Chapter – VI

Experimental studies on Zn$_2$SnO$_4$ thin films

6.1 Introduction

At present, a larger number of extensive research has been focused on the transparent conducting oxides (TCOs), since the transparent electronics is a technology-in-a-hurry. On seeing the electrical and optical properties of TCOs with the band structures of the materials [1], a good performing $n$-type TCO must simultaneously satisfy two requirements: (i) large bandgap as well as large energy separation between the conduction band minimum (CBM) and the second conduction band (SCB), for transparency; (ii) a low CBM with respect to the vacuum level, for high dopability; as well as a small effective mass, for good conductivity. As a consequence of the second condition, a low valance band maximum (VBM), which is a common characteristic of oxides, is also required to meet the first condition. Taking theses criteria into account, the recent growing demand has led to an extensive search for new TCOs with high performance and low cost materials with higher transparency and conductivity [2], for the rapid acceleration of transparent electronics developments towards commercialization. Among many binary and ternary oxides, Cd$_2$SnO$_4$ and Zn$_2$SnO$_4$ have emerged as promising TCO's. As seen in chapter 5, Cd$_2$SnO$_4$ have a high carrier mobility compared to most conventional TCO's. It is believed that Cd$_2$SnO$_4$ warrants further investigation and, perhaps, commercialization, despite concerns about the toxicity of Cadmium. Zn$_2$SnO$_4$ is considered as the nontoxic alternative of Cd$_2$SnO$_4$ [3]. Zn$_2$SnO$_4$ has better optical transparency than Cd$_2$SnO$_4$, although its electrical conductivity is lower [4] than that of Cd$_2$SnO$_4$.

Even though the Zn$_2$SnO$_4$ is considered as a nontoxic alternative of Cd$_2$SnO$_4$, it is very familiar as an amorphous oxide semiconductor (AOS). Since amorphous TCO thin films have smoother surface morphology and cleaner etched profiles compared with crystalline TCO films, amorphous TCO films have inherent advantages for applications such as organic light emitting diode (OLED) and thin film transistor-liquid crystal display (TFT-LCD) if appropriate electrical and optical properties can be
achieved. Zn$_2$SnO$_4$ is the thrust material under research as AOS-TCO, in which the Indium gallium zinc oxide (IGZO) is playing the role, because of its low cost comparing to the indium and gallium. It remains largely remains amorphous, and thus atomically smooth over a wider range of processing conditions. In order to explore the device performance of the amorphous transparent conducting Zn$_2$SnO$_4$ films, it is necessary to study the physical properties of the films, to understand the transparent conducting properties. Hence, this chapter discusses in detail the results of structural, surface morphological, compositional, thermal, optical and electrical properties of the RF magnetron sputtered Zn$_2$SnO$_4$ thin films as a function of varying sputtering parameters i.e., substrate temperature and RF power.

### 6.2 Thickness of Zn$_2$SnO$_4$ films

The physical properties of the thin films are known to be dependent on the thickness of the film. Hence it is necessary to measure the thickness of the prepared films. The thickness of films can be controlled by the sputtering parameters. Since the sputtering parameter - target to substrate distance is kept at constant value as described in the section 5.2, the thickness of the films is expected to be varied with the sputtering parameters such as the substrate temperature and the RF power. The thickness of the RF magnetron sputtered Zn$_2$SnO$_4$ films was measured with Mitutoyo SJ-301 surface roughness tester.

#### 6.2.1 Effect of substrate temperature and RF power on film thickness

The variation of film thickness with the substrate temperature is shown in Fig. 6.1(a). The figure depicts that the thickness of the films is decreasing with increasing substrate temperature. As the substrate temperature increases from the room temperature (RT = 27 °C) to 300 °C, the particle ejected from the target is gaining additional energy from the intentional substrate heating. This causes the diffusion of adatoms into the film surface, hence reduction in the thickness of the films at higher substrate temperatures.

Figure 6.1(b) shows the variation of film thickness with the increasing RF power. Figure 6.1(a) and Figure 6.1(b) clearly depicts that RF power also has immense effect on the film formation. When the RF power increases from 100 W to 300 W, the sputtered atoms will largely collide with the sputtering gas molecules and also with sputtered molecules with each other. This leads to the reduction in the mean free path of
the sputtered molecules. This reduction in the mean free path further minimizes the number of atoms that reaches the substrate, where the films are deposited.

6.3 Structural properties of Zn$_2$SnO$_4$ films

It is well known fact that the structural properties of thin films are known to depend considerably on the preparation conditions. The crystallographic phase and the quality of the films mainly depends on the substrate temperature at which the films are prepared. In the present study, the structural properties of Zn$_2$SnO$_4$ films were studied by the X-ray diffraction analysis and also confirmed with the TEM analysis. The XRD measurements were carried out in PANalytical X'Pert PRO MPD diffractometer with CuK$_{α1}$ radiation. The observed data were confirmed with the ICDD powder diffraction files. The structural studies were further derived from the HRTEM image and the SAED pattern obtained from the Hitachi 8100 electron microscope operating at 200 keV.

6.3.1 X-ray diffraction analysis

6.3.1.1 Effect of substrate temperature and RF power

Zn$_2$SnO$_4$ films deposited at various substrate temperatures were observed to be well adherent to the substrate and posses pinhole free, uniform and smooth surfaces. The crystalline nature of the Zn$_2$SnO$_4$ prepared, was studied by the X-ray diffraction analysis. The XRD patterns of Zn$_2$SnO$_4$ films prepared on glass substrates at various substrate temperature with 100 W, 200 W and 300 W RF power are shown in Fig. 6.2, Fig. 6.3 and Fig. 6.4, respectively. Figure 6.2 shows that all the films deposited with 100 W RF power are amorphous in nature which is irrespective of the increasing substrate temperature. This may be due that the crystallization is not initiated with the increase in the substrate temperature. Similarly, this result has been reported by several coworkers [5 - 10]. Figure 6.3 and Figure 6.4 show that the Zn$_2$SnO$_4$ film deposited with 200 W and 300 W RF power, at room temperature is amorphous in nature whereas, the films deposited with intentional substrate heating are in its first state of crystallization or amorphous. The broad and weak peak present at 2θ in the range 25-35° and at about 2θ=60°, for the film deposited at 300 °C with 200 W RF power indicates that the crystallinity of the films is initiated. The peak in the respective diffraction angle
confirms that the films are in its first state of crystallization. The increase in intensity of the weak and broad peak present at the $2\theta$ value of 23.4°, which is the characteristic peak of the substrate (glass). On increasing substrate temperature, a reduction in film thickness is observed at higher substrate temperature, which may be inferred from Fig. 6.3 and Fig. 6.4.

6.3.2 Transmission electron microscopic analysis
The microstructure of the $\text{Zn}_2\text{SnO}_4$ films deposited at 300 °C with 200 W RF power was confirmed with the high resolution transmission electron microscope (HRTEM) coupled with the selected area electron diffraction (SAED) pattern. The film was peeled off from the substrate and subjected to the HRTEM analysis. The HRTEM image and SAED pattern of the $\text{Zn}_2\text{SnO}_4$ film are as shown in Fig. 6.5 and Fig. 6.6. In the HRTEM image, the absence of ordered lattice fringes confirms that the $\text{Zn}_2\text{SnO}_4$ films deposited at the substrate temperature of 300 °C with 200 W RF power are amorphous in nature. The SAED pattern, shown in Fig. 6.6 also confirms the amorphous nature of the film deposited at 300 °C with 200 W RF power.

The structural properties of $\text{Zn}_2\text{SnO}_4$ films studied from the X-ray diffraction analysis, HRTEM analysis and the SAED pattern confirm that the $\text{Zn}_2\text{SnO}_4$ films in the as-prepared conditions are amorphous in nature. Many researchers [11, 12] reported the similar results in the literature for the RF magnetron sputtered films. Ko et al. [12] reported that the ZTO films exhibited the characteristic profile of an amorphous structure stable even after annealing the films at 450 °C for 1 hr.

6.4 Surface morphological studies
If one think about the device performance of the $\text{Zn}_2\text{SnO}_4$ as a promising AOS TCO, the structural and the surface morphological properties are essential, which are the key factors in deciding the device performance. Hence the RF magnetron sputtered $\text{Zn}_2\text{SnO}_4$ films were subjected to the surface morphological studies. The surface morphological studies were carried out by using the JSM 35 CF Joel scanning electron microscope (SEM) and Veeco digital instruments DI-II atomic force microscope (AFM).
6.4.1 Scanning electron microscopic analysis

The effect of substrate temperatures (RT, 100 °C, 200 °C and 300 °C) and the RF power (100 W, 200 W and 300 W) on the surface morphology of the Zn$_2$SnO$_4$ films were studied by the scanning electron microscope, as the tool is capable of providing information relating to the topographical features and morphology of the films.

6.4.1.1 Effect of substrate temperature

SEM images of the Zn$_2$SnO$_4$ films deposited with 300 W RF power at the substrate temperature of RT, 100 °C and 300 °C are shown in Fig. 6.7. The SEM images show that the Zn$_2$SnO$_4$ films deposited at RT and 100 °C are having a atomically smooth surface without any fragmentation features indicating their amorphous nature of the films, as revealed from the XRD results. The improvement in crystallinity of the films occurs mainly due to the coalescence of the neighboring crystallites driven by the thermal energy acquired from the substrate heating. The SEM images shows that the films are having atomically smooth surface due to the insufficient thermal energy for atomic movement which initiates the rearrangement and alignment of the atoms needed for initiating the crystalline film growth. In the present case of substrate temperatures considered, the thermal energy required for the coalescence may be below the threshold energy for crystallization.

6.4.1.2 Effect of RF power

The SEM images of the Zn$_2$SnO$_4$ films deposited at 300 °C substrate temperature with various RF power (100 W, 200 W and 300 W) are shown in Fig. 6.8. The SEM micrograph of the Zn$_2$SnO$_4$ films prepared with 100 W RF power shows that the films are amorphous which is inferred from the atomically smooth, plain surface (Fig. 6.8(a)). The film prepared with 200 W RF power (Fig. 6.8(b)) confirms that the films are in the first state of crystallinity which enumerated the homogeneously distributed crystal grains, which are changing the surface roughness of the films. Shishiyanu et al. [13] reported the identical surface for the films deposited by SILAR method and after rapid photothermal heating at 650 °C. The film prepared with 300 W RF power (Fig. 6.8(c)) has smooth, netted surface with nano grains. For the films prepared with 100 W RF power, the energy is unavailable to increase the adatom mobility which enhance the coalescence of the neighboring surface atoms. No cracks and holes are observed on the
film surface as a result of substrate temperature and RF power, which indicates the uniformity and pinhole free nature of the films.

6.4.2 Morphological studies by atomic force microscope
The development of the atomic force microscopic (AFM) technique for surface analysis is a study of the surface of materials down to atomic scale because of its exceptionally high vertical resolution. In the present study, AFM was used to monitor the morphological changes of Zn$_2$SnO$_4$ films with substrate temperatures and RF power.

6.4.2.1 Effect of substrate temperature and RF power
AFM images of the Zn$_2$SnO$_4$ films prepared at various substrate temperatures with the RF power 100 W, 200 W and 300 W are shown in Fig. 6.9, Fig. 6.10 and Fig. 6.11, respectively. Figure 6.9 shows the AFM surface morphology and lateral force microscopic (LFM) images of the Zn$_2$SnO$_4$ films deposited with 100 W RF power at $T_s = RT$, 100 °C, 200 °C and 300 °C. The AFM image of the film deposited at room temperature (Fig. 6.9(a)) revealed the formation of smooth surface without grains which may be due to the amorphous nature of the films. With the increasing substrate temperature, the neighboring crystallites tend to form the particles which can be inferred from the Fig. 6.9 (b) and Fig. 6.9 (c). The films deposited at 300 °C substrate temperature (Fig.6.9 (d)) is uniform composed of nano grains.

Figure 6.10 shows the AFM and LFM images of the Zn$_2$SnO$_4$ films deposited with 200 W RF power at $T_s = RT$, 100 °C, 200 °C and 300 °C. Fig. 6.11 shows the AFM and LFM images of the films deposited with 300 W RF power at $T_s = RT$, 100 °C, 200 °C and 300 °C. The AFM images deposited with 200 W and 300 W RF power are identical in surface morphology. The films, deposited with the 200 W and 300 W RF power are uniform with nano grains distributed all over the surface of the films with high density. Nikolic et al. [14] reported similar morphology for the RF magnetron sputtered films at the substrate temperature of 400 °C, with 200 W RF power and film was further annealed at 750 °C for 1 hr. As mentioned in section 5.4.2, the variation in the surface morphology of the films mainly due to the nucleation kinetics which is caused by the substrate temperature and increased RF power. At lower RF power and substrate temperature, few nuclei are formed by the lower energy available. The lower
nucleation density is visible in the AFM micrographs. Large number of nuclei are formed by the continuous diffusion of adatoms leads to the formation of smooth, homogeneous surface with nano grains.

Even though the substrate temperature is not severely affected the surface morphology of the films, it affects the RMS roughness of the films deposited at intentional substrate heating. The variation of RMS roughness with increasing substrate temperature is plotted in Fig. 6.12. The RMS roughness for the films deposited at 300 °C with RF power 100 W, 200 W and 300 W are 1.154 nm, 1.385 nm and 1.88 nm respectively. However, the roughness is high for the films deposited at lower substrate temperature and RF power except for the film deposited at room temperature with 200 W RF power. The reduction of the roughness of the films with the increasing substrate temperature reveals the fact that the films deposited at higher substrate temperature and RF power are smoother than the films deposited at lower substrate temperature and RF power.

6.5 Elemental composition analysis

Elemental composition analysis of the Zn$_2$SnO$_4$ films prepared with 300W RF power at the substrate temperature $T_s = RT$, 100 °C and 300 °C were carried out using the X-ray photoelectron spectroscopy (XPS). The analysis provides information about the elements present in the prepared films and their percentile composition.

The XPS analysis is an unrivaled tool to analyze qualitatively and also quantitatively the chemical composition of the prepared films. XPS survey scan spectra of Zn$_2$SnO$_4$ film deposited at RT, 100 °C and 300 °C are shown in Fig. 6.13. The qualitative XPS survey scan was recorded in the binding energy ($E_B$) range of 0 eV–1100 eV for the Zn$_2$SnO$_4$ films. It is seen from the XPS survey scan spectra of the films (Fig. 6.13), the RF magnetron sputtered Zn$_2$SnO$_4$ films seems not to be contaminated, since there is no impurity peaks other than the Zn$_2$SnO$_4$ films. The binding energies were corrected to compensate for any charge induced shifts by setting the C 1s peak at 284.6 eV. The measured binding energies of Zn 2p$_{3/2}$, Sn 3d$_{5/2}$ and O 1s in the Zn$_2$SnO$_4$ films are tabulated in Table 6.1. Obtained values are in good agreement with the literature [15-17].

The quantitative XPS analysis were also carried out for the Zn$_2$SnO$_4$ films, so as
to deduce the cationic ratio. The XPS narrow scans of Zn 2p$_{3/2}$ and Sn 3d$_{5/2}$ are shown in Fig. 6.14. The intensity of the Zn 2p$_{3/2}$ peak is increasing with the effect of substrate temperature, which is inferred from Fig. 6.14. The cationic ratio was calculated for the films deposited at different substrate temperature using the relation

$$R = \frac{C_{Sn}}{C_{Zn}}$$

where

$$C_{Sn} = \frac{A_{Sn}}{I_{Sn}} + \frac{A_{Zn}}{I_{Zn}}$$

$$C_{Zn} = \frac{A_{Zn}}{I_{Zn}} + \frac{A_{Sn}}{I_{Sn}}$$

$A_{Zn}$ and $A_{Sn}$ are the area of Zn 2p$_{3/2}$ and Sn 3d$_{5/2}$ respectively. $I_{Zn}$ and $I_{Sn}$ are the atomic sensitivity factor for the corresponding core level peak, which were taken from the earlier report [18]. The calculated cationic ratio is tabulated in Table 1. The cationic ratio is decreasing with the increasing substrate temperature. The Sn/Zn ratio reaches the value of 0.469 for the films prepared at 300 °C. This result shows that the near stoichiometric Zn$_2$SnO$_4$ films can be prepared at 300 °C of substrate temperature, with 300 W RF power. Y. Liang [16] reported that the sample sintered at 800 °C was having asymmetric Sn 3d$_{5/2}$ peak, which is attributed to the presence of Sn-O (+2 oxidation state) and SnO$_2$ (+4 oxidation state) chemical bonds and also the presence of metallic tin. In the present study, the Sn 3d$_{5/2}$ peaks are fitted with Gaussian method. The peak fitting confirms that the Sn 3d$_{5/2}$ peak is highly symmetric which in turn confirms the presence of Sn with +4 oxidation state.

Table 6.1 Binding energies of Zn, Sn, O and cationic ratio obtained from the XPS analysis

<table>
<thead>
<tr>
<th>Preparation conditions</th>
<th>Binding energy (eV)</th>
<th>Ratio of Sn/Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>RF power (W)</strong></td>
<td><strong>Substrate temperature (°C)</strong></td>
<td><strong>Zn 2p$_{3/2}$</strong></td>
</tr>
<tr>
<td>300</td>
<td>RT</td>
<td>1021.39</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>1021.05</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>1021.44</td>
</tr>
</tbody>
</table>
Figure 6.15 shows the core level peak position for the O 1s state of Zn$_2$SnO$_4$ films deposited at various substrate temperatures. The O 1s peak is asymmetric, indicating the coexistence of different chemical bonds. The peak present at 531.76 eV may be related to the Sn-O-Zn interactions [16]. The peak present at 531.9 eV and 532.04 eV may due to the surface adsorbed groups. The symmetry of the peak observed at 531.76 eV is increasing with substrate temperature. The symmetry of the O 1s peak for the films deposited at $T_s = 300^\circ$C with 300 W RF power, shows that the films are having only Sn-O-Zn interactions, which confirms the quality of the films.

### 6.6 Thermal properties of Zn$_2$SnO$_4$ films

Since the thermal stability plays a major role in the device performance of the transparent conducting oxides [19], the thermal properties also be derived. The thermal diffusivity is an important parameter that determine the heat transport through the materials and it plays a vital role in the field of TCO in determining the reliability and durability of the materials and also the devices in which they are used as the electrodes or transparent layers. Hence thermal diffusivity should be measured very precisely and frequently. Thermal diffusivity can be measured through many spectroscopic techniques such as Laser flash method and photoacoustic spectroscopy. In the present study, the thermal diffusivity of the Zn$_2$SnO$_4$ films was determined using the indigenously-developed photoacoustic spectrometer. Thermal diffusivity of the films was determined from the photoacoustic depth profiling measurements.

#### 6.6.1 Effect of substrate temperature

The plots of PA phase versus the square root of the modulation frequency of the light, which is the PA depth profiling measurement is shown in Fig.6.16, for the films deposited with 300 W RF power at various substrate temperatures. In the Figure, the curvature present in the PA depth profile curves confirm the thermoelastic bending, which may be due to either the higher thickness of the samples or the lower value value of thermal diffusivity. In the present case, the samples are thin films with thickness in the range of 0.5 $\mu$m. Hence the pronounced thermoelastic bending is due to the much lower value of thermal diffusivity of the Zn$_2$SnO$_4$ films. The thermoelastic bending is also depends on the degree of crystallinity of the films. Since, the Rosencwaig-Gersho theory is valid for the thermally thick regime, the curve is linearly fitted to the higher
modulation frequency region to obtain the thermal diffusivity of the Zn$_2$SnO$_4$ films deposited at various substrate temperatures ($T_s = RT, 100 \, ^\circ C, 200 \, ^\circ C$ and $300 \, ^\circ C$) with the RF power $100 \, W, 200 \, W$ and $300 \, W$.

*Table 6.2* Thermal diffusivity of Zn$_2$SnO$_4$ films prepared at various deposition conditions

<table>
<thead>
<tr>
<th>Preparation conditions</th>
<th>Thermal diffusivity (in $10^{-9}$ m$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF Power (W)</td>
<td>Substrate temperature ($^\circ C$)</td>
</tr>
<tr>
<td></td>
<td>RT</td>
</tr>
<tr>
<td></td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>300</td>
</tr>
<tr>
<td>100</td>
<td>RT</td>
</tr>
<tr>
<td></td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>300</td>
</tr>
<tr>
<td>200</td>
<td>RT</td>
</tr>
<tr>
<td></td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>200</td>
</tr>
<tr>
<td>300</td>
<td>RT</td>
</tr>
<tr>
<td></td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>300</td>
</tr>
</tbody>
</table>

The calculated thermal diffusivity of Zn$_2$SnO$_4$ thin films is tabulated in Table 6.2 and is plotted against the substrate temperature for various RF powers in Fig. 6.17. The Zn$_2$SnO$_4$ films have a mean thermal diffusivity of $1.993 \times 10^{-9}$ m$^2$/s. Since no other experimental data of thermal diffusivity of Zn$_2$SnO$_4$ is available in literature; we cannot compare our results with others. The results of the thermal diffusivity measurement shows that there is a three-order decrease in thermal diffusivity of Zn$_2$SnO$_4$ films compared to Cd$_2$SnO$_4$ films. The particle size of the poor crystalline Zn$_2$SnO$_4$ films are only in few nanometer. So the quantum wavelength of lowest electronic state is constricted and consequently the minimum wavelength is shorter than the high crystalline films. This explains the decrease in thermal properties [20]. Since, the defect density [20] and crystallinity [21], both affects the thermal diffusivity of the materials,
the substrate temperature did not affect the thermal diffusivity mostly, in the present study. It is reported that the increase in oxygen vacancy is the main mechanism for the conduction phenomena in the Zn$_2$SnO$_4$ films. As the substrate temperature increases, the defect density which is the oxygen vacancy is increasing. This further causes the thermal diffusivity to decrease. But the increase in crystallinity, decreases the lattice distortion [22], which pronounces a decrease in phonon scattering, that leads an increase in thermal diffusivity.

6.6.2 Effect of RF power
The variation of thermal diffusivity of Zn$_2$SnO$_4$ films with the RF power is shown in Fig. 6.18. When the RF power is increasing from 100 W to 200 W, the thermal diffusivity is decreasing except for the films deposited at T$_s$ = RT. Further increase of RF power to 300 W, causes the thermal diffusivity to increase. This may be due to the localization of crystalline ordering at higher RF power.

6.7 Optical characterization
The interaction of electromagnetic radiation with matter formed a new branch of science. The interaction mainly varies with the wavelength of radiation. In the present study, the optical properties of amorphous and polycrystalline Zn$_2$SnO$_4$ films were extensively studied for the suitability of the transparent oxide either conducting or non-conducting. Further, the films are engaged to check whether the films are free from lattice trapping centers, impurities and voids. In order to investigate the optical properties of Zn$_2$SnO$_4$ films, the optical absorption spectroscopy (UV-Vis-NIR spectrometry) and the photoluminescence spectroscopy studies were carried out. The results of the optical analysis are presented and discussed elaborately in the following sub-sections.

6.7.1 Optical transmittance
An elaborate investigation on the optical properties of Zn$_2$SnO$_4$ films are essential for their effective device oriented applications. In the present study, the optical transmittance spectra of Zn$_2$SnO$_4$ films prepared at various deposition conditions were studied by using the Ocean Optics HR-2000 fiber optic spectrometer.
The transmittance spectra of Zn$_2$SnO$_4$ films prepared by RF magnetron sputtering technique at various substrate temperatures and with various RF powers are shown in Fig. 6.19, Fig. 6.20 and Fig. 6.21. The interference fringes observed in the transmittance spectra of Zn$_2$SnO$_4$ films prepared at higher substrate temperatures show that the films are highly uniform in thickness. The maximum transmittance observed for the films deposited at lower substrate temperature (T$_s$ = RT and 100 °C) show that the films deposited at lower substrate temperature are amorphous in nature. The average transmittance value of the films deposited at 300 °C are higher when compared to the films deposited at 200 °C. The increase of optical transmittance in lower wavelength region is mainly due to the shift of optical absorption edge to the lower wavelength side which is inferred from Fig. 6.19, Fig. 6.20 and Fig. 6.21. The shift of optical absorption edge to the lower wavelength region is mainly attributed to the well known Moss-Burstein effect [23]. The highest transmittance of 93% was achieved for the films deposited at T$_s$ = 300 °C with 300 W RF power. The highest transmittance reported in literature is ~90% for the films deposited with the substrate heating followed by post heat treatment in high temperature [10,24-26].

### 6.7.2 Optical bandgap

The optical bandgap which is the threshold energy required for the charge transition between the highest nearly filled band and the lowest nearly empty band are essential, since it mainly determines the optical and electrical processes of the transparent and either conducting or non conducting thin films. In the present study, the optical bandgap of Zn$_2$SnO$_4$ films were determined using the UV-Vis-NIR spectroscopy. The procedures and methods for the evaluation of the band-to-band transition energy gap were described in the section 5.7.3. The bandgap values of the optimized as-prepared films were further confirmed with the bandgap values estimated from the wavelength profile of photoacoustic spectroscopy.

The optical bandgap of Zn$_2$SnO$_4$ films were determined from the plot of $(ahv)^2$ vs the photon energy, called the Tauc plot. The Tauc plot of Zn$_2$SnO$_4$ films deposited at various substrate temperatures (T$_s$ = RT, 100 °C, 200 °C and 300 °C) using the RF power 100 W, 200 W and 300 W are shown in Fig. 6.22, Fig. 6.23 and Fig. 6.24, respectively. The Zn$_2$SnO$_4$ films deposited at T$_s$ = RT exhibited no absorption edge in the visible
spectrum of light. Hence the bandgap of the films deposited at RT is not determined. This may be due to the high amorphous nature of the films prepared at room temperature. The evaluated optical bandgap of Zn$_2$SnO$_4$ films prepared with 100 W RF power, at 100 °C, 200 °C and 300 °C are 3.17 eV, 3.64 eV and 3.46 eV, respectively. The bandgap is increasing from 3.17 eV to 3.46 eV with the increasing substrate temperature from 100 °C to 200 °C, indicating the well-known Moss-Burstein effect [23], which may be due to the increase in carrier concentration and decrease in effective mass of the conduction electron. When the substrate temperature is 300 °C, the bandgap decreases to 3.46 eV. This may be mainly due to the increase in crystallinity of the films compared to the films deposited at 200 °C. The optical bandgap of Zn$_2$SnO$_4$ films are 2.92 eV, 3.11 eV and 3.53 eV for the films deposited at 100 °C, 200 °C and 300 °C, respectively. The bandgap for the films deposited with 300W RF power, at 200 °C and 300 °C are 3.34 eV and 3.71 eV, respectively. The bandgap values estimated from optical absorption studies are well agreed with the literature values [10, 11]. Hayashi et al. [10] reported a largest value of bandgap value of 3.6 eV. They further reported that the optical bandgap energy of the amorphous film at minimum resistivity was 3.47 eV.

<table>
<thead>
<tr>
<th>Preparation Conditions</th>
<th>Bandgap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>RF power (W)</strong></td>
<td><strong>Substrate temperature (°C)</strong></td>
</tr>
<tr>
<td>300</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>300</td>
</tr>
</tbody>
</table>

The bandgap of the Zn$_2$SnO$_4$ films deposited with 300 W RF power was also estimated from the photoacoustic wavelength profile measurements done on the films. The PA spectra of Zn$_2$SnO$_4$ films deposited with 300 W RF power are shown in Fig. 6.25. The bandgap values are determined from the dip present in the PA spectra of the Zn$_2$SnO$_4$ films. The PA spectra of the film deposited at room temperature (not shown in figure), exhibited a near straight line response to the incident light, without the dip. This may be due to the near glass nature (amorphous) of the films deposited at room
temperature. The uncertainties present in the PA spectra of Zn$_2$SnO$_4$ deposited at 100 °C also may be due to the amorphous nature of the films. But the presence of dip confirms the crystalline nature of the films deposited with higher substrate temperatures. The bandgap values determined from the PA spectra are tabulated in Table 6.3.

The optical bandgap studies revealed that increasing substrate temperatures mostly yield higher optical bandgap. This increase in optical bandgap shows the Moss-Burstein effect that causes the bandgap widening. It is reported that the oxygen deficiency is the main mechanism that causes the conduction phenomena of Zn$_2$SnO$_4$ films [27]. The increase in bandgap may be also due to the oxygen vacancies, which are positively charged structural defects that capture one or two electrons. The oxygen vacancies occupied by electrons act as donor centers whose levels lie close to valance band, which are responsible for broad band absorption [28].

### 6.7.3 Optical constants

The variations in refractive index $n$ and extinction co-efficient $k$ as a function of wavelength in weak absorption region for the Zn$_2$SnO$_4$ film deposited at different substrate temperature ($T_s = 200$ °C and 300 °C) with the RF power 200 W and 300 W were calculated using the swanepoel method [29] and their variations are shown in Fig. 6.26. The refractive index value varies from 1.45 to 1.64 and the extinction co-efficient varies from 0.0001 to 0.013 and decreasing with increasing wavelength. The significant difference between $n$ and $k$ values leads to enormous changes in the optical parameters [30] of the Zn$_2$SnO$_4$ films. The variation of these parameters between samples not only alter the optical constants but also show differences in structure and material arrangements [11]. Cetingorgu et al. [11] reported the refractive index values which were determined from the spectroscopic ellipsometer data and the oscillator model, as 2.11 to 1.94. They reported that the $k$ values also decreased with increasing wavelengths.

### 6.7.4 Photoluminescence studies

Photoluminescence spectroscopy is an important material characterization tool which probes the electronic properties of the materials. Since the crystallinity of the films affects the photoluminescence measurements, the film deposited at 300 °C with 300 W RF power alone found to be fluoro-active. The photoluminescence emission spectrum
of Zn$_2$SnO$_4$ film was recorded in Varian Cary Eclipse fluorescence spectrophotometer. The photoluminescence emission spectrum of Zn$_2$SnO$_4$ film deposited at 300°C with 300 W RF power, was recorded in the wavelength range of 400 nm - 700 nm, to study the defect levels present in the Zn$_2$SnO$_4$ films. Figure 6.27 shows the photoluminescence spectrum of the Zn$_2$SnO$_4$ film with an excitation wavelength of 380 nm. As seen in figure, the strong blue-green peak present at 2.55 eV is mainly attributed to the oxygen vacancies [31-33]. The presence of two sharp yellow-Orange peaks at 2.17 eV and 2.02 eV indicate that besides the oxygen vacancy-emission, there may be other light emitting mechanism in Zn$_2$SnO$_4$ [31]. Wang et al. [31] reported similar photoluminescence results with two additional peaks at 529 nm and 544nm.

6.8 Electrical properties of Zn$_2$SnO$_4$ films

The electrical properties the materials plays a vital role, since the device performance is mainly depends on its electrical characteristics like resistivity ($\rho$), carrier concentration ($n$) and the mobility of the charge carriers ($\mu$). In the present study, the RF magnetron sputtered Zn$_2$SnO$_4$ films prepared at various conditions were subjected to electrical characterization to derive its electric parameters. The hot probe technique was used to test the type of conductivity of the Zn$_2$SnO$_4$ films. The resistivity measurement were carried out using the Keithley 2000 digital multimeter with linear four probe and heating arrangements. The Hall measurements were carried out using Ecopia Hall effect measurement system model number HMS-3000. The Hall measurements were carried out at room temperature only. The electrical behavior of Zn$_2$SnO$_4$ films with the deposition conditions were elaborately studied and the results are presented and discussed in this section.

The hot probe test results revealed that the Zn$_2$SnO$_4$ films are $n$-type semiconductor which is also confirmed from the Hall effect measurements. The temperature dependance of resistivity (plot of $\frac{1000}{T}$ vs $\ln(\rho)$) of Zn$_2$SnO$_4$ films deposited at different substrate temperature (100 °C, 200 °C and 300 °C) with the RF power of 100 W, 200 W and 300 W are shown in Fig. 6.28, Fig. 6.29 and Fig.6.30, respectively. The resistivity of the films deposited at room temperature ($T_s = RT$) is not measurable with the multimeter. The resistivity value decreases with increasing the temperature, which is inferred from the plot of $\frac{1000}{T}$ vs $\ln(\rho)$, exhibits a
semiconducting nature for the Zn$_2$SnO$_4$ films. The resistivity variations with increasing substrate temperature, may be due to the increasing crystallinity and/or the carrier concentration in the films deposited at higher substrate temperatures [34]. The lowest resistivity of $4.10 \times 10^{-2}$ Ωcm is observed for the films prepared at 300 °C substrate temperature and with 200 W RF power. The resistivity of the Zn$_2$SnO$_4$ films deposited with 100 W and 200 W RF power is in agreement with the reported value of resistivity [24, 25] The room temperature resistivity values of Zn$_2$SnO$_4$ films deposited at various deposition conditions are tabulated in Table 6.4. The resistivity values obtained for the Zn$_2$SnO$_4$ films prepared at higher substrate temperatures are with in the reported values ($\rho = 5.96$ Ωcm to 0.009 Ωcm) [35, 36].

**Table 6.4 Electrical properties of Zn$_2$SnO$_4$ films prepared with various deposition conditions**

<table>
<thead>
<tr>
<th>Preparation conditions</th>
<th>Carrier concentration (in $10^{18}$ cm$^{-3}$)</th>
<th>Mobility (cm$^2$/Vs)</th>
<th>Resistivity (Ωcm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF Power (W)</td>
<td>Substrate temperature (°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>100</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>2.932</td>
<td>1.102</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>75.05</td>
<td>1.885</td>
</tr>
<tr>
<td>300</td>
<td>100</td>
<td>3.893</td>
<td>2.749</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>5.014</td>
<td>4.12</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>5.375</td>
<td>6.393</td>
</tr>
</tbody>
</table>

The carrier concentration and mobility values obtained from the Hall effect measurements are tabulated in Table 6.4 and the values are plotted against the substrate temperature together with the resistivity values in Fig. 6.31. The carrier concentration and mobility values are consistent with the literature values [24, 37]. The carrier concentration is increasing with increasing substrate temperatures which may be mainly attributed to the creation of oxygen vacancies with the removal of more number of interstitial oxygen ions, providing more donor state for conduction [38]. The mobility of the films is increasing with the substrate temperature which may be attributed to the reduction in grain boundary scattering [35] and/or ionized impurity scattering [39] due to the increase in crystallinity with the substrate temperature.
The increase in carrier concentration, which causes the Moss-Burstein effect in heavily doped \( n \)-type semiconductors, affects the optical bandgap determined from the optical absorption spectroscopy. The increase in carrier concentration of \( \text{Zn}_2\text{SnO}_4 \) films with the substrate temperature confirms that the blue shift observed in the bandgap with the increasing substrate temperature is mainly due to the increase in carrier concentration of the films.

### 6.9 Conclusion

The amorphous, transparent conducting oxide (AOS-TCO) \( \text{Zn}_2\text{SnO}_4 \) films were successfully prepared by RF magnetron sputtering technique, from its bulk target material. The films were deposited onto the glass substrate by varying the substrate temperature (\( T_s \)) and the RF power. In this chapter, we have discussed in detail the structural, surface morphological, compositional, thermal, optical and electrical properties of \( \text{Zn}_2\text{SnO}_4 \) films and its control with the substrate temperature (\( T_s = RT, 100 \, ^\circ\text{C}, 200 \, ^\circ\text{C} \) and \( 300 \, ^\circ\text{C} \)) and the RF power (100 W, 200 W and 300 W).

Structural characterizations, carried out using X-ray diffraction (XRD) analysis, High resolution transmission electron microscope (HRTEM) and selected area electron diffraction (SAED) reveal that the films are highly amorphous in nature, irrespective of the substrate temperature. It can be concluded from the structural properties of the films that the \( \text{Zn}_2\text{SnO}_4 \) films are highly stable to the substrate temperature.

The surface morphological properties of \( \text{Zn}_2\text{SnO}_4 \) films show the homogeneity, crack free surface, nano crystal grain and well architectural nature. The obtained micro scale images of scanning electron microscope and atomic force microscope revealed the improved surface nature of the films with respect to substrate temperatures and RF power. All the films sputtered with 200 W and 300 W RF power show a similar surface morphology, irrespective of the substrate temperature and RF power.

The X-ray photoelectron spectroscopic (XPS) analysis revealed that the \( \text{Zn}_2\text{SnO}_4 \) films prepared in the present work are impurity free, because there is no peak observed in the XPS survey scan other than \( \text{Sn}, \text{Zn} \) and \( \text{O} \). The peak positions of \( \text{Zn}, \text{Sn} \) and \( \text{O} \) are well agreed with the literature data. It is also confirmed from the peak position of \( \text{Sn} \) that the RF magnetron sputtered \( \text{Zn}_2\text{SnO}_4 \) films are in single phase (with \( \text{Sn}^{4+} \)) without any constituent binary oxide phases and metallic \( \text{Sn} \). The stoichiometric formulation of the
films was observed from the evaluated Zn and Sn concentration values and it can be concluded that the stoichiometric Zn$_2$SnO$_4$ films can be prepared by varying the substrate temperature.

The thermal diffusivity values of Zn$_2$SnO$_4$ films were evaluated by using the indigenously-developed photoacoustic spectrometer. The determined thermal diffusivity values enumerated the various type of defects present in the Zn$_2$SnO$_4$ films.

The highly transparent nature ($T > 90\%$) of films was identified from the optical transmission studies. The optical bandgap values obtained are in good agreement with the literature. The optical bandgap values obtained from the Tauc plot of optical absorption spectroscopy and the photoacoustic spectroscopy confirms that the increase in optical bandgap with higher substrate temperatures are due to the Moss-Burstein effect and/or increase in oxygen vacancies with the substrate temperature.

The electrical characterizations done on the Zn$_2$SnO$_4$ films reveals that the Zn$_2$SnO$_4$ films exhibit semiconducting nature rather than the conducting nature. The resistivity, carrier concentration and mobility values obtained from the electrical characterizations are in good agreement with the literature values.

References


