Chapter – VIII
Summary, Conclusion and Suggestions for future work

8.1 Summary and Conclusion
Multication metal oxide semiconductors are the interest for fundamental research and many device applications. They have high luminous transmittance, wide bandgap, good electrical conductivity, excellent substrate adherence, hardness and chemical inertness. Transparent conducting oxides of multication metal oxides are the new era of the scientific research, since they are having high transparency and high electrical conductivity along with high mobility. For having high mobility in \( n \)-type wide gap transparent conducting oxides, one of the cation must belongs to \( p \)-block with \( n_s^0 \) electronic configuration such as \( \text{Zn}^{2+}, \text{Hg}^{2+}, \text{Ga}^{3+}, \text{In}^{3+}, \text{Ti}^{3+}, \text{Ge}^{4+}, \text{Sn}^{4+}, \text{Pb}^{4+}, \text{Sb}^{5+}, \text{Bi}^{5+} \) and \( \text{Te}^{6+} \). Among the multication oxides, \( \text{Cd}_2\text{SnO}_4 \) and \( \text{Zn}_2\text{SnO}_4 \) are physically stable and chemically inert; have replaced the \( \text{SnO}_2 \) and \( \text{ZnO} \) materials in the traditional market of the transparent conducting and transparent semiconducting market, respectively.

In the present work, \( \text{Cd}_2\text{SnO}_4 \) and \( \text{Zn}_2\text{SnO}_4 \) thin films were prepared by RF magnetron sputtering technique. The \( \text{Cd}_2\text{SnO}_4 \) and \( \text{Zn}_2\text{SnO}_4 \) powders synthesized from the solid state reactions were used as the target material for the sputtering. The synthesized powders were characterized through X-ray diffraction, Raman spectroscopy and the Electrical measurements like electrical resistivity and Hall effect measurements. The structure solution and Rietveld refinement were done on the powder XRD pattern of the synthesized \( \text{Cd}_2\text{SnO}_4 \) and \( \text{Zn}_2\text{SnO}_4 \) powders. The crystallography results showed that the synthesized \( \text{Cd}_2\text{SnO}_4 \) crystallized in orthorhombic structure with the space group of \( \text{Pbam} \) and the synthesized \( \text{Zn}_2\text{SnO}_4 \) crystallized in cubic inverse spinel structure with the space group of \( \text{Fd} \bar{3}m \). The crystallographic results also suggests the fact that the crystal structure is also the main reason for the conduction properties of the material.

The \( \text{Cd}_2\text{SnO}_4 \) and \( \text{Zn}_2\text{SnO}_4 \) films were deposited onto the preheated glass substrates by varying the RF power. The substrate temperature was also varied from
room temperature to 300 °C to study the physical and chemical properties of the films and to optimize the deposition conditions to prepare the device quality films. Stoichiometric films of Cd$_2$SnO$_4$ and Zn$_2$SnO$_4$ were prepared at the optimized deposition conditions. The optimization of the deposition conditions were done on the electrical and optical properties of the prepared films. The following are the optimized deposition conditions to get uniform, homogeneous and well adherent films.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Cd$_2$SnO$_4$</th>
<th>Zn$_2$SnO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target precursors</td>
<td>CdO &amp; SnO$_2$ in 2:1 ratio</td>
<td>ZnO &amp; SnO$_2$ in 2:1 ratio</td>
</tr>
<tr>
<td>RF power (W)</td>
<td>200</td>
<td>300</td>
</tr>
<tr>
<td>Substrate temperature (°C)</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>Sputtering gas</td>
<td>pure Argon</td>
<td>pure Argon</td>
</tr>
<tr>
<td>Target to substrate distance (cm)</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Sputtering duration (min)</td>
<td>30</td>
<td>30</td>
</tr>
</tbody>
</table>

The prepared Cd$_2$SnO$_4$ and Zn$_2$SnO$_4$ films were systematically characterized with X-ray diffraction, Atomic force microscope, Scanning electron microscope, X-ray photoelectron spectroscopy, UV-Vis-NIR spectroscopy, Photoacoustic spectroscopy, linear four probe resistivity measurement, Hall effect measurements. Some of the prepared films were subjected to high resolution Transmission electron microscope and selected area electron diffraction to confirm the structural properties of the films.

The Cd$_2$SnO$_4$ films prepared at lower substrate temperatures and lower RF power showed the orthorhombic structure whereas the films prepared at higher temperature such as 300 °C exhibited cubic spinel structure. This structural phase transformation was explained on the basis of variation in the RF power and substrate temperature. The Zn$_2$SnO$_4$ films prepared with substrate temperature showed that the films are in its first state of crystallization. HRTEM and SAED analysis results also confirmed the XRD results.

Surface morphology of the prepared Cd$_2$SnO$_4$ and Zn$_2$SnO$_4$ films were analyzed
with the micrographs of SEM and AFM. The surface smoothness and rms roughness were obtained from the micrographs. These pictures showed uniform and well-developed grains for the films prepared at higher substrate temperatures. Elemental composition of the films were analyzed with XPS analysis. All the film prepared under optimized deposition conditions had perfect stoichiometry with out any contamination.

Thermal properties of Cd$_2$SnO$_4$ and Zn$_2$SnO$_4$ films were studied by using the indigenous-developed photoacoustic spectrometer. Very low thermal diffusivity of the films suggest that the films should be thermally inert. The substrate temperature had an effect on thermal diffusivity of the films. Hence thermal properties of the films can be tuned only varying the substrate temperature.

The optical characterizations of prepared oxide thin films were analyzed by taking UV-Vis-NIR transmittance spectra. From the transmittance curve, the optical bandgap of Cd$_2$SnO$_4$ and Zn$_2$SnO$_4$ were obtained. The optical constants $n$ and $k$ were also calculated, found to be very close to the literature values. The optical bandgap of Cd$_2$SnO$_4$ films was found to be 3.3 eV with maximum optical transmittance of ~90% and the optical bandgap of the Zn$_2$SnO$_4$ was found to be 3.71 eV with maximum optical transmittance value of 93%. Photoluminescence emission spectra of Cd$_2$SnO$_4$ films showed the formation of the crystalline phase of Cd$_2$SnO$_4$ at higher substrate temperature. The PL emission spectra of Zn$_2$SnO$_4$ films confirmed the formation of stoichiometric films by the presence of their respective peaks in these spectra.

Electrical measurements were carried out in linear four probe setup and Hall effect measurement system. The electrical resistivity of Cd$_2$SnO$_4$ films was found to be $3.192 \times 10^{-4}$ $\Omega cm$ with high carrier concentration of $6.337 \times 10^{20}$ cm$^{-3}$ and the mobility of 30.86 cm$^2$/Vs for the optimized films. The minimum electrical resistivity of Zn$_2$SnO$_4$ films was found to be $4.410 \times 10^{-2}$ $\Omega cm$ was obtained with the carrier concentration of $7.505 \times 10^{19}$ cm$^{-3}$ and the mobility of 1.885 cm$^2$/Vs.

The $p$-$n$ junction diodes were fabricated based on Cd$_2$SnO$_4$ and Zn$_2$SnO$_4$ films prepared at optimized deposition conditions on the $p$-Si wafer. The I-V characterization done on the $n$-Cd$_2$SnO$_4/p$-Si heterojunction showed that the Cd$_2$SnO$_4$ makes Ohmic contact to any surfaces. Hence it can be successfully used as a promising electrode material for optoelectronic applications. I-V characterization done on the $n$-Zn$_2$SnO$_4/p$-Si confirms the rectifying behavior of $n$-Zn$_2$SnO$_4/p$-Si heterojunction diode.
voltage of the diode was obtained as 1.9 V.

Finally, Cd$_2$SnO$_4$ and Zn$_2$SnO$_4$ thin films prepared at optimized deposition conditions were subjected to the ethanol sensing characterization. Among the two binary metal oxides, Cd$_2$SnO$_4$ films showed slow and notable response to the ethanol vapor, but not very high due to their high conductivity and the high chemical inertness. Zn$_2$SnO$_4$ films showed a high sensitivity to the ethanol vapor and showed a linear relationship to the concentration of the ethanol. The sensor showed relatively high, quick response to the ethanol vapor and also showed quick recovery time.

8.2 Suggestions for future work

In the present study, the properties of Cd$_2$SnO$_4$ and Zn$_2$SnO$_4$ films were studied in as-prepared conditions, since they were deposited on the glass substrates. To increase the crystallinity of the as-prepared films, the films may be subjected to annealing at high temperature ranging from 200 °C to 800 °C in Argon, hydrogen sulfide (H$_2$S) gas atmosphere, by preparing the films on the quartz and alumina substrates. This will also increase the optical and electrical properties of the films.

In the present study, the p-n junction diodes were fabricated as transparent oxide/opaque non-oxide junctions. In future, a proper p-type transparent conducting oxide will be chosen, prepared as thin films and will be characterized to get the device quality optical and electrical properties. The transparent p-n heterojunction diodes will be fabricated based on the n-type Cd$_2$SnO$_4$, Zn$_2$SnO$_4$ and newly chosen p-type oxide. The research may be extended to select and characterize a proper insulating material to fabricate an unipolar transparent thin film transistor based on Cd$_2$SnO$_4$, Zn$_2$SnO$_4$ and insulating thin films.

In the present study, the fabricated ethanol sensor was equipped with a non-solid state heater separately. In future, sensing element with a solid-state heater using integrated technology can be fabricated, to adopt the sensor to the VLSI technology. These compact sensors with high sensitivity can be fitted in automobiles to prior check the legal drink-drive limit of alcohol to avoid the accidents from drunk and drive.
List of Publications:

1. Thermal and optical properties of Cd$_2$SnO$_4$ thin films using photoacoustic spectroscopy
   K. Jeyadheepan, P. Palanichamy, V. Swaminathan, M. Jayachandran and C. Sanjeeviraja

2. Preparation and crystal structures of some A$^{IV}$B$_{III}$O$_4$ compounds: Powder X-Ray Diffraction and Rietveld analysis
   K. Jeyadheepan, V. Swaminathan, M. Jayachandran and C. Sanjeeviraja
   *Acta Crystallographica B. Structural science (Under review) (2010)*

3. Studies on RF magnetron sputtered Cadmium tin oxide thin films with increasing substrate temperature
   K. Jeyadheepan, M. Thamilselvan, Kyunghae Kim, Junsin Yi, M. Jayachandran and C. Sanjeeviraja
   *Applied Surface Science (Under review) (2010)*

4. Automation of Photoacoustic spectrometer for NDE Applications
   P. Palanichamy, P. Kalyanasundaram, K. Jeyadheepan, M. Jeyaprakasam, C. Sanjeeviraja and K. Ramachandran
   *Communicated to Journal of Nuclear Instruments (2009)*

5. Automation of Photoacoustic spectrometer using VEE Pro Software
   *Measurements (2009) (accepted)*

6. Effect of annealing on cold worked D9 alloy by photoacoustics

7. X-ray and photoacoustic studies on Zircaloy-2


8. Ultrasonic, metallographic and photoacoustic studies on Zircaloy-2
