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Electrosynthesis and characterization of WSe_2 thin films

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Abstract

Tungsten diselenide (WSe_2) semiconductor thin films were electrodeposited by the galvanostatic route. Polycrystalline WSe_2 thin films were deposited on chemo-mechanically and ultrasonically cleaned stainless steel (ss) and fluorine doped tin oxide (F:SnO_2 or FTO) coated conducting 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 studied by EDAX analysis. The surface morphology of the films was studied by scanning electron microscopy (SEM). The type of the semiconductor was found to be n-type and confirmed by hot probe technique. Thus the material is strongly applicable in semiconducting devices.

Keywords: WSe_2 ; thin films electrodeposition; X- ray diffraction; SEM EDAX; TEP.

Introduction

Thin films of binary, ternary and mixed/alloyed semiconducting compounds, transition metal dichalcogenides, form a technologically important class of materials owing to their widespread utility in various electronic, optoelectronic and solar energy conversion devices [1-5].Their optical gaps can be tailored to match effectively the maximum span of the solar spectrum. They possess high photosensitivity over a considerable range of energy and a high coefficient of absorption with an allowed direct type of transition [6-7]. Tungsten diselenide thin films have applications in solid state solar cells [8]. Skyllus kazacos et al studied n-MoSe2 and n-WSe2 photoelectrodes for their temperature dependence [9]. C.Sanjeeviraja reported theoretical investigation of the electrical and optical properties of WSe_2 [10]. A variety of thin films deposition methods have been investigated in pursuit of materials for optoelectronic devices. These includes chemical vapour deposition (CVD), RF-Sputtering, Spray pyrrolysis and solid state reactions etc., [11-14]. However amongst these, electrodeposition method is low cost, easy, pollution free and low-temperature method [15]. In this sense electrodeposition is a suitable

method for preparing WSe_2 thin films. But this material is less extensively studied in the form of thin films. From this point of view and considering its applications in solar energy and optoelectronic devices, it is necessary to grow WSe_2 material in the form of thin films and to investigate its characteristics. Hence, the purpose of present investigation is to study the growth, composition and structural characteristics of the electrodeposited WSe_2 thin films.

Materials and Methods

WSe_2 thin films were electrodeposited on to the chemo-mechanically and ultrasonically cleaned stainless steel (ss) and fluorine doped tin oxide (F:SnO_2 or FTO) coated conducting glass substrates from aqueous electrolytic bath containing varied volumes of ammonical solutions of 0.2M H_2WO_4 and 0.1M SeO_2 . The pH of the solution was adjusted to 9.6 by ammonium hydroxide. The uniform and well adherent, grayish black coloured thin films have been deposited at 60^{o}C temperature for about 30 min. Simultaneous deposition of W and Se is possible at constant potential, provided higher concentration of W is used as compared to that of Se.

Electrochemical studies and film deposition were made using a potentiostat (Princeton Perkin-Elmer, Applied Research Versastat-II; Model 250/270) in the three electrode configuration. The reference electrode used was a saturated calomel electrode, graphite as counter electrode (anode) and Stainless steel or FTO coated glass substrates as working electrode (cathode). Optical absorption was carried out in the range 350 to 850 nm with Hitachi-330 UV-Vis-NIR spectrophotometer. The absorption coefficient, band gap and type of transition were determined from these studies. The films were characterized for their structural properties by using Philips X-ray diffractometer PW-1710 (λ= 1.5405 A°) for CuKα radiation in the diffraction angle range 20-90^o. SEM pictures and energy dispersive X-ray analysis were recorded on JEOL-JSM 6360 model. Also the WSe_2 thin films were characterized for their electrical properties. The electrical conductivity of the films was studied by two-probe method in the temperature range 300-500K. The TEP measurement was carried out in the temperature range 300-500 K. Silver contacts were made for the conductivity and TEP measurements.

Results and Discussion

3.1 Growth Mechanism:

The aqueous deposition mixture (electrolyte) consists of tungstic acid and Selenium dioxide in alkaline medium. The induced co-deposition mechanism can be suggested as bellow

$$H_2WO_4 + NH_4OH \rightleftharpoons (NH_4)_2WO_4 + 2H_2O$$

$$(NH_4)_2WO_4 \rightleftharpoons 2\,(NH_4)^+ + WO_4^{2-}$$

$$WO_4^{2-} + (6\text{-}n)\,e^- = W^{n+} \longrightarrow$$

$$SeO_2 + H_2O \rightleftharpoons HSeO_2^+ + OH^-$$

$$HSeO_2 + 2e^- \rightleftharpoons Se_{(s)} + O_2 + -H_2$$

$$Se_{(s)} + 2H_2O \rightleftharpoons HSeO_2^+ + 3H^+ + 4e^-$$

$$H^+ + e\,(ySe) \rightleftharpoons H\,(ySe)$$

$$W^{n+} \text{ ———— } + n\,H\,(ySe) = Wx\,Sey$$

Where n is the oxidation state of W in the intermediate compound ($0 < \eta < 6$) the atomic hydrogen is held by deposited solid selenium on cathode, X and Y are the numbers of tungsten and selenium ions deposited on cathode. In the electrolysis cell, substrate was used as working electrode (cathode) graphite was used as counter electrode (anode) and electrolyte was prepared by mixing 0.2M tungstic acid and 0.1M Selenium dioxide, its pH was adjusted to 9.6 by ammonium hydroxide the electrolysis was carried out with a current density of 6mA/cm^2. Number of depositions over the stainless steel and FTO coated glass substrate were taken by varying i) concentrations of the tungstic acid and selenium dioxide, ii) temperature of the electrolytic bath, iii) pH of the electrolytic bath and iv) time period of deposition. The above parameters were optimized to 0.2M tungstic acid; 0.1M selenium dioxide final pH of the electrolyte 9.6, temperature of the electrolyte for the deposition was maintained at 60^{0}C for 30 minutes. The electrodeposited films were dark gray black, uniform, adhesive and pin whole free. The growth kinetic study was also carried out by changing the deposition parameters. The characterization of thin films was carried out for optical absorption study, x-ray diffraction, scanning electron microscopy, EDAX and electrical properties.

3.2 Optical absorption studies:

The optical absorption spectra of the as-deposited films on FTO coated substrate was recorded in the wavelength range 350 to 850 nm at room temperature. The optical density was converted into absorption coefficient α using predetermined thickness values. The absorption coefficient was of the order of 10^5 cm^{-1} confirming the direct allowed transition. Figure1 shows a plot of $(\alpha h\nu)^2$ versus hν, it is linear at higher energies indicates direct type of transition. The extrapolation of straight line portion to zero absorption (α =0) gives the band gap energy (Eg) of Tungsten diselenide to be 1.5 eV.

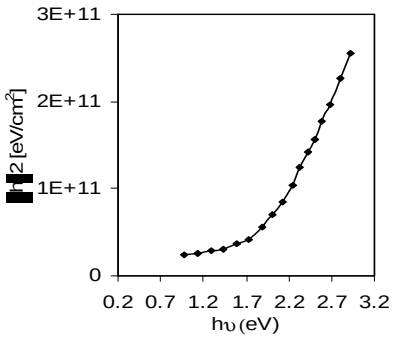

Figure 1 Plot of $(\alpha h\nu)^2$ vs hν

3.3 X- ray diffraction studies:

XRD pattern of electrodeposited tungsten diselenide thin film prepared on stainless steel substrate is shown in Figure 2. The plane indices are obtained from comparison between observed 'd' values and standard 'd' values for WSe_2 which are given by JCPDS file No : 06-0080. The formation of solid solution is expected because both materials crystallises in hexagonal structure. The observed 'd' values are in good agreement with the standard 'd' values for the hexagonal crystal structure of WSe_2. The crystallite size 'D' of the deposits was calculated from the full-width at half- maximum (FWHM) measurement for the prominent X-ray diffraction peaks using the Scherrer formula [16] for the prominent peak assuming that microstrain can be neglected.

$$D = k \lambda / \beta \text{ Cos } \theta \qquad (1)$$

Where, k Constant varies with hkl and crystallite shape but usually nearly equal to 0.94

λ Wavelength of source radiation.

β Full-width at half maximum of the peak, in radian.

θ Bragg's angle.

The calculated crystallite size is 23 nm.

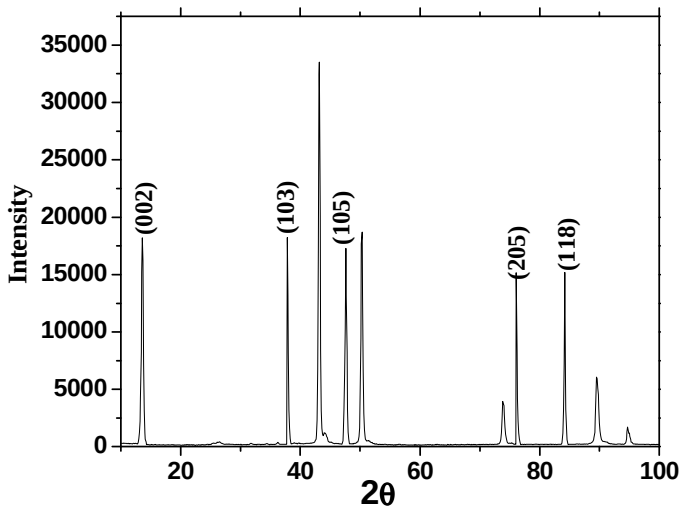

Figure 2 XRD plot of WSe_2 thin film

3.4 SEM / EDS studies:

The SEM micrograph shows homogenous and uniform film surface without cracks and pinholes. Figure 3 shows the typical surface morphology of the WSe_2 thin film prepared on stainless steel substrates under optimized conditions, which exhibits hexagonal platelets of uniform size spread all over the surface.

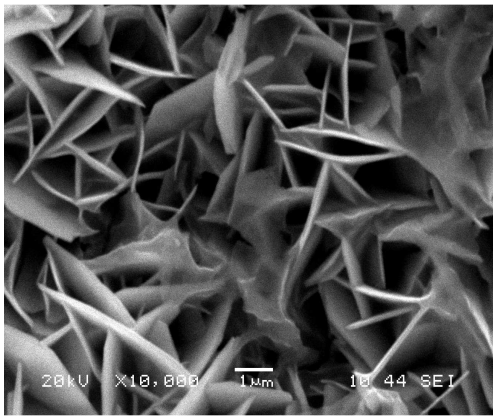

Figure 3 SEM micrograph of WSe_2 thin film

The compositional analysis of the electrodeposited thin film is carried out by EDS technique to study the atomic percentage of the film. Figure 4 shows the EDS pattern of WSe_2 thin film. The EDS spectrum recorded in the binding energy region of 0–10 keV shows the presence of W and Se in the film. From EDS data it is observed that atomic percentage of W and Se is in the ratio of 1:2.

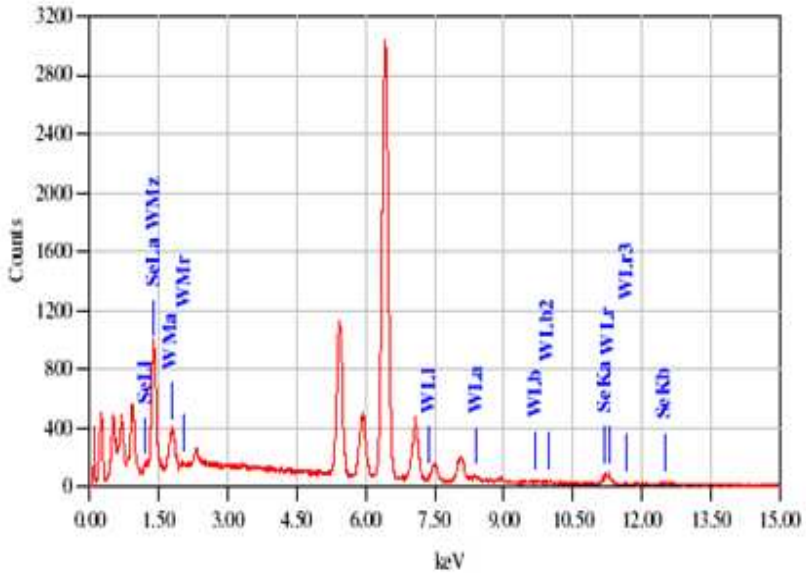

Figure 4 EDS pattern of WSe_2 thin film

3.5 Electrical / TEP studies:

From the point of view of electronic properties; we consider that the electrical conductivity is an important tool for studying the electrical behavior under the influence of an electrical field or temperature. Study of electrical conductivity is carried out by using two-point probe technique by varying the temperature from 300K to 500K. Away from the phase transition region, the electrical conductivity of most insulator and semiconductors is given by the relation,

$$\sigma = \sigma_o \exp^{(-\Delta E / \kappa T)} \qquad (2)$$

Where ΔE is the activation energy for the conduction, κ is Boltzmann constant and σ_0 is the pre exponential constant depending on the material.

Figure 5 is plot of ln σ versus 1000 / T for as deposited WSe_2 thin films and is in good agreement with Eq. (2). At high temperature, there is a non-activated behaviour, which suggests that the conduction is due to the variable range hoping in localized states near the Fermi level. From the slopes of linear plots, activation energy for conduction was calculated which is 0.89 eV.

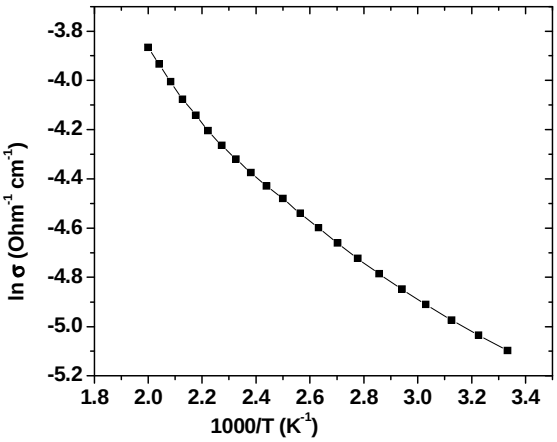

Figure 5 ln s Vs 1000/T Plot for the WSe_2 thin film

The temperature dependence of the thermoelectric power of as deposited WSe_2 film is shown in Figure 6. Thermoelectric power of WSe_2 thin film is negative which indicates that the conduction takes place because of electrons in the valance band and exhibits slight deviation from linearity with increasing temperature. The negative sign indicates the material is n-type charge carriers [7].

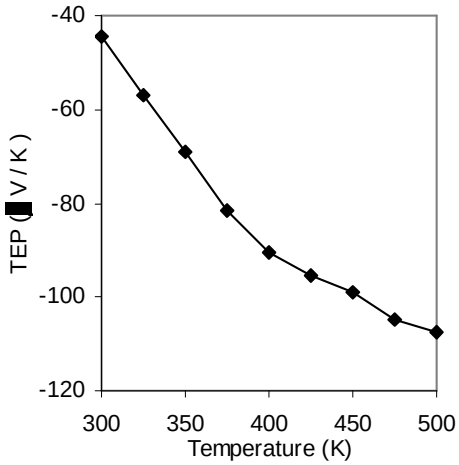

Figure 6 Temperature dependance of Seebeck coefficient for WSe_2 thin film

Conclusion

Using electrodeposition technique WSe_2 semiconducting thin films were successfully deposited on stainless-steel and FTO coated conducting glass substrate from aqueous alkaline bath. WSe_2 thin films are polycrystalline with hexagonal crystal structure and show the n-type semiconducting nature. The optical absorption studies indicate that the as deposited WSe_2 thin film has direct band gap value to be 1.5 eV. EDS analysis shows that the ratio W to Se is 1:2. The SEM micrograph shows homogenous and uniform film surface without cracks and pinholes.

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