"Studies on Thickness dependent transition temperature and Electrical   resistivity of co-evaporated thin films of Ag-Te."

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ABSTRACT: *Thin films of Ag-Te compound of varying composition and thickness have been deposited on glass substrates employing three temperature method. Electrical properties of the films were studied as function of thickness, composition and temperature. The Ag-Te thin films of compositions with Ag >50 at. wt. %, ~50 at. wt. % and <50 at. wt. % has been studied for resistivity measurements at different temperatures and thicknesses. The Ag-Te compound of Ag >50 at. wt. % shows temperature dependent phase change from semiconducting to metallic. The activation energy has been calculated as function of thickness, composition of Ag-Te films. Thickness dependent transition temperature shows increase of thickness decreases transition temperature.*

KEYWORDS: *Ag-Te, thin films, substrate, transition temperature, activation energy, resistivity.*

I.   INTRODUCTION

The Silver–Telluride is a I-VI   compound of narrow band gap semiconductor shows first order phase transition around 420 ^{0}K from semiconducting orthorhombic structure to metallic, cubic (fcc) structure. The phase transition temperatures, as observed during the above semiconductor to metal transition of Ag_2Te reported [1]. The dc conductivity of thermally evaporated $Ag_{10}Te_{90}$ and $Ag_{20}Te_{80}$ thin films has been studied. Measurement of the temperature dependence of the electrical conductivity indicates that the increase of annealing temperature leads to decrease of activation energy [2].

The electrical and structural properties of silver telluride films having stoichiometric composition have been measured as a function of temperature [3, 4]. However these   compounds are less investigated in the form of thin films of different composition and thicknesses. From this point of view and considering application in electronic devices the effect of transition temperature, thickness and composition of Ag-Te films are discussed. We report the measurement of thickness dependent transition temperature, electrical properties such as resistivity and activation energy of Ag-Te thin films of different composition and thicknesses.

II.   EXPERIMENTAL DETAILS

Thin films of Ag-Te for the measurement of electrical resistivity were prepared by the three temperature method [5-10]. Ag-Te films of different compositions and different thicknesses were prepared by vacuum deposition of the constituent elements Ag (99.999% pure) and Te (99.99% pure). Silver metal and tellurium powder were evaporated from two different preheated conical mica baskets which in turn heated externally by nichrome wire. The films were prepared on glass substrate kept at room temperature in a vacuum of the order of 10^{-5} torr with an IBP TORR-120 vacuum unit. After adjusting the flux rates from two sources by varying the source current, films of varying thicknesses and compositions were obtained by overcoming   the   experimental difficulties in adjusting and maintaining evaporation rates of the individual   components. The films obtained were annealed at ~ 423 ^{0}K for 6 to 8 hours for the purpose of uniform distribution of the components of the deposits. The method employed to determine the composition of the film were similar to those reported earlier [7-9]. The composition of Ag from Ag-Te films was determined by employing absorption spectroscopy [11] at 350 nm.

The film thickness (d) was measured by multiple beam interferrometry [12] and gravimetric method [7-10] using the relation,

$$d \; = \; \frac{M}{g \, \times \, A} \; cm$$

where

A = surface area of the film
M = Mass of the film
g = the density of the film material = $x_1 g_1 + x_2 g_2$

where g_1, g_2 and x_1, x_2 are densities and atomic fractions of Ag and Te elements respectively.

III. RESULTS AND DISCUSSION

The resistance of Ag-Te deposits having different compositions and thicknesses have been measured as a function of temperature and the activation energy was calculated. The temperature of measurement varied from 271 to 453 ^{0}K.
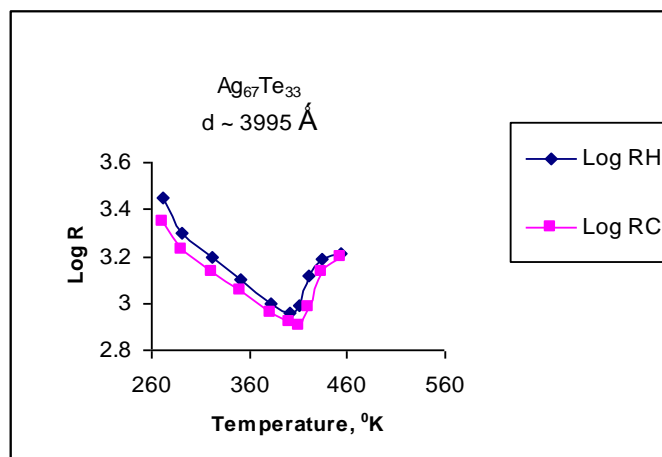
Fig.1: Plot of Log R verses temperature of Ag-Te films of (Ag) > 54 at. wt.% , from 271 to 453 ^{0}K.

Fig.1 shows the variation of Log R with temperature for Ag-Te deposits in the heating and cooling cycles of [Ag] > 54 at.wt. % in the entire temperature range. Similar plots are obtained irrespective of thickness of the deposits. It is seen that electrical resistance decreases with increasing temperature up to a certain temperature, known as transformation temperature exhibits negative temperature coefficient (NTC) of resistance in conformity with semiconducting nature, and then it increases sharply with temperature at an above the transition point exhibits a metallic behavior. During cooling cycle a reversible transformation from metallic to semiconducting behavior is observed. The transition temperature lies between 406 to 421 ^{0}K depending on thickness (d) and composition of Ag-Te thin films. Similar observations have been reported on Ag_2Te thin films by Damodara Das and Karunakaran [13, 14].

From figure-1. It is seen that the temperature of transition during heating is higher than that of cooling, probably due to removal of defects during heating of the specimen.
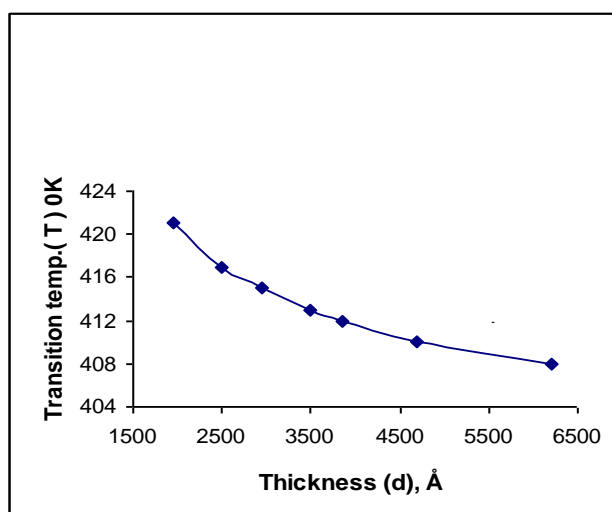

Fig.2: Plot of transition temperature (T) ^{0}K verses thickness (d) Å, of $Ag_{67}Te_{33}$ films

Fig.2 reveals that as the thickness of the deposits increases the transition temperature decreases. This decrease of transition temperature of $Ag_{67}Te_{33}$ films is attributed to decrease of defects with increase of thickness.
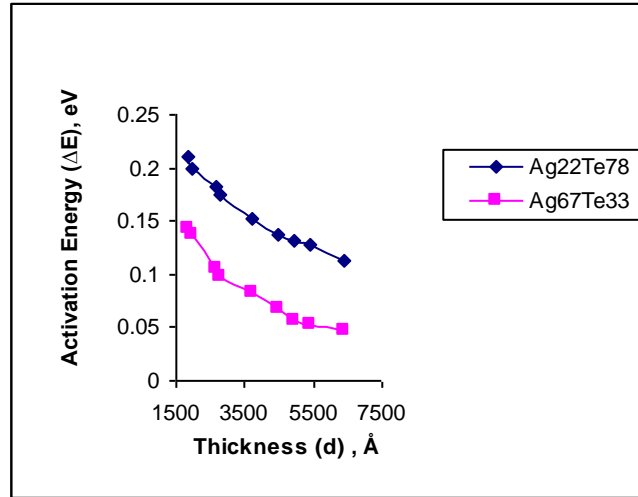
Fig. 3: Plot of activation energy (ΔE) eV verses thickness (d) Å, of Ag-Te films in the temperature range of 271 to 453 [0]K.

Fig 3 shows variation of activation energy (ΔE) as a function of thickness (d) and composition of the films. It is seen that 'ΔE' decreases with increase of film thickness irrespective of compositions.
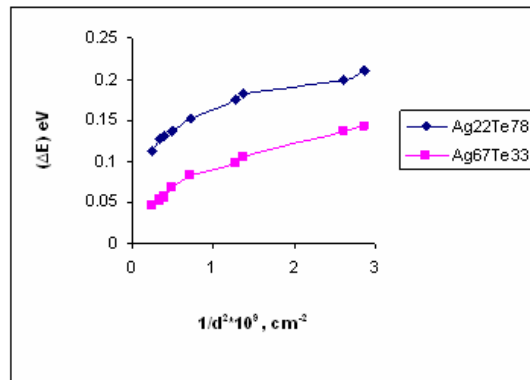
Fig. 4: Plot of activation energy (ΔE) eV verses $1/d^2$ for semiconducting Ag-Te films in the temperature range of 271 to 453 [0]K.

The observation of "band gap change" as a function of thickness can be due to any one combined effects of the following causes as given by Damodara Das and Karunakaran [13]:

1) The change in the barrier height due to the size of the grains
   in a polycrystalline films;
2) A large density of dislocations.
3) Quantum size effect; and
4) Change in stoichiometry.

We will consider the two possibilities, Slater [15] proposed that energy barriers are associated with grain boundaries and their barrier heights can vary because of the charge accumulation at the boundaries. According to him, the increased barrier height is given by

$$\Delta E = \Delta E_0 + C\ (X - fD)^2 \qquad -------------------- (1)$$

Where 'ΔE$_0$' is the original barrier height, C is a term depending on the density of charge carriers, electronic charge and dielectric constant of the material, X is the barrier width of about 200-300 Å, 'D' is the dimension of the grain, and 'f' is a fraction of the order of 1/15 to 1/50 depending upon the charge accumulation, and the carrier concentration .It is known from literature [16] that the grain size is approximately proportional to thickness, and hence increases as thickness increases. Hence if we replace D, the grain size, in the above expression by the film thickness (d) , we find that 'ΔE' should be proportional to $(X - fd)^2$.

However, in the present observations, we find that the band gap varies inversely as the square of the thickness of the film and hence it can be concluded that the observed band gap variation with thickness can be attributed to the above effect.

It is also known that a fairly large number of dislocations are created during the formation of the films and their density increases as the thickness up to a particular thickness, beyond which the density is practically constant. However, the dependence of the dislocation density on thickness has not been quantified and in any case the dependence is complex. It has been suggested [17] that when the dislocation density is fairly high in the case of thin films, there is an increase in the band gap of semiconductor material, because of the presence of dislocations, provided that the dislocations are separated by a distance greater than the inter atomic distance. This separation arises because of the alternate dilation and compression of the lattice on two sides of the dislocation. However, the exact relationship between the dislocation density and /or their separation distance and the change in the band gap has not been established and the magnitude of the separation caused is also unknown. It is however clear that because of the complex nature of the dependence of the dislocation density and the spacing, the variation of band gap with thickness due to above effect will be complex.

As in the present observation we observe a linear 'ΔE' verses $1/d^2$ dependence of the band gap which is expected from the quantum size effect, it is reasonable to disregard the above possibility also.

Sandomirskii [18,19] was the first to consider quantum size effects in semimetallic and semiconducting thin films, and to show that when the thickness of a thin films of any material is of the order of de Broglie wavelength of conduction electrons / holes and is much less than the mean free path of the charge carriers, the material exhibits quantum size effects. In the above situation, the electron / hole momentum component normal to the film is quantized and as a consequence the contribution of motion normal to the film to the kinetic energy of the charge carriers is also quantized and is given by

$$E_z = (\hbar^2 \pi^2/2m^*d^2) n^2 \qquad \text{-------------------- (2)}$$
$$n = 1, 2, 3,\text{----- etc}$$

where $\hbar = h/2\pi$, 'h' is the plank's constant, m^* is the effective mass of the charge carrier, and 'd' is the thickness of the film. 'E' is the kinetic energy contribution due to motion normal to the film plane.

As the lowest momentum component state is non zero, the lowest energy state for this motion is also non zero. As a consequence, the bottom of the conduction band (zero state energy of electrons) and the top of the valence band (zero state energy of holes) in the film state will shift to higher energies with respect to their positions in the bulk state. As a result, if the material is semiconducting in the bulk state, its energy band gap will be increased by an additional amount depending on the thickness of the film. As the increased separation is a function of square of inverse thickness, a plot of band gap verses $1/d^2$ will be linear, as has been observed in the present case.

Gottlieb et al [20] reported the data of effective mass of electrons in Ag_2Te as ~$0.05m_0$ and Fermi energy is of the order of 10^{-2} eV. Hence the de-Broglie wavelength of electrons in Ag_2Te will be of the order of 1000 Å, and has high mobility (over 10000 cm^2 / V Sec at room temperature).

Damodara Das and Karunakaran [13] also showed that the effective mass of electrons is $0.002 m_o$, and largest wavelength found to be 3000 Å. From the slope of the band gap verses $1/d^2$ plot, m^*_e is calculated using the relation

$$\hbar^2 \pi^2/2m^*_e = slope, \qquad \text{------------------------- (3)}$$

assuming 'm_h' to be very large. The largest de Broglie wavelength of the electrons calculated using the relation

$$\lambda = h/p \qquad \text{------------------- (4)}$$

$$p = (2m^*_e E_F)^{1/2} \qquad \text{--------------------------- (5)}$$

where 'p' is the momentum, m^*_e is effective mass of electrons and E_F the Fermi energy of the electrons. Taking E_f to be half the band gap of the film of largest thickness.

In the present study of Ag-Te films of different thicknesses and compositions, it is found that $Ag_{67}Te_{33}$ shows n-type semiconducting nature. [Ag] > 54 at.wt.% of Ag in Ag-Te is n-type, thus the effective mass of electrons in $Ag_{67}Te_{33}$ films is $0.0001035 m_0$, and the de Broglie wavelength corresponding to half the band gap (ΔE) of the film of largest thickness is found using the equations 4 and 5,

$E_F = \Delta E$

we get   P= 0.85117* 10^{-27} hence, $\lambda \sim 7780$ Å

Similar observations are also made for p-type Ag-Te films of [Ag] < 54 at.wt.% of Ag, thus for $Ag_{22}Te_{78}$, the effective mass of holes ($m*_h \sim 2.5 m*_e$),

    P= 1.262* 10^{-27} hence, $\lambda \sim 5248$ Å

The assumption made that $m*_h$ is always greater than $m*_e$ is reasonable and justified in the light of the fact that as reported in the literature [20,3,21]. so that the conductivity observed is large due to electrons in Ag-Te films of [Ag] > 54 at. wt.% and smaller conductivity observed due to holes in Ag-Te films of [Ag] < 54 at. wt.% i.e. in p-type material.

Considering the fourth possibility i.e. stoichiometric change influencing the band gap, it is noted that there is every possibility of inhomogenity or non-stoichiometry in the Ag-Te film studied. In the present investigation [Ag] / [Te] ratio is variable to a greater extent and the effect of dissolved 'Ag' strongly influences the band gap determination. Hence for films of different thicknesses with almost constant composition studied in the same temperature range, the observed variation in 'ΔE' may be due to the effect of variable amounts of dissolved silver getting locked in interstitial sites.
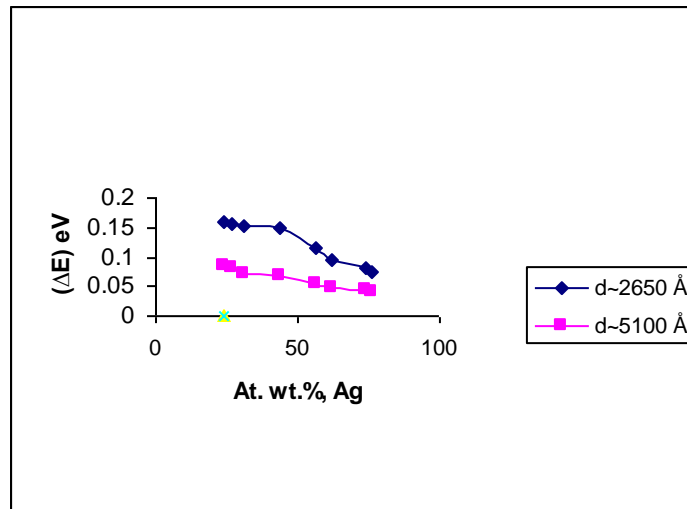
**Fig. 5: Plot of activation energy (ΔE) eV verses at.wt. % of Ag in Ag-Te films in the temperature range of 271 to 453 [0]K**

Fig.5 shows the variation of 'ΔE' with at. wt.% of Ag in Ag-Te deposits over entire temperature range. It shows that 'ΔE' continuously decreases with increase of 'Ag' content.

This probably is due to the increase of interstitial sites occupied by 'Ag' which results in decrease of 'ΔE' with increase of 'Ag' content.

Ag-Te films containing [Ag] > 54 at. wt.% show metallic behavior (Fig.1) in high temperature region. An attempt has been made to fit our observation of metallic behavior to Fuchs-Sondheimer [22,23] and Mayadas and Schatzkes [24] theories. The electrical resistivity of the metallic films can be expressed by FS model as

    $\rho = \rho_o [1+ (3l_o / 8d) (1-p)]$ -------------- (6)

Where 'ρ' is the electrical resistivity of the thin film, 'ρ_o' the electrical resistivity of the bulk material, 'l_o' the electron mean free path, 'd' the film thickness and p the specularity parameter.
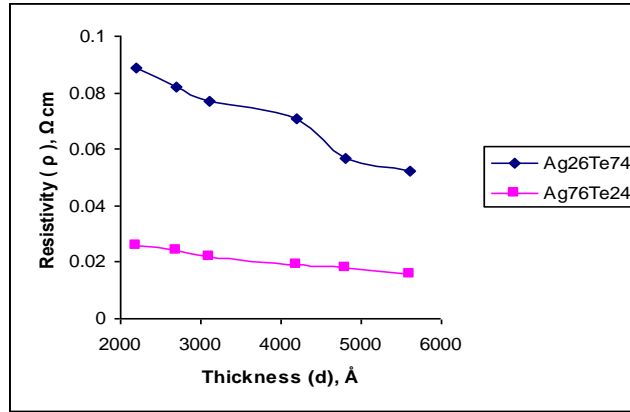
Fig. 6: Plot of resistivity (ρ) verses thickness (d, Å) of Ag-Te films at room temperature (271 to 453 ^{0}K)

The experimentally measured resistivity of thin films as shown by Mayadas and Schatzkes is dependent not only on the ordinary Fuchs size effect but also on the effect of grain boundary scattering. The thin film electrical resistivity given by MS for small ά is

$$\rho = \rho_o [1+ (3/2) \acute{\alpha} +(3l_o/ 8d) (1-p)] \qquad \text{---------------- (7)}$$

where

$$\acute{\alpha} = l_o R/ [d(1-R)] \qquad \text{-------------- (8)}$$

d = average grain diameter
R= grain boundary reflection coefficient.

Fig.6 illustrates the electrical resistivity (ρ) of the films deposited at room temperature and measured at room temperature as a function of thickness. From fig. 6, the electrical resistivity (ρ) is high for lower thickness, and then slowly decreases with increasing thickness. Finally attains a constant value of resistivity for higher thicknesses.

It is also observed from the fig. that, as the at. wt. % of Ag increases in Ag-Te films the resistivity of the films goes on decreasing ultimately conductivity increases.
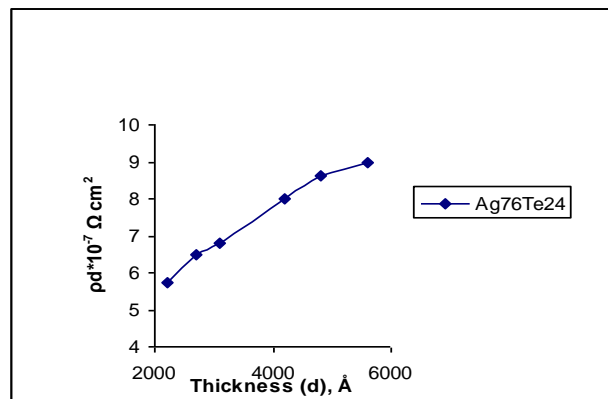
Fig. 7: Plot of (ρ*d) verses thickness (d, Å) of Ag-Te films at room temperature (271 to 453 ^{0}K) .

Fig. 7 shows 'ρd' as a function of 'd'. The slope yields 'ρ$_o$ ' which is electrical resistivity of an infinite thick film, It gives

$$\rho_o = 1.212* 10^{-2} \,\Omega cm.$$

Assuming p=0 for total diffuse scattering, we obtained the value of l_o ~9900 Å, in Ag-Te films. Assuming that the values of ρ_o and $l_o(1-p)$ derived from 'FS' model are also appropriate for the MS model. Equation (8) has been used for estimating the values of $\acute{\alpha}$, Negative values of $\acute{\alpha}$ suggest that MS model is not valid for these films. Higher resistivity in thinner films may be related to smaller crystallite size and larger structural defects.

The effect of thickness on resistivity (ρ) of film can also be explained in terms of Mathiessen rule

$$\rho_{total} = \rho_{ideal} + \rho_{residual} + \rho_{thickness} \qquad \text{------------(9)}$$

Where

ρ_{ideal} depends on the amplitude of the thermal motion of ions, $\rho_{residual}$ is the component strongly dependent on the lattice defects, but independent of temperature as long as these lattice defects are not affected by temperature change, and $\rho_{thickness}$, the component of ρ_{total} that depends on the thickness of the film.

Now as the thickness of the film increases, effect of island structure, quantum size effect and effect like grain size etc. are diminished, thus reducing the contribution of $\rho_{thickness}$ on ρ_{total} . Contribution to ρ_{total} by ρ_{ideal} and $\rho_{residual}$ being characteristics of material may be taken as same for all thicknesses.
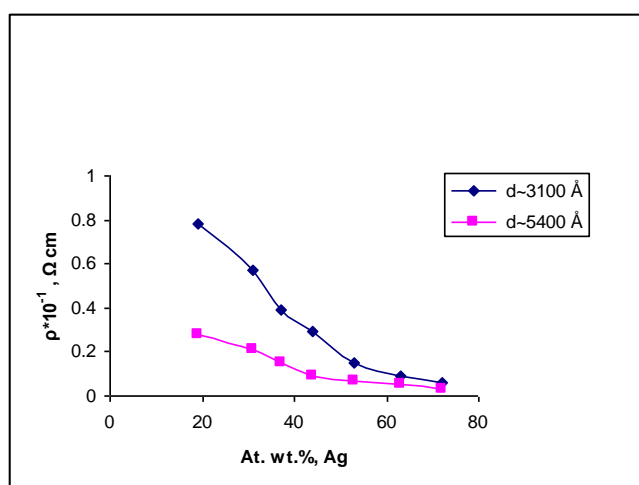Thus ρ_{total} of the film decreases with the increasing film thickness.

Fig.8: Plot of resistivity (ρ) verses At. wt.% of Ag in Ag-Te films in the temperature range 301 to 453^{0}K

The variation of resistivity (ρ) with composition of Ag-Te deposits is shown in fig. 8 It has been observed that resistivity (ρ) decreases with increase of 'Ag' concentration in Ag-Te films. The decrease of (ρ) with increase of 'Ag' concentration may be ascribed to inhomogeneous addition of Ag atoms.

IV. CONCLUSIONS:
Temperature dependent resistivity Shows semiconducting and metallic phase change above 54 At. wt. % of Ag. Thickness and composition dependent activation energy shows inverse relation between them. Thickness and composition dependent resistivity shows also The maximum photocurrent was developed at about thickness of 500nm irrespective of composition and also stoichiometric ZnTe films irrespective of thickness at room temperature.

V. ACKNOWLEDGEMENT

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