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Effect of Annealing Temperatures on the Structural, Optical Properties of Tungsten Selenide Thin Films

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Abstract: Growth and characterization of tungsten selenide (WSe₂) thin films has been active research in photovoltaic and photoconductive devices. The structural and optical properties due to the thermal annealing effects of nanocrystalline WSe₂ thin films are prepared on fluorine doped tin oxide (FTO) substrate by brush plating technique. The parameters like brushing time (45 min), concentration (0.1 N) and current (1 mA) are optimized to get well adherent, polycrystalline films. The films are uniform and matt black in appearance. Slight color change was observed after annealing. The X-Ray Diffraction (XRD) spectra showed the hexagonal structure and the peaks are compared with JCPDS value (06-0080). The As-deposited film was amorphous and the maximum preferential orientation was observed on the (004) plane for the films (annealed to 300 and 500°C). The high intensity peak was observed in the XRD pattern of annealed films. The optical band gap reduced with increase in annealing temperature.

Key words: Tungsten selenide, brush plating, X-ray diffraction, optical properties, photoluminescence

INTRODUCTION

Thin films of mixed/alloyed semiconducting compounds, transition metal dichalcogenides play vital role because of their wide use in various electronic and solar energy conversion devices (Gawale *et al.*, 2010). The transition metal semi conductor WSe₂ belongs to the family of dichalcogenides. Tungsten diselenide also plays an important key role in number of scientific solutions like high temperature solid lubrication and rechargeable batteries (Gawale *et al.*, 2010). Although tungsten diselenide thin film has vast applications, this material is less extensively studied in the form of thin films. By considering its applications in optoelectronic devices and solar energy, tungsten diselenide material is to be prepared in the form of thin films and to investigate its characteristics (Prasad and Srivastava, 1988).

Gawale *et al.* (2010) have reported that tungsten Selenide films were prepared on fluorine doped tin oxide (FTO or F:SnO₂) substrate by electrosynthesis method. Both the as-deposited and the annealed films showed hexagonal structure. Guettari *et al.* (1998) have reported that the WSe₂ thin films were obtained by solid reaction in the presence of a thin nickel layer. Salitra *et al.* (1994) reported that the tungsten selenide thin films were prepared by soft selenization of evaporated WO₃. Boscher *et al.* (2008) reported that WSe₂ thin films were prepared on glass-highly pressure chemical vapour

deposition. Jager-Waldau and Bucher (1991) reported that WSe₂ films were prepared by soft selenization process.

The aim of the present work is to prepare the WSe₂ films on FTO substrate and study the structural (X-ray diffraction analysis) and optical properties (namely UV-visible spectroscopic study, photoluminescence spectrum analysis) of the film by the effect of annealing temperature.

MATERIALS AND METHODS

The tungsten selenide thin films were prepared by brush plating technique. The thin films were coated on conducting (zinc) substrate and on FTO (fluorine doped tin oxide) substrate. The precursors used for the deposition of WSe₂ were WO₃ and SeO₂ and distilled water with 0.1 N concentration. The cotton wrapped with graphite anode was dipped in the precursor mixture and it is brushed on the FTO substrates. The films were deposited at 1 mA current. It takes 45 min to deposit a film. The films were annealed to 300 and 500°C for 2 h. X-Pert PRO diffractometer is used to characterize the films by X-ray diffraction. Optical absorption measurements were done on the thin films which are deposited on the conducting glass substrates. The photoluminescence spectrum was taken using Cary eclipse spectrometer. The transmission spectra were taken using UV-Vis spectrometer.

RESULTS AND DISCUSSION

X-ray diffraction studies: X-ray diffraction spectra of tungsten selenide films on FTO substrate are shown in Fig. 1-3. From the standard 'd' of WSe₂ thin films which are given by JCPDS file No: 06-0080, the plane indices of the observed 'd' are obtained. The standard 'd' values are in good agreement with the observed 'd' values for the hexagonal structure of WSe₂. Peaks corresponding to (004) (102) (106) (110) (108) planes are observed. From the Full-width at Half Maximum (FWHM), the grain size 'D' of the film was calculated for the X-ray diffraction peaks using the Debye-Scherrer formula:

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

Where:

k = Constant varies with hkl and crystallite shape but usually equal to 0.94

λ = Wavelength of source radiation

θ = Bragg angle

β = Full width half maximum of the peak

The peaks are not prominent in the as-deposited film. From the XRD spectrum of as-deposited film (Fig. 1), WSe₂ films seemed to be amorphous. The peaks observed in the annealed film (500°C) are more intense than the annealed film (300°C). The crystallinity nature increases as the films are annealed to higher temperature. The observed planes are compared with the values of WSe₂ thin films, prepared by electrosynthesis method (Gawale *et al.*, 2010).

The observed planes are also comparable with WSe₂ films obtained by solid reaction in the presence of a thin nickel layer (Guettari *et al.*, 1998). The indices are also in good agreement with the WSe₂ films prepared on highly pressure chemical vapour deposition (Boscher *et al.*, 2008).

By the Debye-Scherrer formula the grain size of the films was calculated. The average grain size has been calculated and it varied from 46 to 58 nm. The grain size slightly differed from the reported WSe₂ films prepared by soft selenization process (Jager-Waldau and Bucher, 1991). The grain size was increased as the annealing temperature increased.

The dislocation density of the films was calculated using the formula:

$$\delta = \frac{1}{D^2} \quad (2)$$

The dislocation density decreases with the increasing grain size. The dislocation density observed was between 0.004 and 0.006. This confirms that the dislocation in the films were minimal. The cell parameters of WSe₂ thin film was determined from the peak observed. The determined cell parameters were a = 3.29, b = 12.97. The cell parameters confirm that WSe₂ has hexagonal structure. From the SEM results of WSe₂ films prepared by soft selenization of evaporated WO₃ (Salitra *et al.*, 1994), they are found to be of hexagonal structure.

Optical studies: From the absorption, transmittance and the photoluminescence spectra, the optical properties of the WSe₂ thin films were studied.

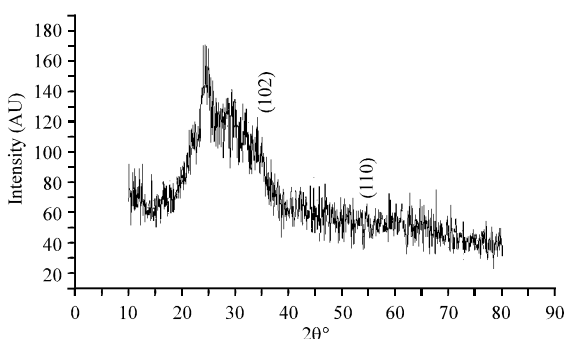


Fig. 1: XRD spectrum of As-deposited film

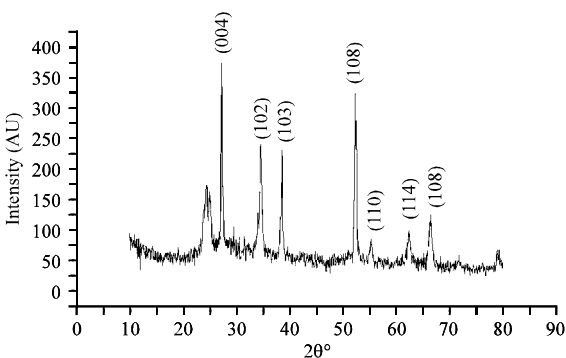


Fig. 2: XRD spectrum of annealed film (300°C)

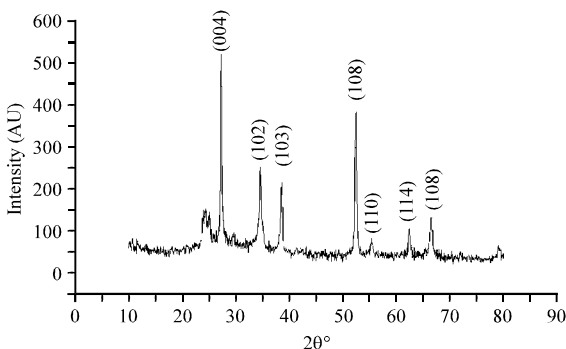


Fig. 3: XRD spectrum of annealed film (500°C)

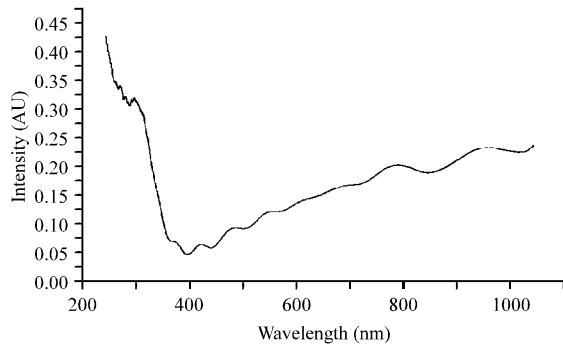


Fig. 4: Absorption spectrum of as-deposited film

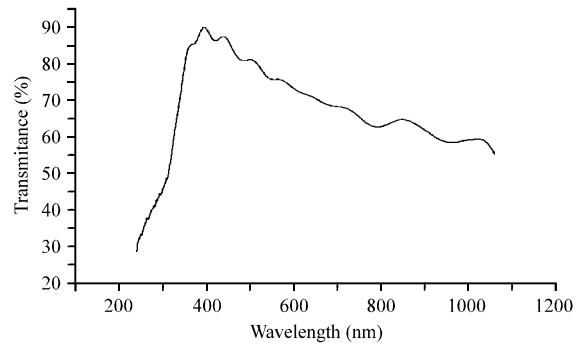


Fig. 7: Transmittance spectrum of as-deposited film

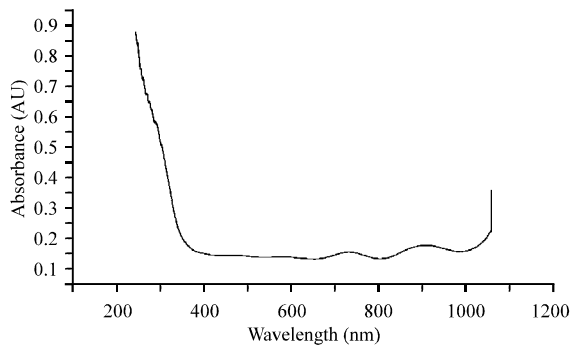


Fig. 5: Absorption spectrum of annealed film (300°C)

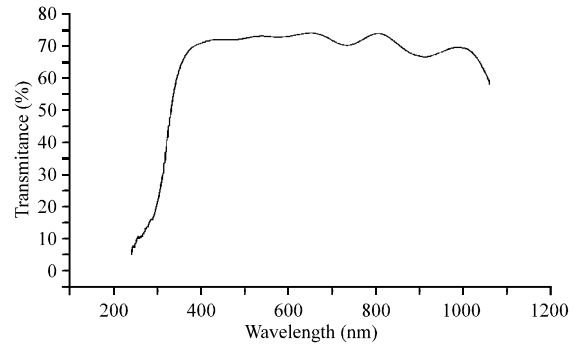


Fig. 8: Transmittance spectrum of annealed film (300°C)

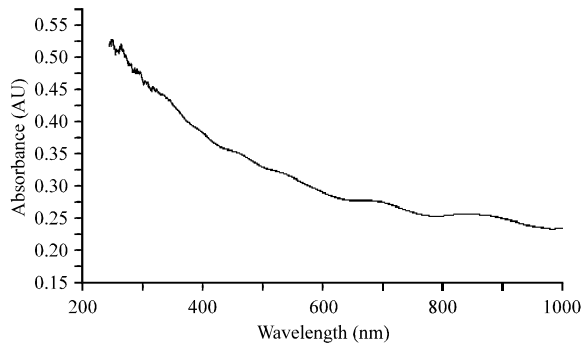


Fig. 6: Absorption spectrum of annealed film (500°C)

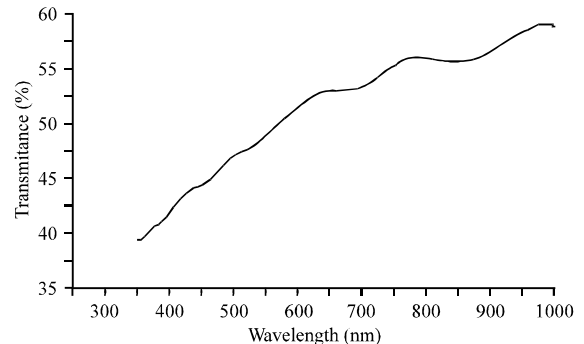


Fig. 9: Transmittance spectrum of annealed film (500°C)

Absorption spectra: The optical absorption spectra of the films on FTO coated substrate was recorded in the wavelength ranging from 200-1100 nm at room temperature. The UV-Vis spectra were plotted for absorption coefficient against wavelength. The Fig. 4 shows the absorption spectra of as-deposited film. The maximum absorption was at the wavelength 243.45 nm. The Fig. 5 and 6 shows the absorption spectrum of annealed to 300 and 500°C films, respectively and the absorption was at the wavelength 244.86 and 247.67 nm, respectively. From the spectra obtained, the curve is shifted towards higher wavelength and hence red shift is observed, thereby leading to decrease in energy gap with increase in annealing temperature.

Transmittance spectra: The transmittance is the fraction of light in the original beam that passes through the sample and reaches the detector. The remainder of the light is the fraction of the light absorbed by the sample is $1-T$.

Figure 7 shows the transmittance spectra of the as-deposited film. Figure 8 and 9 show the transmission spectra of the annealed films. Optical transmission spectrum is shifted towards higher wavelength with the increasing annealing temperature. From the spectra, it is clear that the photons are absorbed in the UV and Vis region up to 400 nm. And the percentage of photons are transmitted are greater in visible region and near IR region. From the Fig. 7-9, the

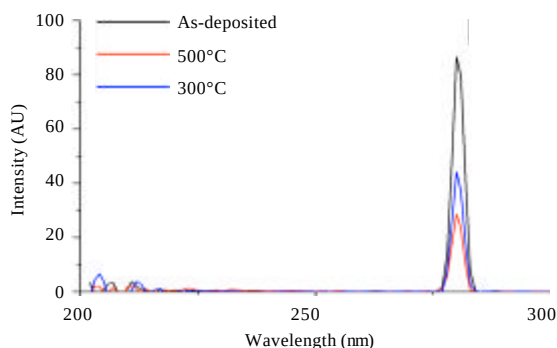


Fig. 10: Photoluminescence (excitation) spectra of WSe₂ thin film: As-deposited and annealed films (Excitation 280 nm at emission)

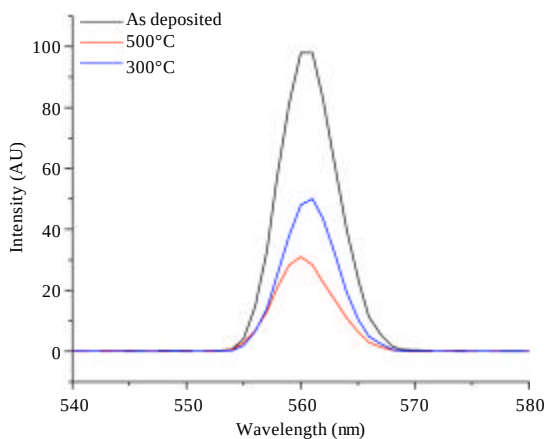


Fig. 11: Photoluminescence(emission) spectra of WSe₂ thin film: As-deposited and annealed films (Emission 561 nm at excitation)

photons are transmitted through the WSe₂ thin films in the wavelength of 400 and 1200 nm.

Photoluminescence spectra: The energy gap can be directly determined from the photoluminescence spectra. The Fig. 10 shows the excitation spectra of WSe₂ films which contain 4 peaks at the wavelengths corresponding to 195 nm, 202 nm, 210 nm and a strong peak at 280 nm.

Figure 11 shows the emission spectra of the films. A strong broad peak is observed in the wavelength 561 nm which corresponds to the energy gap 2.2145 eV.

CONCLUSION

The as deposited WSe₂ films are amorphous in nature. By annealing the films at 300°C the crystalline nature of the films increased and observed different orientations with predominant (004). The intensity of the films observed to be increased by further increasing the annealing temperature to 500°C. The As-deposited and the annealed film showed the hexagonal structure with lattice constant of 'a' 3.29 and 'b' of 12.97 nm. The grain size of the film increased, on annealing. The grain size increased from 46-58 nm. The percentage of photons transmitted through the films were identified from the transmission spectra of the annealed films. The excited wavelength and the emitted wavelength were determined for all the films from the photoluminescence spectra. The band gap energy is determined to be 2.1 eV. As the energy gap reduces when annealed, the WSe₂ thin films can be used as photovoltaic devices, chromic sensors and as solar conversion cells.

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