

Optoelectrical structural properties of Zinc telluride thin films grown by chemical bath deposition method.

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Abstract

Crystalline ZnTe thin film has been deposited using appropriate precursor solution containing Zinc sulphate octahydrate, triethanolamine, sodium hydroxide, ammonia and sodiumtellenosulphate. The effect of parameters such as bath composition, deposition temperature, pH of the solution, speed of the rotation and specificity of complexing agent on growth mechanism were studied. The deposited ZnTe thin film was found to be white gray in colour specular and well adherent to glass substrate. The crystalline phase of the deposited sample was found to be orthorhombic crystal structure. The analysis of optical absorption data shows energy band gap energy 2 eV. ZnTe thin film the positive terminal connected to the cold end therefore, the film shows P- type conductivity. The electrical resistivity of ZnTe thin film to be order of $10^{-8} (\Omega \text{ cm})^{-1}$

Keywords: *Chemical synthesis, Optical, XRD, SEM, ZnTe thin films.*

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I. INTRODUCTION:

The II-VI compound semiconductors are of considerable interest, due to their special electrical and optical properties. Among these compounds zinc telluride is of special importance which is widely used in optoelectronic devices in the visible region [1, 2]. ZnTe thin films grown at high temperature are found to be polycrystalline in nature [3]. These films can be prepared by several techniques including SILAR [4], Molecular beam epitaxy (MBE) [5,6] electrodeposition [7]. Hott wall electrical studies on chemically deposited ZnTe thin film have been made by K.R. Murati et al [8]. A convenient method for deposition of ZnTe thin film is chemical bath deposition. This is due to the possibility of obtaining large surface area deposition at low cost. It does not require any sophisticated instruments. Films prepared by chemical bath deposition can be used in optoelectronic devices due to high purity of deposited material. The deposition ZnTe is based on reaction between Te^{-2} and Zn^{+2} ions with controlled precipitation in equilibrium with the product. Zinc telluride related to ternary alloys like $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ and $\text{ZnSe}_{1-x}\text{Te}_x$ are best materials for optoelectronic devices technology in the visible spectrum [9]. More details of chemical bath deposition method are well documented in literature [10] in the novel synthesis of ZnTe thin films on non-conducting glass substrate from aqueous alkaline medium. We report here the synthesis of ZnTe thin films using chemical bath deposition method and characterization for their optical, structural, surface morphology, compositional analysis, and electrical properties.

II. EXPERIMENTAL DETAILS:

The substrate used for the deposition of ZnTe thin films were non conducting glass slides of dimensions 26×76×2 mm which were cleaned by ethanol and de-ionized water and finally dried in air before use. All chemicals used for the deposition were of analytical grade; it includes zinc sulphate, triethanolamine, ammonia, sodium sulfite and tellurium metal powder. All the solutions were prepared in double distilled water. Sodiumtelenosulfate (Na_2TeSO_3) solution was prepared by refluxing 1g-tellurium metal powder and 2.4g sodium sulfite in 200 mL distilled water for 24 hours at 373K [11].

In actual experimentation, 10mL (1M) zinc sulphate solution was taken in 250mL beaker; 5ml TEA, sodium hydroxide, ammonia, and 10mL (1M) sodium telenosulphate was added in the reaction bath at room temperature. pH of the reaction mixture was found to be 10. The beaker was kept in oil bath, the non-conducting glass substrate were mounted vertically on a specially designed substrate holder and rotated in the reaction mixture with a speed of 60 ± 2 rpm. The temperature of bath was then allowed to increase slowly up to 353 K. After 2 hour 40 minute the slides were removed, washed with deionized water several times, dried naturally and preserved in dessicator. The obtained films were homogenous, well, and adherent to glass substrates.

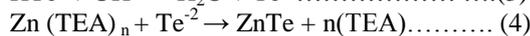
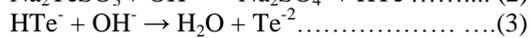
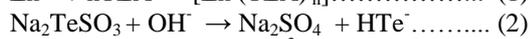
III. SAMPLE CHARACTERIZATIONS:

X-ray diffraction of ZnTe films was carried out in the range of the diffraction angle 10-80° with CuKα1 radiation using Philips PW –1710 diffractometer ($\lambda=1.54056 \text{ \AA}$). The electrical conductivity of ZnTe thin films was measured using a ‘dc’ two-probe method. A quick drying silver paste was applied at the end of the film for ohmic contact purpose. For conductivity measurement the constant voltage of 30V was applied across the sample. The layer thickness of the film was measured by weight difference method. The optical absorbance measurements were made in the wavelength range 400-1200 nm by using a Hitachi-330 (Japan) UV–visible NIR, double beam spectrophotometer at room temperature, uncoated glass substrate placing in the reference beam made substrate correction. A 250 MK-III StereoScon (USA) scanning electron microscope (SEM) was used for the microscopic observations. Thermoelectric power (TEP) measurements and the potential difference between the points separated by 1cm were recorded with a digital micro voltmeter. A calibrated thermocouple probe (Chromel-Alumel 24 gauge) with a digital voltmeter was used to sense the working temperature.

IV. RESULTS AND DISCUSSION:

4.1. Kinetics and growth mechanism:

The deposition of zinc telluride was made using reactive precursor solution containing sodiumtelenosulfate as the source of telluride and zinc sulphate as the source of zinc ions. In the reaction bath Zn^{+2} ions are complexed with TEA in the form of water soluble Zn-TEA complexed and thus control Zn^{+2} concentration. The dissociation of sodiumtelenosulfate as well as Zn-TEA complex in alkaline medium takes place. At room temperature a clear solution is formed and no film formation or precipitates are observed. At low temperature kinetic energy is lower and avoids the precipitation [12]. As temperatures increases slowly, the kinetic energy increases, resulting in decomposition of sodiumtelenosulphate and forming metal complex in alkaline medium in the form of ZnTe thin film. Thermal decomposition of metastable complex releases metal ions while sodiumtelenosulphate hydrolyzes in alkaline solution to yield Te^{-2} ions [13-14] The decomposition takes place when the ionic product Zn^{+2} and Te^{-2} is greater than solubility product [$K_{sp}=10^{-30}$]. The kinetic growth of film can be understood from the following.



If the pH of the bath is in between 7.5 and 13.7 then insoluble $\text{Zn}(\text{OH})_2$ may be present [15]. The presence of $\text{Zn}(\text{OH})_2$ in the reaction mixture is unavoidable due to aqueous alkaline medium of the bath. This results in the inclusion of $\text{Zn}(\text{OH})_2$ in the ZnTe film resulting in the formation of $\text{Zn}_x(\text{TeOH})_y$ thin film rather than ZnTe film [16]. An increase in deposition temperature favours the homogeneous precipitation rather than the film formation, which causes saturation to occur. In growth process no film formation occurs for half an hour. This is due to the induction period required to form nucleation centers on the substrate. The presence of induction period suggests that ion-by-ion growth mechanism instead of cluster by cluster. Fig 1(a) shows the thickness against deposition temperature. This study revealed that homogenous ZnTe thin film has been deposited at 160 minutes with $0.435\mu\text{m}$ thicknesses and saturated for further time. The thickness was measured every 60 minutes and plotted against time as shown in Fig 1 (b). Rotation speed was 60 ± 2 rpm to deposit ZnTe thin films. At lower speed, thick non-adherent films were deposited. Above higher speed, very thin film is deposited. The thickness is found to be $0.435 \mu\text{m}$. The optimum conditions like for temperature and time are at 353K and 160 minutes respectively.

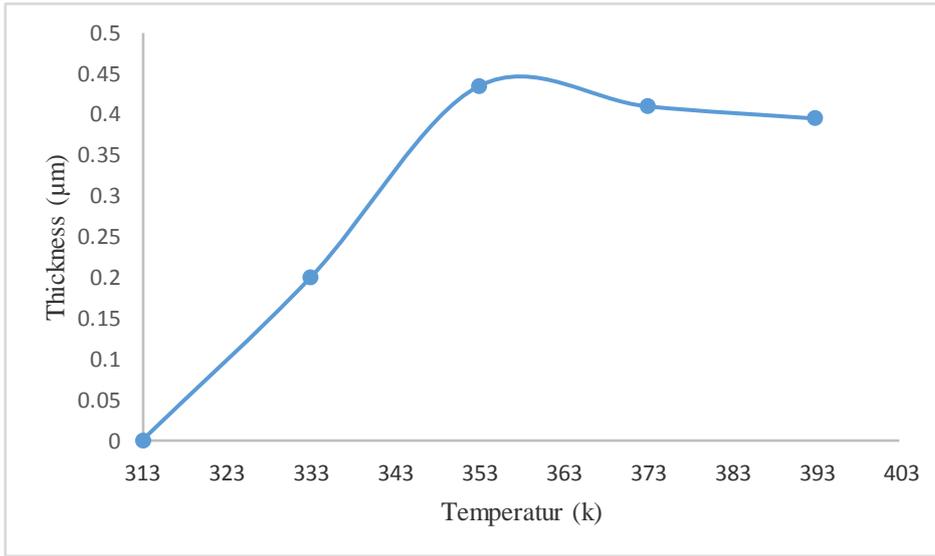


Fig.1. (a). Show deposition of thickness Vs temperature.

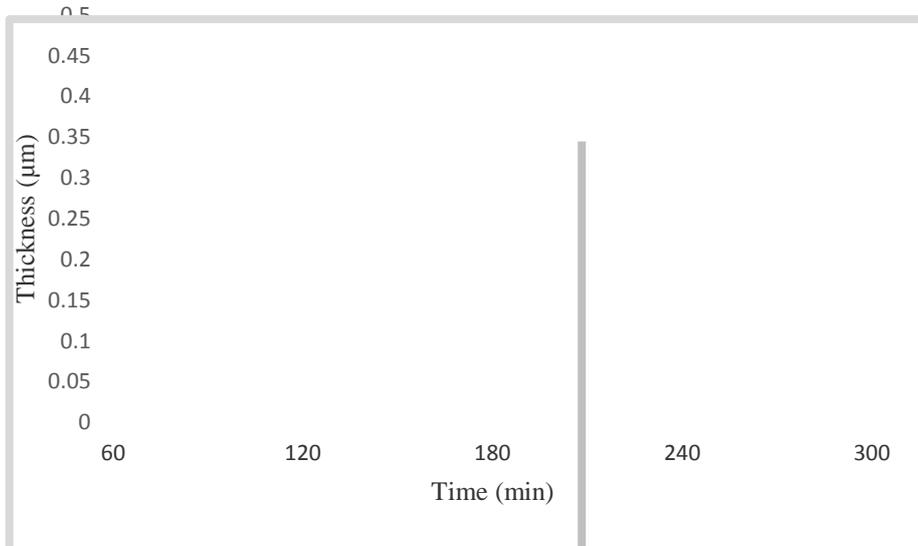


Fig.1. (b). Show deposition of thickness Vs deposition time.

4.2. X-ray diffraction:

XRD pattern of “as deposited” and annealed ZnTe thin films, are shown in Fig 2. The XRD pattern of “as deposited”, film shows very poor crystallinity. The XRD pattern of the annealed sample shows high peak intensity, due to high crystallinity. The diffused background is due to presence of some amorphous glass substrate and also may be due to presence of some amorphous phase in the ZnTe thin film. The observed d-value correspond to 2.861 phase of ZnTe and are indexed according to Orthorhombic structure (JCPDS - 822152). The indices are shown above the reflections in the figure. The XRD pattern shows the highest intensity reflection peak at d=2.861Å (200), Along with (321) plane, (302), (022), (311), (040), (400), peaks are also observed. The significant improvement in crystallinity is due to increased in grain size into effectively crystalline after annealing.

The lattice parameters are a = 4.7244Å, b = 5.8796 Å, c = 5.01Å.

The orthorhombic Phase was calculated by using following equation.

$$1/d^2 = h^2/a^2 + k^2/b^2 + l^2/c^2 \dots \dots \dots (5)$$

The lattice constant was calculated by using orthorhombic crystal structure. The average grain size of the film was evaluated by using Scherrer’s formula.

$$D = K\lambda / \beta \cos\theta \dots \dots \dots (6)$$

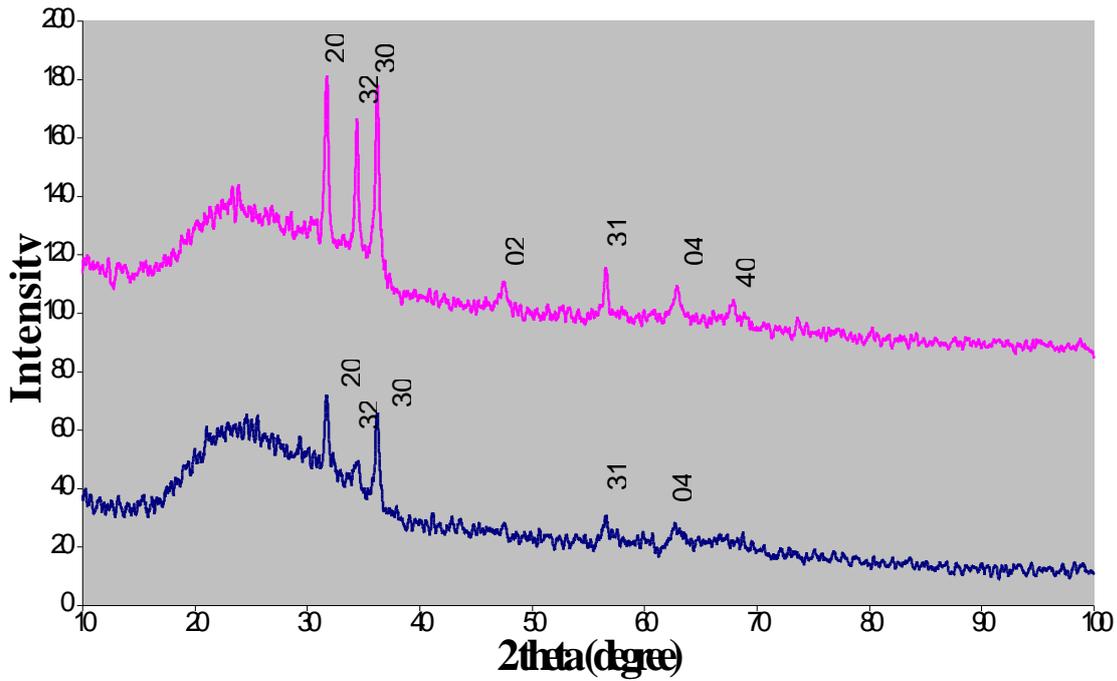


Fig. 2: XRD pattern of ‘as deposited’ and annealed zinc telluride thin film.

Table 1: Crystallographic parameter of ZnTe thin film.

Film	d values (Å)		hkl planes	Grain size (XRD) (Å)	Cell parameter, a ,b,c, (Å)
	ASTM	Observed			
ZnTe	2.869	2.861	200	186	a = 4.7244 b = 5.8796 c = 5.0100
	2.564	2.561	321		
	2.5050	2.499	302		
	1.9189	1.911	022		
	1.6244	1.620	311		
	1.4827	1.487	040		
	1.3647	1.367	400		

Where 'D' is crystallite size, λ is the wavelength used, β is the angular line width at half maximum intensity, θ is Bragg's diffraction angle and K is constant. The average crystallite size was calculated by resolving the highest intensity peak. The average crystallite size of annealing ZnTe thin film at 373 K was found to be 186 Å.

4.3. Scanning electron microscopy:

The SEM micrograph of annealed ZnTe thin film at a 10,000× magnification is shown in Fig.3. (a) 'As deposited' ZnTe thin film is homogeneous, with cracks or pinholes and well covered onto the glass substrate. A uniform distribution of nodular spherical grain of almost similar in size is observed.

Grains are interconnected to each other and no pores are visible. In Fig.3. (b) annealed film the grains are more distinct and of bigger size. The increase in grain size leads to a decrease in the grain boundaries. The presence of fine background is an indication of one-step growth by multiple nucleations. The average grain size of deposited as well as annealed sample is reported in Table 1.

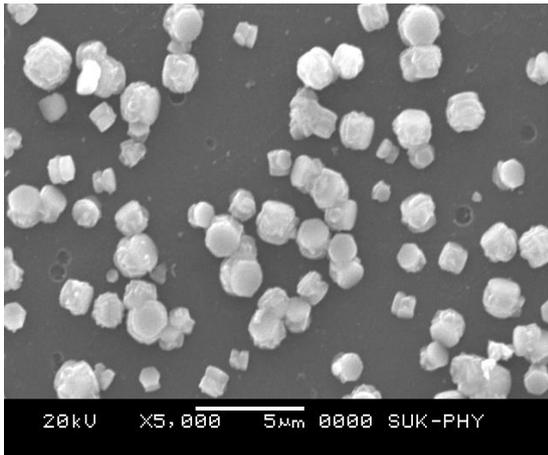


Fig .3. (a) (SEM) ZnTe thin film “as deposited.”

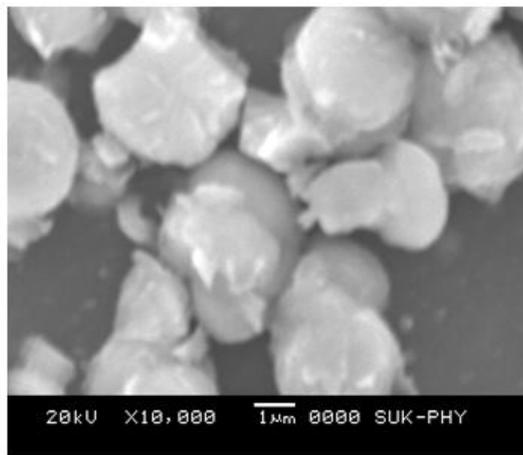


Fig. 3b: (SEM) ZnTe thin film ‘as annealed’.

4.4. Optical studies:

The absorption spectrum of sample was recorded at room temperature in the wavelength range of 400-1200 nm. The optical absorbance of thin film is closely related to its morphology shows the variation of optical absorbance with wavelength. The value of absorption coefficients depends upon radiation energy as well as composition of film. The spectrum showed that the absorption edge for the annealed sample shifts toward lower energy than that of the “as deposited” sample. It is probably due to increase in the grain size leading to reduction in the density of grain boundary trapping centers and the change in the colour form white to gray white. This shift indicates decrease in band gap of the sample.

The data was properly studied in the vicinity of an absorption edge on the basis of three-dimensional model to estimate the band gap by using the following classical relation for near absorption edge in a semiconductor.

$$\alpha h\nu = A (h\nu - E_g)^{1/2} \dots\dots\dots (7)$$

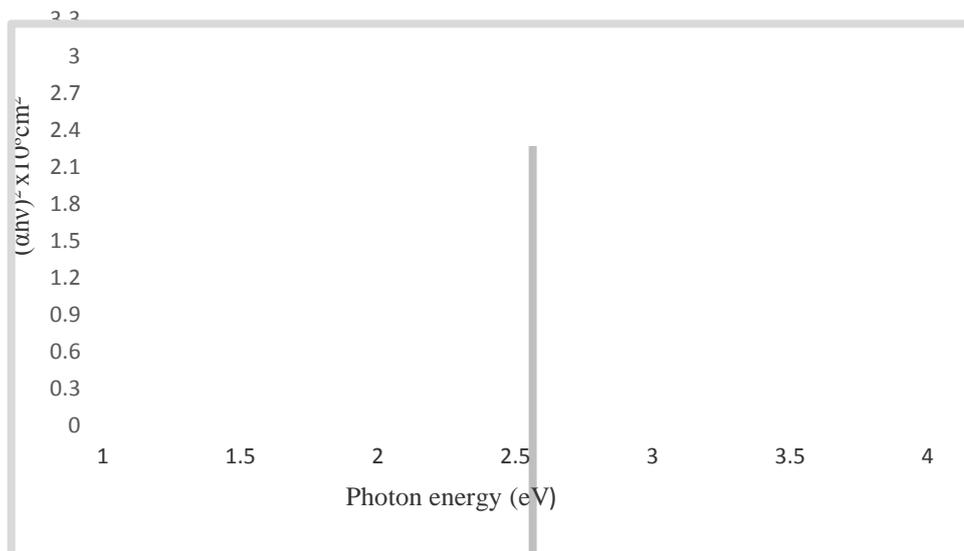


Fig .4. band gap energy $(\alpha h\nu)^2 \times 10^8 \text{ cm}^{-2}$ Vs photon energy (eV).

Where $h\nu$, is the photon energy E_g , is the band gap, A is constant, and depending upon the temperature, phonon energy etc. For allowed direct transition $n = 1/2$ and allowed indirect transition $n = 2$. A plot of $(\alpha h\nu)^2$ Vs $h\nu$ is shown in the Fig. 4. Extrapolation of the linear portion of the curve to $(\alpha h\nu)^2 = 0$ yields the optical band gap. The observed straight-line behavior establishes that the film has a direct band gap of 2 eV. The gap obtained agrees with the results previously reported [8].

4.5. Electrical and transport properties:

The electrical conductivity of ‘as deposited’ ZnTe film was measured in the range of 300-500 K temperature by using dc two probe method. It is well known that electronic properties of polycrystalline thin films are strongly influenced by their structural characteristics [17]. At room temperature the specific conductance was found to be in the order of 10^{-8} ($\Omega \text{ cm}$)⁻¹, which, agrees with the earlier reported value [18]. The conductivity increases with increasing in temperature, indicating semi conducting behavior. The variation of electrical conductivity with temperature during cooling and heating cycles were found to be different and show the ‘as deposited’ films undergoing an irreversible change due to annealing out of non equilibrium defects during first heating. A plot of $\log \sigma$ Vs $(1000/T) \text{ k}$ for the cooling curve is exhibited in Fig 5. The nature of plot is non linear type indicating the presence of two type of conduction mechanism. The temperature dependence of the electrical conductivity is accounted using Arrhenius equation.

$$\sigma = \sigma_0 \exp (- Ea / kT) \dots\dots\dots (8)$$

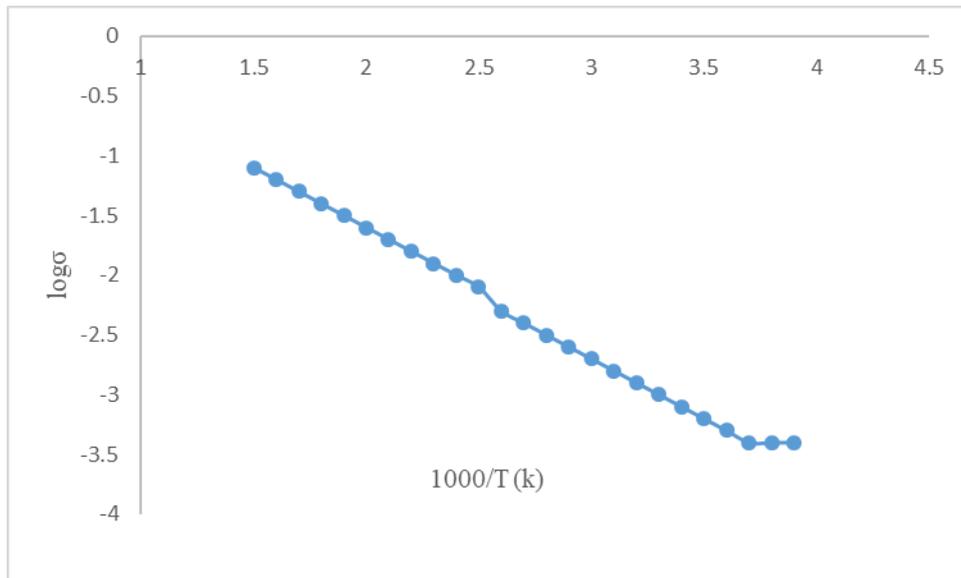


Fig .5. Conductivity of ZnTe thin film $\log \sigma$ Vs $1000/T$ (k).

Table2: Optical and electrical characterization of ZnTe thin film.

sample	Band gap (eV)	Activation energy (eV)		Specific conductance ($\Omega \text{ cm}$) ⁻¹	
		HT	LT	300K	500K
ZnTe	2 (eV)	0.3704	0.0659	1.750×10^{-8}	3.806×10^{-5}

Where Ea' is the activation energy and other terms have their usual meaning. The activation energy of ZnTe thin films was found to be a high temperature 0.370 eV and low temperature 0.065 eV as shown in Table 2. The thermo electrical conductivity of the sample was measured by the open circuit, thermo- voltage generated by the sample where a temperature gradient is applied across a length of the sample was measured using a digital micro voltmeter. The temperature difference between the two ends of the samples causes transport of carriers from the hot to cold end thus creating an electric field, which gives rise to thermo voltage across the ends. From the sign of the potentiometer terminal connected at the cold end, one can deduce the sign of predominant charge carriers. In ZnTe thin film the positive terminal connected to the cold end therefore, the film shows P- type conductivity [23]

CONCLUSION:

Zinc telluride films have been successfully deposited by using chemical bath method. Morphological studies show, as deposited films are uniform, homogenous in crystallinity. The optical absorption studies showed zinc telluride sample have direct band gap of 2 eV. Crystallographic studies revealed zinc telluride thin film are Orthorhombic phase. Electrical conductivity at room temperature of zinc telluride thin film is of the order of 10^{-8} ($\Omega \text{ cm}$)⁻¹. Thermoelectric power measurements indicate p-type conduction for zinc telluride film.

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