The chapter consists of four sections. In the first section, the ageing effects on the gas sensitivity, morphology and microstructure of Cs doped SnO\textsubscript{2} films are discussed in comparison with virgin films. The gas sensitivity results of SnO\textsubscript{2} films doped with Mg, B and Cs are correlated in the second section. In the third section, the electrical, microstructural, morphological, compositional and optical modifications on the film by different dopants are compared in connection with their LPG sensitivity. The mechanism involved in the LPG and methane gas sensing of tin oxide thin films are detailed in the last section.

5.1 Sensor Response Studies on Cs Doped SnO\textsubscript{2} Films

5.1.1 Characteristics of Cs Doped SnO\textsubscript{2} Films

LPG sensing characteristics of spray deposited Cs doped SnO\textsubscript{2} films, along with its structural and morphological features has been reported earlier from our group (Boben et al., 2008). Cesium doping was achieved by adding desired amount of CsCl in to the SnCl\textsubscript{2} solution. Films were deposited by spray pyrolysis method in the temperature range 285°C and 355°C, with Cs concentration varying between 1 % and 4 % by weight. The films were
polycrystalline with thickness ranging between 810 nm and 1260 nm having crystallite size varying in the range 34 nm and 59 nm. FTIR studies revealed that chlorine is not occluded in the film and EDX studies revealed that 82% of Cs added in to the solution is incorporated in the film. The diffraction patterns presented four distinct peaks corresponding to the principal peaks of cassiterite SnO$_2$ at diffraction angles of 26.6° (110), 33.88° (101), 51.78° (211) and 66.1° (301). As temperature of deposition is optimised an increase in (110) and (101) peaks are reported. The lattice parameters of the films correspond to that of bulk tin oxide in tetragonal structure. The SEM micrographs revealed that the doped films are polygon shaped.

5.1.1.(a) LPG Sensitivity of Cs Doped SnO$_2$ Films

The LPG sensing investigations on Cs doped SnO$_2$ films were carried out at an operating temperature of 350°C. The variation in LPG sensor response with deposition temperature and Cs concentration is as shown in figure 5.1 (Boben et al., 2008).

![Figure 5.1](image_url)

*Figure 5.1* LPG sensing variation with deposition temperature for Cs doped films, at operating temperature 350°C
The films doped with Cs when deposited at 355°C, showed a weak LPG sensitivity. In films deposited at 285°C, the LPG sensitivity increase with Cs concentration up to 3 wt. %, whereas for films deposited at 325°C, the sensitivity decrease with Cs concentration above 2 wt. %. Maximum LPG response obtained was 89 % with 2 wt. % Cs doped film deposited at 325°C. The LPG sensitivity is varying between 14 % and 89 % as the Cs concentration is changed between 1 to 4 wt. % and deposition temperature is varied between 285 and 355°C.

5.1.1.(b) Sensor Response vs. Film Resistance

The LPG sensitivity of the Cs doped films was related to the four probe resistance of the film at room temperature. The four probe resistance of the film measured at room temperature varies from 280 Ω and 2090 Ω depending upon deposition temperature and Cs level. Figure 5.2 shows the variation in LPG response of the film with initial resistance (four-probe). It is found that the LPG sensitivity of the film increase with initial resistance of the film.

![Figure 5.2](image-url)
5.1.1.(c) Conclusions from Previous Reports

The effects of deposition temperature on the crystallographic structure of Cs-doped SnO\textsubscript{2} revealed an enhanced preferential growth in (110) direction. The lattice strain is in the range of \(9 \times 10^{-3}\). As the deposition temperature is increased the crystallite size increases and resistance decreases to a great extent. This is reported as due to the better crystallinity resulting from the high temperature deposition and also better amalgamation of Cs\textsuperscript{+} in the SnO\textsubscript{2} grain boundaries. The sensitivity of Cs doped SnO\textsubscript{2} sensors depend significantly on the crystallite size and their response time is found to vary with Cs concentration. The initial resistance and LPG response are found to be highest for 2 wt. \% Cs and minimum for 4 wt. \% Cs. Ageing effects for a period of one year was studied earlier and reported. Cesium doped films are stable and the variation in LPG sensitivity is small during initial one year period of ageing, irrespective of deposition conditions.

5.1.2 Ageing Studies on Cs Doped SnO\textsubscript{2} Films

Long duration ageing effects on Cs doped films are studied and reported here. The variations in LPG sensitivity and micro-structural features of tin oxide films when doped with small concentrations of different dopants viz. Mg, B and Cs are correlated for films deposited at identical temperature.

5.1.2.(a) Effect of Ageing on Film Resistance

The ageing effect on Cs doped films are analysed after eight years of storage in ambient atmosphere. The film shows appreciable adhesion to the substrate surface. The four probe resistances of the film show noticeable
increase in their values. Table 5.1 shows the four-probe resistance of Cs doped SnO\textsubscript{2} films deposited at different concentrations, closely after deposition, after one year of storage and after eight years of storage. After one year storage period in atmosphere, the resistance of the film gets increased by more or less 1 % of its initial value. This is almost uniform for all the samples. But after eight years of storing, the film resistance increased by more than 10 %, when compared with the fresh value.

Table 5.1 Variation in film resistance with storage period for Cs doped films

<table>
<thead>
<tr>
<th>Deposition Temperature (°C)</th>
<th>Cs concentration (wt. %)</th>
<th>Four probe resistance measured at room temperature (Ω)</th>
<th>Percentage increase in resistance after eight years of storage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Post Deposition</td>
<td>After one year storage</td>
</tr>
<tr>
<td>285</td>
<td>1</td>
<td>1230</td>
<td>1242</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1570</td>
<td>1586</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1990</td>
<td>2010</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1885</td>
<td>1904</td>
</tr>
<tr>
<td>325</td>
<td>1</td>
<td>1910</td>
<td>1929</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2090</td>
<td>2111</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1810</td>
<td>1828</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1765</td>
<td>1783</td>
</tr>
<tr>
<td>355</td>
<td>1</td>
<td>480</td>
<td>485</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>530</td>
<td>535</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>340</td>
<td>343</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>280</td>
<td>283</td>
</tr>
</tbody>
</table>

5.1.2.(b) Ageing Effects on LPG Sensitivity

The LPG sensitivity of eight years aged Cs doped samples are examined and found that the sensitivity of the films got decreased by ageing, as anticipated. The figure 5.3 shows the variation in LPG sensitivity for typical Cs doped films with storage period. After the initial one year period of deposition, the change in sensitivity is small. But after an ageing of eight years, the fall in sensitivity is large. For 2 wt. % Cs doped film (deposition temperature – 325°C), which showed maximum sensitivity of
89 % initially, dropped it sensitivity by 56 % of its initial value. The drop is 54 % for 3 wt. % Cs doped film deposited at 285°C and 49 % for 2 wt. % Cs doped film deposited at 355°C.

Figure 5.3 LPG sensitivity variation with ageing period for typical Cs doped SnO₂ films

5.1.2.(c) Surface Modulation in Aged Sensor

The SEM micrographs of Cs doped virgin films and aged films are compared to understand the effect of ageing on the film surface. Figure 5.4
shows the SEM micrograph of 3% Cs doped SnO$_2$ film deposited at 285°C, immediately after deposition and after storage of 96 months.

The aged surface morphology can be differentiated by a very thin layer formed as surface coating. This coating limits the interaction of the active film surface with the exposed gas and may be the reason for the considerable decrease in gas sensitivity of the film by ageing as gas sensing is basically a surface phenomenon. The phenomenon is similar to that observed for Mg and B doped films and hence considered as a behavior related to intrinsic properties of tin oxide film irrespective of the dopants.

5.II Comparative Study on the Effect of Nature of Dopants

5.II.1 LPG Sensitivity Dependence on Ionic Size of Dopants

In previous chapters, the effect of magnesium concentration, boron concentration and deposition temperature on gas sensing characteristics of SnO$_2$ are discussed. It will quiet informative to compare the effect of different dopants on the LPG sensing behavior of the films. The dopants are compared with their ionic radius. The ionic radius of boron (B$^{3+}$) is 41 pm, for magnesium (Mg$^{2+}$) is 86 pm and that for Cesium (Cs$^{1+}$) is 181 pm.

Figure 5.5 shows the variation in maximum LPG sensitivity achieved, with different dopants, for films deposited at different temperatures. For lower ionic size dopant (boron), the sensitivity increases with deposition temperature. For comparatively larger dopant ionic size (magnesium and Cesium), the sensitivity increases with deposition temperature up to 325°C and then decreases. At lower deposition temperature, the LPG sensitivity of larger ionic size dopant Cs is higher for low doping concentrations.
5.II.2 Deposition Condition vs. Ionic Size for Maximum LPG Sensitivity

In figure 5.6 the deviation in dopant concentration to achieve maximum LPG response with the ionic radius of dopant is plotted. The variation in deposition temperature with ionic radius for maximum sensor response is also plotted in the same figure. The smaller the ionic radius, the lesser the dopant concentration required to achieve maximum gas response. The required dopant concentration by wt. %, increase with ionic radius of dopant. When doped with Cs having large ionic radius, 2 wt. % of dopant is required, whereas 0.4 wt. % is required with boron having least ionic radius. The increase in ionic radius may relate to an increase in atomic weight of the dopant. Hence the number of dopant atoms is directly proportional to its wt. % and is inversely proportional to the ionic radius. The deposition temperature at which maximum sensitivity achieved decrease from 355°C for boron, to 325°C for Cs with higher dopant size.
Figure 5.6 Deviation in dopant concentration and deposition temperature with ionic radius of dopant to achieve maximum LPG response

The number of dopant atoms calculated for each dopant concentration in SnO$_2$ for maximum LPG response is tabulated in table 5.2, along with their ionic radius and atomic weights.

<table>
<thead>
<tr>
<th>Dopant atom</th>
<th>Ionic radius (pm)</th>
<th>Atomic weight (amu)</th>
<th>Concentration in SnO$_2$ for maximum LPG response (wt. %)</th>
<th>Number of dopant atoms ($N_A$)</th>
<th>Number of atoms incorporated as per EDX data ($N_A$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>41</td>
<td>10.8</td>
<td>0.4</td>
<td>0.0032</td>
<td>0.0022</td>
</tr>
<tr>
<td>Mg</td>
<td>86</td>
<td>24.34</td>
<td>0.6</td>
<td>0.0021</td>
<td>0.0016</td>
</tr>
<tr>
<td>Cs</td>
<td>181</td>
<td>132.9</td>
<td>2</td>
<td>0.0012</td>
<td>0.0010</td>
</tr>
</tbody>
</table>

The deposited boron doped film with maximum sensitivity contains 0.0022 Avogadro number ($N_A$) of boron atoms. Similarly the Mg doped films contains 0.0016 $N_A$ and Cs doped films contains 0.0010 $N_A$ of respective dopant atoms to attain maximum sensitivity. The number of dopant atoms incorporated to achieve maximum sensitivity decreases with increase in ionic
radius. The attachments of dopant to the grains are contributed by grain boundary effects, surface species and voids. Smaller ionic size dopant can find more void sites to accommodate while the larger ionic size dopant can find comparably fewer sites. The dopant occupation sites in a film are in turn governed by deposition temperature and nature of dopant. If the number of dopant atoms incorporated in to a film is fewer than the number of available accommodation sites, the oxygen adsorption process will not be saturated and therefore the ‘reducing gas’ sensitivity will not attain to a maximum. Also if the dopant atoms are in excess, overflow may happen and that would also affect adversely. As a result, for achieving maximum gas sensitivity, the deposition temperature, dopant ionic size and the concentration has to be harmonised.

5.II.3 Influence of Dopant Ionic Size on Response and Recovery Time

It is also found that the response time and recovery time required for a film depends somewhat on the nature of dopant. To study the effect of nature of dopant on the response and recovery time, the arithmetic mean of these parameters for each of the dopant, are plotted against their ionic size. Figure 5.7 shows the variation in both response and recovery durations with ionic radius of the dopants. Both response and recovery durations are larger for films doped with boron, having minimum ionic radius. The duration decreases together for films doped with magnesium, having intermediate ionic radius among the investigated dopants but show a tendency to increase for film doped with Cs, having larger ionic radius.

The response and recovery periods can be related to the easiness of adsorption and desorption oxygen atoms on to the film surface. It has
already discussed in previous chapters that the (110) and (101) plane of the SnO₂ film possess lowest surface energy when considered with other planes of SnO₂ and the adsorption desorption process of oxygen from these planes will be much easier, and does not involve much change in energy. From the XRD studies of deposited films, it is seen that the texture coefficients of (110) & (101) peaks obtain maximum values when doped with suitable proportion of Mg than with the other two dopants. The increase in texture of these peaks is due to the preferred growth of the film in these orientations. The Mg doped films under suitable conditions are highly oriented in (110) and (101) planes and due to advantage in oxygen adsorption-desorption process, decrease in the response and recovery durations are observed.

Figure 5.7 Variation in average response and recovery time with ionic radius of dopant

5.II.4 Dopant Ionic Size and Lattice Micro-strain

The lattice strains developed on the films are also found to vary with nature of dopant. Figure 5.8 shows the change in lattice strain developed on the
prepared SnO$_2$ films due to change in dopant ionic size. In all the three dopants considered, the lattice strains are of the order of 10$^{-3}$. The minimum micro strain is obtained for films doped with boron (having least ionic radius). For Mg doped films with average ionic size, the micro strain is 2.5 x 10$^{-3}$. The micro strains with larger ionic size Cs doped films (Boben et al, 2008) are larger.

![Figure 5.8](image.png)

**Figure 5.8** Change in lattice strains as a function of dopant ionic radius

The possibilities of the additive to get incorporated as interstitial and substitution can be eliminated by considering the dissimilarity in parameters given by Hume-Rothery rules (Ivanov and Suryanarayana, 2000; Wahl et al, 1997). Substitutional atoms that are larger than the host atoms or interstitial atoms bigger than the interstitial space to occupy will impose a large stress on the surrounding lattice, resulting in variation in lattice constants. (Vogler et al, 1998). Such a large micro strain is not observed in any of the deposited films. Thus the findings in this investigation do not give any comprehensible indication to assume that the additives have occupied the lattice sites.
5.III Recap of Results in the Present Investigation

5.III.1 Doped SnO$_2$ Film by Spray Pyrolysis

For SnO$_2$ film formation by pyrolytic reaction a minimum deposition temperature is required. Lower substrate temperature leads to lower deposition rate, less stoichiometry of the film and poor crystallinity. Films deposited at 205°C possess very poor crystallinity. Good quality polycrystalline SnO$_2$ films are obtained at deposition temperatures above 280°C, irrespective of dopant or the concentration. The spray pyrolysis method is useful for preparing Mg / B / Cs doped or undoped SnO$_2$ nano-structured, transparent polycrystalline thin films with direct band gap and low electrical resistance. All the films are uniformly spread over the substrate. Mg doped films have a very good adherence to substrate and are stable for more than eight years of storage in humid atmosphere, whereas the B doped films have low adherence and less response stability on ageing. The Mg doped films can resist physical aberration more than B doped or undoped films. The optical and electrical measurements carried out indicate that these films are also useful as transparent conducting electrodes. The four-probe resistances of the films vary in the range 0.3 KΩ and 2 KΩ depending upon the nature and concentration of dopant, deposition temperature and crystallite size.

5.III.2 Micro-structural Aspects

The X-ray diffraction patterns of both Mg doped and B doped films reveal that they are preferably oriented in the (110) and (101) direction, whereas the undoped films are oriented along (211) and (301) plane. The temperature of deposition as well as degree of doping and nature of dopant
greatly influence the preferred orientation of micro-crystallites along (110), (101), (200), (211) and (301) planes in polycrystalline films. The sharp and intense XRD peaks observed with the deposited films indicate a high degree of crystallinity for the deposited films. The peak profile of (110), (101), (211) and (301) are found to be more sensitive to deposition parameters in SnO₂ as reported earlier (Murthy et al., 1983; Vishwakarma et al 1989).

It is not much known previously, how different planes of SnO₂ contribute to the gas response in polycrystalline sensor materials. On exposing, most of the planes in SnO₂ contribute to the gas sensing properties in varied amounts. But the experimental observations in this investigation lead to the fact that the films possessing high LPG sensitivities have a preferred orientation in (110) and (101) planes, irrespective of dopant. The preferred growth in these planes under certain deposition conditions are accompanied by a growth deceleration along (211) and (301) directions. In the case of thin films, the increase in reflection intensity of a plane is associated with the preferred orientation of the microcrystallites along the plane. The different preferred orientations of doped SnO₂ films can be correlated to the crystallisation energy in that particular direction. In literature it is reported that the (110) plane can easily release oxygen without distorting the lattice (Matthias et al, 72, 2005). In the present study it is revealed that the (101) plane also has a matching contribution in the oxygen release mechanism, and the process appear to be more efficient if both (110) and (101) planes are grown supportively. Also Beegermayer and Tanaka have performed *ab initio* thermodynamic calculations for the SnO₂ (110) and (101) surfaces and showed that under reducing conditions the
(101) surface actually possess a lower surface energy than the (110) surface. (Bergermayer and Tanaka, 2004).

The lattice constants ‘a’ and ‘c’ of the deposited films are determined from the corresponding XRD data. Their values do not change appreciably for the deposition temperature or dopant variations. The obtained lattice constants are very close to the standard JCPDS data for pure SnO$_2$. The lattice parameters and the unit cell volume estimated for the films correspond to that of bulk tin oxide in tetragonal structure, irrespective of dopant nature or the concentration and suggest that the dopant atoms are not possibly incorporated in to the crystal lattice points (Miki-Yoshida and Andrade, 1993).

5.III.3 Modifications in Optical Properties by Doping

The optical data reported at room temperature show that for the deposited films, irrespective of dopant, the absorption coefficient decreases exponentially with decreasing photon energy and indicates an Urbach characteristics (Abass and Mohammed, 1987). Also the absorbance at higher photon energy varies noticeably with dopant concentration and nature of dopant. The higher value of absorption coefficient for a film can be explained due to the increased absorption of light by charge carriers. In such a situation, the carrier concentration will be higher and can expect a higher band gap energy. The variation in band gap energy for SnO$_2$ films due to doping has been reported earlier (Seif A Nasser, 1999) and is shown along with that obtained in present work as table 5.3.

In the literature it is seen that the undoped SnO$_2$ film have a band gap of 4.11 eV, where as for the doped films they varies from 3.4 eV to 4.21 eV.
depending on the dopant. The modification in band gap energy can be influenced by both the nature and concentration of dopant and the deposition temperature. The reported values suggest that doping may increase or decrease the band gap energy of SnO₂ film. The UV-Visible absorption spectra suggest that the deposited SnO₂ films have direct band gap energy.

<table>
<thead>
<tr>
<th>Table 5.3 Variation in optical band gap energy of SnO₂ films due to doping</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Band gap energy (E₉) for undoped and doped SnO₂</strong></td>
</tr>
<tr>
<td><strong>Earlier reported values (eV)</strong></td>
</tr>
<tr>
<td>Undoped</td>
</tr>
<tr>
<td>F doped</td>
</tr>
<tr>
<td>As doped</td>
</tr>
<tr>
<td>Cl doped</td>
</tr>
<tr>
<td>P doped</td>
</tr>
<tr>
<td>B doped</td>
</tr>
</tbody>
</table>

The difference in band gap energy with the reported value and the present value obtained for B doped samples can be accounted for the difference in deposition temperature of 500°C (Seif A Nasser, 1999). Large shift in the energy band gap is consistent with the fact that the formation of tin oxide with varied excitation energy is possible with dopants having different coordination. The dopant atoms can occupy the acceptor level lying above the valence band or donor level lying below the conduction band depending upon its valency. These levels may overlap with the valence band or conduction band and changes the energy gap. Hence the energy band gap values of doped SnO₂ depend on the type and valency of the doped element in addition to crystallite size of the film. The constituents of valence and conduction band in SnO₂ have been described by Munnix and Schmeits (Munnix and Schmeits, 1983). The width of the valence band is about 9 eV, which has been segmented in these different regions resulting
from, (1) coupling of Sn s orbitals and O p orbitals, (2) mingling of O p orbitals with smaller fraction of Sn p orbitals, and (3) mainly O plane pair orbitals. The Sn s states mainly contribute to the formation of bottom of conduction band and top of conduction band has dominated Sn p character. The above discussion is comprehensible enough to understand s→p direct optical transition in SnO₂ thin films. It can be concluded that in spray deposited films direct s→p optical transmission prevail.

5.III.4 Surface Morphology

The SEM and FESEM images reveal that the grains in undoped SnO₂ films are almost spherical in shape. Mg addition changes the grain shape similar to that of a garden trowel (leafy) shape, yet are of uniform size with enormous voids in between them. In boron doped films, the grains are of pebble-like shaped and of varying sizes. The boron doped films are thickly packed by grains and only fewer voids are visible. This may be one of the reasons for low gas sensitivity for boron doped films, as the dopants are expected to perform mainly at the void space between grains or grain boundaries.

5.III.5 Elements and their Composition

Oxygen deficiency in the crystal lattice of tin oxide can be accounted from the analysis of EDX spectra. Spray pyrolysis deposition technique leads to clearly non-stoichiometric tin oxide films resulting in comparatively low resistance films. This is because the SnO₂ films deposited by spray pyrolysis are more susceptible to oxygen deficiencies, which is the decisive factor for gas sensing application. The obtained [O]/[Sn] ratio greater than 2 on the film surface is due to the oxygen adsorption on the film surface which arises from the lack of oxygen in the
lower layers. The dopant concentration detected from EDX is below what expected and suggest that a few quantity of dopant atom has ejected out during the film formation.

The FTIR investigations on undoped and both Mg and B doped films reveal that chlorine is not occluded in to the film. The entire Cl in the reactant may have converted in to HCl and got escaped during the pyrolytic reaction. This is supportive for the fact that formed film is stannic oxide when the starting materials do not contain other impurities. The concentrations of Mg and boron are very low to be detected in FTIR.

The composition is verified from XPS spectra which explicitly revealed the presence of strong Sn 3d doublet and O 1s peaks. As the binding energy of Mg 1s peak is outside the scan range, the Auger peaks are analysed for endorsing the presence of Mg. However Mg 2s and other weak peaks are observed in the spectra to confirm the inclusion of Mg. Besides B 1s peak is undoubtedly obtained in the spectra of boron doped films. The deconvolution of the Sn 3d peak and O1s peak confirms the less stoichiometric composition of SnO$_{2-x}$ in the deposition.

5.III.6 Effects of Ageing

Ageing of the films largely affect Mg/B/Cs doped and undoped films in diverse amounts. The films surfaces are covered with a thin layer, mainly due to hydroxyl group, with its interaction with humidity. As a result the resistance of the films increased nearly 10 % after six to eight years of storage. The increase in film resistance is in a logarithmic manner. The gas sensitivity of the films is considerably decreased. The interacting gas has to infiltrate this coating layer to get attached with the oxygen previously
adsorbed on to the surface. Plasma etching or annealing (at its deposition temperature) removes this layer almost completely and the original gas response is re-attained. From ageing studies it is understood that Mg doped films are more stable in terms of adherence than undoped, boron doped and or cesium doped films. The boron doped films show least adhesion to the substrate surface and peeling of film at scattered areas is observed after six years of ageing which develop to a total destruction after eight years.

**5.III.7 LPG and Methane Gas Sensitivity**

A good sensitivity is attained with doped films towards low concentration of LPG at an operating temperature of 350°C. The films respond to methane effectively only at a higher operating temperature of 385°C. Hence the prepared films are highly selective between LPG and methane gas. Mg doped samples show a very high response of 93 % to LPG at 350°C but with boron doped film the LPG sensitivity is 56 %, at the same operating temperature. The LPG sensitivity gets increased by more than three times by suitable addition of dopant. But towards methane, even at a higher operating temperature of 385°C, Mg doped films show sensitivities only up to 52% whereas the boron doped films show sensitivities below 22%.

Higher electrically conductive films are not always suitable as a gas sensing material. The electrical conductivity of an n-type polycrystalline tin oxide film is considered as the sum of the electrical conductivity due to the surface, bulk and grain boundary. Compared to bulk, the surface and grain boundary effects dominate in thin films. The conductivity of the film are hence influenced by inter grain resistance and intra grain contacts. In addition, the oxygen vacancies and so the adsorption sites in the layers of
SnO₂ films play an overwhelming role in the sensor response to the gases. In fact, this depends on the deposition parameters of SnO₂ films. It is well known that the gas detection is based on surface reaction between the adsorbed oxygen and the gas to be detected. Oxygen from the air is chemisorbed as O₂⁻, O⁻ and O²⁻, thus decreasing the concentration of electrons near the surface and giving rise to a reducing layer of higher resistance. When exposed to a reducing gas, the mutual interaction between the reducing gas and the adsorbed oxygen result in oxidation of chemisorbed oxygen concentration to impart an increase in conductance. In polycrystalline materials, grain boundary effects greatly contribute to the electrical transport (Hartnagel, 1995). In order to explain the gas detection results upon doping, it may be supposed that dopant atoms are incorporated in to the void space of the SnO₂ grains as there exist least evidence of inclusion in to the lattice. But the compositional analysis reveals the presence of doped atoms and oxygen adsorption shift. Therefore it is assumed that the Mg / B / Cs atoms may be segregated at the grain boundary, acts like a ‘grain boundary activator’ supplying excess oxygen to the grain boundary interface as from the bulk. Further to this, the dopants act as a catalyst for chemisorptions of oxygen on the surface and allow more oxygen species to be adsorbed on the grain surface as compared with undoped tin oxide.

5.IV Involved Mechanism in Gas Sensing

Mainly two species of oxygen get adsorbed on the surface of polycrystalline tin oxide sensors. At temperatures less than approximately 180°C the O₂⁻ species are mainly detected on the surface and highly unstable at higher temperature. The O⁻ species dominate when temperature increases above 200°C
Sensor Response Studies on Aged C, Doped SnO₂ Film and Evaluation of Mg, B and---- (Galdikas et al., 1997). The adsorbed oxygen reacts with the excess electrons in the semiconductor, in the temperature range 150°C - 300°C to give,

\[ \text{O}_2 + 2e^- \leftrightarrow 2\text{O}_{\text{ads}}^- \]  \hspace{1cm} \text{5.1}

the chemisorbed oxygen anions. This adsorbed oxygen creates a space charge region near the film surface by extracting electrons from the material. As the gas sensor is exposed to the reference gas, they oxidised by the chemisorbed oxygen anions O\(^-\) at the grain boundaries to release electrons to the bulk materials.

\[ \text{LPG} + \text{O}_{\text{ads}}^- \rightarrow \text{LPG-O}_{\text{des}} + e^- \]  \hspace{1cm} \text{5.2}

The produced electrons cause an increase in electrical conductivity or a decrease in resistance of the metal oxide. Regarding the details, the first step is the dissociative adsorption of LPG to produce H on the interaction surface that reacts with adsorbed atomic oxygen to produce water. As a result, negative charge carriers are re-injected to the bulk and hence the resistance decreases:

\[ \text{LPG} + \text{O}^-_{\text{(ads)}} \rightarrow \text{CO}_2(\text{air}) + \text{H}_2\text{O} + e^-_{\text{(bulk)}} \]  \hspace{1cm} \text{5.3}

Therefore, by measuring the change in the resistivity of the tin oxide thin films it is feasible detect the reducing gases (Oomman et al., 1999). The sensing process requires an optimal temperature for its operation as the dissociation of these organic gases will not takes place at lower temperatures. When the operating temperature is too high, the carrier concentration increases due to intrinsic thermal excitation and the collision increases to cause a decrease in Debye length. This may be one of the reasons for decreased gas sensitivity at higher temperature (Mizsei J., 1995). Since CH₄ is thermodynamically more stable than most other reducing
gases, it is relatively difficult to detect it with high sensitivity at a lower temperature of 350°C. At the sensor working temperature, the exposure of tin oxide surface to CH₄ results in a surface mediated combustion process. The removal of ionosorbed oxygen increases the electron concentration and hence the surface conductance of the films. The main reaction products are H₂O and or CO₂. A possible reduction reaction that can occur on the sensor surface when exposed to CH₄ can be summarised as follows:

\[
\text{CH}_4 + 2\text{O}^- \rightarrow \text{CH}_3\text{O}^- + \text{OH}^- \quad \text{…………….5.4}
\]

\[
2\text{OH}^- \rightarrow \text{H}_2\text{O} + \text{O}^- \quad \text{…………….5.5}
\]

\[
\text{CH}_3\text{O}^- + \text{O}^- \rightarrow \text{HCHO}^- + \text{OH}^- \quad \text{…………….5.6}
\]

\[
\text{HCHO}^- \rightarrow \text{HCHO} + \text{e}^- \quad \text{…………….5.7}
\]

Thus the presence of methane in the ambient desorbs the oxygen earlier attached to the SnO₂ surface and in turn releases an electron for conduction.

In normal ambiance, oxygen is adsorbed onto less stoichiometric SnO₂ surface by capturing electrons from the conduction band. This adsorbed oxygen induces a consequent potential barrier at a grain contact and a resistive depletion layer is formed which decides most of the sensor resistance. At high temperatures of the order of 270°C, they absorb additional oxygen molecules from the atmosphere which in turn strengthen the potential barrier on the grain surface. Small concentration of dopants can easily find space to occupy in a polycrystalline microstructure. The dopant concentration affects the void occupancy which greatly contributes to the gas sensing operation. But when the amount of dopant is increased, the equilibrium is disturbed on the grain surface and it overflows. Hence the
sensor response saturates or decreases after a particular dopant concentration. The decrease in sensitivity above optimal temperature can be attributed to oxygen diffusion into the grains that affects the oxygen vacancy concentration in the film (Kamp et al., 2005)

One often discussed contribution to the gas-sensing mechanism is the variation of Schottky barriers, at contacts between grains in polycrystalline films (Barsan and Weimar, 2001; Barsan et al., 1999; Malagué et al., 2002; Lantto et al., 2001). The barrier height determines the transmission probability of conduction electrons and thus the conductivity of the film. The Schottky barrier, i.e. the band bending at the surface of SnO$_2$ grains, is a consequence of surface states and charged adsorbates at the surface and is thus influenced by the environment. The surface stoichiometry determines the charge distribution (surface states) and thus the Schottky barrier height and therefore has a strong impact on the gas-sensing mechanism. The results of tailoring electrical and gas sensing properties of this habitually non-stoichiometric 4d metal oxide depend on the nature of doping with impurity ions.