Chapter – IV

Photoconductivity study of ZnTe thin films and its correlative assessment with structural characterization
4.1 Introduction

The study of binary II-VI compounds has attracted wide interest because of their wide applications in a variety of solid state devices. Among these, ZnTe is of considerable interest chiefly for its use as light emitting diodes in short wavelength region. In addition to this p type ZnTe thin film sample has been used for fabricating high efficiency CdS/CdTe/ZnTe solar cells/1-15/. The properties of the films depend on the growth parameters as well as trapping and recombination centers that may be present in the band gap. For a total investigation of electrical conductivity of the films, substrate temperature of film growth and other growth parameters and ambient applied conditions must be taken into consideration. The growth parameters of importance are the thickness of the film, substrate temperature, rate of deposition, source temperature, spacing between the source and substrate.

It is found that the high quality ZnTe films can be produced by evaporation of ZnTe powder onto glass substrates heated to 873K/16-20/. The substrate temperature (T_s), at which a thin film is grown, is an important factor for formation of grains of different sizes in the thin films prepared by thermal evaporation/21-30/.

Thermally deposited ZnTe thin films at high T_s are found to be polycrystalline with preferential orientation of (111) plane parallel to the substrate/31/, in addition to other two sets of prominent planes (220) and (311). Polycrystalline ZnTe thin films contain grains of various sizes along different orientations. The lattice parameter, grain size, average internal stress, microstrain, residual stress and strain, dislocation density are the important structural attributes of the thermally deposited ZnTe thin films. Structural attributes such grain sizes, grain orientations, grain boundary potential barriers, localized strains and dislocations of the films particularly of vacuum evaporated type, play important roles in both dark and photoconductivity processes. The grain boundaries contain fairly high densities of interface states, which trap free carriers /32/. Thermal annealing also improves the degree of crystallinity of polycrystalline ZnTe thin films. Due to thermal annealing resistivity of the films also changes.

In this study of the photoresponse characteristics and other related properties of ZnTe thin films at different ambient temperatures, substrate temperatures were selected in the range 300K – 500K and the thickness range of the thin films was 700 Å-4000 Å. The
electronic and optoelectronic properties of the films are dependent on the structural properties of the films. The structural characteristics and in turn determined by various growth parameters. Hence a correlative study of structural and optoelectronic properties is required for a clear understanding of the interdependence of these characteristics attributes. The present work is an attempt in this direction.

4.2 Results and discussions

4.2.01 Structural characterization of ZnTe thin films

Different structural parameters were analyzed from XRD data of the fresh and annealed ZnTe thin films, taking the diffractograms of the bulk ZnTe samples as the basic reference. Various structural parameters of the thin film samples are elaborated in chapter III and some salient features are highlighted below.

(a) Lattice plane (hkl) and lattice constant “a”

The Bragg angle of diffraction lattice planes of the ZnTe thin films were determined using reciprocal lattice method. Accurate value of lattice constant of ZnTe in thin films was evaluated from the Nelson Riley (N – R) plot.

(b) Grain size

Grain size ‘D’ of the zinc telluride thin films in fresh as well as after annealing were calculated considering Cauchy, Gaussian and Intermediate Parabolic form of distribution with the help of the following relation

\[ D = \frac{0.89\lambda}{\beta \cos \theta} \]  

Where \( \lambda \) is the wavelength of the diffracted X-ray, \( \beta \) is the Full Width at Half maximum of the prominent peaks and \( \theta \) is the Bragg angle of diffraction. The evaluated values of the grain sizes lie within the range 75 Å - 400 Å.

(c) W – H (Williamson-Hall) plot

W- H plots between \( \beta^* (\beta \cos \theta / \lambda) \) vs. \( d^* (2 \sin \theta / \lambda) \) indicates that X-ray line broadening is due to size effect as well as the presence of strain in the thin film samples.

(d) Strain and stress

Average strain and stress of the fresh and annealed thin films were evaluated considering Cauchy, Gaussian and Intermediate Parabolic form of distribution-

\[ S = \frac{[(a - a_0) / a_0] E}{2v} \]  

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respectively, where \( a \) and \( a_0 \) are the lattice constants of the thin film sample and the bulk sample respectively and \( E \) and \( v \) are the Young’s modulus and Poisson’s ratio of the bulk sample. The evaluated values of the average strain and stress lie in the ranges of \( 3.29 \times 10^8 \text{ N/m}^2 \) – \( 6.46 \times 10^8 \text{ N/m}^2 \) and \( 3.69 \times 10^3 \) – \( 6.18 \times 10^3 \).

(e) Residual stress and strain

(i) Residual stress and strain of ZnTe thin films were determined using \( \sin^2 \psi \) method with the help of the following relation –

\[
\frac{d - d_o}{d_0} = \varepsilon_r - \frac{(1 + v)}{E} \sigma_r \sin^2 \psi
\]

The evaluated values of the residual stress and strain lie in the ranges of \( 4.75 \times 10^8 \text{ N/m}^2 \) – \( 18.16 \times 10^8 \text{ N/m}^2 \) and \( 3.01 \times 10^3 \) – \( 13.70 \times 10^3 \) respectively.

(ii) Residual stress and strain of ZnTe thin films were determined using grazing incidence X-ray diffraction geometry with the help of the following relation –

\[
\frac{d - d_o}{d_0} = \left( \frac{(1 + v)}{E} \right) \sigma_r \cos^2 \alpha \sin^2 \psi + \left( \frac{(1 + v)}{E} \right) \sigma_r \sin^2 \alpha - \left( \frac{2v}{E} \right) \sigma_r
\]

The evaluated values of the residual stress and strain lie in the ranges of \( 7.72 \times 10^8 \text{ N/m}^2 \) – \( 20.85 \times 10^8 \text{ N/m}^2 \) and \( 14.35 \times 10^3 \) – \( 40.88 \times 10^3 \) respectively.

(f) Dislocation density

Dislocation density of the fresh and the annealed ZnTe thin films were measured considering Cauchy, Gaussian and Intermediate Parabolic form of distribution with the help of following relation –

\[
\rho_{hkl} = \left[ 3nKb^2 / D^2b^2F^2 \right]^{1/6}
\]

along different preferred orientations, where \( n \) is the no. of dislocations, \( K \) is a constant which depends upon the strain distribution function, \( b \) is the Burgers vector of dislocations and \( F \) is an interaction parameter \((= n)\) and \( b = d_{hkl} = a / (h^2 + k^2 + l^2)^{1/6} \). The calculated values of the dislocation densities for fresh and annealed ZnTe thin films lie in the range \( 0.229 \times 10^{12} \text{ cm}^{-2} \) – \( 4.708 \times 10^{12} \text{ cm}^{-2} \).

4.2.02 Dark and photoconductivity characterization

(a) Study of electrode-film contacts

To get the ohmic contact with ZnTe thin films electrodes of several of metals was utilised by different worker. Bellakhder et al used silver electrodes for getting ohmic contact with ZnTe thin films deposited by r. f. sputtering /I/. Kazuhiro Mochizuki et al
and Takes Ohtsuka et al. /33,34/ used gold as the electrode material in chemically deposited ZnTe thin films under different ambient conditions. Palladium metal was utilised as the electrode material by different workers/35,36/ for getting ohmic contact with p-type ZnTe thin films prepared by different techniques. Many workers have been utilizing aluminum as electrode material for a long time for getting ohmic contact with thermally evaporated ZnTe thin films to study electrical conduction mechanisms under various ambient conditions/24,25,31,37,38/. In this work before starting the optoelectronic measurements, the ohmic nature of the electrode contacts was confirmed by recording the $J_d - V_a$ characteristics ($J_d$ is the dark current density and $V_a$ is applied bias) at different ambient temperatures over a wide range of voltage of both the polarities under dark condition. Figure 4.01 and 4.02 show the $J_d - V_a$ plots at different ambient conditions of typical films of thickness 1900Å and 1400 Å grown at 303K to 475K ($T_s$). The distinct linearity over the entire bias range and symmetrical nature about the zero applied bias of these plots show that the electrode contacts are ohmic in the whole range of the applied voltage.

(b) $J_d$ versus $V_a$ and ln$J_d$ versus $F^{1/2}$ characteristics

The dark current density $J_d$ versus applied bias ($V_a$) characteristics of the ZnTe thin films were found to be linear within the range of the applied bias (-110 volt - 0 - +110 volt). The $J_d$ versus $V_a$ plots for films grown at room temperature and higher substrate temperature in fresh and annealed conditions are also shown in Figure 4.01. Which also indicates that the aluminum electrode contact with ZnTe thin films is ohmic for dark conductivity. As a cross checking measure natural logarithm of dark current density is plotted against square root of the applied field as shown in Figure 4.03. The graphs are totally nonlinear within the entire range of applied field. This implies that there is no exponential region of dependence of $J_d$ on $F$ in the applied field range from 0 to $1.57 \times 10^4$ Volt/m. This picture leads ample support to the observations depicted in the Figure 4.01 and 4.02 to the fact that the electrode contacts to the ZnTe thin film samples are ohmic/39/.
Figure 4.01: Dark current density ($I_D$) versus applied bias ($V_B$) characteristics for fresh and annealed ZnTe thin films of thickness 1900Å, deposited at $T_s = 303K & 375K$ (at room temperature).
Figure 4.02: Dark current density ($J_D$) versus applied bias ($V_a$) characteristics corresponding to different ambient temperatures for ZnTe films of thickness 1400Å deposited at 303K and 375K.
Figure 4.03: \( \ln J_d \) versus \( F^{1/2} \) characteristics at different ambient temperature for ZnTe thin films of thickness 1900Å, deposited at \( T_s = 303K \) & 375K.

(c) \( \ln J_{ph} \) versus \( \ln \phi \) characteristics

Figure 4.04 and 4.05 i.e. \( \ln J_{ph} \) versus \( \ln \phi \) plots represent the intensity dependence of photocurrent density of two representative films of thickness 1900Å deposited at room temperature (303K) and higher temperature (\( T_s = 375K \)). These plots reveal that the photocurrent density (\( J_{ph} \)) has a sub-linear dependence on the intensity of light (\( \phi \)).
Figure 4.04: $\ln I_0$ versus $\ln \Phi$ plots for fresh and annealed ZnTe thin films deposited at different substrate temperature (ambient temperature = 303K).
The power law relationship between $J_{ph}$ versus $\phi$ can be written as

$$J_{ph} = C\phi^\gamma,$$

(7)

where $J_{ph} = J_L - J_D$, $J_L$ is the current density under illumination, $J_D$ is the dark current density, $\gamma$ is the power factor and $C$ is a constant of proportionality. The values of power

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factor \( \gamma \) were calculated from the slopes of \( \ln J_{\text{ph}} \) versus \( \ln \phi \) graphs for different films at different applied biases and at different ambient temperatures. From the plots of \( \ln J_{\text{ph}} \) versus \( \ln \phi \) it has been observed that the values of \( \gamma \) ranges between 0.5-0.6. Hence the photoconductivity in these thin films is of defect-controlled type. The calculated values \( \gamma \) for ZnTe thin films deposited at different \( T_s \) and experiments performed at different ambient temperatures are given in the Table 4.01.

**Table 4.01**: Calculated values of power factor (\( \gamma \)) for films of thickness 1900 Å under white light illumination at bias 9 Volts and 63 Volts.

<table>
<thead>
<tr>
<th>Samples at different condition</th>
<th>( \gamma ) at different applied bias</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>9 Volt</td>
</tr>
<tr>
<td>Fresh ([T_s = \text{RT}(303K)])</td>
<td>0.58</td>
</tr>
<tr>
<td>Annealed ([T_s =303K])</td>
<td>0.54</td>
</tr>
<tr>
<td>Fresh ([T_s = 375K])</td>
<td>0.52</td>
</tr>
<tr>
<td>Annealed ([T_s =375K])</td>
<td>0.55</td>
</tr>
<tr>
<td>Ambient temperature 325K</td>
<td>0.58</td>
</tr>
<tr>
<td>Ambient temperature 360K</td>
<td>0.58</td>
</tr>
</tbody>
</table>

(d) \( J_{\text{ph}} \) versus \( V_s \) characteristics and study of field effect

The photocurrent density \( J_{\text{ph}} \) is defined as \( J_L - J_D = J_{\text{ph}} \), where \( J_L \) and \( J_D \) are the light and dark current densities respectively. The dependence of photocurrent density \( J_{\text{ph}} \) on applied bias (\( V_s \)) for four different intensity of white light at room temperature for fresh and annealed ZnTe thin films deposited at RT (=303K) and higher \( T_s (=375K) \) are shown in the figure 4.06. In Figures 4.07(a)&(b) and 4.08(a)&(b), the \( J_{\text{ph}} \) versus \( V_s \) characteristics for different ambient temperatures are shown for two fixed intensities of illumination (1100lx and 4400lx) for ZnTe thin films deposited at room temperature substrates and higher temperature (375K).
Figure 4.06: Photocurrent density ($J_{ph}$) versus applied bias ($V_a$) characteristics at different intensity of white light illumination and at room temperature for fresh and annealed ZnTe films deposited at different $T_*$.
Figure 4.07(a): Photocurrent density \( (J_{ph}) \) versus applied bias \( (V_a) \) characteristics (intensity of illumination fixed at 1100 lux) for different ambient temperatures for ZnTe thin films deposited at 303K\((T_a)\).

Figure 4.07(b): Photocurrent density \( (J_{ph}) \) versus applied bias \( (V_a) \) characteristics (intensity of illumination fixed at 1100 lux) for different ambient temperatures for ZnTe thin films deposited at 375K\((T_a)\).
Figure 4.08(a): Photocurrent density ($J_{\text{ph}}$) versus applied bias ($V_a$) characteristics (intensity of illumination fixed at 4400 lux) for different ambient temperatures for ZnTe thin films deposited at 303K($T_a$).

Figure 4.08(b): Photocurrent density ($J_{\text{ph}}$) versus applied bias ($V_a$) characteristics (intensity of illumination fixed at 4400 lux) for different ambient temperatures for ZnTe thin films deposited at 375K($T_a$).
From these figures it is clear that \( J_{ph} \) versus \( V_a \) characteristics obey two distinct conduction mechanisms in different bias regions. There is a low voltage range (for both the polarities) in which the \( J_{ph} \) versus \( V_a \) plots are linear and pass symmetrically through the origin. Thus in the low field region the conduction mechanism is ohmic. Beyond the low voltage range the photocurrent density is found to increase nonlinearly with the applied bias. The nonlinear dependence of photocurrent density with applied bias indicate the predominance of Poole-Frenkel or Schottky effects /42/. The present results can be suitably interpreted in terms of Poole-Frenkel effect.

The Poole-Frenkel effect is the field lowering of the built-in potential barriers. This results in a traditional conductivity expression /43/

\[
J = \sigma_0 F \exp \left( \frac{\beta F^{1/2}}{kT} \right)
\]

Here \( k \) is the Boltzmann constant, \( T \) is the absolute temperature, \( F \) is the average applied field, \( \sigma_0 \) is the low field conductivity, which depends on the carrier mobility and donor activation energy and \( \beta \) is the Poole-Frenkel coefficient. The Poole-Frenkel coefficient is given by

\[
\beta = \left( \frac{e^3}{\pi \varepsilon \varepsilon_0} \right)^{1/2}
\]

where \( e \) is the electronic charge, \( \varepsilon_0 \) the permittivity of free space and \( \varepsilon_r \) the relative permittivity of the material. In the studied ZnTe thin films, beyond the low voltage range the photocurrent density was found to increase nonlinearly with applied bias. In the nonlinear region of the \( J_{ph} \) vs. \( V_a \) characteristics the \( \ln J_{ph} \) versus \( F^{1/2} \) plots appear as shown in the Figure 4.09, 4.10 and 4.11. The \( \ln J_{ph} \) versus \( F^{1/2} \) graphs were found to be linear in high field region. Which indicates the predominance of Poole-Frenkel type of conduction mechanism. Since the increase in \( J_{ph} \) with \( F \) is normally significantly less than that with the exponential term of equation (8), therefore current density due to Poole-Frenkel type of conduction mechanism can be expressed as

\[
J_{ph} = J_0 \exp \left( \frac{\beta_{PF} F^{1/2}}{kT} \right)
\]
where $J_0 (= \sigma_0 F)$ is the low field current density, $\beta_{PF}$ is the Poole-Frenkel coefficient and other symbols have their usual significance. Due to the presence of potential barriers localized at the grain boundary regions, the mobility of the carriers are modulated by these potential barriers. In such a case the mobility can be expressed as an effective mobility given by

$$\mu^* = \mu_0 \exp \left( - \frac{q \phi_b}{kT_0} \right)$$

(11)

where $T_0$ is a characteristic constant of the barriers having the dimension of temperature, $\mu_0$ is the mobility of the carriers with no barriers effect. Therefore, it is clear that the effective mobility contributes another exponential factor to the Poole-Frenkel conductivity, as a result of which the effective Poole-Frenkel conductivity becomes a strong function of the illumination level. The effective current density can now be written as,

$$J_{ph} = n q F \mu^* \exp \left( \frac{\beta_{PF} F^{1/2}}{kT} - \frac{q \phi_b}{kT_0} \right)$$

(12)

where $n$ is the majority carrier density. Since the grain boundary potential barrier $\phi_b$ is reduced by the photogenerated carriers, therefore, at a constant applied field the photocurrent density increases exponentially with illumination. In high applied bias the exponential behaviour in case of $J_{ph}$ vs. $V_*$ characteristics (the linear regions in case of $\ln J_{ph}$ vs. $F^{1/2}$ plots) increases with the increase of illuminations as well as the ambient temperatures. The plots of $\ln J_{ph}$ versus $F^{1/2}$ ($F$ is the field corresponding to the applied bias) yield a slope $m = \frac{\beta}{kT}$. Using these experimental results, the values of Poole-Frenkel coefficients ($\beta_{PF}$) were calculated. The Poole-Frenkel coefficients ($\beta_{PF}$) calculated from this relation for fresh and annealed films deposited at RT and higher $T_*$ are shown in Table 4.02 and 4.03. These values of experimental $\beta_{PF}$ being higher than those predicted theoretically suggest the existence of localized electric fields in the films, which make the effective field higher than mean field $\bar{F} = \frac{V}{d}$. Such localized fields may be present as the result of a number of different effects; band bending in the region.
Figure 4.09: \( k \alpha \) versus \( \eta \alpha \) plots under different feed intensity of illumination for fresh and annealed ZnTe thin films deposited at different T's.
Figure 4.10: In $J_{ph}$ versus $F^{1/2}$ plots for ZnTe thin films deposited of different $T_s$ under different ambient temperature (intensity of illumination fixed at 1100lux).
Figure 4.11: In $J_{ph}$ versus $F^{1/2}$ plots for ZnTe thin films deposited of different $T_s$ under different ambient temperature (intensity of illumination fixed at 4400lux).
Figure 4.12: Plots of $m$ (slope of $\ln J_{ph}$ versus $F^{1/2}$ plot) versus $1000/T$ at different fixed intensity of illumination for ZnTe thin films deposited at 303K.

Figure 4.13: Plots of $m$ (slope of $\ln J_{ph}$ versus $F^{1/2}$ plot) versus $1000/T$ at different fixed intensity of illumination for ZnTe thin films deposited at 375K.
Table 4.02: Calculated value of Poole-Frenkel coefficient ($\beta_{PF}$) for the fresh and annealed ZnTe thin films of thickness 1900Å deposited at RT (303K) and higher temperature (375K) under different illumination level (observations taken at RT).

<table>
<thead>
<tr>
<th>Intensity of illumination (in lux)</th>
<th>Poole-Frenkel coefficient ($\beta_{PF}$) in $10^{-4}$ eV V$^{-1/2}$m$^{-1/2}$ deposited at $T_s$=303K</th>
<th>Poole-Frenkel coefficient ($\beta_{PF}$) in $10^{-4}$ eV V$^{-1/2}$m$^{-1/2}$ deposited at $T_s$=375K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Fresh$</td>
<td>$Annealed$</td>
</tr>
<tr>
<td>1100</td>
<td>3.907</td>
<td>3.921</td>
</tr>
<tr>
<td>4400</td>
<td>4.961</td>
<td>4.852</td>
</tr>
<tr>
<td>11000</td>
<td>5.724</td>
<td>5.134</td>
</tr>
<tr>
<td>22000</td>
<td>6.286</td>
<td>5.986</td>
</tr>
</tbody>
</table>

Table 4.03: Calculated values of Poole-Frenkel coefficient ($\beta_{PF}$) for the ZnTe thin films of thickness 1900Å deposited at RT (303K) and higher $T_s$ (375K) under two different illumination level and at different ambient temperatures.

<table>
<thead>
<tr>
<th>Ambient temperature</th>
<th>Poole-Frenkel coefficient ($\beta_{PF}$) in $10^{-4}$ eV V$^{-1/2}$m$^{-1/2}$ at intensity of illumination 1100lx</th>
<th>Poole-Frenkel coefficient ($\beta_{PF}$) in $10^{-4}$ eV V$^{-1/2}$m$^{-1/2}$ at intensity of illumination 4400lx</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_s$=303K</td>
<td>$T_s$=375K</td>
</tr>
<tr>
<td>303K</td>
<td>3.921</td>
<td>4.673</td>
</tr>
<tr>
<td>325K</td>
<td>3.952</td>
<td>4.565</td>
</tr>
<tr>
<td>340K</td>
<td>5.102</td>
<td>5.664</td>
</tr>
</tbody>
</table>

of the contacts due to the difference in work functions between the metal and semiconductor is one possibility, while the different localized environments of individual trapping centres in the grain boundary regions of the film are unlikely to result in an exactly linear variation in potential on a microscopic scale and thus in a spatially constant electric field.
Thus the uniform distribution of localized electric fields results in the following expression for current density

\[ J_{\text{ph}} = \frac{2J_0kT}{\alpha \beta F^{1/2}} \exp \left( \frac{\alpha \beta F^{1/2}}{kT} - \frac{q\phi_0}{kT_0} \right) \]  \quad (13)

which is also known as modified Poole-Frenkel relation/43/. Where \( J_{\text{ph}} \) = Photocurrent density, \( \beta \) = Poole-Frenkel coefficient, \( \alpha \) = a constant which depends on the field strength known as field enhancement factor and the other terms have usual significance. One can obtain the above relation in the form

\[ \ln J_{\text{ph}} = \ln \frac{2J_0kT}{\alpha \beta F^{1/2}} + \frac{\alpha \beta F^{1/2}}{kT} - \frac{q\phi_0}{kT_0} \]

\[ = C + mF^{1/2}, \]  \quad (14)

where \( C = \ln \frac{2J_0kT}{\alpha \beta F^{1/2}} - \frac{q\phi_0}{kT_0} \) and \( m = \frac{\alpha \beta}{kT} \).

A check for the consistency in the temperature dependence of conductivity has been performed by deriving a series of values of “m” for a sample at different ambient conditions. A plot of m against 1/T thus yields a straight line with slope m' given by \( m' = \frac{\beta}{k} \). The plot of the experimental values of m vs. 1/T yields a straight line as shown in the Figure 4.12 and 4.13. This leads further to the fact that photoconduction mechanism in these ZnTe thin films are of a modified Poole-Frenkel type. The m vs. 1/T graphs then yield another slope m' such that \( m' = \frac{\alpha \beta}{k} \). Thus values of (\( \alpha \beta \)) under different level of illumination are calculated for the films deposited at different T, of thickness 1900Å and are shown in the Table 4.04. Thus the derived value of \( \beta \) calculated from equation (10) will be multiplied by the factor \( \alpha \) if modified Poole-Frenkel mechanism is operational in the studied ZnTe thin films.
Table 4.04: Calculated value of $(\alpha \beta)$ for the films of thickness 1900Å deposited at RT and higher $T_s$ under different illumination levels.

<table>
<thead>
<tr>
<th>For samples grown at different $T_s$ (in K)</th>
<th>Values of $(\alpha \beta)$ in $10^{-4}$ eV V m$^{-1/2}$ m$^{-1}$ for different illumination level.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1100 lx</td>
</tr>
<tr>
<td>303</td>
<td>7.001</td>
</tr>
<tr>
<td>375</td>
<td>5.882</td>
</tr>
<tr>
<td>423</td>
<td>4.654</td>
</tr>
<tr>
<td>473</td>
<td>3.997</td>
</tr>
</tbody>
</table>

(e) Temperature dependence of photoconductivity

The thermally evaporated ZnTe thin films were kept in the deposition chamber in dark for 24 hours or more before being mounted to the sample holder so that the samples could attain thermodynamic equilibrium state. A constant d c voltage of 27 volt was applied for dark and photoconductivity measurement of the thin film samples. The dark conductivity $\sigma_D$, and conductivity under illumination $\sigma_L$ for films of thickness 1900Å grown at different $T_s$ were measured at different ambient temperatures ranges from 300K to 475K. The variation in d c conductivity ($\ln \sigma_D$ or $\ln \sigma_L$) as a function of temperature 1000/T of ZnTe thin films deposited at room temperature (303K) and at higher $T_s$ (375K) are shown in the in Figure 4.14 and 4.15 and is representative for all the samples. It has been observed from these plots that conductivity plots can be divided into two distinct linear regions with the break occurring at ~340K.

As the conductivity $\sigma$ cannot be represented by a single exponential form, so the transport mechanism is assumed to be a double activated process of the form

$$\sigma = \sigma_{01} \exp\left(-\frac{E_1}{kT}\right) + \sigma_{02} \exp\left(-\frac{E_2}{kT}\right)$$

(15)
Figure 4.14: In $\sigma$ versus $1000/T$ characteristics for ZnTe thin films deposited at 303K($T_s$).

where $E_1$, $E_2$, and $\sigma_{01}$, $\sigma_{02}$, are the activation energies and 0 K extrapolated electrical conductivities corresponding to lower and higher temperature regions respectively. The calculated values of $E_1$ and $E_2$ for all films of thickness 1900Å deposited at different $T_s$ are shown in the Table 4.05. It is seen that the dark as well as photo activation energies decreases with the elevation of substrate temperature. The different values of activation energy can be explained as follows.
The conductivity and mobility of carriers in polycrystalline films are influenced by the effects of the various scattering processes at different lattice imperfections like dislocations, surface potential barriers and grain boundaries. In ZnTe thin films two major defects are found to be Zn interstitials and Zn-site vacancy defects. Various kinds of traps may arise from these Zn vacancies. The trapping centres at the grain boundaries capture free carriers and these charged centres, create barriers that limit the carrier transport.
Table 4.05: Activation energies ($E_a$) at dark and under illumination of white light for the films of thickness 1900Å grown at different $T_a$.

<table>
<thead>
<tr>
<th>For samples grown at different $T_a$ (in K)</th>
<th>Average grain size in Å</th>
<th>Activation energy ($E_a$→$E_1$&amp;$E_2$) in eV.</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Under dark</td>
<td>At 11000 lx</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R_1$</td>
<td>$R_2$</td>
</tr>
<tr>
<td>303</td>
<td>168</td>
<td>1.71</td>
<td>0.97</td>
</tr>
<tr>
<td>375</td>
<td>220</td>
<td>1.55</td>
<td>0.81</td>
</tr>
<tr>
<td>423</td>
<td>250</td>
<td>1.33</td>
<td>0.67</td>
</tr>
<tr>
<td>473</td>
<td>300</td>
<td>1.32</td>
<td>0.65</td>
</tr>
</tbody>
</table>

$R_1$: It is the temperature range from 345K to 450K.

$R_2$: It is the temperature range from 300K to 345K.

The transmission of electric charge through polycrystalline films is governed by the density and also with the mean height $\phi_B$ of the barriers connected with the grain boundary regions/47/. The variations of ($\phi_B - \Delta\phi$) in the mean height of these potential barriers provoked by an external field influence the static electrical characteristics of these polycrystalline thin films. For a bias of 18 volt was applied between the electrodes of separation 7mm. The average grain size in these films is about 240Å(approx). Therefore average applied bias per grain is $\sim$6.5×10⁻⁵ volt (or more). Hence the energy received by the charge carriers due to the applied voltage is much lower than thermal energy ($\sim$0.02eV) in this temperature range. So the transmission of electronic charge through ZnTe thin films mainly due to thermoionic emission. The relevant conductivity is given by/34-37/:

$$\sigma = Dq^2 n \left[ \frac{1}{2\pi m^*_a kT} \right]^{1/2} \exp \left[ -qV_B/kT \right], \quad (16)$$

where $D$ is the grain size, $m^*$ is the effective mass of the carrier, $n$ is the average carrier concentration, $V_B$ is the average barrier height measured with respect to the top of the
valence band and $q$ is the electronic charge. Using the relationship of $\sigma = q\eta\mu$, the effective mobility, $\mu_{\text{eff}}$ is given by

$$\mu_{\text{eff}} = Dq \left[ \frac{1}{2\pi m^*_{\text{e}} kT} \right]^{1/2} \exp \left[ -\frac{E_B}{kT} \right], \quad (17)$$

where energy barrier $E_B = qV_B$. From the equation (16) and (17) it is seen that the change in conductivity with temperature may be either due to change of carrier density or mobility or change of both of these parameters together. Therefore the evaluated activation energy in the used temperature range is the total conductivity activation energy. The activation energy for all films was found to reduce under illumination and conductivity was higher than the corresponding dark conductivity. This can be explained by the reduction of grain boundary potential barrier ($\phi_b$) under illumination. The potential barriers localized at the grain boundary modulate the conductivity in the polycrystalline ZnTe films. At any temperature the conductivity under illumination is higher than the dark is mainly due to two contributing factors i.e. (i) contribution from the excess photogenerated carriers and (ii) barrier modulation by the photogenerated minority carriers. It may be noted that the majority carrier density is not much affected by the presence of grain boundaries but the mobilities are altered. The excess photogenerated minority carriers effectively recombine with the grain boundary states that act as fast recombination centers and thereby deplete potential barrier height $\phi_b$.

In other words we may write $\phi_D > \phi_L$, where $\phi_D$ and $\phi_L$ are the grain boundary potential barrier height under dark and under illumination respectively. Due to reduction of the barrier height the effective mobility $\mu_{\text{eff}}$ under illumination gets enhanced. The effective mobility may be written as,

$$\mu_{\text{eff}} = \mu_0 \exp \left( -\frac{q\phi_b}{kT_0} \right), \quad (18)$$

where $T_0$ is a characteristics temperature which depends on the film system. Hence the $q\phi_b$ is the mobility activation energy. Because of this mobility activation due to illumination, the current density under illumination increases from the corresponding dark values. The effective mobilities under dark and illumination respectively are given by
\[ \mu_D^* = \mu_0 \exp \left( -\frac{q\phi_D}{kT} \right) \]  
\[ \mu_L^* = \mu_0 \exp \left( -\frac{q\phi_L}{kT} \right) \]  

Table 4.06: Mobility activation energy due to illumination of white light of intensity 1100 lx for the films of thickness 1900Å grown at different T_s.

<table>
<thead>
<tr>
<th>For samples grown at different T_s (in K)</th>
<th>Mobility activation energy in eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>At intensity of illumination 1100 lx</td>
<td></td>
</tr>
<tr>
<td>R1</td>
<td>R2</td>
</tr>
<tr>
<td>303</td>
<td>0.78</td>
</tr>
<tr>
<td>375</td>
<td>0.63</td>
</tr>
<tr>
<td>423</td>
<td>0.51</td>
</tr>
<tr>
<td>473</td>
<td>0.39</td>
</tr>
</tbody>
</table>

The change in mobility due to illumination is \( \Delta \mu_{eff}^* = \mu_L^* - \mu_D^* \). Since \( \phi_D > \phi_L \), therefore \( \mu_D^* < \mu_L^* \). Here \( \Delta \mu_{eff}^* \) is a positive quantity which is reflected in the increase of conductivity under illuminations. From the Table 4.03 it is seen that the grain boundary barrier heights have less significant effect on the light and dark activation energies in low temperature region. But in the high temperature regions corresponding activation energies get reduced significantly. The reduction in the grain boundary potential barrier will reduce the energy needed to activate the charge carriers for conduction besides the thermally activated carriers, which are responsible for the increase in conductivity with temperature.

4.2.03 Correlative assessment of structural and photoconductivity process

Various structural and electrical parameters, which were described above, are correlated with each other.

(a) Dependence of grain size on thickness

It has been observed that the effects of both small particle size and micro strain are quite prominent in thermally evaporated ZnTe thin films under investigation and there
is a gradual increase of the effective particle sizes and a gradual decrease non-uniform lattice strains in these type of films as the films increases in thickness and approach the bulk. This is quite understandable from the point of view of thickness dependence of grain size and also the lattice imperfections content in which discrete domains which appear at the initial stage coalesce to form larger domains with a subsequent increase in the effective domain size and a slight removal of strains in the domains as the thickness increases. Plots of grain size versus thickness of different ZnTe thin films of different thickness deposited at different constant $T_n$ as shown in the Figure 4.16 indicate that there is no direct relationship between them. But in some of present experimental films it has observed that there is a trend of increase in the grain sizes with film thickness.

(b) Dependence of photoconductivity on grain size

Reports on the photoelectrical measurements of polycrystalline semiconductors, particularly, ZnTe thin films with due consideration to grain boundary effects are not exhaustive. The effect of grain boundaries in polycrystalline ZnTe thin films on the absorption spectrum is reflected in the broadening of the band tail due to the presence of inherent space charge regions at the interfaces. The nature and magnitude of the above broadening depends on the grain size and grain distribution and would necessarily contain the information on the grain boundary effects in thermally evaporated ZnTe thin films/48-53/. This would mean that for a meaningful determination of the grain boundary effects on the photoconductive properties of polycrystalline ZnTe thin films, one should carry out measurements at photon energies less than the band gap. In the present study the photoconductivity of zinc telluride thin films is found to increase exponentially with the grain sizes for the films of different thickness. These experiments have been carried out for films deposited at different substrate temperatures and are depicted in the Figure 4.17.

(c) Poole-Frenkel coefficient versus grain size

From the present experimental analysis it has been found that photocurrent increases linearly with bias in low field region and exponentially in high field region. The photoconductivity of the films is a function of mobility, which is also dependent on the grain size/49-60/. In the high field region due to the mobility activation process Poole-Frenkel coefficients are found to decrease in the ZnTe thin films deposited at different...
Figure 4.16: Variation of grain size with thickness for ZnTe thin films deposited at different $T_s$. 

$T_s = RT(303K)$

$T_s = 373K$

$T_s = 423K$

$T_s = 473K$
Figure 4.17: Photoconductivity ($\sigma_{ph}$) versus grain size ($D$) characteristics for ZnTe thin films deposited at different $T_s$. 
growth conditions. Poole-Frenkel coefficients can be calculated in the thin film samples, at different ambient temperatures and at different illumination levels. But in the present experiment average Poole-Frenkel coefficients of each film is calculated from the observation of photoconductivity under different illumination levels. The present results include the variation of Poole-Frenkel coefficient with grain size of different films of different thickness deposited at different substrate temperature (T_s). It has also been observed from the present experimental data that Poole-Frenkel coefficients has linear relationship with the grain size with a negative slope i.e. Poole-Frenkel coefficient decreases gradually with the increase in grain sizes as shown in the Figure 4.18.

(d) Average strain versus average dislocation density

Figure 4.19 shows the variation of average strain with dislocation density of the ZnTe thin film samples deposited at different constant substrate temperatures (T_s). From this experimental work it is also clear that with dislocation density, average strain increases linearly for films of different thickness. It is also confirmed that in thin film samples containing smaller grain size the number of dislocation density is more.

(e) Average dislocation density versus grain size

The present experimental study reveals that average dislocation density of the thermally evaporated ZnTe thin films decreases exponentially with the grain size. It is also found that the average dislocation decreases in the ZnTe thin film samples deposited at higher substrate temperature (T_s). As a result of annealing also the number of dislocation density near grain boundary is reduced. There is a very small decrease in dislocation density with the increasing thickness. As the thickness increases the grain size also increases as it is observed and from the Figure 4.20, it is also confirmed that the dislocation density decreases with the increase of grain size.

(f) Photoconductivity versus dislocation density

In the polycrystalline samples dislocated atoms occupy the regions near the grain boundaries. The effect due to the presence of dislocated atoms or molecules near grain boundary on the electronic structure and optical properties of polycrystalline semiconductor is mainly determined by the following three factors: (a) crystal structure distortions (bond angle and bond length deviation); (b) the presence of mechanical stresses due to structural defects, dislocations at grain boundary etc.; (c) internal electric
Figure 4.18: Poole-Frenkel coefficient ($\beta$) versus grain size ($D$) characteristics of ZnTe thin films deposited at different $T_s$. 

$D_{(m \text{~Å})}$
Figure 4.19: Average strain ($\varepsilon$) versus dislocation density ($\rho$) plots for ZnTe thin films deposited at different $T_s$. 

$T_s = RT(302K)$ 

$T_s = 373K$ 

$T_s = 423K$ 

$T_s = 473K$
Figure 4.20: Average dislocation density ($\rho$) versus grain size ($D$) plots of ZnTe thin films deposited at different $T_s$. 

$T_s = 373K$

$T_s = 473K$

$T_s = 423K$
Figure 4.21: Photoconductivity ($\alpha_{\text{ph}}$) versus average dislocation density ($\rho$) plots of ZnTe thin films deposited at different $T_s$. 
Figure 4.22: Variation of average strain with grain size (D) for ZnTe thin films deposited at different T_s.
Figure 4.23: Variation of residual strain with grain size (D) for ZnTe thin films deposited at different Ts.
Figure 4.24: Photoconductivity ($\sigma_{ph}$) versus average strain plots of ZnTe thin films deposited at different $T_s$. 
Figure 4.25: Photoconductivity ($\sigma_p$) versus residual strain plots for ZnTe thin films deposited at different $T_s$. 
fields arising as a result of screening of the charge near the grain boundary/61/. In the present experimental results i.e. the plots of photoconductivity versus average dislocation density in thermally evaporated ZnTe thin films of different thickness deposited at different constant substrates temperatures are shown in the Figure 4.21. It is also found that the photoconductivity of the thin film sample decreases exponentially with the average dislocation density. It can therefore be concluded that the increase in the number of dislocation enhance the contribution of defects which in turn reduce the photoconductivity of the studied ZnTe thin film samples.

**(g) Average strain versus grain size**

From experimental observation it has been confirmed that the grain size of the thermally evaporated ZnTe thin films increases with substrate temperature when thickness is kept constant at a particular value. In the present study on thermally evaporated ZnTe thin films, variation of strain with grain size has been observed for the samples of different thickness. From these plots of the average strain versus grain size, it is found that average strain of the studied thin film samples it is observed that there is a tendency of increase of strain with grain size, as shown in the Figure 4.22.

**(h) Residual strain versus grain size**

In the present experimental study thin film samples were prepared on glass substrates keeping them at different $T_e$. As both the glass substrate and ZnTe sample has different thermal expansion coefficients there occurs residual strain in between them mainly due to lattice mismatch. It is also found that these residual strains highly influence various morphological and photoelectrical properties of thin film samples. As a part of experimental work, residual strain has been plotted as a function of grain size of different films having different thickness, as depicted in Figure 4.23. From these plots of the residual strain versus grain size, it can also be concluded that there exists no direct relationship between residual strain and grain size in studied ZnTe thin film samples.

**(i) Photoconductivity versus strain and residual strain**

From the plots of photoconductivity versus strain and photoconductivity versus residual strain, it is seen (Figures 4.24 and 4.25) that there is an increasing trend of photoconductivity with strain and residual strain.
4.3 References

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