Journal of Ovonic Research Vol. 7, No. 1, January - February 2011, p. 21 - 27

EFFECT OF THICKNESS ON THE OPTICAL BAND GAP OF SILVER TELLURIDE THIN FILMS

M. PANDIARAMAN, N. SOUNDARARAJAN*, C.VIJAYAN
Department of Microprocessor and computer, School of Physics, Madurai Kamaraj University, Madurai-625 021, India

Silver telluride thin films of thickness between 16 nm and 150 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, confirmed by x-ray diffractogram. Transmittance spectra of silver telluride thin films were recorded in the wavelength range between 300 nm and 900 nm. High absorption coefficient of silver telluride thin films determined from the analysis of transmittance spectra indicates the presence of direct band gap. The band gap of silver telluride thin films is also determined from transmittance spectra. The optical band gap of silver telluride thin films is thickness dependent; it is proportional to the 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.

(Received January 31, 2011; accepted February 23, 2011)

Keywords: Semiconductor, thin films, quantum size, band gap, thickness, effective mass

1. Introduction

Silver telluride (Ag_2Te) is non-magnetic, self doped, degenerate semiconductor [1]. The increased attention on I-VI semiconducting compounds is due to their potential applications in semiconductor technology [2-4]. Silver telluride undergoes structural phase transition around 420 K from monoclinic structure to cubic structure with hysteresis [3,4]. In monoclinic structure, silver telluride exhibits semiconducting behaviour with high electron mobility and low lattice thermal conductivity [5,6]. Studies show that silver telluride with excess tellurium is extrinsic p-type semiconductor at low temperature and becomes n-type at higher temperatures [7,8]. Aliev and Nikulin [9] have measured thermoelectric power of silver telluride in the temperature range from 2 K to 90 K in order to study the phonon drag effect by carriers in Ag_2Te. Thermoelectric power of silver telluride increases linearly with the increase in temperature from 300 K to 415 K confirming degeneracy of carriers [9,10]. Chuprakov and Dahmen [11] have observed large magnetoresistance in silver telluride thin films in low temperature, from 2 K to 300 K. Xu et al [12] have also reported large magnetoresistive effect in silver chalcogenides which extended the GMR/CMR family to non-magnetic compounds. Optical memory effects of semiconducting tellurium alloy films have been investigated and utilized for various applications. Interesting enhanced Raman scattering phenomenon has been observed during the investigation of Raman spectra of silver telluride [5]. The presence of defects in thin films gives rise to change in optical and electrical properties of material [13]. The study of optical absorption spectra of solids provide essential information about band structure and energy gap of non-crystalline and crystalline materials [14]. Earlier, Appel [15] studied optical absorption of silver telluride and determined optical band gap as 0.67 eV at room temperature. Richard Dalven [16] has also reported the optical band gap of silver telluride as 0.64 eV at 300 K. Recently, Prabhune and Fulari [17] reported the optical band

*Corresponding Author: thinfilmlab.mkuphysics@yahoo.com

gap of silver telluride thin film prepared by chemical method is 1.7 eV. The differences in the reported band gap of silver telluride is instrumental for the present work. The present work is carried out to determine the optical band gap of thermally evaporated silver telluride in thin film form and also to study the effect of thickness on the optical band gap of silver telluride.

2. Experimental

Silver telluride (Ag_2Te) thin films were prepared by thermal evaporation technique from Ag_2Te powder of 99.99% purity purchased from M/s Sigma-Aldrich. The Silver telluride thin films of thickness between 16 nm and 150 nm were prepared on well cleaned glass substrates of dimension (0.01 m X 0.03 m) at the deposition rate of 0.2 nm/sec under high vacuum better than 10^{-5} mbar. The glass slides were well cleaned by rinsing in hot chromic acid for about forty five minutes then rinsed with distilled water and cleaned with acetone and then again with distilled water. The XRD of these films were recorded using powder X-ray diffractometer to verify structure of prepared Ag_2Te thin films. The atomic force microscopic (AFM) images were recorded to confirm polycrystallinity of prepared Ag_2Te thin films. Transmittance of Ag_2Te films was recorded from 300 nm to 900 nm using UV-VIS double beam spectrophotometer. These experimental measurements were analyzed to determine the optical band gap of silver telluride thin films and the effect of thickness on the optical band gap of silver telluride.

3. Results and discussion

Fig (1) is X-ray diffractogram of Ag_2Te thin films of 100 nm thickness. It reveals that silver telluride thin films are polycrystalline and on comparing XRD data with Pearson's crystal data, the structure of silver telluride is monoclinic. Similar diffraction patterns have been observed for other prepared Ag_2Te thin films confirming that silver telluride thin films are polycrystalline and have monoclinic structure without any preferred orientation. Prabhune and Fulari [17], Damodara das and Karunakaran [18], Gnandurai et al [2] have also observed that silver telluride thin films prepared over amorphous or polycrystalline substrates are polycrystalline with monoclinic structure. But Richard Dalven and Richard Gill [7] have observed that silver telluride thin films prepared over crystalline substrate exhibits a few percent of hexagonal "empressite" structure. Fig (2), the AFM picture of silver telluride thin film of thickness 100 nm confirms the polycrystalline nature of Ag_2Te thin films.

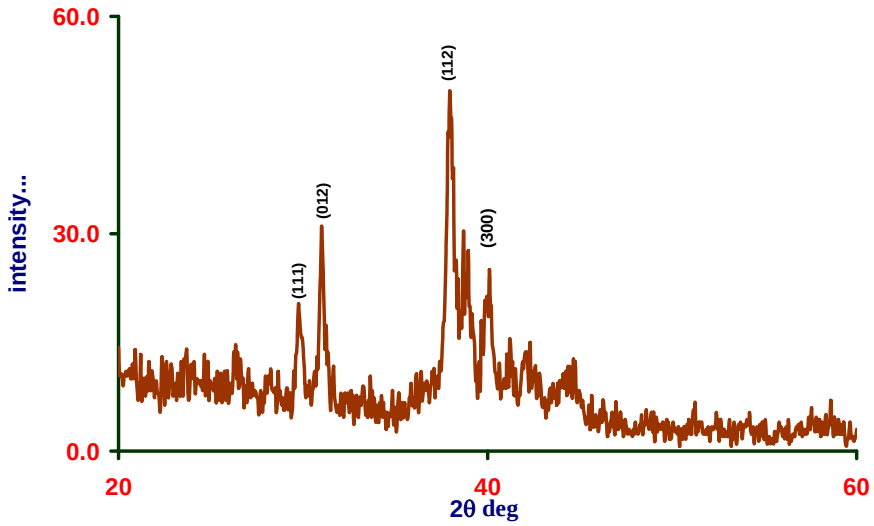

FIG.1. Powder X-ray diffractogram of Ag_2Te thin film of thickness 100 nm

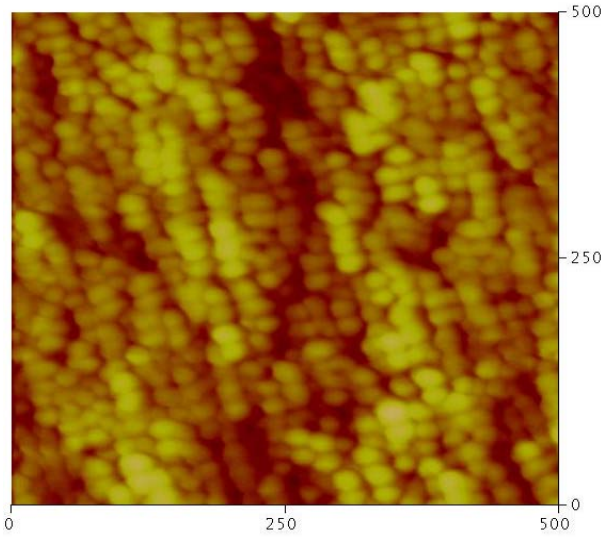

FIG. 2. AFM image of Ag_2Te thin film of thickness 100 nm

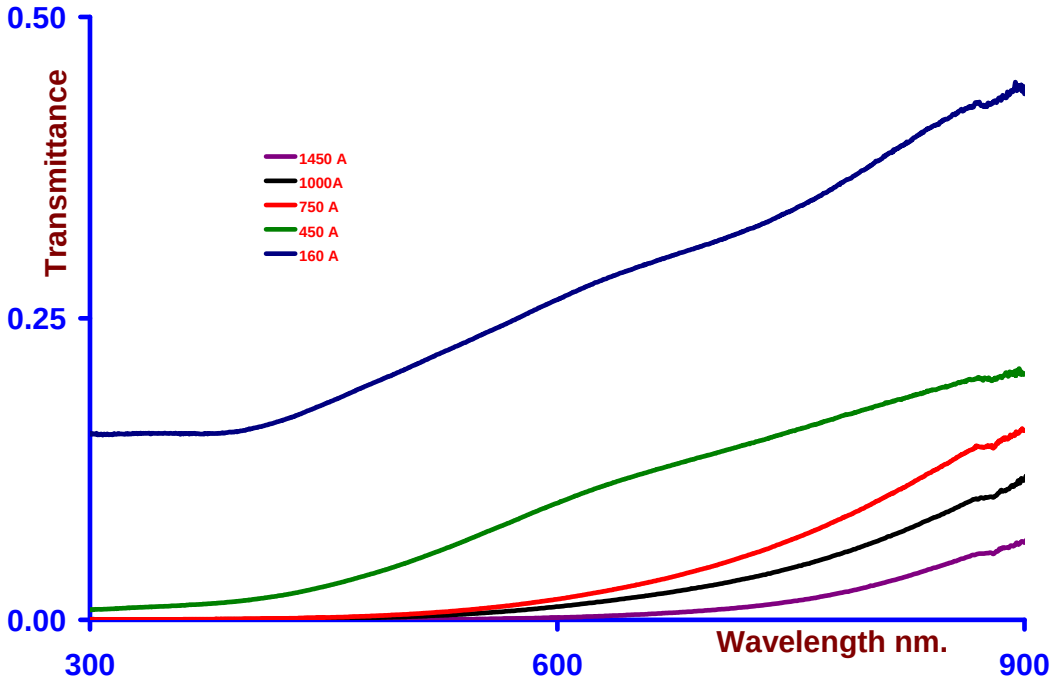

Fig. 3. Transmittance spectra of Ag_2Te thin films of thickness from 16 nm to 145 nm

Fig (3) is the transmittance spectra of silver telluride thin films of different thicknesses from 16 nm to 145 nm in the wavelength range from 300 nm to 900 nm. It shows that transmittance of silver telluride thin films increases monotonically with the increase in wavelength; but decreases monotonically with the increase in film thickness. Absorption coefficient of silver telluride thin films has been calculated using transmittance spectra. The high value of optical absorption coefficient about 10^4 cm^{-1} confirms that silver telluride has direct band gap. Prabhune and Fulari [17] have also observed that silver telluride has direct band gap.

Depending on the band structure of material, direct or indirect optical transitions are possible. Assuming parabolic bands, the absorption coefficient varies with the energy of radiation [19] as

$$\alpha h\nu = A(h\nu - E_g)^n \qquad (1)$$

where
α – absorption coefficient (cm^{-1})
$h\nu$ – energy (eV)
E_g - band gap (eV)
and 'n' takes 1/2 or 2 depending on the kind of transition. 'n' is equal to 1/2 if the transition is direct and allowed. It is 2 if the transition is indirect and allowed. From a plot of Ln (α) against $h\nu$, the region in which the absorption is saturated due to band transition is first identified. Then the wavelength range close to the onset of saturation is chosen for curve fitting. Since, only in this region, the parabolic band approximation holds. A plot of $(\alpha h\nu)^2$ against $h\nu$ shown in fig (4) is used to determine band gap of silver telluride. It is found that the band gap of silver telluride thin films is thickness dependent. It decreases with the increase in film thickness. Silver telluride thin films are polycrystalline. In thin films the particle size of crystallites is of the order of film thickness and proportional to thickness of films. Since grain size influences the energy level of electrons, the band gap will be dependent on thickness of films. Fig (5) is the plot of band gap of silver telluride thin films as a function of reciprocal of square of thickness. It is linear.

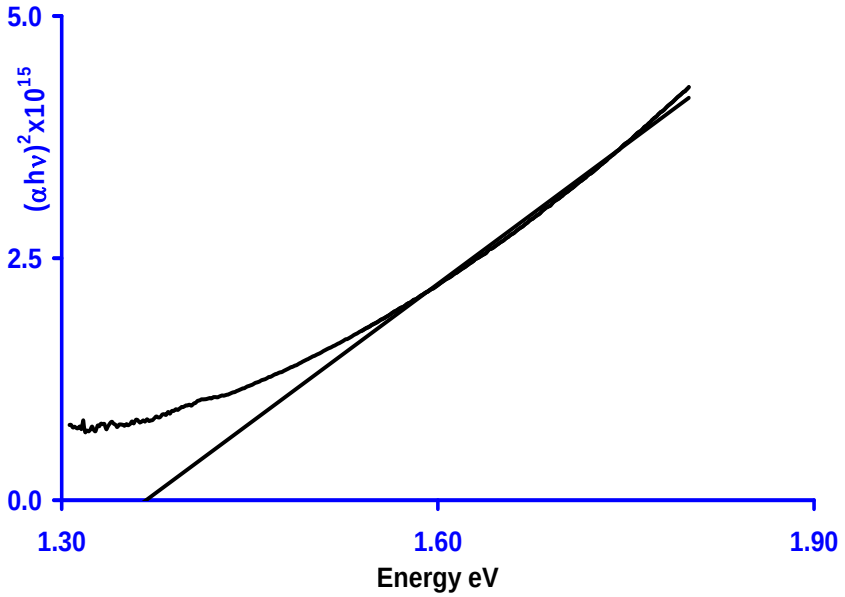

Fig.4. $(\alpha h\nu)^2$ Vs $h\nu$ plot of Ag_2Te thin film of thickness 100nm.

Earlier studies reveal that silver telluride is semiconductor in its monoclinic phase with high carrier concentration and high mobility. Damodara das and Karunakaran [20] 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 [7] have reported band gap of silver telluride is 0.064 eV by Hall coefficient measurement. By optical studies, Dalven [16] has calculated band gap of silver telluride as 0.064 eV. Appel [15] have measured the optical band gap of Ag_2Te to be 0.7 eV by transmission studies. Prabhune and Fulari [17] has observed that silver telluride has an optical band gap of 1.7 eV at 300 K. The optical band gap of silver telluride in the present work is

between 1.34 eV to 1.72 eV. These values are in agreement with the reported value of Prabhune and Fulari [17].

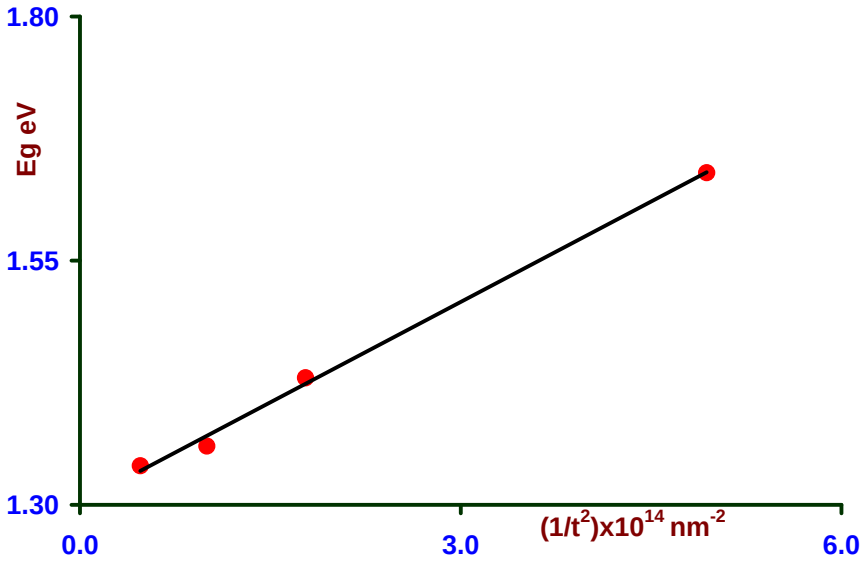

Fig.5. Optical band gap of Ag_2Te thin films as a function of $1/t^2$.

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 [21] 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

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

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 [22] 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

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

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 figure (5) the band gap of silver telluride thin film varies as $1/t^2$ exhibiting quantum size effect. From the slope, effective mass of electrons is estimated which is less than the rest mass of electrons. It is $0.002m_o$. This value agrees well with observations of Damodara das and Karunakaran [20].

4. Conclusion

Silver telluride thin films have been polycrystalline with monoclinic structure. The films have no preferred orientation. The high absorption coefficient of silver telluride thin films of about $10^4 cm^{-1}$ confirms that silver telluride has direct band gap. Since in thin films, the grain size is proportional to the thickness of films, the band gap will be dependent on the thickness of films. In silver telluride thin films, band gap varies as the reciprocal of square of film thickness exhibiting quantum size effect. The estimated effective mass of electrons in silver telluride is 0.002 m_o.

Acknowledgement

The authors acknowledge UGC for their financial support through UGC-DRS to install thin film preparation unit and UV-Vis spectrophotometer; also thankful to Dr.V.Ganesan, UGC-Consortium for scientific research, Indore for helping us to record the AFM on our samples. The author Mr.M.Pandiaraman is thankful to UGC for providing the UGC-RGNSR Fellowship.

References

[1] L. Jiang and E.R. Nowak, Fluctuations and Noise Letters, **4**, L465 (2004)
[2] M. Pandiaraman, N.Soundararajan, C.Vijayan, C.Kumar and R.Ganesan, Journal of Ovonic Research, **6(6)**, 285 (2010)
[3] M. Ohto and K. Tanaka J. Vac. Sci. Technol. B, **14**, 3452 (1996)
[4] Ruizhi Chen, Dongsheng Xu, Guolin Guo and Linlin Gui, J.Mater. Chem., **2**, 2435 (2002)
[5] Aimiao Qin, Yeuping Fang, Pingfang Tao, Jianyong Zhang and Chengayong Su, Inorganic Chem., 46, 7403 (2007)
[6] Ruizhi Chen, Dongsheng Xu, Guolin Guo, Youqi Tang, Chemical Physics Letters **377,** 205 (2003)
[7] R. Dalven and R. Gill, Phys. Rev. **143,** 666 (1966)
[8] C. Wood, V. Harrap, and W.M. Kane, Phys. Rev., **121**, 978 (1961)
[9] S.A. Aliev and E.I. Nikulin, Inorg. Mater., **13**, 607 (1977)
[10] V. Damodara das and D. Karunakaran, Physical Review **B, 30**, 2036 (1984)
[11] I.S. Chuprakov and K.H. Dahmen, Appl.Phys Lett., **72**, 2165 (1998)
[12] R. Xu, A. Husmann, T.F. Rosenbaum, M.L. Saboungi, J.E.Enderby and P.B.Littlewood, Nature (London), **390**, 57 (1997)
[13] A. Abu EL-Fadl, M. M.Hafiz, M.M. Wakaad, A.S. Aashour, Radiation Physics and Chemistry, **76,** 61 (2007).

[14] G.A. Amin, S.M. El-Sayed, H.M. Saad, F.M. Hafez, M. Abd-El- Rahman, Radiation measurements, **42**, 400 (2007)
[15] J. Appel, Z.Naturforsch, **10a**, 530 (1955)
[16] Richard Dalven, Physical Review letters, **16**, 311 (1966)
[17] V.B. Prabhune and V.J .Fulari, Optics Communication, **282**, 2118 (2009)
[18] V. Damodara das and D. Karunakaran, J.Appl Phys., **66**, 1822 (1989)
[19] A. Goswami, Thin Film Fundamentals (New Age International (P) Ltd., (1996)) P.No. 421
[20] V. Damodara das and D. Karunakaran, J.Appl Phys., **54**, 5252 (1983)
[21] J.C. Slater, Phys. Rev., **103**, 1631 (1956)
[22] V.B. Sandomirskii, Sov.Phys**.** JTEP, **25**, 101 (1967)