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Effect of Thallium Ratio on The Properties of Some Chalcogenide Thin Films

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Abstract:- **The chalcogenide systems $As_{25}Se_{75-x}Tl_x$ (x= 8,15,22,29 and 33%) were prepared as thin films with the same thickness (250 nm) by using melt quench technique, and sedimentation was made by electron beam evaporation technique. It is found that, the residual dielectric constant ε_∞, effective mass $\frac{N}{m^*}$, and the free carrier concentration N increase with increasing thallium ratio. In addition, the density *d* increased with decreasing the heat of atomization, and many parameters affected by changing of thallium ratio will be examined.**

Key words: thallium ratio, Chalcogenide thin films, residual dielectric constant, effective mass, free carrier concentration.

I. INTRODUCTION

It is reported that chalcogenide glasses offer transparency in the wavelength region from 3-5 to 8-14 μm [1-3]. Their high refractive index and low optical losses permit their development as infrared optical materials and optical fibers within the range from 2 to 12 μm [4-13]. Many models have been proposed to explain the compositional dependence of various physical properties of chalcogenide network glasses [14-19]. In these models, the properties of the chalcogenides can be discussed in terms of the average coordination number r , which is indiscriminate of the species of valence bond. In the constrain model, by equating the number of operative constraints to the number of degree of freedom, it was found that the value of coordination number r of the most stable glass is shown to be $\approx$ 2.4. The region of glass formation of As-Se-Tl is considered wide [20,21]. The effect of thallium ratio on the optical properties of thin films of AsSeTl and GeSeTl has been studied [22, 23]. The electrical properties of the As25 Se75-x Tlx system are studied too [24-29].

It is intended to study the effect of thallium content on the optical properties and other parameters of As25 Se75-x Tlx (x= 8,15,22,29 and 33%) thin films evaporated by electron beam.

II. EXPERIMENTAL

High purity (99.999) of As, Se and Tl were used for preparing bulk amorphous samples of the system As25 Se75-x Tlx (x = 8, 15, 22, 29 and 33%) . Appropriate mole percentages of the three elements were mixed and enclosed in 10 mm diameter silica tube sealed under vacuum of the order of 10-5 torr and then heated in an oven. The temperature was raised to the maximum required value in three steps, first, the temperature was raised up to 300 oC at a rate of 3-4 oC/min and then kept at this temperature for 3 hr. Secondly, and the temperature was then raised up to 600 oC at the same rate and kept at this temperature for 12 hr. Finally, the temperature was raised up to 950 oC, where alloying was performed at this temperature for 24 hrs. Thin films of the prepared compositions were deposited at room temperature of thickness 250 nm by electron-beam evaporation at 10-5 torr using an Edwards high – vacuum coating unit model E306A. The rate of deposition was $\sim$ 1-2 nm/s. Ultrasonicaly cleaned glass was used as a substrate. The film thickness was controlled by means of an Edwards TM200Maxtek high-vacuum film thickness monitor. A Jasco model V-

570 (UV-visible-NIR) double beam spectrophotometer was employed to record the transmission T and reflection R spectra over the wavelength range from 200 to 2000 nm at normal incidence. The microstructure analysis was carried out using x-ray diffractometer type Philips model PW 1710 showed that all the films under test revealed amorphous structure where there were no peaks representing crystallites.

III. RESULTS AND DISCUSSIONS

The absorption coefficient $\sim(\mu)$ of the optical absorption near the band edge shows an exponential dependence on photon energy $h\mu$ and obeys Urbach's empirical formula [30]

$$\sim(\mu) = \sim_o \exp(\hbar\mu / E_u) \qquad (1)$$

Where $\sim_o$ is constant and E_u the Urbach energy which represents the width of the band tails of the localized states in the band gap, $\sim(\mu)$ can be determined directly from the spectrophotometer readings using the formula [31]

$$\sim = \frac{2.303}{d}\log_{10}\left(\frac{1-R}{T}\right) \qquad (2)$$

where d is the film thickness, T is the transmittance and R is the reflectance of the film.
The optical energy gap is estimated from the optical measurements by analyzing the optical data with the expression for the optical absorbance, and the photon energy, $h\neg$ using the following equation:

$$(\sim h\neg) = A(h\neg - E_g)^n \qquad (3)$$

Where $\sim$ represents the absorption coefficient, h is the Plank's constant, A is a constant and E_g is the optical energy band gap, which can be obtained by extrapolating the linear portion of the plots of $(\sim h\neg)^{1/n}$ versus $h\neg$ to $\sim$ = 0. The exponent n can be assumed to have values of 1/2 , 3/2, 2 and 3, depending on the nature of electronic transition responsible for the absorption: the value 1/2 for allowed indirect transition, 3/2 for forbidden direct transition, 2 for allowed direct transition and 3 for forbidden indirect transition [31].

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Using Drude's theory of the dielectrics, the real part $(£_1)$ of the complex dielectric function £ can be written as [32]

$$£_1 = n^2 - k^2 = £_\infty - \frac{e^2}{4®^2 £_0 c^2}\frac{N}{m^*}a^2 \qquad (5)$$

where $£_\infty$ is the residual dielectric constant, c is the light velocity, N and m^* are the free carrier concentration and its effective mass respectively e is the electronic charge.

$$\mu_p = \left(\frac{e^2 N}{£_o £_\infty m^*}\right)^{1/2} \qquad (7)$$

is the plasma resonance frequency for one kind of free carriers, ε_∞ the high frequency dielectric constant, c the velocity of light, $£_o$ the free space dielectric constant, $\frac{N}{m^*}$ the ratio of free carrier concentration N_c to the free carrier concentration effective mass m^*.
The variations of the transmittance T and reflectance R with incident wavelength are measured, from which the absorbance is calculated. The plots of $(\sim h\neg)^{1/2}$ versus $(h\neg)$ for different values of x for As_{25} Se_{75-x} Tl_x (x = 8, 15, 22, 29 and 33%) thin films are shown in Fig.1 from which the optical energy gaps are estimated and recorded in table 1. The optical energy gap found to decrease from 1.5 eV down to 1.3 eV with increasing the ratio of thallium from 8% up to 33%. It is cleared that the optical gap is strongly

dependent on the fractional concentration of atoms where E_{op} decrease with increasing Tl content which could be due to the effect of compositional disorder [33]. Besides, decreasing the values of E_{op} with increasing thallium content is due to more creation of localized states in the bang gap. Also, increasing Tl content is associated with an increase of the extent of the band tailing, and therefore the optical gap decrease. Using equation (1), and plotting the relation $Ln(\sim)$ versus $(h\neg)$, it was found straight lines as shown in Fig.2, where the values of the width of the band tails of the localized states in the band gap E_u are calculated and recorded in table 1. The width of the band tails of the localized states in the band gap E_u found to increase with increasing thallium content revealing that the localized states increase, therefore the optical gap decrease.

The coordination number r can be calculated using the equation [17-18, 34];

$$r = xCN(As) + yCN(Se) + zCN(Tl) \qquad (8)$$

Where x, y, z are the ratios of As, Se and Tl in the compositions under study. Also, the heat of atomization H_s can be calculated using the equation [35]:

$$H_s = xH_s^{As} + yH_s^{Se}zH_s^{Tl} \qquad (9)$$

Since, H_s^{As}, H_s^{Se} and H_s^{Tl} are the heat of atomization of As, Se and Tl elements.

The coordination number r, the density d, the parameter which determine the deviation from stiochiomtry Z and the average number of bonds per atom N_{av} are calculated and recorded in table 1. It is noticed that the composition of 8% thallium is the most stable composition. It is seen that the values of *d, r,* N_{av} increase with increasing Tl content which result from enriching with Tl. On the other side, E_{op} and H_s decreases with increasing the coordination number r which can be explained as follows, the bond strength of the three bonds (As-As), (Se-Se) and (Tl-Tl) are 43.4, 44 and 15.4 K cal. mol^{-1} respectively, by addition of Tl to As – Se system, the average bond strength of the compound decrease and hence E_{op} will decrease [36], also the properties of semiconductors such as the energy gap which essentially reflect the bond strength must be directly related to the heats of atomization. Further, there exists a linear correlation between the energy gap and the average heat of atomization [37].

It is noticed from table 1, except of the film of 8% thallium, all values of Z are less than unity of such glass under test indicating chalcogen-poor materials, meanwhile, increasing Tl content is accompanied with decreasing the values of Z.

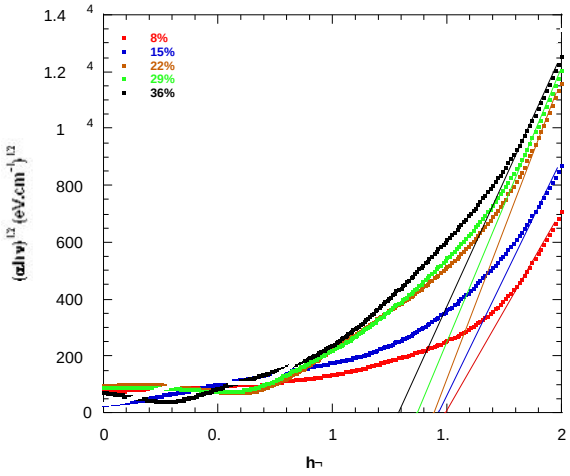

Figure1 Plots of ($\alpha h\nu)^{1/2}$ **vs.** h ν for as-deposited $As_{25}Se_{75-x}Tl_x$ thin films of different ratio of thallium.

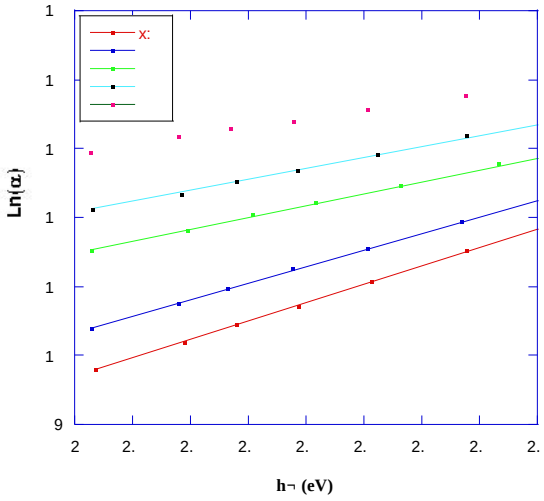

Figure 2 Plots of Ln (α) vs. photon energy for as-prepared $As_2Se_{75-}Tl_x$ thin films of different ratio of thallium.

To determine the ratio $\frac{N}{m^*}$ and the residual dielectric constant $£_\infty$, the variation of the real part of the dielectric constant $£'$ with a^2 are drawn, and found to be straight lines verifying equation (5) as shown in Fig. 3, from their slopes and intercepts , values of $\frac{N}{m^*}$ and $£_\infty$ can be determined.

Table 1 Values of optical and other parameters of amorphous As_{25} Se_{75-x} Tl_x films.

x%	d	r	Z	H_S	E_{op}	E_u	$\frac{N}{m^*}$ $x10^{46}$	μ_p $x10^{11}$
8	**5.053**	**2.49**	**1.17**	**39.31**	**1.50**	**0.38**	**3.15**	**1.07**
15	**5.604**	**2.70**	**0.80**	**37.31**	**1.47**	**0.42**	**4.98**	**1.12**
22	**6.154**	**2.91**	**0.57**	**35.31**	**1.45**	**0.58**	**5.65**	**1.19**
29	**6.704**	**3.12**	**0.42**	**33.31**	**1.37**	**0.63**	**6.92**	**1.20**
33	**7.019**	**3.24**	**0.35**	**32.16**	**1.30**	**0.80**	**7.67**	**1.21**

To determine the ratio $\frac{N}{m^*}$ and the residual dielectric constant ε_∞, the variation of the real part of the dielectric constant ε' with a^2 are drawn, and found to be straight lines verifying equation (5) as shown in figure (3), from their slopes and intercepts values of $\frac{N}{m^*}$ and ε_∞ can be determined and recorded in table 1. It is found that both values of ε_∞ and $\frac{N}{m^*}$ increase with increasing thallium content which can be attributed to the relatively higher concentration. Furthermore, the plasma frequency μ_p increase with increasing thallium content which may be owed to the increase of the carrier concentration N when taking in consideration that the effective mass m^* is constant.

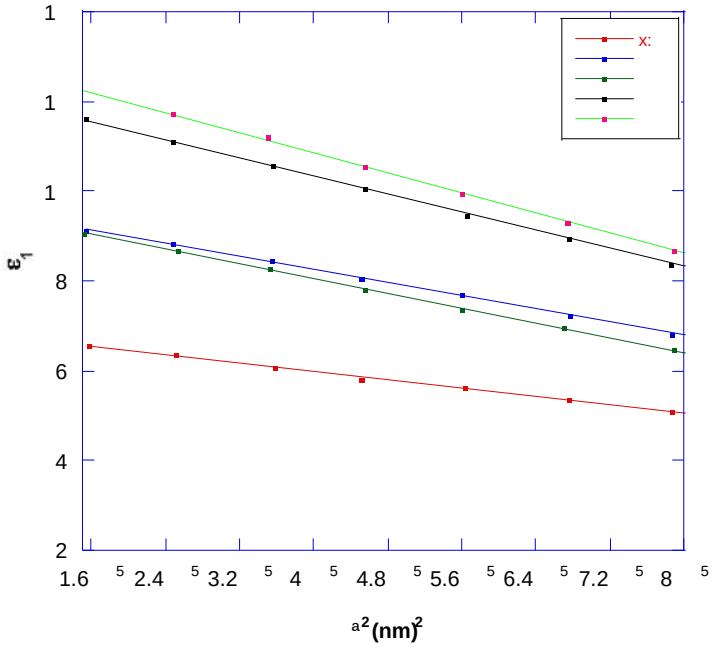

Figure 3 Plots of ε_1 **vs.** a^2 for as-prepared $As_2Se_{75-x}Tl_x$ thin films of different contents of thallium

IV. CONCLUSION

It can be concluded that:

(1)- The system $As_{25}Se_{75-x}Tl_x$ is chalcogen-poor for the considered ratio (x= 15, 22, 29 and 33%).

(2)- Optical gap E_{op} decrease with increasing the density d and the coordination number r of the considered compositions.

(3)- The width of the band tails of the localized states increase with more enriching of Tl content.

(4)- The free carrier concentration N and the plasma frequency μ_p increase with more enriching of Tl.

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