INVESTIGATION OF SUBSTRATE TEMPERATURE EFFECTS ON PHYSICAL PROPERTIES OF ZnTe THIN FILMS BY CLOSE SPACED SUBLIMATION TECHNIQUE

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Zinc telluride thin films were grown on well-cleaned glass substrates by closed space sublimation technique. ZnTe powders having 99.99% purity were used as a precursor. The effect of changing the substrate temperature was studied using X-ray diffraction (XRD) method, UV/VIS/NIR spectroscopy, electrical properties using Hall measurements and FTIR analysis. The films possessed the (111) orientation preferably as indicated by the XRD patterns. The variation in energy band gap was observed by changing the substrate temperatures. The electrical resistivity, mobility and the carrier concentration were found to be dependent on the substrate temperature. Resistivity decreases by increasing the substrate temperature.

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1. Introduction

Zinc Telluride (ZnTe) is a semiconductor compound belongs to II-VI group. Over the years ZnTe have attracted many researchers, because it is widely used in fabrication of solar cells, photo detectors, photo diodes, light emitting diodes, and opto-electronic devices. To design opto-electronic devices ZnTe possess the required optical and electrical properties. At room temperature Zinc Telluride have a band gap (E_g) of 2.6eV [1, 2] in the electromagnetic spectra it is the pure green region. The band gap of ZnTe allows it a primary candidate for manufacturing of green light emitting diodes (LEDs) [3–8]. ZnTe is useful in detection and production of tetra hertz radiation, because of high electro-optic co-efficient [3, 7]. Higher efficiency can be achieved in CdTe solar cells by using ZnTe as a back contact material, because in CdTe and ZnTe a very small valence band offset (0.1eV) occurs [8]. ZnTe films fabricated by using a numeral fabrication techniques including electron beam [9], electro-deposition [10], SILAR method [11], pulsed laser deposition [12], thermal evaporation [13], Molecular beam epitaxy (MBE) [14], sputtering [15], MOCVD [16], brush plate [17], magnetron sputtering [18], and closed space sublimation [19].

However, Closed Space Sublimation (CSS) technique is economical and a simple technique as compared to other techniques for improved quality ZnTe films, depending on if we organize the deposition parameter in a proper way. Temperature of the substrate is one of the important parameter in the CSS technique. Crystallanity and composition of the deposited films is very much varied by substrate temperature. So the effect of temperatures of substrate is of great

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importance on the ZnTe films properties deposited by CSS. Main emphasize of this research is to study electrical, optical and structural properties of ZnTe films deposited by CSS, under different temperatures of substrate, to determine the optimal growth conditions of these films with good optical quality.

2. Experimental

ZnTe fine powder was used with purity 99.99% as base material for ZnTe thin films deposition on soda lime glass substrates (2.5 cm x 5 cm) by the CSS technique. Before deposition, the substrate slides were cleaned with Iso-Propanol (I.P.A) in an ultra-sonic bath (60°C bath temperature and sonications for 20 minutes) and dried. A small amount of source material (ZnTe fine powder) was placed in graphite boat. The ZnTe powder was heated by 1000 W halogen lamp. The substrate and source heaters were linked through separate triacs to the main. Gates triacs were linked directly to the temperature controllers. In graphite substrate supporter and source graphite boat we inserted K-type thermocouples. The distance between source and substrate is kept 5 mm. The chamber was cleaned well with acetone to remove dust particles and impurities. After cleaning, closed the chamber and by the help of rotary pump evacuated the chamber to $\sim 1 \times 10^{-2}$ mbar. The substrate slides were reserved at three different temperatures 300˚C, 330˚C and 360˚C. The time of deposition was kept three minutes. Before starting the substrate and source heating firstly chamber was evacuated for half an hour. After depositing film for three minutes, turned off the source heater while the substrate heater was maintained at deposition temperature for half an hour to avoid further deposition. The films were kept in vacuum till temperature of source was minimized to room temperature, to avoid the films to get oxidized.

Deposited films had good adhesion and have uniformity. Deposited ZnTe films at different substrate temperatures were characterized by different analysis techniques. The ZnTe deposited films XRD characterization was done by PANalytical X'Pert PRO XRD (CuKα radiation). The UV–VIS-NIR spectrophotometer (Perkin Elmer Lamda 950) was used to determine the transmission. Electrical characterization such as resistivity, mobility and carrier concentration of ZnTe thin films was studied by Ecopia HMS-3000(at room temperature). By using silver paste four silver contacts on corner of films (1cm x 1cm) were made. Good ohmic contacts of silver were found on the ZnTe films. Hall measurements were made for ZnTe thin films by four probe method [20].

3. Results and discussion

3.1. Structural properties

XRD pattern of films deposited at three substrate temperature (300, 330 & 360ºC) are shown in Fig. 1. All the three ZnTe films have cubic structure with preferred orientation is in (111) direction. We calculated lattice parameter for highly preferred orientation of (111) planes and it was found to be 6.108 Å which is matched with the value mentioned in JCPDS reference card. From XRD patterns we calculated grain size of films. The increased in grain size value, or we can also say that the film crystallanity increases with the increase in substrate temperature. As the substrate is heated the mobility of atoms increases which consequences in less significant amount of nucleation centers [21]. The deposited films composition depends on the number of Zn and Te atoms adsorb to the surface and impinge on substrate. At lower substrate temperature tellurium is in excess because of difference in sticking co-efficient and vapor pressure of Zn and Te. By increasing the temperature of substrate sticking co-efficient of Zn increases and Te atoms which are in excess re-evaporates resulting in a balance between Zn and Te.

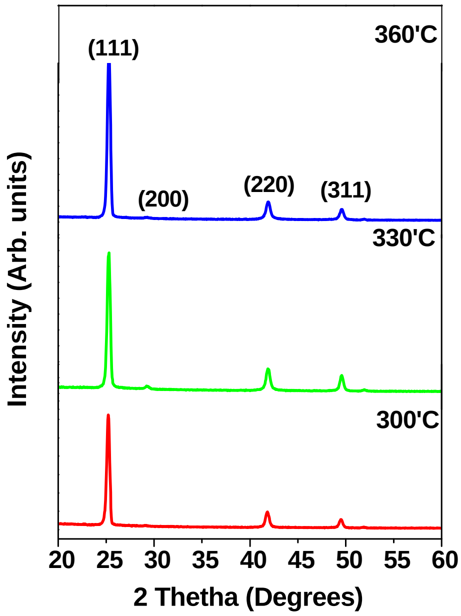

Fig. 1 XRD spectrum of ZnTe films deposited at different substrate temperatures.

The lattice parameter 'a' for (hkl) has been calculated by the following expression [22]

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Where d is the interplanar spacing of the atomic plane whose Miller indices are (hkl).

Debye Scherrer formula as mentioned in equation 2 is used to calculate the grain size (D) of the ZnTe films

$$D = \frac{k\lambda}{\beta \, Cos\theta} \qquad (2)$$

Where k is a constant to be taken 0.49 λ, β, and θ are the X-ray wavelength (=1.5406Å), FWHM and Bragg angle respectively. The dislocation density (ρ), which represents the amount of defects in the crystal, is estimated from the following equation 3:

$$\rho = \frac{1}{D^2} \qquad (3)$$

Strain (ε) of the thin film is determined from equation 4:

$$\varepsilon = \frac{\beta Cos0}{4} \qquad (4)$$

The lattice constant (a), crystallite size (D), dislocation density (ρ), strain (ε) were calculated and mentioned in Table 1. As the temperature of the substrate increases Strain, dislocation density and lattice constant decreases while the crystallite size increases.

Table 1. Structural parameters of the ZnTe films deposited at three substrate temperature (300, 330 & 360ºC).

Substrate temperature (˚C)	Lattice constant 'a' (Å)	Crystallite Size 'D' (nm)	Dislocation Density ($x10^{-04}$ nm^{-2})	Strain ($x10^{-04}$)
300	**6.112**	**37.16**	**7.24**	**9.32**
330	**6.108**	**44.20**	**5.12**	**7.84**
360	**6.105**	**63.32**	**2.49**	**5.47**

3.2. Optical properties

Transmission spectra of ZnTe films deposited at various substrate temperatures and transmission Spectra of ZnTe films deposited at 300ºC & 330 ºC with angle variation shown in Fig. 2 & Fig. 3 respectively.

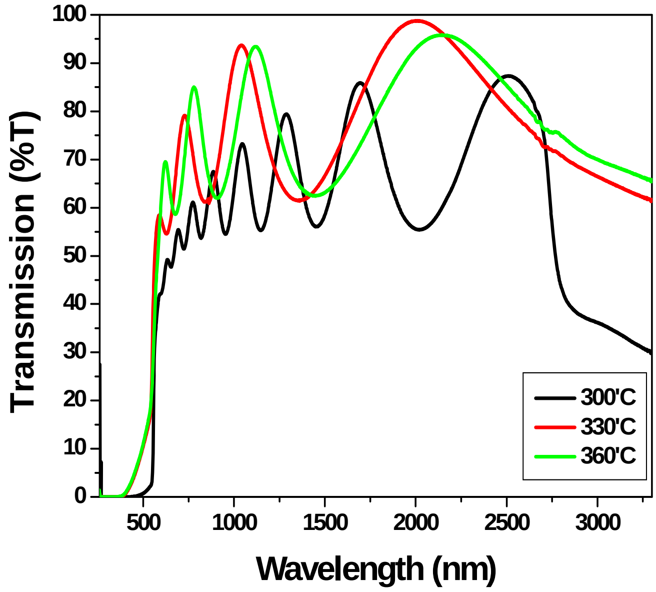

Fig. 2 Transmission Spectra of ZnTe films deposited at different substrate temperatures

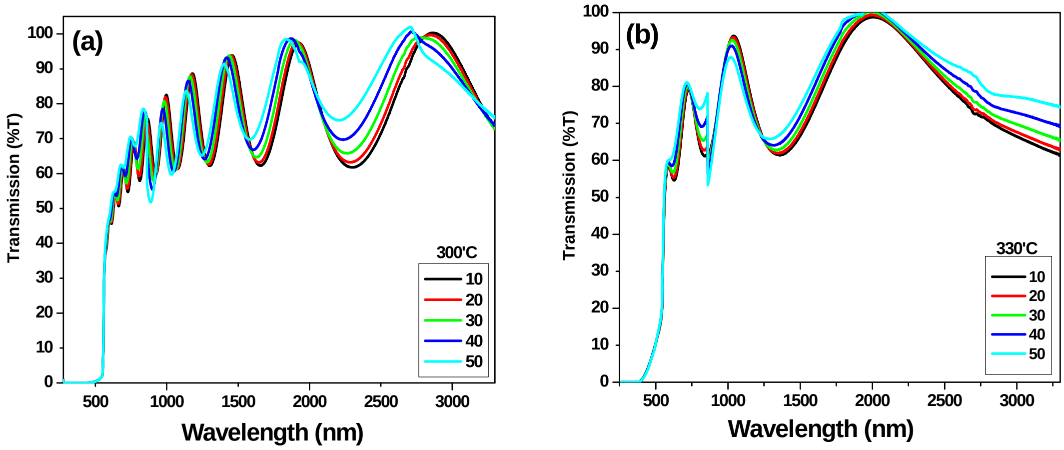

Fig. 3 Transmission Spectra of ZnTe film with angle variation (a) 300ºC and (b) 330ºC.

The absorption co-efficient (α) is related to the optical band gap (E_g) by the relation[24],

$$\alpha h\nu = B(h\nu - E_g)^n \tag{5}$$

In the above equation B is a constant having value 1 because optical transition is direct for ZnTe films ,n is a constant number, ν is frequency of the radiation and h is Plank's constant.In Fig. 4 $(ah\nu)^2$ vs. hν plots shows a linear portion indicating that the relation in equation 4 holds good for ZnTe films. By extrapolating linear portions of curves we easily calculate the band gap (Fig. 4). As we increases the substrate temperature the optical band gap increases from 2.22eV and approaches to 2.25eV.

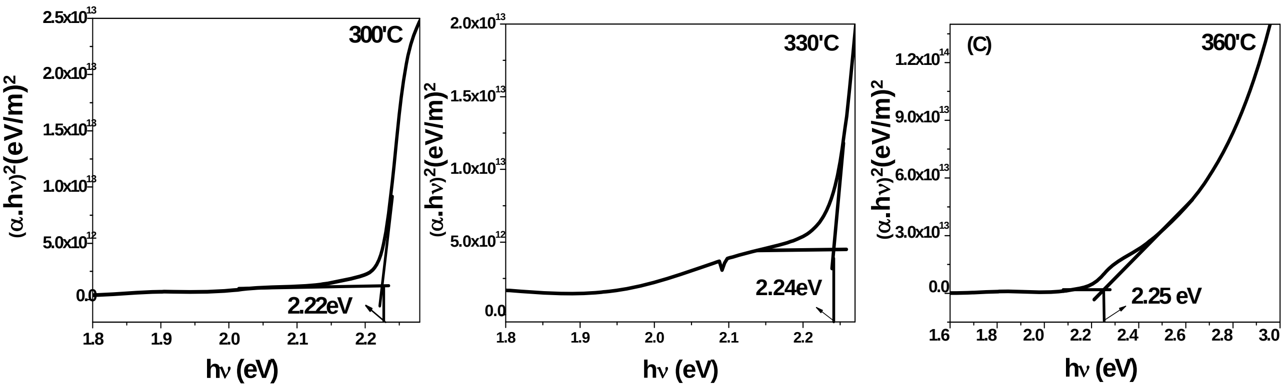

Fig. 4 Optical Band Gap of ZnTe films deposited at (a) 300ºC, (b) 330ºC and (c) 360ºC

As we increase the substrate temperature the refractive index of the films decreases because the films were more stoichiometric and uniform. The stoichiometry and enhancement in films crystallanity of the films at elevated substrate temperature consequences shift in optical band gap [23]. The films which are deposited at relatively higher temperature of substrate have larger grain size and are almost stoichiometric so their band gap is nearly equal to bulk material. Optical conductivity of ZnTe films can be easily calculated from the relation (6)

$$\sigma_o = \frac{\alpha . n . c}{4\pi} \tag{6}$$

Where α is the absorbance co-efficient, n is refractive index and c is speed of light. Optical density (OD) is the measure of transmittance of an optical medium for a given wavelength. optical density calculated by the relation (7)

$$O.D = Log_{10} \frac{1}{T} \tag{7}$$

Where T is transmittance. The higher the optical density the lower the transmittance. OD is related to refractive index of a material. A higher value of refractive index means higher OD as shown in fig.5a.

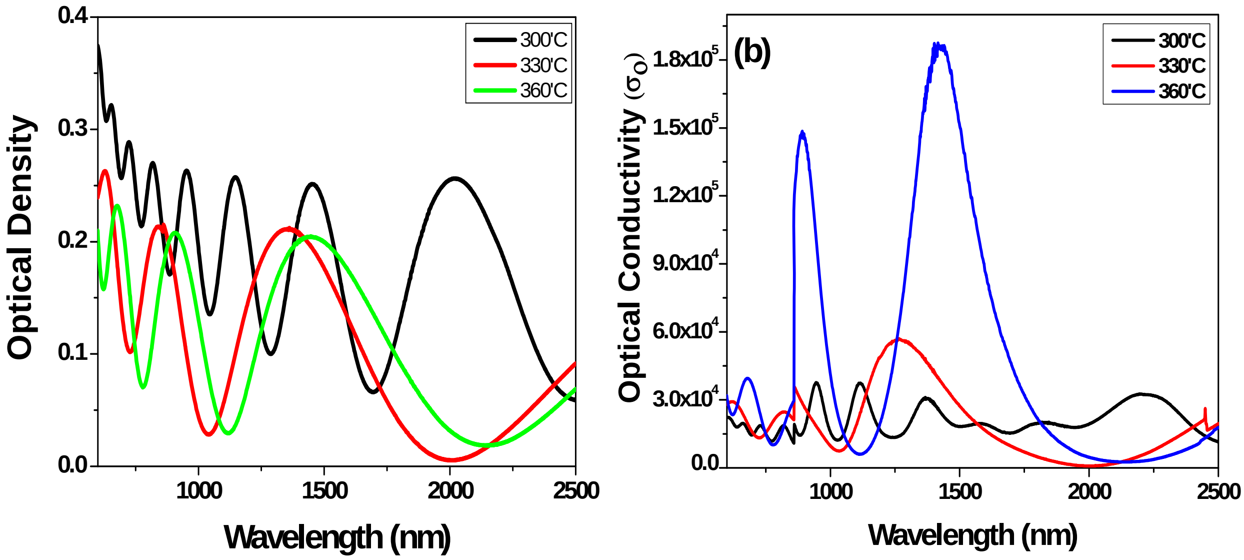

Fig. 5 (a)Optical Density and (b) Optical Conductivity of ZnTe films deposited at three substrate temperature (300, 330 & 360ºC).

Table 2. The band gap, refractive index and optical conductivity of the ZnTe films deposited at three substrate temperature (300, 330 & 360ºC).

Substrate temperature (˚C)	**Band Gap (eV)**	**Refractive Index**
300	**2.22**	**2.57**
330	**2.24**	**2.53**
360	**2.25**	**2.50**

3.3. Electrical properties

Vander Paw-Four probe method was used to measure the electrical properties. ZnTe films are of p-type determined by the carrier concentration [25]. The resistivity, mobility and carrier concentration of films are given in Table 3. Resistivity of the deposited films decreases which we deposit at higher temperature of substrate are more stoichiometric and have improved crystallanity which fallout in increase in the conductivity of the films due to the decrease in the defect states. Larger grain boundary region and small grain size were noticed in lower substrate temperature deposited films. Films which are grown at lower temperature of substrate have large number of defects due to the grain boundary region disordering. [26].

Table 3. Carrier Concentration, Resistivity and Mobility of ZnTe films at three substrate temperature (300, 330 & 360ºC).

Substrate temperature (˚C)	Carrier Concentration (cm^{-3})	Resistivity (Ω.m)	Mobility ($cm^2V^{-1}s^{-1}$)
300	**$4.01x10^9$**	**$2.3x10^5$**	**$1.69x10^2$**
330	**$3.11x10^{10}$**	**$1.72x10^5$**	**$2.74x10^2$**
360	**$1.44x10^{11}$**	**$1.58x10^5$**	**$6.63x 10^2$**

3.4. FTIR of Zn-Te Films

Zn-Te films deposited at three substrate temperature (300, 330 & 360ºC) showed the characteristics peak for Zn-O stretching mode at 481, 476.1 and 456.8cm^{-1} [16, 17]. Physisorbed water present on the surface of films showed its appearance by giving vibrational signal of O–H in the IR region at 1595.2, 1595.0 and 1595.5 cm^{-1} [27, 28, 29]. Presence of CO_2 molecules in air showed its FT-IR signature peak at 2358.9, 2359.2 and 239.3 cm^{-1} [27, 28]. The Zn-O appeared in all samples which showed that by varying substrate temperature there is no effect on the formation of film.

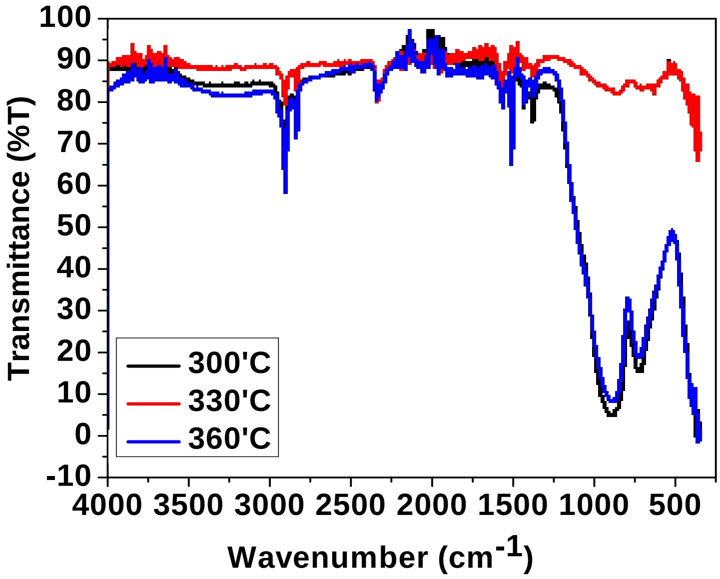

Fig. 6 FTIR of ZnTe films deposited at different substrate temperatures.

Table 4. FTIR of ZnTe films at three substrate temperature (300, 330 & 360ºC).

Substrate temperature (°C)	CO_2 in air (cm^{-1})	O-H bending of adsorbed water (cm^{-1})	Zn-O stretching (cm^{-1})
300	**2358.9**	**1595.2**	**481**
330	**2359.2**	**1595.0**	**476.1**
360	**2359.3**	**1595.5**	**456.8**

4. Conclusion

Closed Space Sublimation (CSS) was selected as a deposition technique for depositing thin films of ZnTe on soda lime glass substrates. The main tool is temperature of substrate for couture the structural, optical and electrical properties of deposited films. The films exhibit a cubic structure and were polycrystalline.XRD shows peak intensity and the crystallite size increases with increasing substrate temperature. The transmission coefficient was found to be strongly affected by substrate temperature due to tellurium micro crystallites presence in films (analyzed by XRD patterns) having greater absorbance in the visible domain. This effect consequently leads to increased in the optical band gap width with increasing temperature of substrate. It has been observed that the high frequency dielectric constant decreases by increasing the temperature of substrate. The band gap analysis shows that the optical data was allowed direct transitions. The band gap increases from 2.22eV to 2.25 eV by increasing the temperature of substrate. FT-IR analysis is not suitable for the study of ZnTe film as it can't show Zn-Te characteristic peak (which appears in the range of 160-175 cm^{-1}) which is beyond its usual limit.

Larger grains were noticed in films deposited at higher substrate temperatures and were nearly have stoichiometric composition. Optical and electrical properties of films were found to enhance by these improvements. Thus stoichiometric composition and good crystallanity can be achieved in closed space sublimation (CSS) fabricated ZnTe films by rising the temperature of substrate in a suitable manner, which are basic requirement for device quality films.

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