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STUDIES ON ELECTRICAL RESISTIVITY OF VACUUM EVAPORATED Zn-Te THIN FILMS.

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ABSTRACT

Thin films of Zn-Te compound of varying compositions and thicknesses have been deposited on glass substrates employing three temperature method. Electrical resistivity have been studied as function of thickness, composition and temperature of films. Zn-Te thin films show effect of annealing temperature, composition and thickness of the films. The Zn-Te films of compositions Zn >50 at. wt. %, ~50 at. wt.% and < 50 at. wt.% have been studied for resistivity measurement at different temperatures and thicknesses. The activation energy has been calculated as function of thickness and composition of Zn-Te films. From energy of activation, conduction mechanisms have been predicted.

Keywords: Zn-Te, thin films, thickness, composition, transition temperature, activation energy, resistivity.

1. INTRODUCTION

The Zn-Te is a II-VI semi conductor compound has a direct band gap of 2.26 eV at room temperature. Thin films of Zn-Te have been made by several workers from the crystallization point of view and application considerations [1,2]. The polycrystalline compound semiconductor films are of considerable technological importance and play a major role in the fabrication of electronic devices, both from purely scientific and application points of view, it is used in detectors, IR filters, Solar cells, switching devices, diodes and high speed stable integrable thin film transistors. Zinc Telluride is a promising semiconductor material for fabrication of high efficiency thin film solar cells and other optoelectronic devices due to its suitable optoelectronic band gap [3,4].

The crystallite size in evaporated films can be improved by employing a higher deposition temperature of the substrate and also by post deposition thermal treatment, the usefulness of thermally treated films may be reduced as a result of cracking and pinhole effects .Thermal electrical conductivity measurement and activation energy calculation of ZnTe and Zn-Te films were made by several workers [5-11] .

From a survey of the literature it is found that no attempt has been made to study the electrical properties of Zn-Te system over entire range of composition in its thin film state. Therefore we have taken the investigation of an electrical property such as resistivity of Zn-Te films of varying composition and thickness prepared by using the three temperatures method [12-15].

II. EXPERIMENTAL DETAILS

II. 1. Preparation of Zn-Te thin films

In the present work Zn-Te thin films were prepared by three temperatures method [12-15]. Zn-Te films of different compositions and different thicknesses were prepared by thermal evaporation technique of the constituent elements Zn (99.999 % pure) and Te (99.99 pure) in a vacuum of 10^{-6} torr in an IBP TORR-120 vacuum unit. Zinc and tellurium powders were evaporated from two different preheated conical mica baskets which were heated externally by nichrome wire filament. The films were prepared mostly on glass substrate kept at room temperature in a vacuum, after adjusting the flux rates from two heating sources by varying the source current, films of varying compositions were obtained. Overcoming the experimental difficulties in adjusting and maintaining evaporation rates of the individual components to obtain films of different compositions having nearly same thickness and films of different thicknesses and nearly same

composition, films of the required compositions and thicknesses were obtained. The films deposited were annealed at ~423 K for 6 to 8 hours for the purpose of uniform distribution of the components in the deposits.

II. 2. Measurement of Thickness and composition

The method employed to determine the composition, thickness and uniformity of the film were similar to those reported earlier [12-15]. The composition of the film was determined by employing absorption spectroscopy at a wavelength of 550 mμ with an accuracy of ±1 at.wt.%. The film thickness (d) was measured by using multiple beam interferometry and also by gravimetric method [12-15] (±100Å) using the relation

$$d = \frac{M}{g \times A} cm \qquad (1)$$

where notations are
A: surface area of the film
M: mass of the film material
g: density of the film material,
which verifies $g = x_1 g_1 + x_2 g_2$
with g_1, g_2 and x_1, x_2 are the densities and atomic fractions of Zn and Te elements of the film material respectively.
Both techniques of thickness measurements agreed within ±10% for very thin films and ± 5% for thick films (>500 Å).

II. 3. Electrical properties

Electrical measurements such as resistivity of the annealed ZnTe films of different thicknesses and compositions were made at temperatures ranging between 271 to 301 K and 301 to 423 K in vacuum of 10^{-6} torr using digital multimeter (MECO) as described elsewhere.

III. RESULTS AND DISCUSSION

As mentioned before the measurements on Zn-Te films were carried out after appropriate annealing. A typical plots of log(R) versus 1/T for temperature regions 271 to 301 K and 301 to 423 K for different compositions are shown in Figures-1 and 2 respectively.

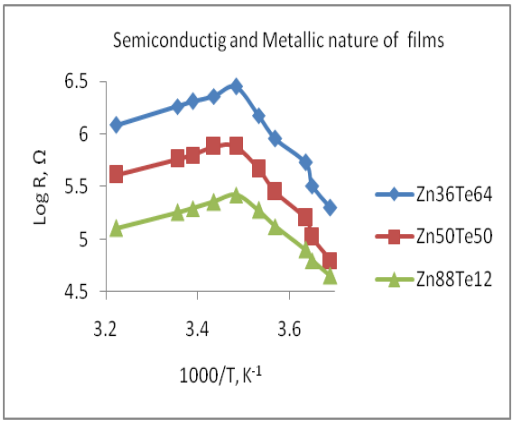

Fig. 1: Plot of Log(R) versus 1/T of Zn-Te thin films in the temperature range of 271 to 301 K.

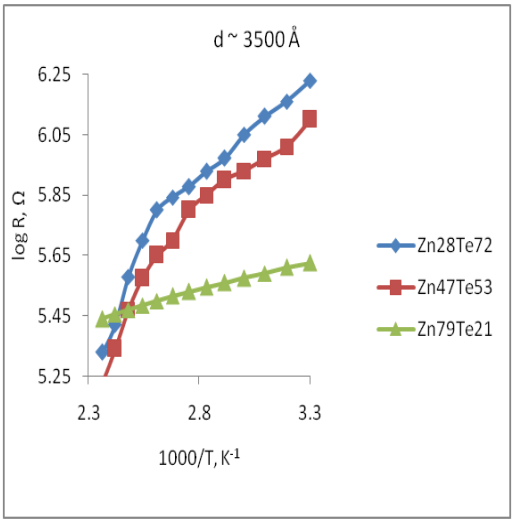

Fig. 2: Plot of Log(R) versus 1/T of Zn-Te thin films in the temperature range of 301 to 423 K.

A close perusal of fig.1 and fig.2 reveals interesting results. Zn-Te thin films of different compositions show semiconductor and metallic behavior in the temperature range 271 to 301 K. However, the Zn-Te films in the temperature range of 301 K to 423 K show only semiconducting behavior with two distinct energy of activation values. The activation energy (ΔE) is calculated by using the relation,

$$R = R_0 \exp(\Delta E / KT) . \qquad (2)$$

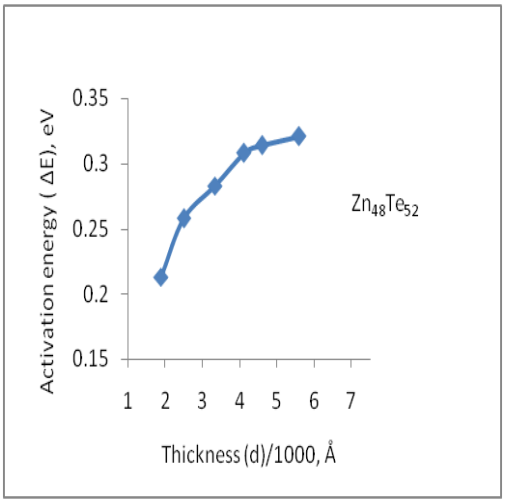

Fig. 3: Plot of activation energy (ΔE) versus thickness (d) of Zn-Te thin films in the temperature range of 287 K to 301 K.

It is observed that the activation energy (ΔE) is thickness and composition dependent. From fig.3 it is seen that (ΔE) increases with increase of film thickness in the temperature range of 287 to 301^{0}K and it is due to large number of dislocations created during the formation of the film and their density increases as the thickness increases up to particular value beyond which the density of dislocations practically constant.

Similar inhomogeneous observations have been reported by [13,15], again the films studied are inhomogeneous or non-stoichiometric. But for the temperature region 301 K to 423 K the energy barriers are associated with grain boundaries and their barrier heights can vary because of the charge accumulation at the boundaries.

From the quantum size effect (QSE) in semi-metallic and semi-conductor thin films, an expression for the increase in the energy band gap is obtained as

$$\Delta Eg = \hbar^2 \pi^2 / 2md^2 \qquad (3)$$

where d is the film thickness and ΔEg the band gap. This can again be as a function of island structure theory [16].

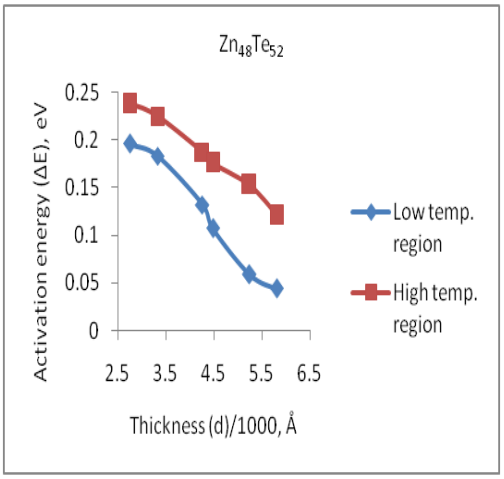

Fig. 4: Plot of activation energy (ΔE) versus thickness (d) of Zn-Te thin films in the temperature range of 301 K to 423 K.

However, fig.4 shows that ΔE values are decreased with increased film thickness in the temperature range 301 K to 423 K. The band gap change as a function of thickness can be due to one of combined effects of the following causes:

1. change in the barrier height due to the size of the grains in a polycrystalline films;
2. large density of dislocation;
3. quantum size effect; and
4. change in stoichiometry.

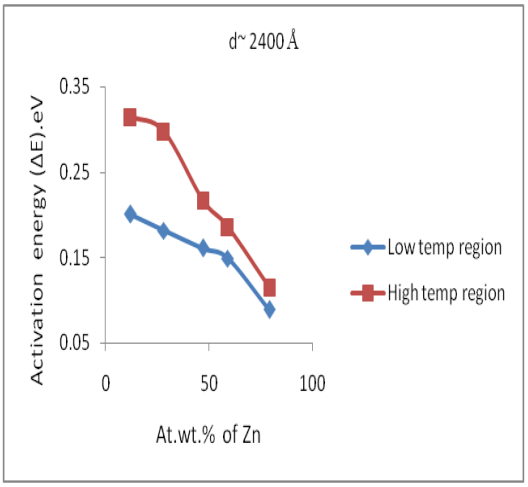

Fig. 5: Plot of activation energy (ΔE) versus at.wt.% of Zn in Zn-Te films in the temperature range of 287 K to 423 K.

The variation of ΔE with at. wt .% of Zn shown in fig.5 represents increased concentration of Zn in Zn-Te films decreases ΔE, because of trap centers in the forbidden energy gap shifts towards conduction band with addition of Zn

into Te causing lower energy of activation of carriers.

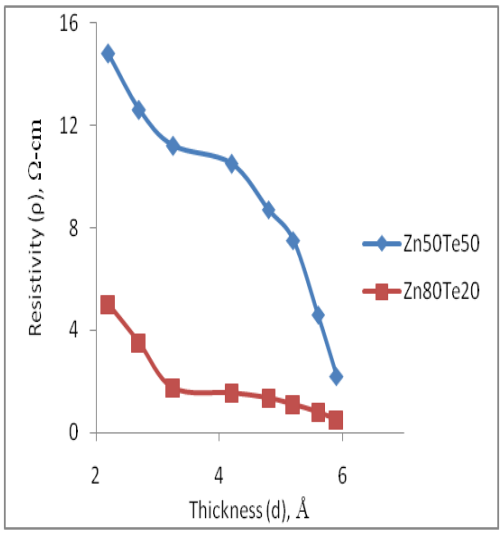

Fig. 6: Plot of resistivity (ρ) versus thickness (d) of Zn-Te films at 313 K in the temperature range of 301 K to 423 K.

Fig. 6 shows variation of resistivity (ρ) with thickness (d) of Zn-Te thin films. It is seen that resistivity decreases sharply with increase of thickness of deposits irrespective of its composition and temperature range of measurement.

The sharp decrease of ρ, for thinner films may be due to island structure and higher defect density in the films. The effect of thickness (d) on resistivity (ρ) of film can be explained by Mathiessen rule.

$$\rho_{total} = \rho_{ideal} + \rho_{residual} + \rho_{thickness}$$

where ρ_{ideal} depends on amplitude of 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 thickness of the film.
Now as the thickness of the film increases, effect of island structure, quantum size effect and effect like grain size 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 film thicknesses. Thus ρ_{total} of the film decreases with the increasing film thickness.

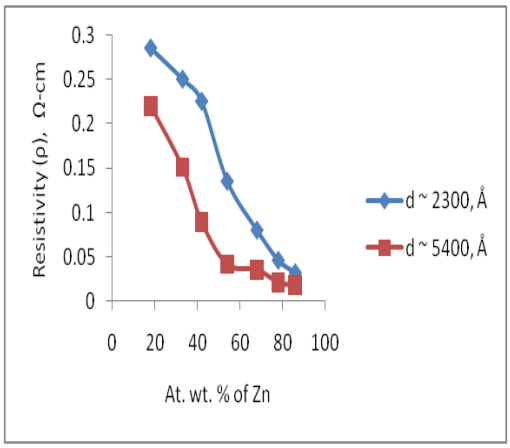

Fig. 7: Plot of resistivity (ρ) versus at.wt.% of Zn in Zn-Te films at 273 K in the temperature range of 271 K to 287 K (metallic region).

Fig. 7 shows variation of ρ with at. wt. % of Zn in Zn-Te thin films in metallic region (271 to 287 K). It is seen that ρ decreases exponentially with increase of Zn concentration. This sharp fall of resistivity may be attributed to increase of Zn, in Zn-Te thin films. The electrical resistivity (ρ) of thin metallic film can be expressed by [17]

$$\rho = \rho_o [\, 1+ (3l_o / 8d) (1-p)] \qquad (4)$$

where ρ is the electrical resistivity of the film; $\rho_{o,}$ the electrical resistivity of the bulk material; l_o the electron mean free path; d, the film thickness and p is the specularity parameter.
The experimentally measured resistivity (ρ) of thin metallic films as shown by Mayadas and Shatzkes (MS model) is dependent not only on the ordinary Fuchs size effect but also on the effect of grain boundary scattering. The electrical resistivity of thin metallic film given by MS for small α' is

$$\rho = \rho_o [1+(3/2)\, \alpha' + (3\, l_o / 8d) (1-p)] \qquad (5)$$

where $\alpha' = l_o\, R'/ d(1-R')$, d is the average grain diameter and R' the grain boundary reflection coefficient.
Assuming P= 0 for total diffuse scattering, we obtain the value of l_o as 7700 Å in Zn-Te films. Assuming that the values of ρ_o and l_o (1- p) derived from Fuchs model are also appropriate for the MS model. Eq.5 has been used for estimations of the values of α' for different thicknesses. In the present investigation α' obtained using eq. 5 yield negative values, there by indicating non obeying MS model for resistivity of metallic Zn-Te films and therefore

it is only the Fuchs and Sondheimer (FS) model describing size effect on resistivity of metallic Zn-Te films.

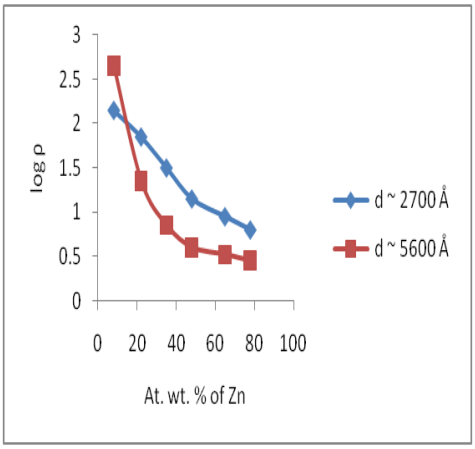

Fig. 8: Plot of resistivity (ρ) versus at.wt.% of Zn in Zn-Te films at 313 K in the temperature range of 301 K to 423 K (semiconductor region).

Fig. 8 shows variation of ρ with at. wt. % of Zn of semiconductor Zn-Te thin films in the temperature region 301 K to 423 K . It is seen that ρ decreases exponentially with increase of Zn concentration. This sharp fall of resistivity may be attributed to increase of metallic Zn, in Zn-Te thin films.

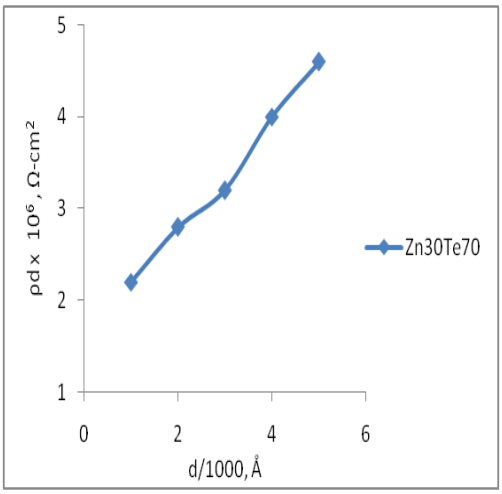

Fig. 9: Plot of (ρd) versus thickness (d) of Zn-Te films in the temperature range of 271 K to 423 K.

Fig.9 shows ρd as a function of d. The intercept on the y-axis yields (3 l_o /8d)(1-p) while the slope yields ρ_o = 0.05 Ωcm which is the electrical resistivity of an infinitely thick film.

IV. CONCLUSION

Zn-Te films have been well prepared by three temperature method. These films showed temperature dependent semiconducting and metallic behavior. Activation energy increases with increase of film thickness for low temperature region and decreases in high temperature region. The activation energy decreases with increases of at wt.% of Zn in the films. Resistivity decreases with increase in thickness as well as increases in wt.% of Zn.

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