a mixed phase of 2H and 3R of p-WS_2 film is observed in electrodeposition technique. WS_2 thin films prepared by Ennaoui et al. [2] by vapour transport technique show peaks of (0 0 ℓ) planes only. But films prepared by electrodeposition method, show the peaks of (1 0 0), (1 0 1), (1 1 6) in addition to (0 0 ℓ) planes. Jager-Waldau et al. [8] reported similar type of peaks corresponding to type-I and type-II texture for WS_2 thin films prepared by sulphurisation method. In the case of WS_2 films deposited on molybdenum

target by ion beam sputtering, Genut et al. [7] observed predominantly type-I texture films. As the films are coated on CTO coated glass substrate its respective peaks at $2\theta = 26.5^\circ$, 37.8° and 61.6° (JCPDF : 21-1250) are also observed. The crystallite sizes of the as-deposited films are observed to vary from 12 to 35 nm as calculated using Debye-Scherrer formula. The annealed films showed an increase in the intensities of most of the peaks showing improved crystalline nature of the film [11]. But the grain size was unaffected on vacuum annealing at 300°C.

The EDAX was recorded in the binding energy region of 0.8–9.0 keV. The spectrum reveals the presence of prominent peaks at 8.41 and 2.29 keV which confirms the presence of elemental W and S in the film. The ratio of the weight percentage of W and S is nearly two, approaching the stoichiometry at the optimised condition.

The SEM micrographs show well adherent and uniform film surface without cracks and pinholes. Fig. 3 shows the surface morphology of the WS_2 thin film which exhibits granular grains of uniform size of 0.17 μm spread all over the surface. This type of surface morphology reveals that the orientation of the crystallites, constituting the grains, is with the *c*-axis perpendicular to the substrate which is corroborated by the XRD results discussed earlier. This is in accordance with the observation made by Jager-Waldau et al. [8]

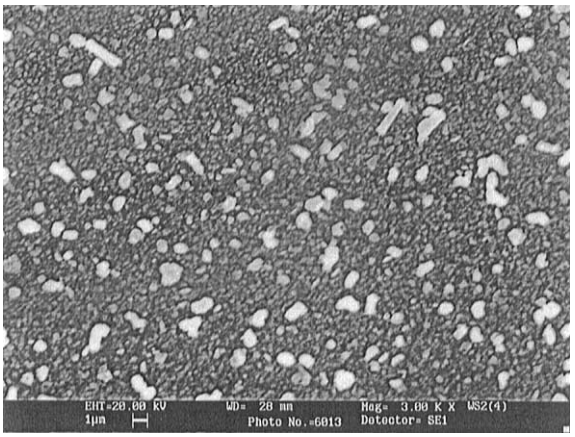

Fig. 3. Scanning electron micrograph of 2H-WS_2 thin film.

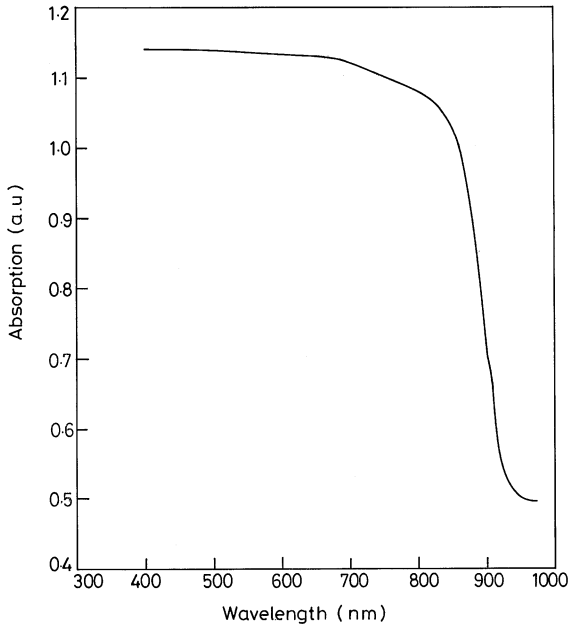

Fig. 4. Absorption spectrum of WS_2 thin film.

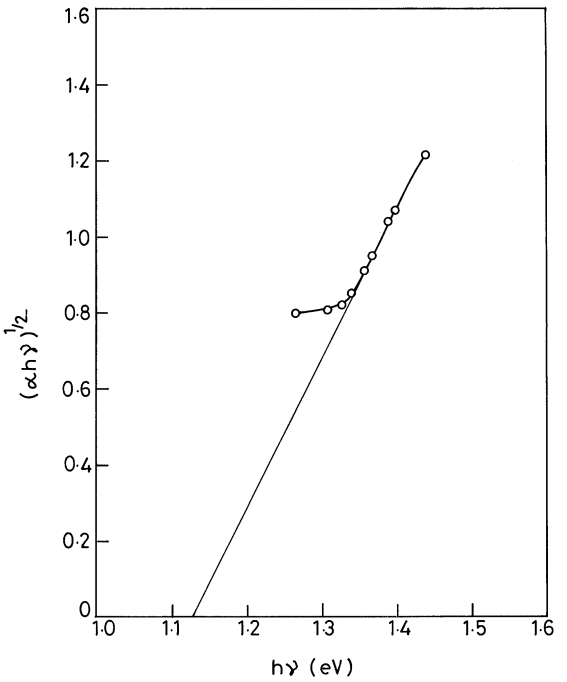

Fig. 5. Photon energy ($h\nu$) vs. $(\alpha h\nu)^{1/2}$ of WS_2 thin film.

for the WS_2 films prepared by sulphurisation of W films.

The optical absorption curve shows that the absorption band edge is near the IR region (Fig. 4). The photon energy ($h\nu$) and $(\alpha h\nu)^{1/2}$ are calculated and a graph is drawn between them taking ($h\nu$) in the x-axis and $(\alpha h\nu)^{1/2}$ along the y-axis. It shows that the electrodeposited WS_2 film is an indirect band gap material (Fig. 5). The extrapolation of the linear portion of the curve is intercepted at $(\alpha h\nu)^{1/2}=0$, which gives an indirect band gap of 1.12 eV and is in good agreement with the reported values [14,16].

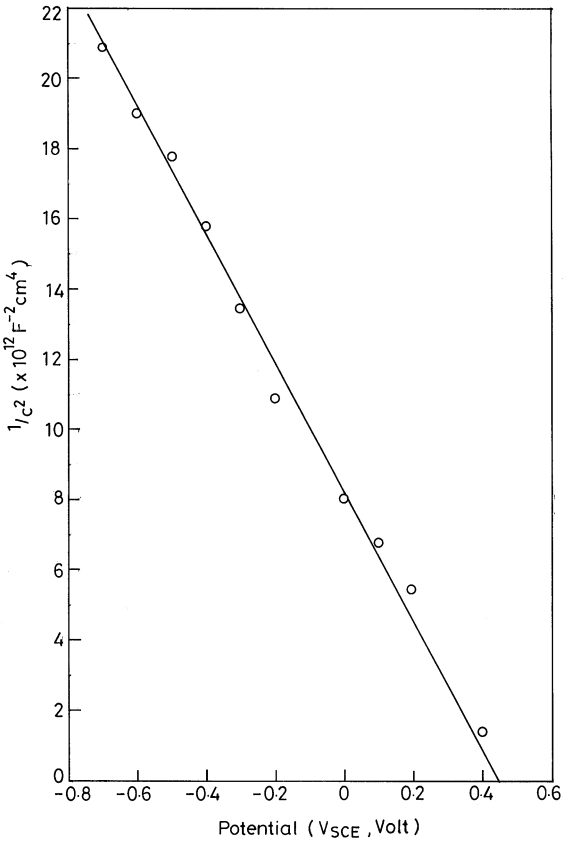

Fig. 6. Mott–Schottky plot for p-WS_2 thin film in 0.2 M Na_2SO_4.

Fig. 6 shows the Mott–Schottky (MS) plot drawn between $1/C^2$ and the potential with respect to SCE. The MS behaviour of all the films showed p-type semiconducting nature. The flat band potential (V_{fb}) is found to be 0.44 V_{SCE} and the acceptor density (N_A) as $9.7687\times10^{17}\,cm^{-3}$ which compares well with the reported values [12,13,15]. Baglio et al. [15] calculated the semiconductor parameters with different liquid electrolyte interfaces for WS_2 single crystals which are also comparable with our values. In Table 1 the reported semiconductor parameter values for WS_2 thin films prepared by different techniques and single crystal are presented along with the values for the electrodeposited WS_2 films studied in the present work.

4. Conclusion

Polycrystalline WS_2 thin films are prepared by electrodeposition technique on CTO coated glass plates. Films prepared at optimised deposition parameters show (0 0 4) preferential orientation, which shows that the c-axis is perpendicular to the substrate. The films have both the 2H-hexagonal and 3R-phase. The annealing treatment of the film in the vacuum at 300°C shows the improvement in the polycrystalline nature of the film. All the films prepared in this method are p-type with indirect optical bandgap of 1.12 eV. The SEM micrographs show the device quality nature of the surface

Table 1
Comparison of semiconductor parameters with the reported values

No	Material	Technique	Type of conduction	Acceptor density N_D (cm^{-3})	$E_{fb}(V_{SCE})$	Ref.
1.	Thin film	Electrodeposition	p	9.7×10^{17}	0.44	Present work
2.	Thin film	Thermal decomposition of WS_3	p	1.0×10^{18}	0.45	[13]
3.	Thin film	CVT	p	7.0×10^{17}	0.60	[12]
4.	Single crystal	CVT	p	1.0×10^{18}	0.65	[15]

without any pinholes and the semiconductor parameters, optical and structural properties of the electrodeposited WS_2 films are in very good agreement with that the single crystals, this film can be used for the fabrication of PEC solar cells.

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