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ELLIPSOMETRIC STUDIES ON SILVER TELLURIDE THIN FILMS

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Silver telluride thin films of thickness between 45 *nm and* 145 *nm were thermally evaporated on well cleaned glass substrates at high vacuum better than* 10^{-5} *mbar. Silver telluride thin films are polycrystalline with monoclinic structure was confirmed by X-ray diffractogram studies. AFM and SEM images of these films are also recorded. The phase ratio and amplitude ratio of these films were recorded in the wavelength range between* 300 *nm and* 700 *nm using spectroscopic ellipsometry and analysed to determine its optical band gap, refractive index, extinction coefficient, and dielectric functions. High absorption coefficient determined from the analysis of recorded spectra indicates the presence of direct band transition. The optical band gap of silver telluride thin films is thickness dependent and proportional to square of reciprocal of thickness. The dependence of optical band gap of silver telluride thin films on film thickness has been explained through quantum size effect.*

Keywords: *ELLIPSOMETRY, THIN FILMS, BAND GAP, OPTICAL CONSTANTS*

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1. INTRODUCTION

Studies on the I-VI semiconducting compounds have received much attention because of their potential applications in semiconductor technology. Silver telluride exhibits interesting behaviour like phase transition and high carrier concentration and high mobility of carriers [1]. Damodaradas and Karunakaran [1], Gnanadurai et al [2] have reported the structural phase transition from monoclinic to cubic structure in silver telluride by DSC analysis. Silver telluride exhibits thermal hysteresis in the structural phase transition [1-3]. Silver telluride undergoes phase transition around 420 K from monoclinic structure to cubic structure during heating [1-5]. Silver telluride in its monoclinic phase exhibits semiconducting property with high electron mobility and high carrier concentration [6]. Damodaradas and Karunakaran [4] have studied the electrical properties of silver telluride thin films and have found that the activation energy varies from 0.4 eV to 0.8 eV as a function of thickness of films. Aliev and Nikulin [7] have studied the thermoelectric power of silver telluride in the low temperature ranges from 2 K to 90 K in order to study the drag effect on carriers in

silver telluride. Gnanadurai et al [8] have studied the seebeck coefficients of silver telluride thin films as a function of thickness and reported that silver telluride exhibits hysteresis in the phase transition. Thermoelectric power of silver telluride increases with increasing temperature from 300 K to 415 K confirming the degeneracy of carriers [9]. Silver telluride exhibits large magnetoresistance from low temperature 2 K to 300 K. Silver telluride exhibits p-type semiconducting behavior [10, 11]. Dalven [12] have calculated the band gap of silver telluride to be 0.064 eV by optical studies. Appel [13] has measured the optical band gap of silver telluride to be 0.7 eV by transmission studies. Prabhune and Fulari [14] have observed that silver telluride has an optical band gap of 1.7 eV at 300 K. Spectroscopic ellipsometry is a best tool for characterizing and understanding the optical properties of semiconducting materials [15-18]. The present work is to study the effect of thickness on the optical band gap, refractive index and extinction coefficient of silver telluride thin films using spectroscopic techniques.

2. EXPERIMENT

Silver telluride thin films of thickness from 45 nm to 145 nm were prepared by thermally evaporating 99.99 % spectroscopic pure silver telluride purchased form 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. The substrates were well cleaned by immersing in hot chromic acid for 45 min, then cleaned with distilled water followed by acetone. Again it is cleaned well with distilled water and dry cotton. Thickness and the deposition rate of the prepared films were monitored by using digital quartz crystal thickness monitor. The X-ray diffractogram of silver telluride thin films of thickness 100 nm was recorded. The XRD were analysed to confirm the structure of silver telluride thin films. Atomic Force Microscopy (AFM) images of the silver telluride thin films were recorded to determine the grain size. The SEM image of the silver telluride thin films was recorded to confirm the smoothness of the surface 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. It is non destructive technique to optically characterize the thin films. The amplitude ratio (ψ) and Phase change (Δ) spectra of silver telluride thin films of thickness form 45 nm to 145 nm were recorded in the wavelength range from 300 nm to 700 nm.

3. RESULTS AND DISCUSSION

X-ray diffractogram of silver telluride thin film of thickness 100 nm is shown in Fig. 1. By comparing the recorded data with pearson's crystal data, the structure of silver telluride thin films is found to exhibit monoclinic structure without any preferred orientations. X-ray diffractrogram of silver telluride thin films of various thicknesses shows the similar pattern and it also confirmed to exhibits monoclinic structure with polycrystalline nature. Prabhune and Fulari [14], Damaodaradas and Karunakaran [1, 4], Gnanadurai et al. [2] have also observed silver telluride thin films prepared over amorphous or polycrystalline substrates are polycrystalline with monoclinic structure. Fig. 2 shows the AFM image of

silver telluride thin film of thickness 100 nm. The grain size of silver telluride is found to be around 24 nm. The SEM images of the silver telluride thin films are also recorded and the image of 100 nm silver telluride thin film is shown in Fig. 3. This image confirms that the silver telluride thin films prepared over glass substrates are smooth and free from voids.

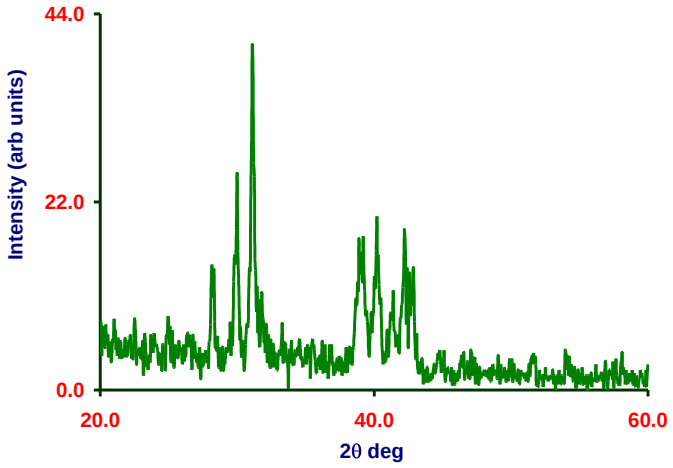

***Fig.* 1** – *XRD of Silver telluride thin film of thickness* 75 *nm*

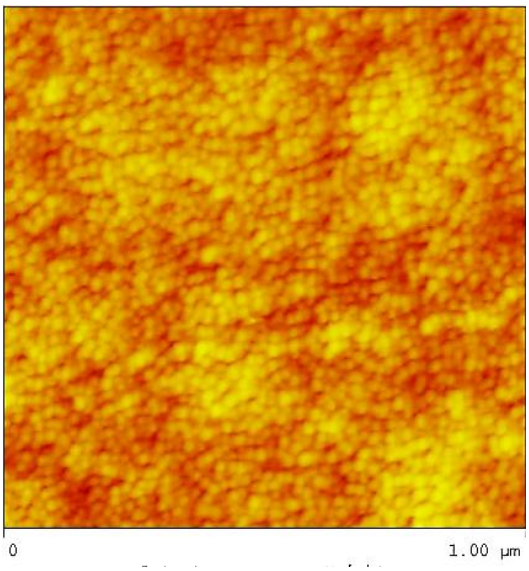

***Fig.* 2** – *AFM image of Silver telluride thin film of thickness* 75 *nm*

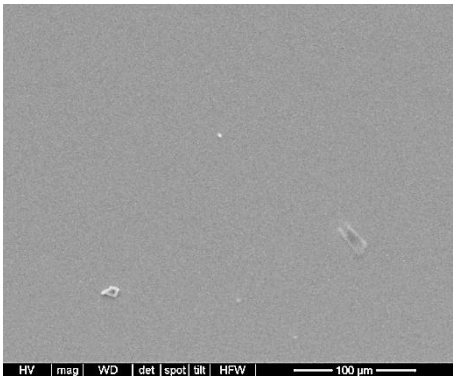

Fig. 3 – *SEM image of Silver telluride thin film of thickness 75 nm*

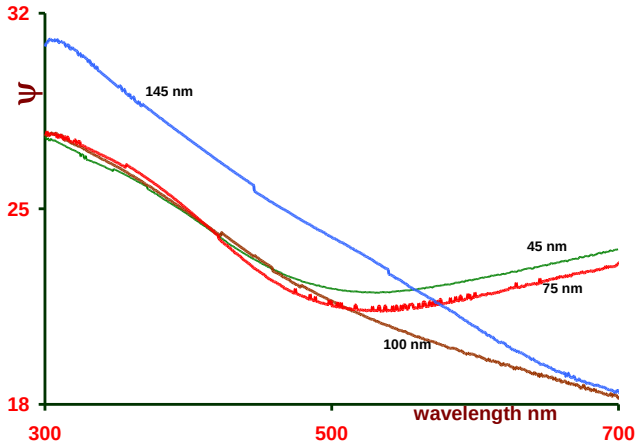

Fig. 4 – *Amplitude ratio spectra of silver telluride thin films*

Main 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 telluride thin films has been determined. In spectroscopic ellipsometer, the refractive index (n), extinction coefficient (k) and dielectric functions can be determined from 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 [19, 20]. Here our material is confirmed to be polycrystalline nature from XRD, AFM, SEM studies. So we determine the optical constants of silver telluride thin films by crystalline and optically active and absorbing relations from recorded ellipsometric data.

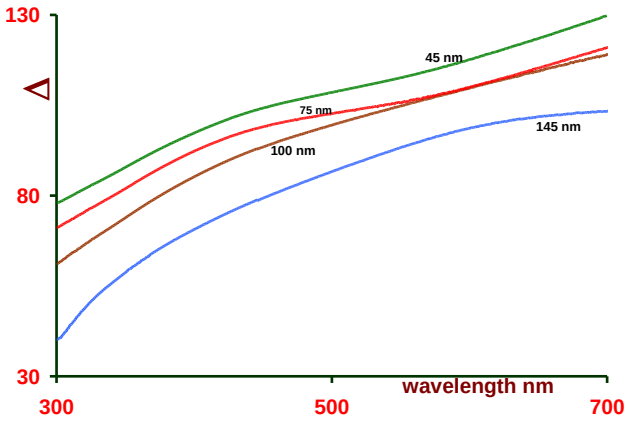

Fig. 5 *– Phase change spectra of silver telluride thin films*

From the value of ψ and Δ, we determine the refractive index of the silver telluride thin films using the relation [20]

$$n^2 = n_0^2 \sin^2\theta\left[1 + \frac{\tan\theta - \cos 2\psi}{(1 + \sin 2\psi \cos\Delta)^2}\right], \qquad (1)$$

here n – refractive index of the material, n_0 – refractive index of the substrate, ψ – amplitude ratio, Δ – phase ratio, θ – incident angle (70°)

The refractive index of the silver telluride is determined to be in the range between 2.0 to 4.0 for the wavelength range between 300 nm and 700 nm. The refractive index is found to increases with increase in wavelength and decreases with the increase in thickness of films as shown in Fig. 6. The 'n' value of silver telluride thin films of thickness from 45 nm to 145 nm, increases monotonically with increase in wavelength from 300 nm to 700 nm. This may occur due to the presence of defects, voids in lower thickness films. From Fig. 6, it is confirmed that silver telluride shows positive dispersion in the wavelength range between 300 nm and 700 nm.

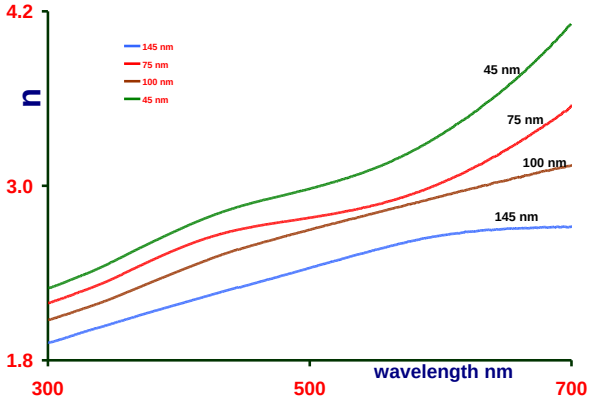

Fig. 6 *– The dependence of refractive index (n) of silver telluride thin films on the incident wavelength*

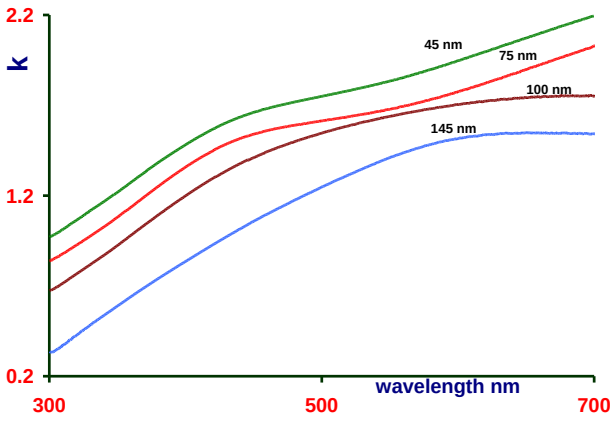

Fig. 7 *– The dependence of extinction coefficient (k) of silver telluride thin films on the incident wavelength*

The extinction coefficient (*k*) of silver telluride 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 coefficient of silver telluride increases monotonically with increase in wavelength from 300 nm to 700 nm and it decreases with increases in thickness of the films. Its values vary from 0.2 to 2.0 depending on the incident wavelength and thickness of the films.

The absorption coefficient of silver telluride is determined from the extinction coefficient of the silver telluride determined from the ψ and Δ spectra. The relation between the extinction coefficient and absorption coefficient of a material [21] is given as

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

This value is found to be in the order of 10^5 cm^{-1}, which confirms the presence of direct band transition in silver telluride [22]. Prabhune and Fulari [14] also determined that silver telluride exist direct band transition from UV-Vis studies. Neyvasagam et al. [15] have determined the optical band gap of tellurium alloy from the extinction coefficient of tellurium alloy determined using spectroscopic ellipsometer [15]. The optical band gap of silver telluride thin films were calculated from the absorption coefficient of silver telluride. By assuming the parabolic bands, the absorption coefficient varies with the energy in the relation [20]

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

where, α is the absorption coefficient (cm^{-1}); $h\nu$ is the energy (eV); E_g is the 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 telluride thin film of thickness of 100 nm film. Similar procedure was carried out to determine the optical band gap of silver telluride thin films of thickness between 45 nm and 145 nm and is found to vary from 1.33 eV to 1.64 eV. Prabhune and Fulari [14] have also reported that the optical band gap of silver telluride as 1.7 eV.

Earlier studies reveal that silver telluride is semiconductor in its monoclinic phase with high carrier concentration and high mobility. Damodara das and Karunakaran [23] have measured electrical band gap of silver telluride thin films and found to be between 0.02 eV and 0.08 eV in Ag_2Te thin films. Dalven and Gill [24]have reported band gap of silver telluride is 0.064 eV by Hall coefficient measurement. By optical studies, Dalven [12] have calculated band gap of silver telluride as 0.064 eV. Appel [13] has measured the optical band gap of Ag_2Te to be 0.7eV by transmission studies. Such low band gap value suggests that silver telluride is intrinsic with high electron and hole concentration. But high Lorentz number, due to low thermal conductivity, indicates that there may be only one type of carrier concentration in silver telluride contributing to its transport properties. Prabhune and Fulari [14] has observed that silver telluride has an optical band gap of 1.7 eV at 300 K. These observations are possible if and only if silver telluride is relatively wide band gap defect semiconductor so that it has high concentration of one type of carriers. Moreover, at low temperature Te excess silver telluride is p-type semiconductor with high resistivity. With the increase in temperature, it turns into n-type above 200 K. Undoped stoichiometric Ag_2Te is n-type.

The optical band gap of silver telluride in the present work is between 1.33 eV to 1.64 eV. Our studies also confirm that silver telluride is relatively wide band gap defect semiconductor with defects acting as donors. The high absorption near band edge is due to the presence of more defects. It also found that the optical band gap of silver telluride thin films were dependent on the thickness of the films as shown in Fig. 9.

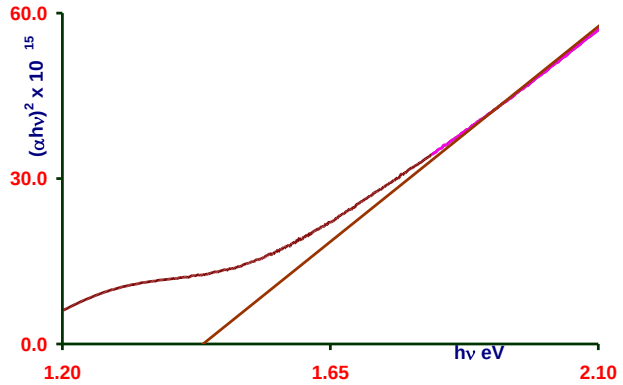

Fig. 8 – *Plot of* $(\alpha h\nu)^2$ *vs* $h\nu$ *eV of thin film of* 100 *nm silver Telluride thin film*

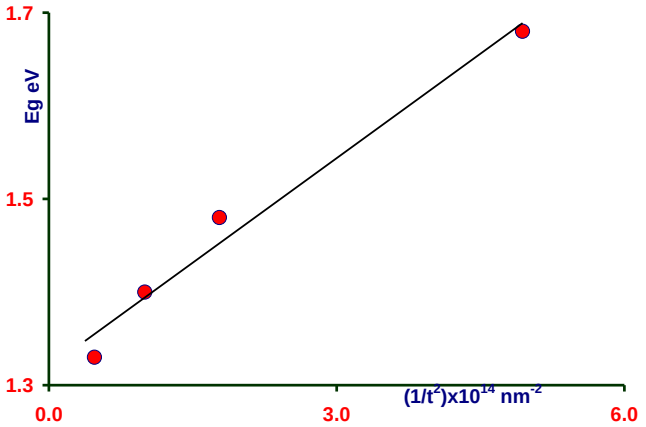

Fig. 9 *– Dependence of optical band gap (eV) on the thickness of the films*

Generally band gap is finger print of a material. But in thin films, it has been observed that band gap varies with film thickness because of changes in barrier height at grain boundaries with thickness, due to high density of dislocations and/or quantum size effect. Slater [25] proposed that charge accumulation at grain boundaries influences energy barrier associated with grain boundaries and affect barrier height. According to him, the increased barrier height is

$$E = E_0 + c(\chi - fD)^2 \qquad (5)$$

where, E_0 is original band width, χ is barrier width, D is grain size (nm), c and f are constants that depend on carrier concentration and amount of charge accumulation on boundaries. Since in thin films, the average grain size is proportional to thickness of films it is expected that the band gap of thin semiconducting films will increase quadratically if charges are accumulated at grain boundaries. The decrease in the band gap with the increase in film thickness in our study indicates there is no charge accumulation at grain boundaries in silver telluride thin films.

When dislocation density is very high, it causes dilation in spacing of atoms that influences band gap of materials. It has been suggested that when dislocation density is very high there is increase in band gap with the increase in film thickness, as dislocation density increases with film thickness. As the band gap of silver telluride films decrease with the increase in film thickness, it is obvious that dislocation density is not high in silver telluride thin films, which is also confirmed by narrow peaks of diffraction in X-ray diffractogram.

As in the present work, the band gap varies linearly with the reciprocal of square of thickness ($1/t^2$), the quantum size effect is the possible cause for the change in band gap in silver telluride thin films. Sandomirskii [26] was the first to propose that when thickness of thin film is of the order of de Broglie wavelength of conduction electrons and much less than the mean free path of charge carriers, material exhibits quantum size effect. As electrons in silver telluride have high mobility, it has high mean free path. Hence silver telluride is an ideal material to observe quantum size effect.

Because of quantum size effect, the energy component along thickness is quantized and is given by

$$E_t = \frac{\hbar^2 \pi^2}{2m} \frac{1}{t^2} n^2; n = 1, 2, 3, \ldots \quad (6)$$

where, m is the mass of electron in Ag_2Te (g); t is the film thickness (nm); E_t is the energy component along thickness (eV)

The lowest states of valence band edge and conduction band edge get shifted to lowest non-zero state leading to the increase in band gap as a function of the reciprocal of square of thickness. As shown in Fig. 9 the band gap of silver telluride thin film varies as $1/t^2$ exhibiting quantum size effect.

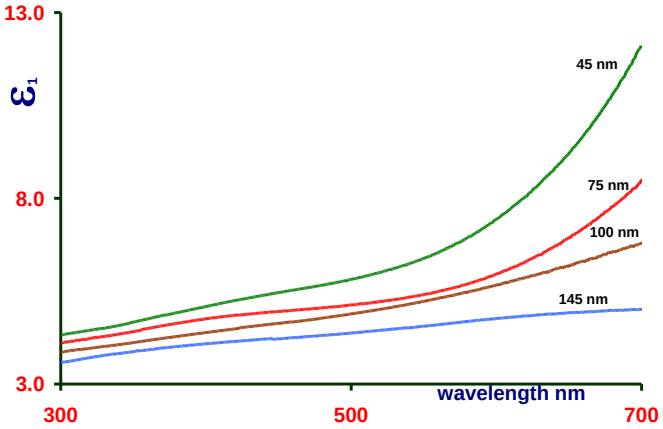

Fig. 10 – *The dependence of real part of dielectric function on the incident wavelength*

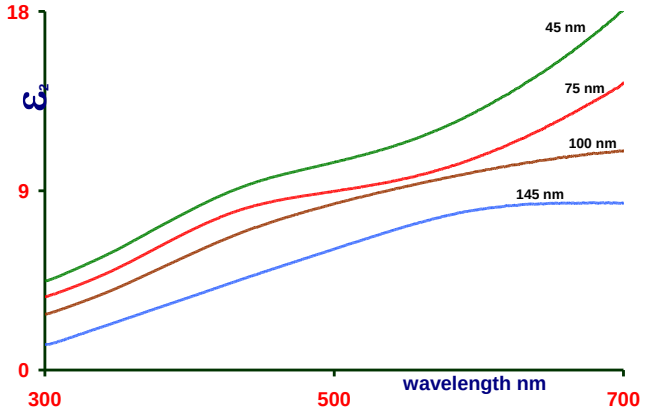

Fig. 11 – *The dependence of imaginary part of dielectric function on the incident wavelength*

The low absorbing material like silver telluride has the complex dielectric functions in the form [21]

$$\varepsilon_1 = n^2 - k^2;\ \varepsilon_2 = 2nk, \tag{7}$$

where n– refractive index; k– extinction coefficient of the material.

The real part of dielectric function can be determined from $n^2 - k^2$ and imaginary part of dielectric function can be deduced from $2nk$. The corresponding spectra of ε_1 and ε_2 as a function of incident wavelength shown in Fig. 10 and Fig. 11 respectively. From these figures, the real and imaginary part of the dielectric function is found to decreases with increase in thickness and increases with increase in wavelength.

4. CONCLUSION

Silver telluride thin films were prepared by thermal evaporation method and it is confirmed to exhibit polycrystalline nature with monoclinic structure. The high absorption coefficient value of silver telluride thin films of order $10^4 cm^{-1}$ confirms silver telluride exhibits direct transition. From spectroscopic ellipsometry studies, the refractive index of the silver telluride thin films are in the range between 2.0 to 4.0 with respect to incident wavelength and it shows positive dispersion in the wavelength range between 300 nm and 700 nm. Extinction coefficient and complex dielectric functions are also determined from the recorded data. The optical band gap of silver telluride thin films varies from 1.33 eV to 1.64 eV with decreasing thickness from 145 nm to 45 nm. In silver telluride thin films, band gap varies as a function of the reciprocal of square of film thickness is linear and exhibiting quantum size effect. The estimated effective mass of electrons in silver telluride is 0.002 m_0.

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