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Abstract Silver selenide, a phase-changing chalcogenide material, is prepared using electro deposition method for various molarities. X-ray diffraction studies show the cubic lattice of the material. The micro-structural properties such as grain size, strain, dislocation density, and texture coefficient are examined. The lattice constant is calculated using Nelson-Relay function. Morphological studies are done and uniform distributions of grains are observed. High purities of thin films are confirmed by energy dispersive X-ray analysis. The band gap is calculated using UV-vis spectroscopy and photoluminescence technique, and hence, the Stokes's effect is observed in silver selenide thin films. It is the first time that the lattice constant and the Urbach energy for various molarities in the case of silver selenide thin films are reported.

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1 Introduction

The semiconducting materials show unique structural and optical properties when the electron motion is confined in at least any one direction. The size-dependent structural, optical, and electrical properties of semiconductors play an important role in the field of science and technology. Phase-changing chalcogenide materials have a wide range of applications in the field of optics and electronics [1] (http://www.jtaphys.com/content/6/1/7). Silver selenide belongs to group I–VI semiconductor which is a super ionic conductor [2]. It has an orthorhombic structure at low temperature and undergoes a phase transition to cubic structure at 400 K [3]. It has a wide range of applications such as IR detectors, photovoltaic cells, magnetic resistive sensors, electrochemical potential memory devices, semiconducting optical devices, solid electrolyte in photochargeable batteries, non-linear optical devices, and biological imaging [4–9]. Different synthesis methods are available to prepare silver selenide thin films such as chemical bath deposition, adsorption-reduction method, electrodeposition, flash evaporation, vacuum evaporation, and explosive evaporation [3, 10–15]. In this paper, we report the preparation, structural, morphological, and optical properties of silver selenide thin films which are prepared by electro deposition method. The micro-structural properties are examined. Nelson-Relay function is employed to calculate the lattice constant. Morphological and chemical compositional analyses are done. Band gap and the Urbach energy are calculated using absorption spectrum. Photoluminescence technique is also used to find the band gap of the material. Lack of data on lattice constant and the Urbach energy for various molarities induce us to do this work. The abovementioned parameters are reported for the first time.
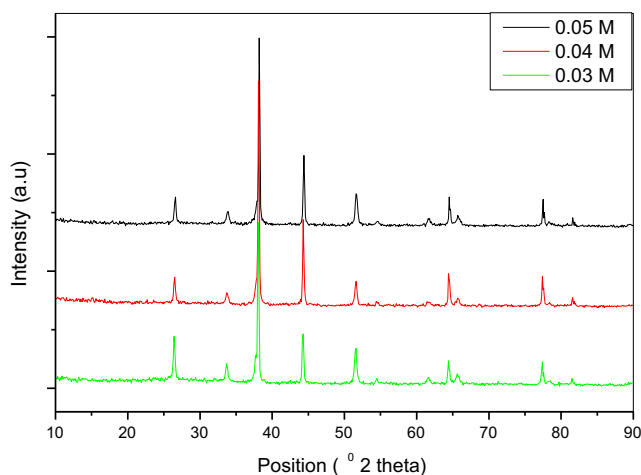
Fig. 1 XRD pattern of silver selenide thin films

2 Experimental Procedure

The preparation of the silver selenide thin films is carried out using an electrodeposition procedure. The deposition is done in a three-electrode system in which SnO_2-coated indium tin oxide (ITO) plate is used as the working electrode, graphite is used as the counter electrode, and saturated calomel electrode (SCE) serving as the reference electrode. All the chemicals are of AR grade and are used without further purification. The precursor solution of 0.03 M is prepared by dissolving $AgNO_3$, SeO_2, and ethylenediaminetetraacetic acid (EDTA) in double distilled water. Subsequent stirring and the addition of ammonia is carried out until the powder is totally dissolved in the water. The depositions are carried out potentiostatically at a potential of −650 mV/SCE for about 90 min. The above procedure is repeated for the concentrations of 0.04 and 0.05 M. The films are annealed at 500 °C for about 5 h. The annealed samples are used to characterize the materials.

3 Results and Discussions

3.1 Structural Investigations

Figure 1 shows the X-ray diffraction (XRD) pattern of silver selenide thin films. The XRD pattern coincidences with the standard cubic phase of silver selenide (JCPDS no: 65–7789).

No other peak of impurity is observed. This indicates that highly pure form of silver selenide thin film can be prepared by the electrodeposition method.

The grain size of the material is found from Debye-Scherrer's formula [16]:

$$D = \frac{0.9\lambda}{\beta\cos\theta},$$

where λ is the wavelength of Cu-Kα line, β is the full-width at half-maximum in radians, and θ is the Bragg angle. $\beta\cos\theta$ is plotted against $2\sin\theta$ and the slope of the line gives the strain ε. The dislocation density $\delta=1/D^2$ is calculated [16]. The grain size of the material is also calculated using Williamson-Hall equation [16]:

$$D = \frac{0.9\lambda}{\beta\cos\theta - 2\varepsilon\sin\theta}.$$

The preferential crystal orientation is obtained from the texture coefficient (TC) and it is defined as follows [16]:

$$TC = \frac{I/I_0}{(1/n)\sum I/I_0},$$

where n is the number of diffraction peaks considered, I(hkl) is the XRD intensity, and I_0(hkl) is the intensity of the XRD reference of the randomly oriented grains.

As the molar concentration increases, the grain size which is calculated from Debye-Scherrer's formula and Williamson-Hall equation decreases, but the dislocation density, strain, and the texture coefficient increase. The high value of the texture coefficient indicates the crystalline nature of the material. The calculated results are tabled in Table 1.

The Nelson-Riley function (NRF) can be calculated using the following expression [17]:

$$NRF = \frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right).$$

The true value of the lattice constant can be calculated by plotting NRF along x axis and the lattice constant along y axis. The extra plotting of the line to the y axis

Table 1 Micro-structural properties

| Micro-structural properties	0.03 M	0.04 M	0.05 M
Grain size using Debye-Scherrer's formula (nm)	32.51	31.03	28.79
Grain size using Williamson-Hall equation (nm)	41.79	39.89	37.01
Strain	1.98×10^{-3}	2.53×10^{-3}	3.13×10^{-3}
Dislocation density (/m^2)	9.46×10^{14}	10.39×10^{14}	12.07×10^{14}
Texture coefficient	2.86	2.94	3.04

Fig. 2 Lattice constant vs. molarity
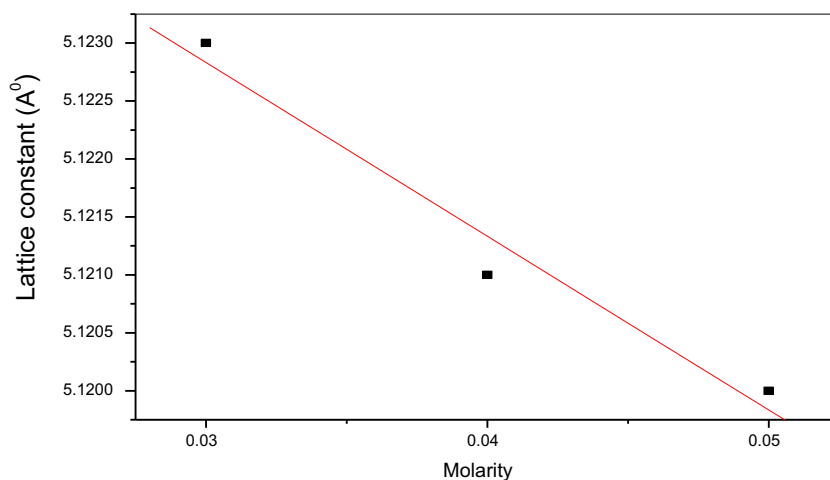
gives the value of the true lattice constant. The calculated lattice constant is 5.123, 5.121, and 5.120 Å for the molarity of 0.03, 0.04, and 0.05 M, respectively, and is shown in Fig. 2. It is interesting to note that as the molarity increases, the lattice constant decreases, but the change is negligible.
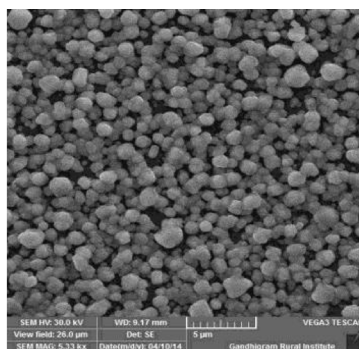
3.2 Surface Morphology and Compositional Studies

The surface morphological studies of thin films are done by scanning electron microscope (SEM). Figure 3(i) shows the SEM image of silver selenide thin films. The spectra are recorded at 30 kV. The uniform distributions of grains are
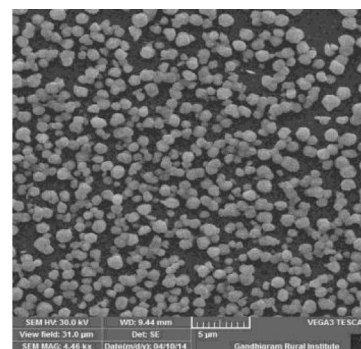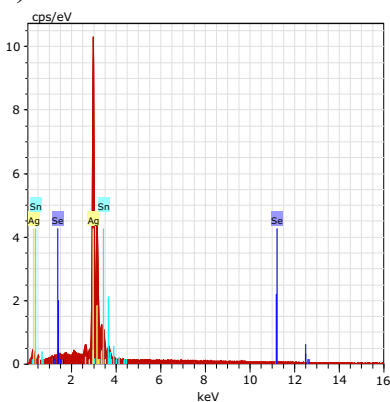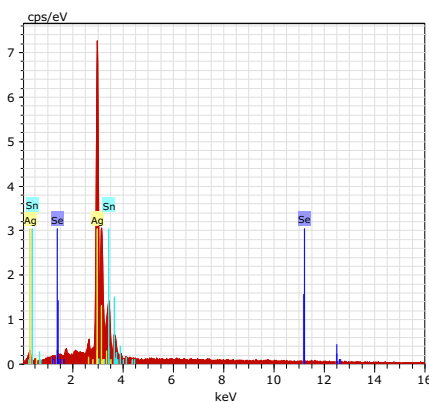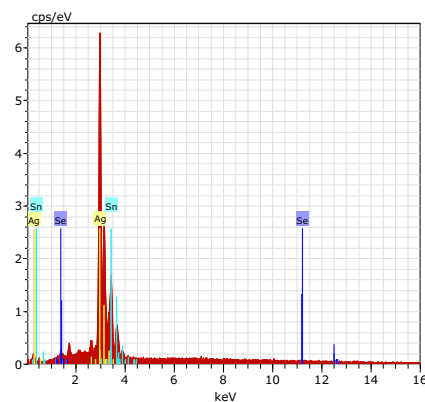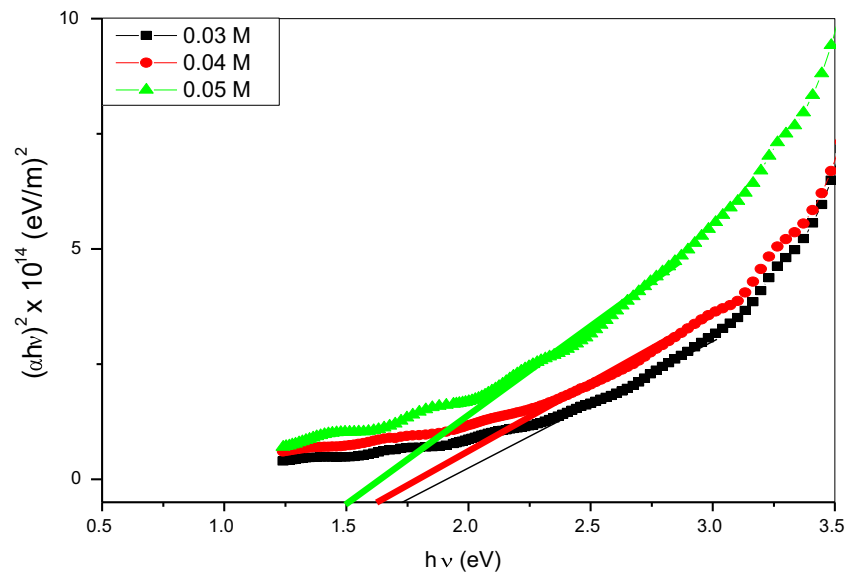
(i)
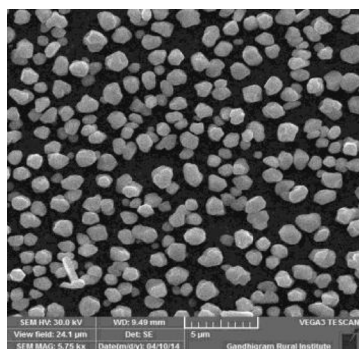
(a) (b) (c)

(ii)

(a) (b) (c)

Fig. 3 (*i*) SEM image of silver selenide thin films *a* 0.03 M, *b* 0.04 M, and *c* 0.05 M. (*ii*) EDX spectrum of silver selenide thin films *a* 0.03 M, *b* 0.04 M, and *c* 0.05 M

Fig. 4 $(\alpha h\nu)^2$ vs. hν

observed in the micrographs. As the molar concentration increases, the size of the grain decreases, and it is visually observed. This suggests that increase in molarity favor both particle growth and aggregation.

Figure 3(ii) shows the energy dispersive X-ray analysis (EDX) spectrum of AgSe thin films. The presence of Ag and Se are confirmed, and no impurities are observed.

Table 2 Optical properties

Optical properties	0.03 M	0.04 M	0.05 M
Band gap from optical absorption (eV)	1.75	1.62	1.50
Band gap from PL (eV)	1.51	1.49	1.48
Urbach energy (eV)	3.88	3.26	3.08

3.3 Optical Studies

The optical absorption as a function of wavelength is the simplest way to study the optical properties of the material. The absorption coefficient is related to the incident photon energy by the relation, $(\alpha h\nu)^{1/n} = A(h\nu - E_g)$, where E_g is the band gap of the material and A is a constant [17]. In order to determine the band gap of the direct allowed transition, the graph between $(\alpha h\nu)^{1/n}$ and hν is plotted by setting $n = 1/2$. The plot between $(\alpha h\nu)^2$ vs. hν is shown in Fig. 4. The extrapolation of the straight line portion of the graph to the horizontal axis gives the value of the band gap. The calculated band gap ranges from 1.75 to 1.50 eV as the molar concentration increases from 0.03 to 0.05 M. The results are given in Table 2. The relationship between the absorption coefficient and the photon energy is given by the following [17, 18]:

Fig. 5 ln(α) vs. hν
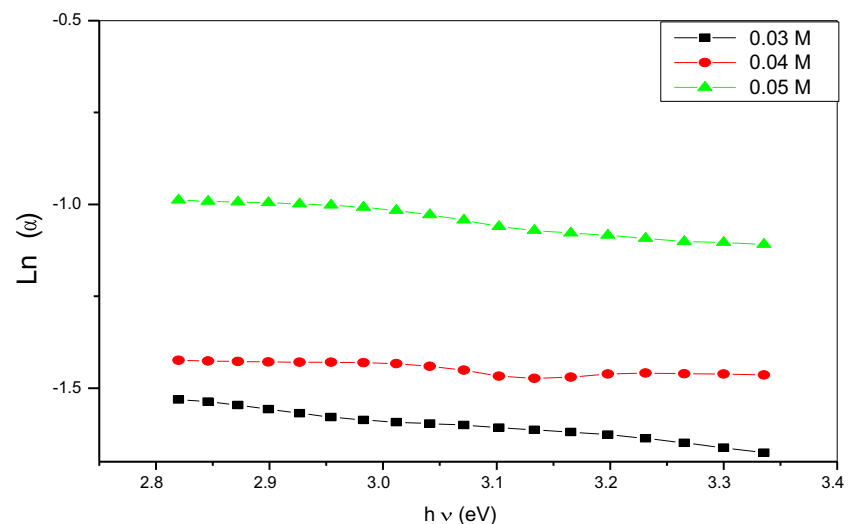
Fig. 6 Intensity vs. wavelength
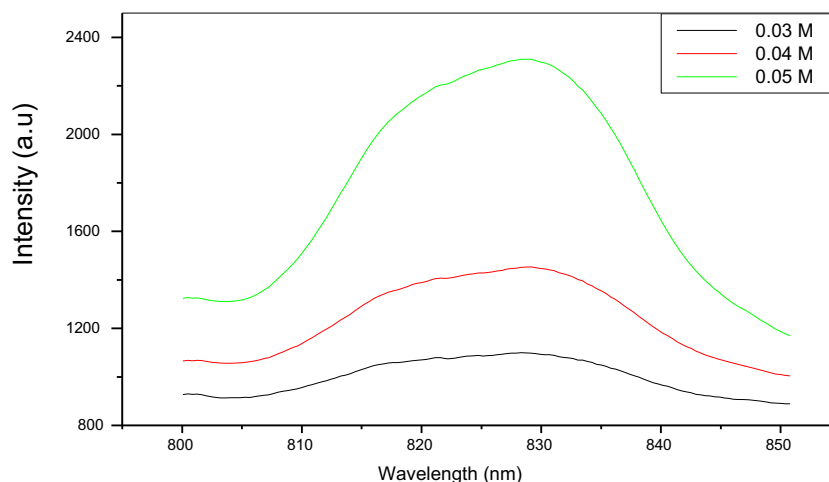
$$\alpha = \alpha_0 \exp\left[\frac{h\nu}{E_U}\right],$$

where E_U is the Urbach energy. The plot of $\ln(\alpha)$ vs. $h\nu$ is shown in Fig. 5. The reciprocal gradient of the straight line portion gives the value of Urbach energy. The calculated Urbach energy is 3.88, 3.26, and 3.08 eV for the molar concentrations of 0.03, 0.04, and 0.05 M, respectively.

Photoluminescence originates due to the recombination of surface states. Figure 6 shows the photoluminescence (PL) spectrum of silver selenide thin films. The intensity of the silver selenide thin film increases as the molar concentration increases. The band gap is calculated using the fundamental relation $E = hc/\lambda$, where h is Planck's constant, c is the speed of light in vacuum, and λ is the wavelength where the maximum absorption takes place.

The calculated band gap using the photoluminescence spectrum ranges from 1.51 to 1.48 eV as the molar concentration increases. The decrease in the band gap is observed as the molarity increases in both optical absorption and photoluminescence spectrum. The calculated optical parameters are given in Table 2.

The difference in the band gap which is calculated from the optical absorption and the photoluminescence spectrum is due to Stokes's effect. Though Stokes's effect is observed in the silver selenide thin films, the deviation is negligible for the molar concentration of 0.05 M and above. It is believed that this work will trigger further research in the field of phase-changing chalcogenide materials.

4 Conclusion

Molarity based micro-structural, morphological, and optical properties of silver selenide thin films have been investigated. Lattice constant was calculated using Nelson-Relay function and reported for the first time. High purity of samples has been confirmed by EDX. The optical properties such as band gap and Urbach energy have been calculated, and the Stokes effect is observed.

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