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SPECTROSCOPIC STUDIES ON SILVER SELENIDE THIN FILMS

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Silver selenide thin films of thickness between 80 nm and 160 nm were prepared by thermal evaporation technique at a high vacuum better than $2x10^{-5}$mbar on well cleaned glass substrates at a deposition rate of 0.2 nm/sec. Silver selenide thin films were polycrystalline with orthorhombic structure. Ellipsometric spectra of silver selenide thin films have been recorded in the wavelength range between 300 nm and 700 nm. Optical constants like refractive index, extinction coefficient, absorption coefficient, and optical band gap of silver selenide thin film have been calculated from the recorded spectra. The refractive index of silver selenide has been found to vary between 1.9 and 3.2 and the extinction coefficient varies from 0.5 to 1.6 with respect to their corresponding thickness of the films. Transmittance spectra of these films have been recorded in the wavelength range between 300 nm and 900 nm and its spectral data are analysed. The photoluminescence studies have been carried out on silver selenide thin films and the strong emission peak is found around 1.7 eV. The calculated optical band of thermally evaporated silver selenide thin films is found to be around 1.7 eV from their Ellipsometric, UV-Visible and Photoluminescence spectroscopic studies.

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Keywords: Optical properties, Thin films, Emission, Band gap

1. Introduction

Silver selenide, I-VI semiconductor compound, belongs to the family of super ionic conductors. It has high carrier concentration and finds attractive applications like magnetic resistive sensors, non-volatile memories, IR detectors, photoconducors, photovoltaic cells, electrochemical potential memory devices semiconducting optical devices for visible region etc. [1-3]. Silver selenide undergoes a phase transition from low temperature orthorhombic structure to high temperature cubic structure around 420 K [4,5]. It also exhibits phase transition with hysteresis [6,7]. Leon et al [8] have studied the effect of nanoscale confinement on the phase transition temperature increases with the decrease in the grain size of the silver selenide. Silver selenide is found to exhibit only n-type semiconducing property at 4.2 K even with 0.37% excess selenium [9]. It is impossible to dope silver selenide to be p-type from their thermoelectric power measurements with different amount of doping of different elements [10]. Xu et al [11] have observed that silver chalcogenide has linear and large magnetoresistance effect. The study of optical absorption of solids provides essential information about band structure and energy gap in both non-crystalline and crystalline materials [12]. Earlier, Dalven and Gill [13] have studied the absorption spectra of Ag_2Se at very low temperatures and found that the band gap is direct. The energy gap of sintered Ag_2Se film is reported as 0.2 eV [14]. From resistivity measurements, Damodara das and Karunakaran [15] have reported the energy gap of Ag_2Se is between 0.04 eV and 0.08 eV. The optical band gap of reactive evaporated Ag_2Se is 1.58 eV is reported by SantoshKumar and Pradeep [16]. Nanocrystalline Ag_2Se thin film has optical band gap of 1.8 eV

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[17]. Kulkarni et al [18] have determined the band gap of silver selenide as 1.3 eV from the optical studies on annealed and unannealed films of silver selenide. In 2010, the optical constants of silver selenide thin films were determined and reported by Santosh Kumar and Pradeep [19]. The difference in the reported optical band gap of silver selenide motivates us to determine the optical band band gap of thermally evaporated silver selenide thin films.

Spectroscopic ellipsometry is a non-destructive technique used to characterize the optical property of thin films [20-22]. The thickness dependence on the optical constants of tellurium alloys have been reported recently by Neyvasagam et al [23]. The present work is to determine the optical constants and optical band gap of silver selenide films using spectroscopic ellipsometric measurements.

2. Experimental

Silver selenide thin films of thickness from 80 nm to 160 nm were prepared by thermally evaporating 99.99% spectroscopic pure silver selenide purchased from M/s Sigma-Aldrich at a vacuum better than 10^{-5} mbar. These films were deposited at a deposition rate of 0.2 nm/sec on well cleaned glass substrates. Thickness and the deposition rate of the prepared films was monitored using microprocessor controlled digital quartz crystal thickness monitor. The X-ray diffractogram of silver selenide thin film was recorded and analysed to confirm the structure of silver selenide thin films. Atomic Force Microscopy (AFM) images of the silver selenide thin films were recorded to confirm the polycrystalline nature of films. Scanning Electron Microscopic images of silver selenide thin films were recorded to confirm the continuity and surface smoothness of the films.

The ellipsometry measurements have been carried out on these films using spectroscopic ellipsometer (SE850 model supplied by SENTECH instruments, GmbH, Berlin) at room temperature. The amplitude ratio (ψ) and Phase change (Δ) spectra of silver selenide thin films of thickness from 80 nm to 160 nm were recorded in the wavelength range from 300 nm to 700 nm. Transmittance spectra of silver selenide thin films have been recorded using Schimazdu UV-Vis double beam spectrophotometer. The emission spectra of silver selenide thin films have been recorded at room temperature using Shimazdu RF 8100 spectrofluorometer.

3. Results and discussion

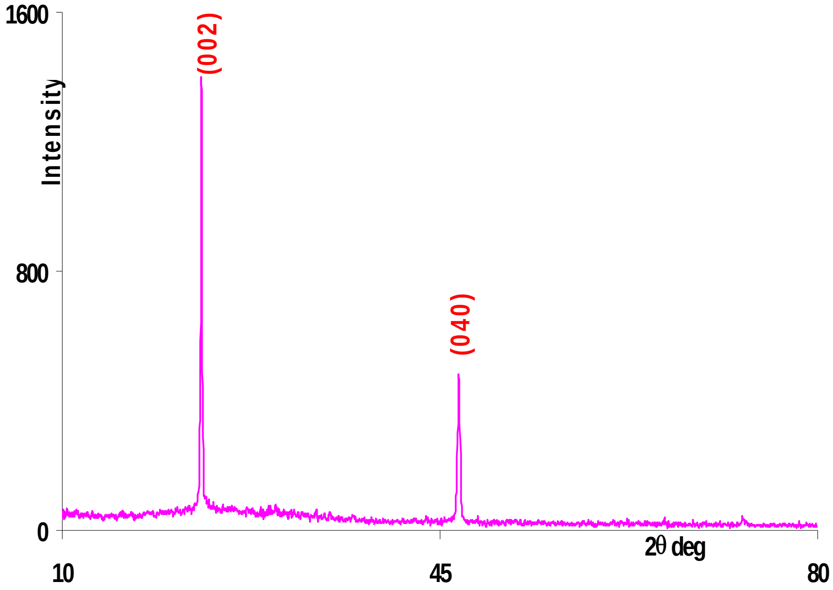

Fig.1. XRD of Silver selenide thin films.

Fig.1 is the powder X-ray diffractogram of silver selenide thin film of 120 nm thickness. It reveals that silver selenide film is polycrystalline. Comparison of the positions of peaks in X-ray diffractogram with Pearson's crystal data reveals that the structure of silver selenide film is orthorhombic. XRD pattern of other Ag_2Se thin films also shows similar diffraction pattern confirming the polycrystalline nature with orthorhombic structure. Structural studies on silver selenide thin films have been studied and reported that silver selenide thin films prepared over amorphous or polycrystalline substrates exhibits orthorhombic structure [6,9,18]. The existence of monoclinic structure in silver selenide thin film was reported by Gnanadurai et al [7]. From earlier studies, the existence of uncertainty in the structure of silver selenide thin films is confirmed. Baer et al [24] propose the existence of two low temperature phases β1 and β2 with a transition temperature of 90^0C. Atomic Force Microscopic images of the silver selenide thin films were shown in fig (2). The particle size of the silver selenide thin films was found to be about 500 nm, from atomic force microscopic studies. The surface of the silver selenide thin films was found to be uniform and exhibits polycrystalline nature. In thermally evaporated silver selenide thin films on glass substrates, the grains were found to be uniformly distributed from the recorded SEM image of the silver selenide thin films and it is shown in fig (3).

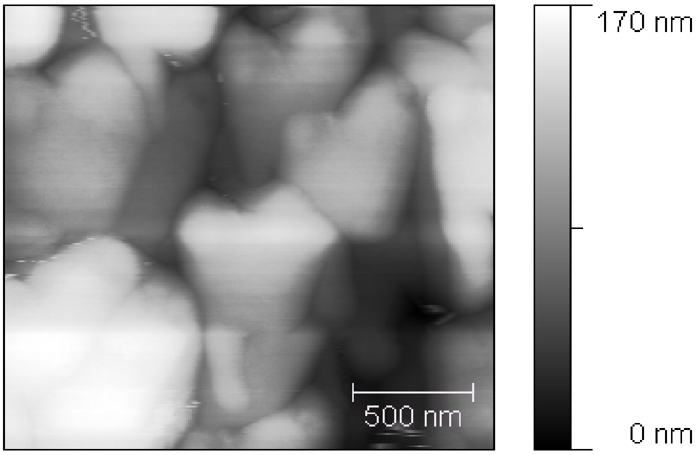

Fig. 2. AFM image of Silver selenide thin films.

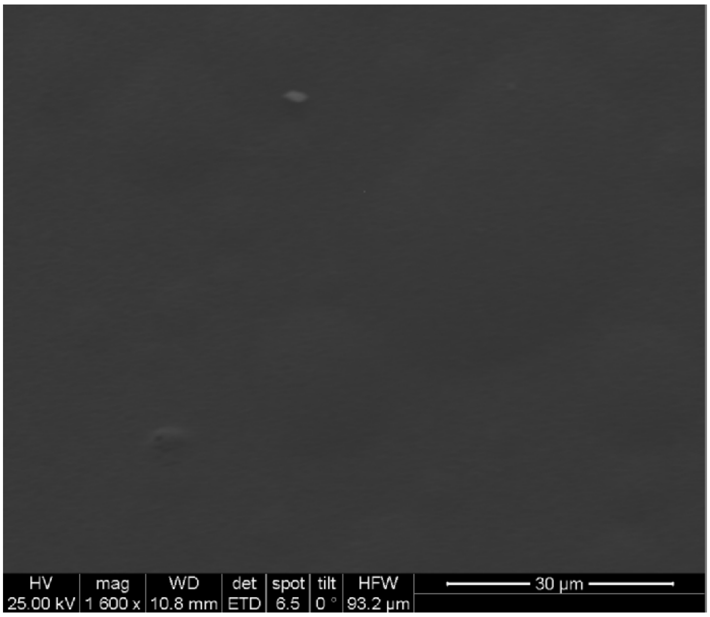

Fig. 3. SEM image of Silver selenide thin films.

3.1 Spectroscopic Ellipsometry studies

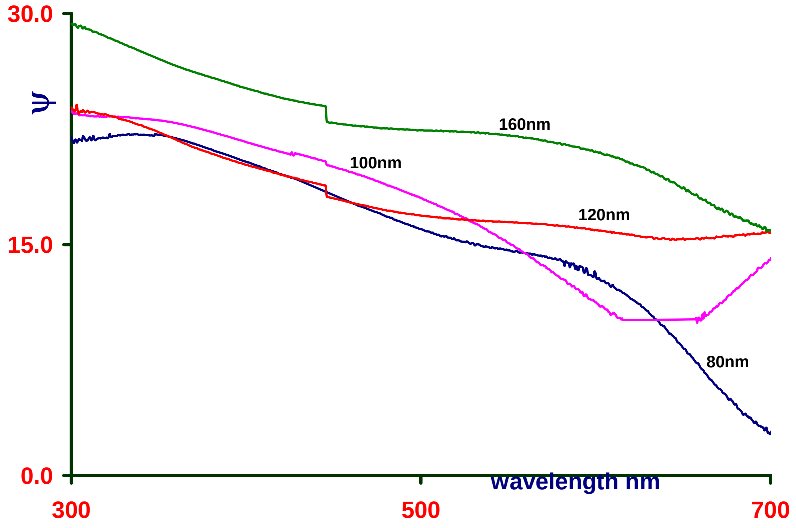

Fig. 4. Amplitude ratio spectra of silver selenide thin films as a function of incident wavelength

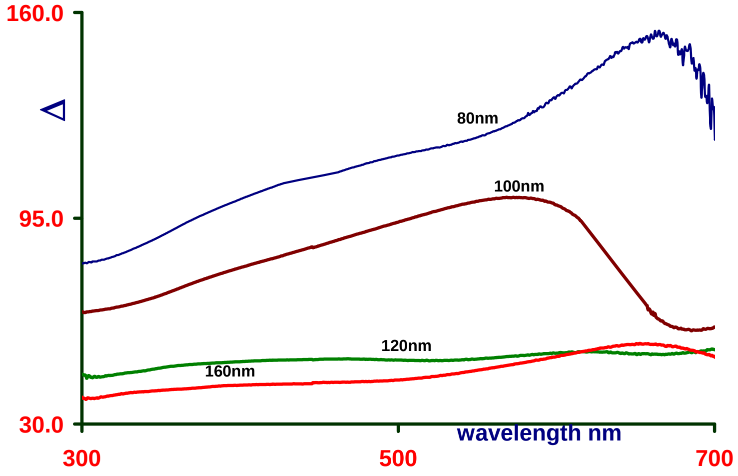

Fig. 5. Amplitude ratio spectra of silver selenide thin films as a function of incident wavelength

Spectroscopic ellipsometry data, amplitude ratio (ψ) and the phase ratio (Δ) as a function of wavelength between 300 nm and 700 nm has been recorded and shown in fig (4) and fig (5) respectively. The amplitude ratio (ψ) decreases monotonically with the increase in wavelength and increases with increase in thickness of the film. The phase ratio (Δ) increases with the increase in wavelength and it also decreases with the increase in thickness of the films. Using these two recorded data from ellipsometer, the optical constants like refractive index (n), extinction coefficient (k) and Dielectric functions (ε_1) and (ε_2) of silver selenide thin films has been determined. In spectroscopic ellipsometer, the refractive index (n), extinction coefficient (k) and dielectric functions can be determined form the theoretical relations which vary depending on the nature of the compounds. The separate relations are available for amorphous, crystalline optically active and absorbing material, absorbing and non-optically active materials [25,26]. Here our material is confirmed to be polycrystalline nature from XRD, AFM, SEM studies. So we determine the optical constants of silver selenide thin films by crystalline and optically active and absorbing relations from recorded ellipsometric data.

$$n^2 = n_o^2 \sin^2\theta \left[1 + \frac{\tan\theta - \cos 2\psi}{(1+\sin 2\psi \cos\Delta)^2} \right] \qquad (1)$$

From the value of ψ and Δ, we determine
the refractive index of the silver selenide thin films using the relation [26]
Where

n	-	refractive index of the material
n_o	-	refractive index of the substrate
ψ	-	amplitude ratio
Δ	-	phase ratio
θ	-	incident angle (70^o)

Fig. 6 shows the dependence of refractive index on the incidence wavelength ranges between 300 nm and 700 nm. The refractive indexes of silver selenide thin films were found to vary from 1.9 to 3.1. The refractive index of silver selenide determined using ellipsometric data was found to agree with the transmittance and reflectance analysis of Santosh kumar and Pradeep [19] recently. The value of 'n' founds to decrease with increasing the thickness of the films from 80 nm to160 nm. Silver selenide thin films also shows positive dispersion in the wavelength ranges between 300 nm and 700 nm and it is shown in fig (6).

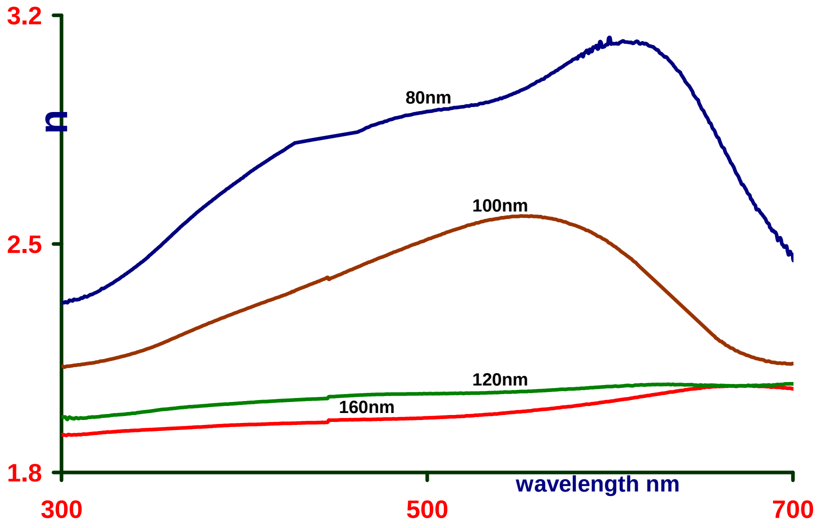

Fig.6. The dependence of refractive index (n) on the incident wavelength

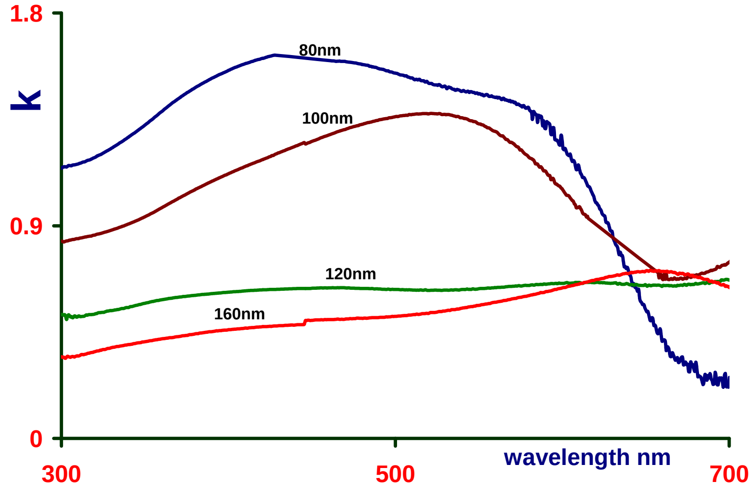

Fig.7. The dependence of extinction coefficient (k) on the incident wavelength

The extinction coefficient (k) of silver selenide also determined from the recorded data using the equation (2) and its spectral dependence is shown in fig (7).

$$k=\frac{\sin^2\theta\tan^2\theta\sin 4\psi\sin\Delta}{2n(1+\sin 2\psi\cos\Delta)^2} \tag{2}$$

The extinction coefficients of silver selenide thin films were determined from the recorded data using the relation given in equation (2). The dependence of the extinction coefficient of the silver selenide on the incident wavelength was shown in fig (7). The value of extinction coefficient of silver selenide thin films was found to vary from 0.4 to 1.6. It is found to increase with incident wavelength and also found to decrease with the increase in the thickness of the films. The absorption coefficient of the silver selenide thin films was determined from the extinction coefficient of the silver selenide from the relation given in equation (3).

$$\alpha = \frac{4\pi k}{\lambda} cm^{-1} \tag{3}$$

Neyvasagam et al [23] have determined the optical band gap of metallic chalcogenide thin films from their extinction coefficient determined using spectroscopic ellipsometer. The value of the absorption coefficient is found to be in the range between 10^4 cm^{-1} and 10^5 cm^{-1}. This value confirms that the silver selenide films exhibits direct band transition. Several authors also observed and reported that the silver selenide thin films exhibits direct band transitions. From the absorption coefficient value the optical band gap of silver selenide thin films were determined using the relation given in equation (4). The optical band gap of silver selenide thin films were calculated from the absorption coefficient of silver selenide. By assuming the parabolic bands, the absorption coefficient varies with the energy in the relation [26]

$$\alpha h\nu = A(h\nu - E_g)^n \tag{4}$$

where, α – absorption coefficient (cm^{-1}); $h\nu$ – energy (eV); E_g - band gap (eV)
'n' takes the value as ½ for direct and allowed transition and 2 for indirect and allowed transition. A plot of $(\alpha h\nu)^2$ vs $h\nu$ was shown in fig (8) used to determine the direct band gap of the silver selenide thin film of thickness of 100 nm film. Similar procedure was carried out to determine the

optical band gap of silver selenide thin films of thickness between 80 nm and 160 nm and is found to be 1.7 eV.

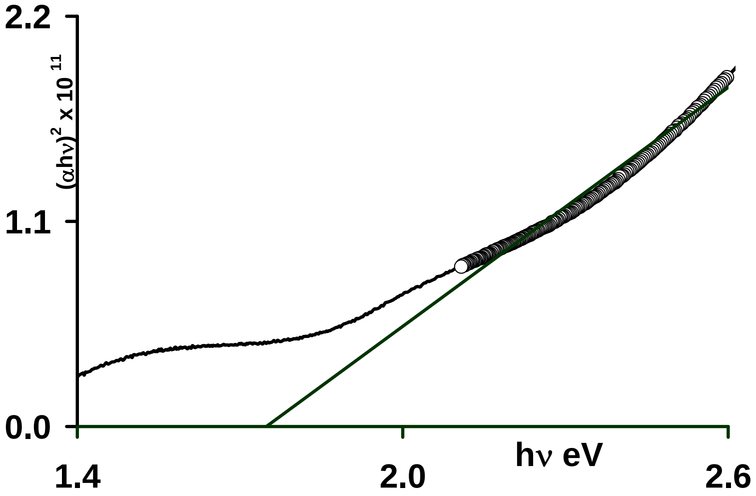

Fig.8. Plot of $(\alpha h\nu)^2$ *vs* $h\nu$ *eV of thin film of 120 nm silver selenide thin films*

Earlier studies reveal that the low temperature phase of silver selenide is semiconductor with orthorhombic structure and its carrier concentration is $10^{17}cm^{-3}$ to $10^{19}cm^{-3}$ with high mobility. The electrical band gap of Ag_2Se thin films was determined to be vary from 0.04 eV to 0.08 eV and reported by Damodara das and Karunakaran [15]. From Hall coefficient measurements, Dalven and Gill [13] have reported the band gap of Ag_2Se as 0.07 eV at 0 K and they have calculated the optical band gap of silver selenide as 0.13 eV at low temperatures by absorption studies.

Santosh Kumar and Pradeep [16] have reported that the optical band gap of silver selenide thin film is 1.58 eV at room temperature from the analysis of absorption spectra. From absorption studies, the optical band of silver selenide thin films prepared by chemical methods was found to be 1.3 eV for annealed and unannealed films [18]. The optical band gap of silver selended thin film prepared by SILAR method was determined to be 1.2 eV and reported by Pathan and Lokhande [27]. The optical band gap of electrodeposited Ag_2Se thin film was determined as 1.62 eV and it is reported by Pawar et al [28]. The optical band gap of nanocrystalline silver selenide film is found to be 1.72 eV by Batabyal et al [29].

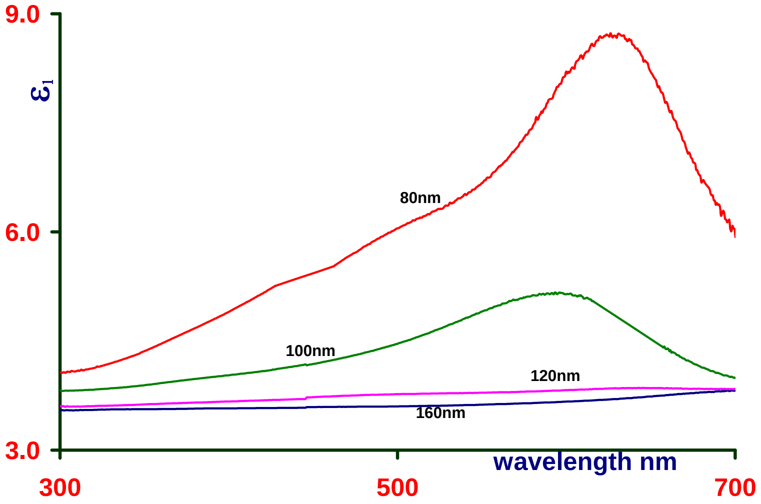

Fig.9. the dependence of real part of dielectric on the incident wavelength

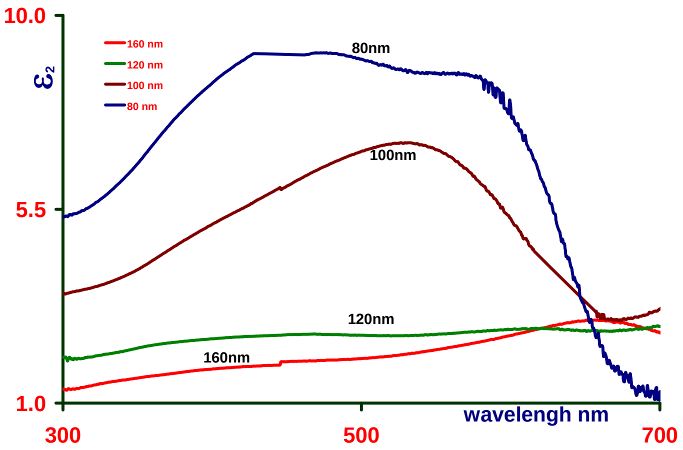

Fig.10. The dependence of imaginary part of dielectric on the incident wavelength

In earlier studies on electrical and optical properties of silver selenide, the band gap of silver selenide has been estimated between 0.04eV and 0.13eV. But recent studies on optical properties of silver selenide show that optical band gap of silver selenide exists between 1.2eV and 1.8eV. In our studies also optical band gap of thermally evaporated silver selenide films have been found to be 1.7eV and independent of thickness of films.

$$\varepsilon_1 = n^2 - k^2;\ \varepsilon_2 = 2nk \qquad (5)$$

From the calculated refractive index and extinction coefficient of the silver selenide, its complex dielectric function can be determine using the relation given in equation (5). The spectral dependence of ε_1 and ε_2 on the incident wavelength between 300 nm and 700 nm is shown in fig (9) and fig (10). The real part of the dielectric function varies from 3.5 to 9 and the imaginary part of the dielectric function varies from 1 to 9. The dielectric functions were found to decrease with the increase in thickness of the films.

3.2 UV-Vis Spectrophotometer studies

Fig (11) is the transmittance spectra of silver selenide thin films of different thicknesses from 80 nm to 160 nm in the wavelength range from 300 nm to 900 nm.

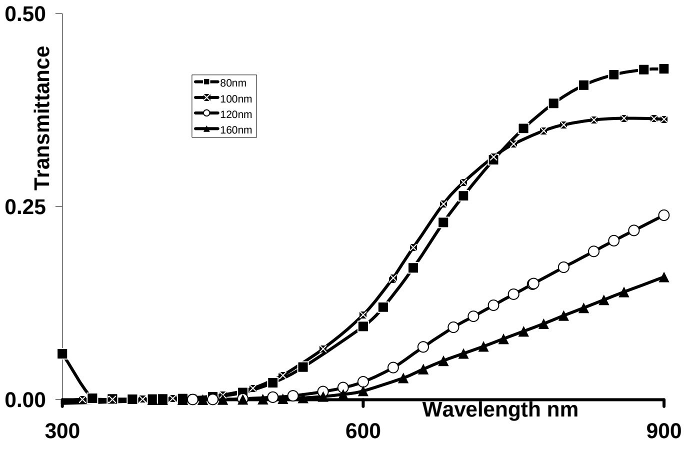

Fig. 11. Transmittance of Silver selenide thin films of thicknesses between 80 nm and 160 nm.

Fig. (11) shows that transmittance of silver selenide thin films increases monotonically with the increase in wavelength; but decreases monotonically with the increase in film thickness. Absorption coefficient of silver selenide thin films has been determined from the recorded transmittance spectra using the relation given in equation (8).

$$T = e^{-\alpha t} \tag{6}$$

where T – Transmittance; t – Thickness of the film (nm) ; α – absorption coefficient (cm^{-1})

The high value of optical absorption coefficient about 10^4 cm^{-1} confirms that silver selenide thin films have direct band gap. Many authors have also observed that silver selenide has direct band gap. A plot of $(\alpha h\nu)^2$ against hν shown in fig (12) is used to determine band gap of silver selenide. The optical band gap of silver selenide thin films have been found to be 1.7 eV and also found to be independent of thickness of the films between 80 nm and 160 nm.

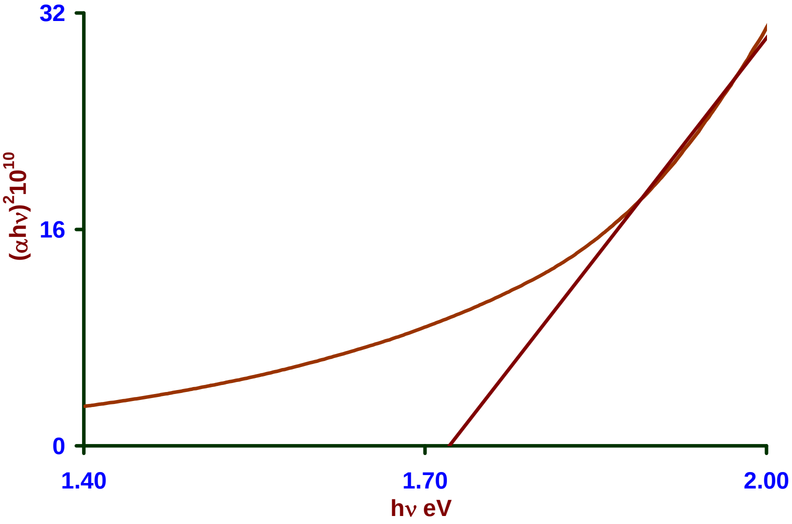

Fig.12. Plot of $(\alpha h\nu)^2$ vs $h\nu$ eV of thin film of 120 nm silver selenide thin films

3.3 Photoluminescence studies

The photoluminescence spectra of silver selenide thin films of thickness between 80nm and 160nm were recorded at room temperature with the excitation wavelength of 484nm and its emission spectra was shown in fig (13).

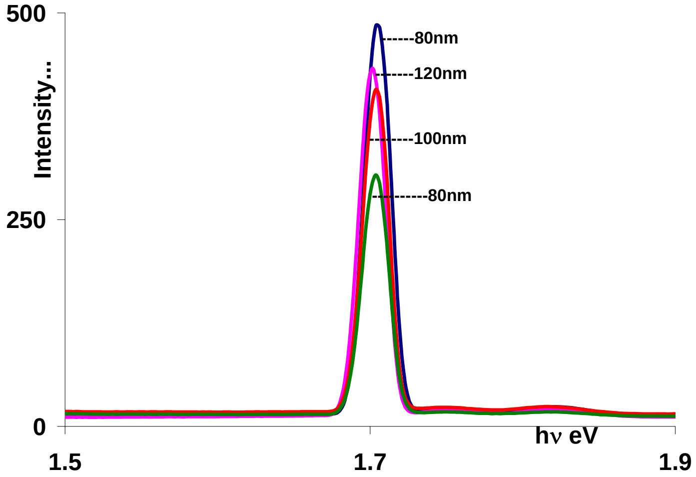

Fig.13. Emission spectra of silver selenide thin films

From the emission spectra of silver selenide it is observed that silver selenide shows a strong emission peak around 1.7eV. The PL intensity of the silver selenide thin films also found to increase with the increase in thickness of the films. This sharp emission peak around 1.7eV may occur due to the band edge emission. If a light particle has energy greater than the band gap energy, then it can be absorbed and thereby raise an electron from the valence band upto the conduction band across the forbidden energy gap. In this photoexcitation, the electron generally has excess energy which it loses before coming to rest at the lowest energy in the conduction band. At this point the electron eventually falls back down to the valence band. When it falls down, the energy lost by the electron will converted into a luminescent photon which is emitted from the material. Thus the energy of the emitted photon is a direct measure of the band gap of the material. The emission peak of silver selenide thin films of thickness between 80nm and 160nm is present around 1.7eV and there is no appreciable shift in the emission peak with respect to their corresponding thickness of the films. The optical band of silver selenide thin films is found to be around 1.7eV from its emission spectra. This value also found to agree with the transmittance analysis on these films.

In earlier studies on electrical and optical properties of silver selenide, the band gap of silver selenide has been estimated between 0.04eV and 0.13eV. But recent studies on optical properties of silver selenide show that optical band gap of silver selenide exists between 1.2eV and 1.8eV. In our studies also optical band gap of thermally evaporated silver selenide films are about 1.7eV and independent of thickness of films.

Optical band gap of silver selenide thin films have been found to be independent of thickness which indicates that there is no charge accumulation at the grain boundaries and the presence of density dislocations are also not dominant. Since the grain size is in the order of thickness of films, the mean free path is about film thickness and hence the quantum size effect does not exist in silver selenide thin films.

4. Conclusions

The prepared silver selenide thin films are polycrystalline with orthorhombic structure confirmed from powder X-ray diffractogram. The optical constants like refractive index, extinction coefficient, absorption coefficient and the dielectric functions of the silver selenide thin films were determined. The refractive index of the silver selenide is determined from the ellipsometric data were found to agree with the reported values of silver selenide. Silver selenide has direct band to band optical transition with high absorption coefficient value of $10^4 cm^{-1}$. The optical band gap of silver selenide is found to be 1.7 eV from the recorded ellipsometric data. The complex dielectric function of the silver selenide is also determined from the ellipsometric measurements. From photoluminescence studies, the optical band gap of silver selenide thin films is found to be around 1.7eV. The optical band gap of silver selenide thin films is about 1.7 eV and is also found to be independent of thickness of films prepared at the rate of 0.2 nm/s.

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