Magnesium doped SnO$_2$ thin films are prepared by spray pyrolysis and their LPG and methane sensitivity and selectivity are compared with that of undoped samples. In order to verify the doping, the composition of the deposited films is investigated by EDX, XPS and FTIR. The doping effectiveness in the films is studied in relation to deposition temperature and Mg concentration. To find the doping location in the deposited films, the structure has been analysed by XRD. Preferential orientation growth of the films by Mg incorporation is also evaluated. The crystallite size of the films is estimated as a function of deposition temperature and Mg concentration. The morphology of the films is studied by utilising SEM and FESEM. The electrical and optical parameters are explored as a factor of deposition temperature. The sensitivity is measured at different operating
temperatures in 1000 ppm LPG and in methane for doped films deposited at different temperatures. Ageing of films are investigated and the fall in gas sensitivity is probed in relation to surface compositional variation.

Tin (Sn) is a post-transition metal with atomic number 50 and a stable ionic state of $4^+$ with an ionic radius of 83 picometre (pm) and a less stable ionic state of $2^+$ with an ionic radius of 118 pm. It forms two types of oxides namely stannous oxide (SnO) and stannic oxide (SnO$_2$). Magnesium is an alkaline earth element with atomic number 12. It has a common oxidation number of $2^+$ with ionic radius of 86 pm, which is comparable with the size of Sn $4^+$.  

3.1 Film Preparation

The method employed for the preparation of SnO$_2$ thin films is spray pyrolysis. It is one of the relatively simple and inexpensive methods, which can easily be adopted for mass production of uniform large-area coatings for industrial applications. In this method, the process parameters highly govern the film properties. The important control parameters that affect the quality of films are the nature and surface temperature of substrate, spray solution composition, carrier gas pressure, solution flow rates, deposition duration and the nozzle-to-substrate distance.

3.1.1 Substrate and Solution

Glass slides having size 7.6 cm x 2.5 cm x 1.1 mm are cleaned thoroughly. For this they are initially washed with Teepol® – a laboratory glassware cleaning liquid, to remove any oil, grease, or dirt particles on its surface. It is then washed in distilled water. The slides after been dried are
dipped in concentrated nitric acid to dissolve any unreacted water insoluble ions. The slides are then washed repeatedly in deionised water. They are then dipped in acetone solution and dried in dust free atmosphere.

The basic ingredient of the spray solution is stannous chloride. 10 gm of SnCl₂·2H₂O (Qualigens, Guaranteed Reagent grade, 99.9% pure, product number 15844) is dissolved in distilled, de-ionised water at 100°C. A few ml. of conc. HCl (Merck GR grade) is added to dissolve residual precipitates if any. Subsequently isopropyl alcohol (Merck GR grade) is added in abundance to form the spray solution of 90 ml. Alcohol will enhance the spreading of the solution during spraying and aids to achieve uniform films. Doping with Mg is achieved by adding desired concentration of MgCl₂ (Qualigens, GR grade, 99.9% pure) to the SnCl₂ solution (Boben et al, 2004).

3.1.2 Spray Pyrolysis Setup

![Experimental setup of spray pyrolysis technique](image_url)
A simple inexpensive spray pyrolysis set up is constructed in the laboratory, whose schematic diagram is shown in figure 3.1. The experimental arrangement consists of an atomiser, temperature controlled hot plate and an air compressor. The atomiser is made up of a flat bottomed glass bulb with a spray nozzle of diameter $\approx 0.3$ mm with provision for admitting compressed air. Substrates are mounted on the hot plate. The temperature of substrate is continuously monitored using a chromel-alumel thermocouple, which is calibrated to $\approx 0.04$ mV/$^\circ$C.

Purified atmospheric air at 30 Kg/cm$^2$ pressure is used as carrier gas. The solution is sprayed intermittently so that the variation in substrate surface temperature is within $\pm 3^\circ$C. Tin oxide film is formed on the substrate by the pyrolytic decomposition. The reaction is summerised as follows:

$$2\text{SnCl}_2 + 2\text{H}_2\text{O} + \text{O}_2 \rightarrow 2\text{SnO}_2 + 4\text{HCl} \uparrow \text{ ..................3.1}$$

The spray duration is 10 minutes and the solution flow rate is 9 ml/minute. The films are allowed to cool at a constant rate of 10 $^\circ$C per minute. A number of samples were prepared at different deposition temperatures for various dopant concentrations. For each level of MgCl$_2$ in the spray solution, the temperature of pyrolysis was fixed at 285, 325, 355, 385 and 425$^\circ$C. Reproducibility of films is well achieved by controlling the deposition parameters.

3.2 Physical Properties

3.2.1 Visible Nature of the Film

The films are observed to be transparent without any abruptions as examined by naked eye. By reason of formation of films the roughness of
the surface increases. The transparency and absorbance of films are studied in detail by UV-VIS spectroscopy as discussed in section 3.7. Original photograph of undoped and Mg doped films along with plane substrate are shown in figure 3.2.

![Photograph of (a) plane substrate, (b) undoped film and (c) Mg doped typical film (virgin) (d) eight years aged Mg doped film](image)

**Figure 3.2** Photograph of (a) plane substrate, (b) undoped film and (c) Mg doped typical film (virgin) (d) eight years aged Mg doped film

### 3.2.2 Film Thickness

Thicknesses of the films are measured by an in-house interferometry set up and are confirmed using Sloan Dektak 6M profilometer. It is seen that the film thickness is not affected by magnesium concentration but is influenced by deposition temperature and spray nozzle to substrate distance. It is observed that variation of temperature in the range ± 3°C do not affect the film parameters in the spray pyrolysis deposition. The films deposited with spray nozzle to substrate distance 60 cm are analysed for LPG sensing which has thickness in the range of 0.8 to 1.2 μm.
3.3 Structural Characterisation – XRD

3.3.1 Texture Coefficients, Crystallite size and Lattice Parameters

The micro-structural properties of the films are studied by computer controlled Rigaku MiniFlex 600 X-ray diffractometer using Cu Kα (1.5406 Å) radiation. The diffractogram is plotted for angle 2θ, varying from 5° to 90° at a voltage of 30 KV and current of 10 mA. The step size of goniometer is 0.1° and the speed is 4°/minute. The diffractogram data is analysed with PDXL2 Rigaku data analysis software for obtaining FWHM, peak intensity, d spacing values for each peaks and also for structural identification.

![Figure 3.3 XRD of undoped SnO₂ film spray deposited at 205°C](image)

It is observed that a temperature above 200°C is required for uniform film formation. Figure 3.3 shows the XRD pattern for undoped film prepared at 205°C. At this temperature the films depicts less intense peaks corresponding to (110), (111) and (211) planes of SnO₂ tetragonal cassiterite structure, showing that the film has poor crystallinity. As the temperature of deposition in increased, higher intensities are observable. The diffractograms of undoped films deposited at higher temperatures of 285°C,
325°C, and 355°C are shown below as figure 3.4 (a) – (c). They contain characteristic peaks corresponding to (110), (101), (200), (211), (310), (301), (321) and (312) of SnO₂ tetragonal cassiterite structure (JCPDS data card no. 21-1250).

![Diffractograms of undoped SnO₂ films prepared at (a) 285°C, (b) 325°C and (c) 355°C](image)

**Figure 3.4** Diffractograms of undoped SnO₂ films prepared at (a) 285°C, (b) 325°C and (c) 355°C

The presence of peaks corresponding to (220) and (202) depend on deposition temperature. The undoped film growth is preferably oriented along (211) and (301) planes. The intensity of peaks corresponding to (101) and (110) planes evidences a weak texture in these orientations for the undoped films.
Table 3.1 Crystallite size, lattice constants and texture coefficients of prepared undoped samples in the temperature range 285°C to 355°C

<table>
<thead>
<tr>
<th>Deposition temperature (°C)</th>
<th>Crystallite size (nm)</th>
<th>Lattice constants</th>
<th>Texture coefficient of planes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>a Å</td>
<td>c Å</td>
</tr>
<tr>
<td>285</td>
<td>43</td>
<td>4.749</td>
<td>3.21</td>
</tr>
<tr>
<td>325</td>
<td>41</td>
<td>4.749</td>
<td>3.20</td>
</tr>
<tr>
<td>355</td>
<td>45</td>
<td>4.747</td>
<td>3.21</td>
</tr>
</tbody>
</table>

The texture coefficients of the peaks for undoped films (figure 3.4.) along with their lattice constants and crystallite size are given as table 3.1. It is seen that the lattice constants are unaffected by deposition temperature, but the crystallite size and textures are influenced. The crystallite size as calculated using Debye Scherrer formula on the lowest angular peak (110) is least for films prepared at 325°C.

The effect of magnesium doping by the pyrolysis, on the film formation has been analysed. Figure 3.5 shows the XRD patterns of 0.3 wt. %, 0.6 wt. % and 0.9 wt. % Mg doped films deposited at 285°C. The tetragonal cassiterite structure is not disturbed by the presence of Mg in small quantities. Same diffraction peaks as in undoped samples are obtained and there is no noticeable shift seen due to Mg addition. The intensities of peaks (110), (200), (211) and (301) are significantly altered by the concentration of Mg. At this formation temperature, the (310), (321) and (312) peaks are not much influenced by the addition of Mg.
The XRD patterns of 0.3 wt. %, 0.6 wt. % and 0.9 wt. % Mg doped films deposited at 325°C is shown in figure 3.6. At this deposition temperature, the film growth is preferably oriented in the (110), (101) planes. The growths in both the planes are foremost for 0.6 wt. % Mg doping. Such an orientation is unique for this narrow temperature range and is not noticed for any other deposition conditions. At this deposition temperature range, the growth along the planes (211) and (301) are significantly suppressed.
Chapter 3

Figure 3.6 X-ray diffractograms of SnO₂ films doped with (a) 0.3 wt. %, (b) 0.6 wt. % and (c) 0.9 wt. % Mg, deposited at 325°C

At a deposition temperature of 355°C, the growth along (211) plane is maximum, irrespective of Mg level. Figure 3.7 shows that at this deposition temperature, an increase in Mg concentration decreases the growth along (110) and (101) plane.

From the above discussions it is obvious that both deposition temperature and Mg concentrations can influence the growth profile of polycrystalline SnO₂ films by spray pyrolysis. Small quantities of Mg do not disturb the formation of tetragonal cassiterite structure. By suitably tuning these deposition parameters highly oriented films can be achieved. The intensities of peaks (220), (310), (202), (321) and (312) are very small compared to major peaks. The preferential growth obtained along the (110) and (101) plane by suppressing the growth along (211) and (301) plane is an
achievement of this investigation, as the film growth plays a major role in the gas sensing action of SnO$_2$ films which is detailed later in section 3.9.

![Image](image.png)

**Figure 3.7** X-ray diffractograms of SnO$_2$ films doped with (a) 0.3 wt. %, (b) 0.6 wt. % and (c) 0.9 wt. % Mg, deposited at 355°C

The variation of texture coefficients for low angle reflections corresponding to (110) and (101) plane with Mg addition and deposition temperature are plotted in figure 3.8. For undoped films both the peaks have a very low texture. For 0.6 wt. % Mg doped film deposited at 325°C (here onwards termed as ‘SnO$_2$:Mg-0.6(325) film’) superior gas sensing is obtained and interrelated with the texture coefficient of planes (110) and (101). At this condition the texture for (301) shows a smaller value while that of (211) depicts a moderate value, as evident from figure 3.6.
Figure 3.8 Variation of texture coefficients for (110) and (101) planes with deposition temperature and Mg concentration

Figure 3.9 Variation of texture coefficients of planes for 0.6 wt. % Mg doped films deposited in the temperature range 285°C to 425°C
The variation in texture coefficient for the major peaks for 0.6 wt% Mg doped films deposited in the temperatures range 285°C to 425°C is plotted in figure 3.9. It is implicit from the figure that the growth along (301) plane and (211) planes are suppressed by adding suitable amount of Mg and in turn contributed to the growth of (110) and (101) plane, when deposited at 325°C.

The diffractograms of samples deposited at 385°C and 425°C are also recorded. It is observed that the peak profile is similar to that of the samples deposited at lower temperatures. In both the temperatures, the growth along (211) plane is the higher.

The crystallite size are calculated from both the lower angle peaks at (110) and (101) and are discussed in table 3.2 along with the estimated lattice constants. In Mg doped films, for deposition temperatures 285°C and 355°C the crystallite size (average from 110 and 110 planes) initially increase with Mg concentration up to 0.6 wt. % and then decreases with Mg addition. But for films deposited at 325°C, the average crystallite size initially decrease up to 36 nm for 0.6 wt. % of Mg and then increases. For higher deposition temperatures, the crystallite size is little affected by dopant concentration. Hence it may be concluded that the function of Mg dominates the effect of temperature in grain growth, at comparably lower temperatures. Considering (110) plane alone, the minimum crystallite size obtained is 29 nm where as the maximum is 51 nm.

The lattice constants are calculated from the major peaks (110) and (211). From table 3.2, it is evident that the constants ‘a’ and ‘c’ are indecisively affected by Mg addition even at higher concentration and
deposition temperatures. The XRD peak positions are also not shifted. From the obtained results, it is likely to assume that either there is no inclusion of Mg in to lattice structure or the effects are not immense enough to be detected by XRD technique.

Table 3.2 Crystallite size, lattice constants and cell volume of the films deposited at different temperatures and Mg concentrations

<table>
<thead>
<tr>
<th>Deposition temperature (°C)</th>
<th>Mg concentration wt. %</th>
<th>Crystallite size determined from the planes using Scherrer formula (nm)</th>
<th>Estimated lattice constants (tetragonal structure)</th>
<th>a/c value</th>
<th>Cell volume</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(110)</td>
<td>(101)</td>
<td>a (Å)</td>
<td>c (Å)</td>
<td>Å³</td>
</tr>
<tr>
<td>285</td>
<td>0.3</td>
<td>38</td>
<td>36</td>
<td>4.751</td>
<td>3.199</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>49</td>
<td>43</td>
<td>4.748</td>
<td>3.201</td>
</tr>
<tr>
<td></td>
<td>0.9</td>
<td>51</td>
<td>35</td>
<td>4.746</td>
<td>3.202</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>44</td>
<td>36</td>
<td>4.747</td>
<td>3.203</td>
</tr>
<tr>
<td>325</td>
<td>0.3</td>
<td>49</td>
<td>33</td>
<td>4.748</td>
<td>3.198</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>29</td>
<td>43</td>
<td>4.749</td>
<td>3.201</td>
</tr>
<tr>
<td></td>
<td>0.9</td>
<td>38</td>
<td>37</td>
<td>4.747</td>
<td>3.202</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>42</td>
<td>36</td>
<td>4.746</td>
<td>3.201</td>
</tr>
<tr>
<td>355</td>
<td>0.3</td>
<td>51</td>
<td>40</td>
<td>4.750</td>
<td>3.198</td>
</tr>
<tr>
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<td>53</td>
<td>46</td>
<td>4.748</td>
<td>3.200</td>
</tr>
<tr>
<td></td>
<td>0.9</td>
<td>44</td>
<td>38</td>
<td>4.751</td>
<td>3.201</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>46</td>
<td>35</td>
<td>4.751</td>
<td>3.198</td>
</tr>
<tr>
<td>385</td>
<td>0.3</td>
<td>54</td>
<td>59</td>
<td>4.747</td>
<td>3.199</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>59</td>
<td>56</td>
<td>4.750</td>
<td>3.198</td>
</tr>
<tr>
<td></td>
<td>0.9</td>
<td>55</td>
<td>52</td>
<td>4.751</td>
<td>3.197</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>57</td>
<td>51</td>
<td>4.751</td>
<td>3.196</td>
</tr>
<tr>
<td>425</td>
<td>0.3</td>
<td>58</td>
<td>53</td>
<td>4.750</td>
<td>3.196</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>56</td>
<td>59</td>
<td>4.747</td>
<td>3.198</td>
</tr>
<tr>
<td></td>
<td>0.9</td>
<td>55</td>
<td>53</td>
<td>4.750</td>
<td>3.199</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>51</td>
<td>56</td>
<td>4.751</td>
<td>3.189</td>
</tr>
</tbody>
</table>

Similar profiles are obtained with films prepared with higher concentrations of Mg varying from 3 wt. % to 7.5 wt. % (Table 3.3). The films show preferential orientation in (211) and (301) planes. Mg
addition slightly alter the growth profile and hence the texture of the films. Very small shifts found in the peak position are accounted due to the micro strains developed during crystal formation.

Table 3.3 Crystallite size, lattice constants and texture coefficients of films with higher concentrations of Mg, varying from 3 wt. % to 7.5 wt. % deposited at temperatures 285°C and 325°C

<table>
<thead>
<tr>
<th>Deposition temperature (°C)</th>
<th>Mg level (wt.%)</th>
<th>Crystallite size (nm)</th>
<th>Lattice constants</th>
<th>Texture coefficient of planes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>a (Å)</td>
<td>b (Å)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>d (°)</td>
<td>g (°)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(110)</td>
<td>(101)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(200)</td>
<td>(211)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(220)</td>
<td>(310)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(301)</td>
<td>(321)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(312)</td>
<td></td>
</tr>
<tr>
<td>285</td>
<td>3</td>
<td>4.746 3.201</td>
<td>0.675 0.328 1.53 1.8 0.30 0.34</td>
<td>2.5 0.71 0.61</td>
</tr>
<tr>
<td></td>
<td>4.5</td>
<td>4.748 3.196</td>
<td>0.663 0.243 1.32 1.3 0.38 0.31</td>
<td>3.14 0.3 -</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>4.746 3.202</td>
<td>0.692 0.299 0.49 1.3 0.54 0.60</td>
<td>2.24 0.55 -</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>4.744 3.195</td>
<td>0.61 0.55 1.41 1.5 0.56 0.69</td>
<td>1.71 0.65 -</td>
</tr>
<tr>
<td>325</td>
<td>3</td>
<td>4.744 3.201</td>
<td>1.065 0.318 1.21 1.2 0.73 0.27</td>
<td>3.58 0.51 0.13</td>
</tr>
<tr>
<td></td>
<td>4.5</td>
<td>4.746 3.199</td>
<td>1.275 0.34 1.52 1.0 0.67 0.91</td>
<td>1.91 0.76 0.24</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>4.747 3.203</td>
<td>0.936 0.672 0.97 1.6 0.49 0.66</td>
<td>2.71 0.61 0.39</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>4.740 3.202</td>
<td>0.562 0.483 0.78 1.2 0.40 0.48</td>
<td>3.07 0.56 0.49</td>
</tr>
</tbody>
</table>

There are no significant variations in lattice constant for higher Mg concentrations but a small increase in crystallite size can be observed. It is evident that an increase in Mg level beyond 3 wt. % does not influence the growth profile much. This may point out that, the Mg is likely get occupied at the grain boundaries or voids. If excess Mg is added, saturation occurs and it may be expelled out of the crystalline formation.

Both the undoped and Mg doped films can be indexed to tetragonal rutile phase belonging to space group P4_2/mmm. No obvious peaks from impurities or metallic Sn is observed. Addition of low concentration of Mg favours privileged growth at lower temperature. According to theoretical and experimental studies (Agoston Peter, 2011; Lupan O., 2008) it is suggested that the surface energy sequence of SnO_2 is \( \varepsilon(110) < \varepsilon(100) < \varepsilon(101) < \varepsilon(001) \). Thus the SnO_2 (110) surface, which has the lowest surface
energy is thermodynamically most stable (Slater et al., 1999) and the plane (110) would be expected to feature privileged growth predominantly when in the tetragonal phase. The stimulated growth of (110) can be described by this approach. The variation in crystallite size may be due to the break out of oxygen from stoichiometry resulting from the higher kinetic energies of reactants, at deposition temperature, where the fusing of the agglomerates take over.

3.3.2 Standard Deviation

![Figure 3.10](image)

**Figure 3.10** Variations in standard deviations in microstructure with Mg concentration for films deposited at temperatures 285°C – 425°C

The standard deviation (SD) of X-ray profiles discussed previously are determined and are plotted as a function of deposition temperature and Mg concentrations in figure 3.10. For undoped SnO₂ films the standard deviation is more when deposited at 325°C where as for Mg doped films it shows a minimum at 325°C.
3.3.3 Micro-strain (Lattice Strain)

Micro-strains are developed on the grains and can be visualised from the feeble peak position shifting in the XRD spectra. To study the lattice strain, graph is drawn by $\sin \theta$ versus $\beta_t \cos \theta$, for all the peaks in a diffractogram, where $\theta$ is the half angle of the concerned peak and $\beta_t$ is the corresponding FWHM. The lateral strain is then calculated as $\eta = \beta_t \cot \theta$. The Williamson-Hall plot for SnO$_2$:Mg-0.6(325) film is shown below as figure 3.11. The micro strain, $\eta$ is calculated from the slope of the graph and is obtained as $1.66 \times 10^{-3}$. The crystalline size is also determined by extrapolating the graph. The Y-intersection gives $\eta = \frac{k \lambda}{D}$, from which the crystalline size $D$ is calculated where $k$ is a constant (here taken as 0.9) and $\lambda$ is the wave length of X-ray source. The obtained value is 44 nm and is in well agreement with that obtained from XRD.

![Figure 3.11](image_url)  
*Figure 3.11 Williamson-Hall plot for 0.6 wt% Mg doped SnO$_2$ film deposited at 355°C*

The micro-strains are determined for all the prepared films. They are plotted as a function of deposition temperature and Mg concentration in figure 3.12. The lattice strains are of the order of $10^{-3}$, and non-linear with
the variation of Mg addition. If Mg is to be in the lattice points, the strain should be higher than the value obtained and likely to be some function of Mg concentration.

Figure 3.12 Variation in micro strain with deposition temperature and Mg concentration

3.4 Surface Morphology - SEM

The SEM micrographs of the as-deposited films are taken and compared to investigate the modification brought about on the size and shape of the grain due to Mg addition and the variation in deposition temperature. Electron micrographs of the deposited films are recorded by employing JEOL JSM 6390LV and Hitachi S 2400.

3.4.1 Micrographs of Undoped Films

Figure 3.13 shows the micrographs of undoped SnO2 films deposited at 205°C and 425°C. The micrographs explain that temperature 205°C is too small for well defined grain formation. At temperature 425°C, grains of varying size with a combination of flattened and fuse together features are
obtained accompanied by voids in between them. These may be due to the over temperature and the softening of grains at that higher temperature.

![Figure 3.13 SEM micrographs of undoped SnO$_2$ films deposited (a) at 205 °C and (b) at 425°C](image)

![Figure 3.14 Micrographs of undoped SnO$_2$ films deposited at temperatures (a) 285°C, (b) 325°C, (c) 355°C and (d) 385°C](image)

The micrographs of undoped films deposited at 285°C, 325°C, 355°C and 385°C are shown in figure 3.14. In these films, the grains are almost
spherical in shape. The micrograph establishes that the undoped SnO$_2$ thin films are homogeneous and uniform with regard to the surface topography. Numerous void regions are viewed between the grains. At 325°C and 355°C, the grain seems to contain pointed corners.

3.4.2 Micrographs of Mg Doped Films

The variation in grain shapes due to deposition temperature for 0.6 wt. % Mg doped SnO$_2$ films are illustrated in figure 3.15. Mg addition greatly affects the grain formation, both in size and shape. The grains become flattened and forms leafy shape or garden trowel shape. The grains develop in an irregular pattern at 425°C and this may be due to the softening of grains at this higher temperature.

![Figure 3.15](image)

**Figure 3.15** Micrographs of 0.6 wt. % Mg doped SnO$_2$ films deposited at temperatures (a) 285°C, (b) 355°C, (c) 385°C and (d) 425°C
The electron micrographs of SnO$_2$:Mg-0.6(325) films with different magnifications are shown in figure 3.16. The grains are garden trowel shaped. The grain size as seen from SEM varies in the range 110 nm and 190 nm.

![Figure 3.16 Micrographs of SnO$_2$:Mg-0.6(325) films with magnifications of (a) x 10000 and (b) x 15000](image1)

The grain manifestation for higher Mg concentrations (3 wt. % to 7.5 wt. %) when deposited at 325°C is shown as figure 3.17. As the Mg

![Figure 3.17 SEM images of higher Mg concentrations films deposited at 325°C, (a) 3 wt. %, (b) 4.5 wt. %, (c) 6 wt. % and (d) 7.5 wt. % Mg](image2)
concentration is increased, the uniformity in grain distribution is disturbed. A mixture of very small and very large grains is obtained. Larger grains are fewer in number and are of the order of 240 nm in the case of film with 6 wt. % Mg.

The grain size is determined from the SEM by intercept technique. For this, a random straight line is drawn though the micrograph. The number of grain boundaries intersecting the line is counted. The average grain size is found by dividing the number of intersections by the actual line length.

\[
\text{Average grain size} = \frac{\text{(actual length of the line)}}{\text{(number of intersections)}}
\]

where actual line length = (measured length) / (magnification scale).

3.5 FTIR Analysis

The elemental identification via characteristic frequencies is carried out by recording the Fourier transform Infra-Red spectra using Bruker Tensor 27 spectrophotometer with ATR.

![FTIR spectra of SnO2:Mg-0.6(325) film in the range 340 to 4000 cm⁻¹](image)

*Figure 3.18* FTIR spectra of SnO₂:Mg-0.6(325) film in the range 340 to 4000 cm⁻¹

Figure 3.18 shows the FTIR spectra of SnO₂:Mg-0.6(325) film in the wave number range 340 – 4000 cm⁻¹. No prominent bands appear in the range 4000-1000 cm⁻¹ due to OH and Sn-O vibrations. For detailed analysis
of the peaks in shorter wave number region, the spectra of figure 3.18 is enlarged in the range of 370 to 600 cm\(^{-1}\) and shown in figure 3.19. In the range of 520- 400 cm\(^{-1}\), Sn-O-Sn bands of various depths appear as the result of tin oxide film formation. The spectrum shows the characteristic bands at 487 and 484 cm\(^{-1}\), which appear due to Sn-O-Sn stretching modes (Uche et al., 2010), whereas peaks at 441 and 414 cm\(^{-1}\) shows the metal – oxygen vibrational frequency (Kaur et al., 2013). The weak peak at 465 cm\(^{-1}\) can be ascribed to \(\nu\)(Sn-O) vibrations. Again weak peaks appear in the spectrum at 454 cm\(^{-1}\) and also in the ranges of 477- 465 and 459- 403 cm\(^{-1}\) can be assigned to various \(\nu\)(Sn-O) stretching frequencies.

![Figure 3.19 FTIR spectra (shorter wave number region) of 0.6 wt. % Mg doped film deposited at 325°C](image)

The variation in spectra reported under different deposition conditions can be ascribed to changes in the size and the shape of the SnO\(_2\) particles. But no strong stretching band of Sn-Cl bond at 417 cm\(^{-1}\) or 390 cm\(^{-1}\) corresponding to chlorine (Pilling et al., 1999; Sutopo et al., 2012), is noticed. A very weak band appear at 378-376 cm\(^{-1}\) is indicative of C-O vibrations present (I-Chih et al., 1996).
3.6 Compositional Analysis - EDX

The elemental identification and their quantitative analysis are done side by side with SEM by employing EDX. For this Oxford Inca Energy and JEOL JED 2300 are utilised.

![EDX spectrum of undoped SnO₂ film deposited at 325°C, with its elemental composition in inset](image)

The EDX spectrum for undoped film deposited at 325°C is shown in figure 3.20 with its elemental composition given in inset. The peaks corresponding to Sn at 3.44 KeV and O at 0.52 KeV are obtained in the spectra. There is no peak corresponding to chlorine at 2.62 KeV, suggesting the absence of unreacted SnCl₂ in the deposition process. The (O)/(Sn) ratio is 2.07. The excess of oxygen is accounted due to the adsorption of atmospheric oxygen on the film surface.

The EDX spectrum of 0.3, 0.6 and 0.9 wt% Mg doped SnO₂ film deposited at 325°C are shown in figure 3.21 with its elemental composition given in inset. The characteristic peak of Mg is observed at 1.25 KeV. The Mg level is seen to increase with the increase in doping level. The amount of Mg incorporated in to the film formation slightly varies in the range 85 – 95 % depending on dopant concentration. The EDX spectrum for films prepared
at lower and higher deposition temperatures are also recorded and similar peaks are observed. The \([O]/[Sn]\) ratio is a factor of both deposition temperature and Mg concentration. The ratio itself has a key role in the gas sensing ability of a film.

Figure 3.21 EDX spectrums of (a) 0.3 wt% Mg; (b) 0.6 wt. % Mg; and (c) 0.9 wt. % Mg doped SnO\(_2\) film deposited at 325°C, with their corresponding elemental composition in insets’
Table 3.4 shows the variation in \([\text{O}] / [\text{Sn}]\) ratio with Mg concentrations in films deposited at 325°C, and with deposition temperature for films with 0.6 wt. % Mg concentration.

The ratio is greater for Mg doped films when compared with undoped films, is largest for SnO\(_2\):Mg-0.6(325) film and is 2.48. This shows that increasing the amount of Mg to certain extent favours the oxygen adsorption on the surface. The amount of oxygen adsorbed on to film surface depends on its deviation from stoichiometry. This is consistent with the intensity of (110) diffraction peak, which increases with increasing oxygen concentration. As the lattice is not disturbed, it would imply that the excess oxygen may be situated at the grain boundaries or at the film surface to cause the improved gas sensing detected, as they can be easily desorbed without any delay.

Amount of Sn and O in SnO\(_2\) thin films change with deposition temperature indicating non-stoichiometric behaviour of the films. The amount of non-stoichiometry and hence, the number of Sn\(^{4+}\) ions in the lattice is a function of formation temperature assisted by the dopant
Investigations on Mg Doped Tin Oxide Films for Sensing LPG and Methane

concentration. The EDX, measurement in this study yields SnO$_x$ with $x = 2.07$ to 2.48, suggesting that the films adsorb oxygen in addition to post depositional cooling to room temperature. Oxygen can be adsorbed on the surface of tin oxide films by the following process when the temperature is $< 100^\circ$C (Babar et al, 2011);

\[ \text{O}_2 \text{ gas} + e^- \rightarrow \text{O}_2^-_{\text{ads}} \quad \text{...............3.2} \]

The adsorbed oxygen has O$_2^-$ character and an accumulation layer is formed at the surface of grains. As the temperature is raised above 240$^\circ$C, the O$_2^-$ (ads) transforms to O$^-$ and O$_2^-$ by absorbing electron from the film, which displays an increase in resistance. On exposure to LPG adsorbed O$_2^-$ species interacts with the gas, resulting in release of captured excess electrons to demonstrate the sensor response.

3.7 Optical Properties and Band Gap Energy

The UV-Vis absorbance spectra of the samples are recorded by employing PerkinElmer Lambda 650 spectrometer, in the wave length range 180 - 900 nm. Spectra are similar in appearance irrespective of deposition temperatures and Mg concentrations. Spectra corresponding to films deposited at 325$^\circ$C are shown in figure 3.22. The absorbance is very poor in the wavelength range 400 nm to 900 nm and the mean transmittance is high to get a value of 79 %. The absorbance shows a rise at a wavelength smaller than 400 nm and attains a peak in the range 280 nm and 290 nm. The positions of the peak show a slight blue shift with magnesium concentration and it suggests that the addition of magnesium alter the band gap energy of the system.
3.7.1 The Tauc Plot

To analyse the band gap engineering effect of Mg doped SnO$_2$ film, Tauc plot are constructed for a direct band gap condition by taking the energy, $h\nu$ of the incident wave along X-axis and $(\alpha h\nu)^2$ along Y-axis.

Figure 3.22 Absorbance spectrum of undoped and Mg doped SnO$_2$ films deposited at 325°C

Figure 3.23 Tauc plot for undoped SnO$_2$ films deposited in the temperature range 285°C - 425°C
The Tauc plot for undoped SnO$_2$ films deposited in the range 285°C and 425°C are shown in the figure 3.23. The band gap is found to increase slightly with deposition temperature. The Tauc plot is constructed for all the samples and their band gap energies are determined. Band gap energies thus obtained for the prepared films are tabulated as table 3.5, for comparative study. The minimum band gap energy obtained is 3.56 eV and is obtained for undoped film deposited at 285°C, whereas the maximum obtained $E_g$ is 4.26 eV and is obtained for 0.9 wt. % Mg doped film deposited at 385°C. For undoped films the band gap energy increases with increase in deposition temperature from 285°C to 425°C. Small concentration of Mg increases the energy gap, but as the Mg level is increased in excess, the energy gap decreases.

<table>
<thead>
<tr>
<th>Deposition temperature (°C)</th>
<th>Band Gap Energy ($E_g$) - eV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>undoped</td>
</tr>
<tr>
<td>285</td>
<td>3.56</td>
</tr>
<tr>
<td>325</td>
<td>3.66</td>
</tr>
<tr>
<td>355</td>
<td>3.85</td>
</tr>
<tr>
<td>385</td>
<td>3.91</td>
</tr>
<tr>
<td>425</td>
<td>3.96</td>
</tr>
</tbody>
</table>

An increase of the temperature may lead to the decrease of the density of the defects, as decrease of the optical absorbance is clearly obtained in the spectrum. The shift in the absorption edge can be accounted for by the increase in carrier concentration and blocking of low energy transitions. Sn$^{4+}$ ions are more concentrated in films prepared with a higher temperature, results in an increase in the free electron concentration, but the presence of other phase in trivial quantities does not affect the concentration to a great extent. Accordingly less number of the unsaturated defects at
higher deposition temperature in the range 285 to 425°C gives out a ‘blue shift’ in optical band gap ($E_g$) from 3.56 to 4.26 eV.

3.8 Electrical Characterisation

3.8.1 D.C. Conductivity

To evaluate the electrical transport, the dc electrical conductivities of the prepared films are analysed. To enable a comparative study, the resistances of the films are measured by different techniques. In two-probe method, the lead wires are silver pasted to the films with a separation of 10 mm between the leads. For four-probe measurements, the current leads are silver pasted to the film at a constant separation (10 mm) and the voltage leads are pasted in perpendicular to that (separation 10 mm). The two-probe electrical measurements are carried out by employing Meco 45P digital multimeter and the four-probe electrical measurements are carried out by computer controlled Keithley 2400 source meter.

3.8.1.1 Undoped films

It is found that the both the two-probe and four-probe resistance of the films are of the order of few Kilo Ohms. Over the lower resistance region, as expected, the four-probe resistance of the films is lower than the two-probe measured resistance. Initially the resistances are measured at room temperature. The two-probe and four-probe resistance of undoped films deposited in the temperature range 285°C and 425°C as shown in table 3.6. For undoped films the resistances are found to decrease with increase in deposition temperature. But as the deposition temperature is increased to 425°C, the resistance slightly increases.
**Table 3.6** Two-probe and four-probe resistance of undoped films deposited at temperatures in the range 285°C and 325°C

<table>
<thead>
<tr>
<th>Resistance measurement</th>
<th>Deposition temperature</th>
<th>285°C</th>
<th>325°C</th>
<th>355°C</th>
<th>385°C</th>
<th>425°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Two-probe (Ω)</td>
<td></td>
<td>2612</td>
<td>2156</td>
<td>1953</td>
<td>1812</td>
<td>1887</td>
</tr>
<tr>
<td>Four-probe (Ω)</td>
<td></td>
<td>1593</td>
<td>1080</td>
<td>956</td>
<td>826</td>
<td>888</td>
</tr>
</tbody>
</table>

### 3.8.1.2 Mg doped films

The two-probe and four-probe resistance in Mg doped films are also determined. The variation in two-probe resistance is plotted as a function of deposition temperature and added Mg, in figure 3.24. Mg doping increases the resistance of films. Maximum resistance is obtained for films deposited at 325°C and the least for that deposited at 385°C.

![Figure 3.24](image)

**Figure 3.24** Variation of two-probe resistance of films with deposition temperature and Mg concentration

For films deposited in the range 285°C and 355°C, the two-probe resistance initially increases with increase in Mg concentration up to 0.6 wt.
%, and then decreases with Mg addition. For films deposited at higher temperatures, the resistance continuously falls with increase in Mg level.

The four-probe resistances of the Mg doped films are tabulated in table 3.7. As in the case with undoped films, for Mg doped films also, the four-probe resistance is much small when compared with two-probe resistance. The variation in four-probe resistance of the films with deposition temperature and Mg level is similar to that with the variation of their two-probe resistance.

**Table 3.7** Four-probe resistances of doped SnO₂ films for different deposition temperatures and Mg concentrations

<table>
<thead>
<tr>
<th>Deposition Temperature (°C)</th>
<th>Four-probe resistance at room temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mg concentration</td>
</tr>
<tr>
<td></td>
<td>0.3 wt. %</td>
</tr>
<tr>
<td>285</td>
<td>2015</td>
</tr>
<tr>
<td>325</td>
<td>1450</td>
</tr>
<tr>
<td>355</td>
<td>1921</td>
</tr>
<tr>
<td>385</td>
<td>1741</td>
</tr>
<tr>
<td>425</td>
<td>1774</td>
</tr>
</tbody>
</table>

**Figure 3.25** Ohmic resistance (four-probe) variations with crystallite size of films
It is seen that the crystallite size has major role in determining the resistance of the Mg:SnO$_2$ films. To investigate the relation, the four-probe resistances of the films are plotted as function of average crystallite size, determined from XRD (110) and (101) peaks and is shown as figure 3.25. The third order polynomial trend line fits the variation and shows that the four-probe resistance of films increases drastically when crystallite size falls below 40 nm and decreases for crystallite size below 55 nm. This suggests that the grain boundary effects influence the electrical conductivity of the films.

The resistance of the films measured by two-probe method and four-probe method for higher concentrations of Mg deposited at temperature range 285 ± 3°C and 325 ± 3°C is shown in table 3.8. It is observed that higher concentrations of Mg do not alter the electrical conductivity of the films excessively. The resistance of the films shows a small decrease with increase in Mg level from 1.5 wt. % to 7.5 wt. %.

<table>
<thead>
<tr>
<th>Deposition temperature</th>
<th>Measurement method</th>
<th>Resistance of film (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>285°C</td>
<td>Two-probe</td>
<td>3715 3645 3633 3601 3591</td>
</tr>
<tr>
<td></td>
<td>Four-probe</td>
<td>1480 1435 1427 1407 1400</td>
</tr>
<tr>
<td>325°C</td>
<td>Two-probe</td>
<td>3806 3752 3658 3615 3628</td>
</tr>
<tr>
<td></td>
<td>Four-probe</td>
<td>1538 1503 1443 1415 1424</td>
</tr>
</tbody>
</table>

3.8.2 A.C. Characteristics

The a.c. characteristics of the films are carried out by QUADTECH 1920 precision LCR meter. The a.c. conductivity, capacitance and dissipation factor are measured by varying the frequency in the range 20 Hz to 1 MHz.
3.8.2.(a) Frequency vs. a.c. conductance

The variation of ac conductivity with frequency (taken in log\textsubscript{10} scale) for the SnO\textsubscript{2}:Mg-0.6(325) film is plotted to obtain figure 3.26. The ac conductivity is very small up to a frequency of 500 KHz and shows a sharp increase above it. The maximum conductivity obtained is 0.032 Seimens/metre indicates that a film has only low capacitance.

![Figure 3.26 Variation of ac conductivity with frequency (log scale) for SnO\textsubscript{2}:Mg-0.6 (325) film](image)

The frequency dependence of ac conductivity and its variation with deposition temperature for 0.6 wt. % Mg doped SnO\textsubscript{2} films are plotted in figure 3.27. The conductivity is small for all the films below 200 KHz. In between 200 KHz and 500 KHz the conductivity increases linearly with ac frequency regardless of the temperature of deposition. But for higher frequencies, the ac conductivity changes with film deposition temperature. The a.c. conductivity reaches maximum for films deposited at 325°C. The gradual increase in ac conductivity with increase in frequency and its variation with deposition condition suggests that it must be related to the oxygen deficient stoichiometries present in the sample and the conduction of
charge carriers among these phases due to hopping and is consistent with earlier hopping reports.

![Figure 3.27 Variation of ac conductivity with frequency for 0.6 wt. % Mg doped SnO$_2$ film deposited at various temperatures](image)

**Figure 3.27** Variation of ac conductivity with frequency for 0.6 wt. % Mg doped SnO$_2$ film deposited at various temperatures

### 3.8.2.(b) Dissipation factor vs. frequency

![Figure 3.28 Variation of dissipation factor with frequency for films deposited at 325°C](image)

**Figure 3.28** Variation of dissipation factor with frequency for films deposited at 325°C

The dissipation factor (denotes the power dissipation and hence loss factor) variations with frequency of a.c. as a function of deposition conditions are determined. The profiles are almost similar for all the deposition conditions, especially in higher frequencies. Figure 3.28 shows the variation of dissipation factor with frequency for samples deposited at 325°C. The dissipation factor
Chapter 3

decreases up to frequency 1 KHz and keeps a low profile up to 10 KHz. The factor thereafter increases to reach a maximum value at 100 KHz and then decreases subsequently till the measurement cutoff of 1 MHz. The decrease of loss factor at lower frequencies (up to 1 KHz) may be due to fact that the ions, or states at the grain boundaries, require more energy to transfer electrons whereas at higher frequencies grain conduction itself play a dominant role where hopping require less energy. The loss factor is found to decrease in the highest frequency region, which may be due to the effect of contact or lead resistances.

3.8.2.(c) Frequency vs. capacitance

![Figure 3.29 Variation of capacitance with a.c. frequency (log. scale), for films prepared at 325°C](image)

The variation of capacitance with frequency in the range 20 Hz to 1 MHz for undoped and doped films prepared at 325°C are shown in figure 3.29. It is found that for all Mg concentrations, the capacitance of the films decreases with increase in frequency up to 1 KHz and attains a steady negligible value for all higher frequencies. Both for the Mg doped and undoped samples, the higher capacitance at lower frequencies is evident. The
higher value of capacitance at lower frequency can be explained on the basis of interfacial / space charge polarisation due to porosity and grain interface present in the films. At very high frequencies the polarisation decreases and then drops to a constant value owing to the increased hopping between metal ions of different types (Sn$^{2+}$, Sn$^{4+}$) and barriers cannot follow the changing field. It has also observed that the value of capacitance remains steady with the increase in dopant concentration. It may be due to the fact that the dielectric polarisability is not altered by small amount of doping.

3.9 Gas Sensing Characterisation

One of the main objectives of this research is to determine the organic gas sensitivity (LPG and methane) of the deposited films. After determining the sensor response of each deposited film, their response variation is thoroughly co-related with the previously discussed characteristics of the film. This gives out a way of understanding the gas sensing mechanism of the film and emerges out ideas for improving the sensor characteristics. The organic gases undertaken for sensitivity test belong to two groups. One group contains gases that are liquifiable at room temperature in dissimilarity with the second group that cannot be liquifiable. In spite of that both must contain comparable chemical species. Selection based on this categorisation results in LPG (liquified petroleum gas) and methane gas. Hence the sensor response towards both the gases are analysed separately and are discussed in this section.

3.9.1 Sensor Response to LPG

3.9.1.(a) Operating temperature

For determining their sensor response of films, the as-deposited films loaded in the sensing chamber with four-probe leads attached. It is found that the film conductivity is not affected at room temperature by the presence of LPG. Hence a higher temperature known as ‘operating temperature’ is needed
for the analysis. For this the film is heated inside the chamber with atmospheric air as ambient and then in the ambience of LPG. The graph shown in figure 3.30 shows the variation of four-probe resistance of SnO$_2$:Mg-0.6(325) film in the presence and absence of LPG (1000 ppm). It is seen that the resistance of the sample continuously decreases with increase in temperature up to 270°C, irrespective of the ambient atmosphere. This may be due to the normal characteristics of SnO$_2$ as a semi conductor. But when the temperature is increased above 270°C, the film depicts different electrical characteristics, with ambient gas. Above 285°C with air as ambient gas, the resistance of the film increases with temperature, and practically saturates at 385°C. This possibly may be due to the fact that the oxygen in the atmospheric air may have adsorbed in to the film surface could attach some of the free electrons. This adsorption mechanism can be enhanced by temperature of the film surface. When the temperature is too high, further adsorption may not be possible or the desorption of previously adsorbed oxygen may take place due to high excitation energy of the electrons.

![Figure 3.30](image.png)

**Figure 3.30** Resistance (four-probe) variation of 0.6 wt. % Mg doped SnO$_2$ film with temperature in the presence and absence of LPG
When the temperature of the film is raised above 275°C, in the presence of LPG, a decrease in film resistance is observed. This provides a means of sensing LPG ambience by the film. On exposure to reducing gas like LPG the film interact with the previously adsorbed oxygen on the surface to release the electron held by the oxygen ion. This increases the electrical conductivity of the film. For the process, dissociation of LPG is required which occur above 300°C.

The variation of film resistance with different composition and deposition temperatures is analysed and the plots almost similar to that in figure 3.30 are obtained. The four-probe resistance of the film observed in air at a particular temperature below 270°C and above depends on its initial resistance at room temperature. In the presence of LPG, the temperature upon which the rapid decrease in resistance of doped film starts around 295°C.

The sensor response (sensitivity) varies with the surface temperature of the film, hereafter called as ‘operating temperature’. The variation in sensor response with operating temperature is analysed by plotting a graph between them.

![Figure 3.31](image) The deviation of sensor response with operating temperature, for SnO₂ Mg-0.6(325) film
3.9.1.(b) Sensor response variation with deposition condition

Figure 3.31 shows the variation of sensor response with operating temperature for SnO$_2$:Mg-0.6(325) film. The curve drawn attains a peak value at an operating temperature of 350°C. Further increase in operating temperature may not be advantageous and causes a decrease in sensor response. Films with different deposition conditions are also analysed and almost similar results are obtained. Hence the operating temperature for further analysis is fixed at 350°C in the entire investigations. Each of the deposited films is loaded in to the sensing chamber for determining their LPG response. The operating temperature is maintained at 350°C and 1000 ppm of LPG is admitted into the chamber. The four-probe resistance of the film is continuously monitored every 5 seconds for 10 minutes. The resistance values so obtained are plotted against the sampled time. Figure 3.32 shows the resistance decrease profile of films deposited at 325°C with various Mg concentrations with sampling time after exposure to 1000 ppm of LPG. For all the samples, resistance continuously falls off for the initial 55 to 70 seconds, to attain a minimum saturation value as shown in the graphs.

![Figure 3.32](image.png)  
*Figure 3.32* Resistance variations in film with exposure time to 1000 ppm of LPG; for films deposited at 325°C
The variation in resistance is smallest in undoped films. For Mg doped films the resistance variation is more rapid and higher than that of undoped films. The percentage resistance variation obtained is largest for SnO$_2$:Mg-0.6(325) film. Its four-probe resistance, which is 3255 ohms initially, falls to 292 ohms with 70 seconds after exposed to 1000 ppm of LPG. The obtained most favorable value of sensor response is the basis of using the mentioned condition for doped film formation, for a detailed study.

The sensor response (sensitivity) of the films is defined as

\[ S\% = \frac{\text{Initial resistance at operating temperature} - \text{saturation resistance after feeding gas}}{\text{Initial resistance at operating temperature}} \]

The sensor response is determined for films deposited at temperatures in the range 285°C and 425°C for Mg concentration varying from 0 (undoped) to 1.2 wt. %. It is found that the LPG sensitivity of the film greatly depend upon the deposition conditions. The enhancement in sensitivity due to suitable concentration of Mg addition dominates the effect due to deposition temperature. Figure 3.33
shows the growth of sensor response of typical samples with exposure time. The sensor response in only 34 % for undoped film deposited at 325°C whereas it is 93 % for SnO\textsubscript{2}:Mg-0.6(325) film. In all cases nearly 80 % of its sensor response is achieved within 55 to 59 seconds after LPG exposure. The saturation of sensor response is achieved within exposure duration of 60 to 72 seconds.

The sensor response variations in 1000 ppm of LPG for films deposited at different temperatures and typical Mg concentrations are shown in figure 3.34. The LPG sensitivity achieved by SnO\textsubscript{2} film varies widely with Mg doping and deposition temperature. For all deposition temperatures in the range 285 – 425°C, the sensitivity of undoped samples are the least when compared with Mg doped samples at same temperature. Mg addition up to 0.6 wt. % favours LPG sensing for the investigated deposition temperatures. It has been noted that adding higher Mg concentration does not usually deliver favourable results.

![Figure 3.34 LPG sensitivity variations, as a function of deposition temperature and Mg concentration](image)

For the analysed samples, the sensitivity increase with deposition temperature up to 325°C and then gradually falls until 425°C, irrespective of the Mg concentration. The structural, morphological, compositional and
electrical characterisation of the films discussed in earlier sections also illustrate that, these characteristics widely vary with deposition conditions. Hence it can be believed that the LPG sensing is mainly governed by the structural and stoichiometric variations of the films.

3.9.1.(c) Correlation of sensor response with four-probe resistance

The four-probe resistance of the films at room temperature is correlated with the sensitivity of the film. Figure 3.35, shows the variation of film sensitivity at 350°C with corresponding four-probe resistances at room temperature. Most of the samples have a moderate resistance in the range $1600 \, \Omega$ to $1900 \, \Omega$ and have a moderate LPG sensitivity in the range 23 % to 62 %. Maximum sensitivity of 93 % is obtained for film with maximum resistance. When more oxygen is adsorbed on a film surface, more electrons get secured by this means and the conductivity will be least. When such a surface is exposed to reducing gas like LPG, electrons get released will be larger in number which in turn increase the conductivity to a great extent.

![Figure 3.35](image_url)  
*Figure 3.35 Dependence of sensor response towards LPG, on initial four-probe resistance of film*
3.9.1.(d) Correlation of sensor response with growth along (110) & (101) plane

The oxygen adsorption is more in certain sample surface and is less in certain other sample surface. The growth of crystallites in particular orientations may enhance oxygen adsorption. Figure 3.36 shows the variation of peak intensity of (110) and (101) plane with regard to sensor response. An increase in intensity for reflection from a plane refers to extended crystal orderliness in that orientation. It is obvious from the figure that the higher the peak intensity of these planes in comparison to other reflections, better is the sensitivity. To attain a sensor response above 80 %, both the planes should have a large texture value and the intensity of (110) should be explicitly at a higher value than (101).

It is already discussed from figure 3.8 that the texture coefficients of both (110) and (101) planes shows a hefty value for 0.6 wt. % Mg doped sample deposited at 325°C than film deposited at any other conditions. In figure 3.9, it is unambiguously disclosed how the growth along (211) and (301) planes are suppressed and subsequently contributed to the growth along (110) and (101) plane, when deposited at 325°C. This points out to the fact that the preferential growth along (110) and (101) planes favour the sensor response of the film positively by enhanced oxygen adsorption on the surface.
The size of crystallites determined from (110) and (101) planes are plotted against the sensor response of the films is shown in figure 3.37. For (110) plane, the maximum sensitivity is obtained when films are formed in smaller crystallite size of 29 nm. As the grain develop to bigger in size, the sensitivity of the film decreases. Calculating from the (101) plane broadening, it is observed that as the crystallite size increases, the sensitivity initially increases up to 43 nm and then decreases.

3.9.1. (e) Response time and recovery time

The response time and recovery time are analysed for the prepared samples. The response time is defined as the time interval taken to attain 80
% of sensitivity after exposed to LPG. The recovery time is defined as the duration taken to regain 80% of initial resistance (at the operating temperature) after LPG is pumped out. Figure 3.38 shows the loosing and regaining of sensor resistance when LPG is injected in (ON) and pumped out (OFF) of the sensing chamber, for SnO$_2$:Mg-0.6(325) film for successive cycles. When LPG is ON, the resistance suddenly falls and attains saturation. The response time is 59 seconds for this film. When LPG is pumped out, the sensor resistance tries to regain its initial value. The recovery time is 71 seconds and the resistance gets saturate at 95 % of its initial value. Similarly the response time and recovery time remains almost constant for repeated cycles.

![Figure 3.38 Loosing and gaining of sensor resistance with LPG exposure duration and recovery duration for SnO$_2$:Mg-0.6(325) sensor](image)

The response and recovery durations are determined for other samples also. It is seen that the response time slightly increases with sensitivity of the film. The smaller the sensitivity of the film, the smaller will be its response
time. However this is not a speedy sensing, because 0.8 fraction of sensitivity of poor response film will be equivalent to 0.2 fraction of the sensitivity of the privileged film. The recovery duration required for all the films are greater than their response time. The recovery time required also increases with sensitivity or in other words, the higher the response time, higher is its recovery duration. Variation of response time and recovery time with sensitivity is shown in figure 3.39. The difference between response time and recovery time is least for the films with minimum sensitivity and it increases for films with larger sensitivity.

![Figure 3.39 Response time and recovery time variations with sensor response](image)

**Figure 3.39** Response time and recovery time variations with sensor response

### 3.9.2 Sensor Response to Methane

#### 3.9.2.(a) Operating temperature

As methane is not a component of LPG, the sensor response towards methane is separately analysed. For efficient practical sensing the operating temperature is to be determined. Methane being more stable than LPG, a higher temperature is required for the dissociation.
Figure 3.40 Variation in sensor response with operating temperature towards methane gas, for Mg:SnO$_2$-0.6(325) film

The temperature is maintained at different values in the range 275°C and 400°C and the sensor response towards 1000 ppm of methane gas for SnO$_2$:Mg-0.6(325) film is determined. Figure 3.40 shows the variation in sensor response with operating temperature towards methane gas, for 0.6 wt. % Mg doped SnO$_2$ film deposited at 325°C. The sensor did not respond to methane when the operating temperature is below 300°C and the response is less than 10 % when the operating temperature is raised to 325°C. Maximum sensor response is obtained at an operating temperature of 385°C. It has verified that further increase in operating temperature does not give appreciable improvement. From figure 3.30 it is concluded that the increase in sensor resistance with temperature in air ambience gets saturated at 385°C. In concurrence with this, the methane sensitivity is also not to get increased above the particular operating temperature.

3.9.2.(b) Methane response at 350°C

To compare the sensor response to methane with that of LPG, sensor response of all the samples are determined at 350°C. To get an indication
about the change in sensitivity for methane, the films are analysed at the operating temperature 385°C also. Figure 3.41 shows the actual variation in resistance (four-probe) of films deposited at 325°C with exposure-duration in 1000 ppm of methane gas, at the operating temperature 350°C. As earlier observed, the response is very feeble for the undoped film. Maximum variation is obtained for 0.6 wt. % Mg and the resistance falls from 3240 Ω to 2820 Ω in 120 seconds.

At the operating temperature of 350°C, the variation in sensor response in methane with deposition temperature and Mg concentration is shown in figure 3.42. At this temperature, the film response is very poor for undoped sample which is nearly 2 %. Maximum response is obtained with SnO$_2$:Mg-0.6(325) film for methane is 13.2 %. For lower deposition temperatures the sensitivity increases with Mg concentration up to 0.6 wt. % and then decreases with increase in Mg addition.
Chapter 3

Figure 3.42 Variation of sensor response in methane with deposition temperature and Mg concentration, at operating temperature of 350°C

At higher deposition temperature, Mg addition above 0.3 wt. % has no appreciable benefit. For all the samples, the sensitivity to methane gas is much smaller when compared with its sensitivity to LPG. Hence if the sensor is operated at 350 °C temperature, a good selectivity can be achieved for both the reducing gases.

3.9.2.(c) Methane response at 385°C

Maximum sensitivity is achieved in methane gas when operated at 385°C. The variation in four-probe resistance for films deposited at 325°C, when exposed to 1000 ppm of methane gas is shown in figure 3.43. The sensitivity of both doped and undoped samples increases to a reasonable value at this operating temperature. For 0.6 wt. % Mg doped film, a maximum sensitivity of 52 % is obtained in methane. It resistance falls from 3356 Ω to 1611Ω in 80 seconds. It is evident from the responses that the increase in operating temperature from 350°C to 385°C reduces the response time for methane gas sensing.
The variation in sensor response for methane gas with deposition temperature and Mg concentration, when operated at 385°C is shown in figure 3.44. For 0.6 to 0.9 wt. % Mg doped films, the methane response increases with deposition temperature from 285°C to 325°C and thereafter decreases with increase in deposition temperature. For undoped and higher Mg concentration (1.2 wt. %), the sensitivity increases with deposition temperature up to 355°C and then decreases with higher deposition temperatures. Maximum sensitivity is achieved for 0.6 wt. % Mg doped film at all deposition temperatures. This is somewhat similar with the results obtained with LPG sensitivity at 350°C. In short the Mg doped films show more sensitivity than undoped films when deposited below 400°C. Mg doped films in all deposition temperatures show methane response which increases with Mg concentration level up to 0.6 wt. % and then decreases. The response is 32 % for undoped film deposited 355°C whereas 53 % for SnO₂:Mg-0.6(325) film.
Figure 3.44 Variation of sensor response towards methane at an elevated operating temperature of 385°C, with deposition temperature and Mg concentration.

Figure 3.45 shows the growth of sensor response of typical samples with methane exposure time. In all cases nearly 80% of its sensor response is achieved within 60 seconds of gas exposure. The saturation of sensor response is achieved within exposure duration of 70 to 80 seconds.
3.9.2.(d) Response time and recovery time

The response and recovery durations are determined for methane gas also. Figure 3.46 shows the losing and regaining of sensor resistance when methane gas is injected in (ON) and pumped out (OFF) of the sensor chamber, for SnO$_2$:Mg-0.6(325)film in successive cycles. When methane gas is ON, the resistances suddenly falls and attains saturation. The response time is 59 seconds for this sample and is identical to that for LPG. The initial resistance of 3356 Ω (at 385°C) falls to 1611 Ω in 74 seconds and attains saturation. When methane is pumped out, the sensor resistance tries to regain its initial value. The film regained 3221 Ω 88 seconds after removing the methane gas. The recovery time is 80 seconds and the resistance gets saturate at 96 % of its initial value. Similarly the response time and recovery time remains almost constant for repeated cycles. As in the case with LPG, the methane response time slightly increases with the sensitivity of the film. The recovery duration required for all the films are greater than their response time.

![Figure 3.46 Loosing and gaining of four-probe sensor resistance with methane gas exposure duration and recovery duration (for SnO$_2$:Mg-0.6(325)film)]
3.9.2. (e) Dependence of methane response on four-probe resistance

Similar to what obtained with LPG, the sensor response to methane gas at 385°C depends on the room temperature resistance of the film. Figure 3.47 shows the dependence of methane gas sensitivity on the four-probe resistance (room temperature) of films. For the films having four-probe resistance between 1500 Ω and 2000 Ω, their methane sensitivity will be in between 28 % and 48 %. For films with lower resistance, the sensitivity decrease up to 23 %. It is evident from figure 3.47, that as the resistance increase above 2000 Ω, the methane sensitivity increases uniquely. The resistance related changes can be related to the compositional variations of the film.

![Figure 3.47 Dependence of sensor response to methane with four-probe resistance (at room temperature) of sensor film](image)

3.9.3 Comparison between LPG and Methane Sensitivity

With magnesium doped films, maximum sensitivity is obtained with films deposited at 325°C. A comparison of sensitivity of the films in LPG and methane is done to evaluate the selectivity of these sensors among the studied gases at this deposition temperature. Figure 3.48 shows the variation in LPG sensitivity at 350°C, and methane sensitivity at both 350°C and
385°C, with different Mg concentration. In all cases, the LPG sensitivity is above that of methane sensitivity. With 0.6 wt. % of Mg, the LPG sensitivity at 350°C is double than its methane sensitivity at an elevated temperature of 385°C. Hence the present doped films posses’ high level of selectivity between these two gases.

![Figure 3.48](image)

**Figure 3.48** Comparison of LPG and methane sensitivity for films deposited at 325°C, with different dopant concentrations and operating temperatures

### 3.10 Stoichiometry Analysis from X-Ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy is a good analytical tool for elemental analysis, as the binding energy (BE) values of core levels are, to a certain extent dependent on the molecular environment. Hence the stoichometry of the SnO$_2$ films are analysed by using XPS. Typical broad-scan XPS spectrum within the BE range of 0–1000 eV, for the SnO$_2$:Mg-0.6(325) film, which showed maximum sensor response to LPG is shown in figure 3.49.
Figure 3.49 XPS wide scan spectrum for SnO$_2$:Mg-0.6(325) film with prominent photoelectron peaks labeled. Inset shows enlarged low binding energy region.

The spectrum primarily shows the Sn 4d, Sn 3d$_{5/2}$, Sn 3d$_{3/2}$, O 1s, sharp intense peaks located at 25.8, 486.4, 494.8, and 530.5 eV respectively, besides minor peaks from Sn 3p$_{3/2}$, Sn 3p$_{1/2}$ respectively at 716.8 and 757.8 eV, to confirm the presence of Sn and O (Themlin et al., 1992; Moulder et al., 1995; Jin Ku et al., 2010). Mg KLL characteristic peak measured in the binding energy 304.8 eV shows the presence Mg. Lower energy portion of the XPS scan is shown in the inset, which clearly provides convincing evidence for the presence of Mg 2p$_{3/2}$ at 50.7 eV and Mg 2s at 91 eV (Sebastian et al., 2011).

A small feature near C 1s observed can be assigned to the C KLL peak at 275 eV (Hye Yoon and Yong-Cheol, 2007). A very broad peak is also distinct at 977.8 eV which is usually assigned to O Auger (KLL) (Rusu et al., 2010). The peaks at 476.8 eV and 518 eV are assigned to satellite peaks and are consistent with the fact that the highest intensity peak is often flanked by satellites (Vladimer and Geoffrey, 1995).
3.10.1 Deconvolution of C 1s, O 1s and Sn Peaks

A close analysis of the spectra, by fitting of the peaks using software, can be used to determine the Sn electron state and the degree of oxidation. The SnO$_2$ electron states are curve-fitted, by deconvolution with Gaussian and Lorentzian (GL 30) contributions for the peak shapes with Vision processing software© through an iterative minimisation procedure. In the plots, dark solid line correspond to experimental data, the coloured fainted line/s demonstrate the deconvoluted peak and dashed line correspond to numerical sum of the peak fits.

![Graph showing C 1s peaks of SnO$_2$:Mg-0.6(325) film with computer fitted curves. The C 1s recorded spectrum is shown in black solid line (peaks at 284.8 eV), the violet line demonstrates the GL 30 deconvoluted peak and the fit sum in dashed red line (both peaks at 284.8 eV)](image)

**Figure 3.50(a)** Narrow scan XPS C1s peaks of SnO$_2$:Mg-0.6(325) film with computer fitted curves. The C 1s recorded spectrum is shown in black solid line (peaks at 284.8 eV), the violet line demonstrates the GL 30 deconvoluted peak and the fit sum in dashed red line (both peaks at 284.8 eV)
The symmetrical C 1s core line, which is due to surface carbon contamination of the sample in open air, as evidenced by the variation of peak intensities with store up time, can be fitted by a single Voigt function, figure 3.50(a), and designated to carbon atoms bonded to carbon and/or hydrogen atom (Li et al, 2009).

In the O 1s core level peak, the binding energy value lower than expected, indicates that there are oxygen vacancies in the doped material (Reddy et al, 2007). The high resolution scan of O 1s peak, a slight asymmetry in the form of a high energy tail, apparent for all the samples investigated, suggests the presence of multiple valence oxygen in the metal oxide (Pan and Fu, 2001). Thus, the O 1s spectrum is fitted to Gaussian / Lorentzian (GL 30) peaks, in order to determine the peak positions and relative abundance of the different oxygen sites.

The complex data envelope in oxygen peaks in figure 3.50(b) can be resolved into doublet component corresponding to two different types of oxygen sites present in these films (Bonnelle et al, 1975). Components corresponding to O 1s of 531.0 eV belonging to SnO$_{2-x}$ structural O atoms or oxygen inside non-stoichiometric oxides within the surface region of the material, while 532.7 eV corresponds to adsorbed oxygen, identified as ‘chemisorbed oxygen’ (Liu P. Y. et al, 2004; Marcus Kennedy, 2004). The adsorbed oxygen exists on the grains or surface of the SnO$_2$ crystallites from O$_2$ molecules of the ambient atmosphere. In samples containing more oxygen deficiency, the peak appears at a slightly lower binding energy of 531eV which is caused by O 1s of tin oxide in lower coordination.
Figure 3.50(b) Narrow scan XPS O1s peaks of SnO$_2$:Mg-0.6(325) film with computer fitted curves. The O 1s peak recorded spectra shown as black solid line (peaks at 530.5 eV) and the GL 30 deconvoluted peaks as blue line (peaks at 531.0 eV) and dashed red line (peaks at 532.7 eV) respectively.

Resolving the Sn 3d$_{5/2}$ main peak asymmetry in a similar way as above, it can be deconvoluted into two Voigt components (figure 3.50(c)), to represent the chemical bonding states of tin species. The best GL30 fit to the XPS peaks of the Sn 3d$_{5/2}$ lines resulted into two distinct peaks as shown. The deconvolution spectra suggest that the distribution contains two oxidation states (all found with an energy difference of less than 1 eV between the Sn$^{4+}$ and Sn$^{2+}$ states) and observed that their intensities change with the deposition parameters.
The Sn 3d$_{5/2}$ asymmetric peak (~ 486.4 eV) supports the heterogeneity in bonding within the formation (Yoshitake Masuda, 2012). The deconvoluted B.E. value of 486.4 eV and 486.1 eV attributed to the presence of SnO$_2$-$x$ major phase along with the existence of Sn-oxidation state less than +4, in the films. The reported binding energy 487.1 eV for SnO$_2$ is identical, but the 486.9 eV for SnO with additive is slightly higher (Punnoose et al, 2005) by 0.4 eV with the present values. Furthermore, no peak for elemental tin (484.2 - 485 eV) is observed indicating that only phase variation occur in all the blends. This is further supported by the fact that energy difference between the Sn 3d$_{5/2}$ and O 1s peaks for the samples
is 43.85 eV. As the oxygen deficiency increases, the peak position of Sn 3d shifts to a lower binding energy. Sample with, SnO$_{1.69}$, which has a low [O] / [Sn] ratio, exhibits a shoulder peak at a binding energy close to 485 eV, which corresponds to the Sn-Sn binding energy (Lee et al, 2000).

The deconvolution of narrow-scan analysis of Sn 3d$_{3/2}$ spectra at 494.8 eV, is also presented in figure 3.50(c). The large binding energy usually indicates more oxidised metals. The formation of tin oxide is unambiguously detected by the XPS spectra but the accurate determination of SnO$_2$, SnO, and Sn$_2$O$_3$ amounts in the films, could not be done due to the similarities in binding energies of these compounds (Walter et al, 2005). The separation between the Sn 3d$_{5/2}$ and Sn 3d$_{3/2}$ binding energy 8.40 eV is in agreement with the reported value (8.5 eV) of SnO$_{2-x}$ thin films (Humaira et al, 2012; Qi-Hui et al, 2007).

Table 3.9 Measured XPS peak values and the computer fit values for 0.6 wt% Mg doped SnO$_2$. The BEs and the FWHMs of the peaks obtained by a Gaussian/Lorentzian fit

<table>
<thead>
<tr>
<th>Peak analysed</th>
<th>Binding energy (eV)</th>
<th>FWHM (eV)</th>
<th>Peaks fitted by Voigt analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Curve 1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Binding energy (eV)</td>
</tr>
<tr>
<td>C1s</td>
<td>284.8</td>
<td>1.917</td>
<td>284.8</td>
</tr>
<tr>
<td>Sn3d$_{5/2}$</td>
<td>486.4</td>
<td>1.431</td>
<td>486.8</td>
</tr>
<tr>
<td>Sn3d$_{3/2}$</td>
<td>494.8</td>
<td>1.445</td>
<td>494.8</td>
</tr>
<tr>
<td>O1s</td>
<td>530.5</td>
<td>3.087</td>
<td>531.0</td>
</tr>
</tbody>
</table>

Table 3.9 show the BE and FWHM values, resulting from the selection of constituent line profile functions Gaussian / Lorentzian, for the deconvolution of XPS peaks. The results from deconvolution indicate that Sn is predominantly in an oxidised state (Sn$^{4+}$ or Sn$^{2+}$) at the surface. As the difference of the peak position of Sn$^{2+}$ and Sn$^{4+}$ is very small, these states cannot be differentiated from one other. In summary, the
XPS results obtained in this report confirm that the pre-adsorbed oxygen in the sensor plays a crucial role in the electrical properties of SnO$_2$:Mg films and provide useful means in understanding the gas sensing mechanism of the material.

### 3.10.2 Quantification from Peak Area Analysis

The ratio of atomic concentrations \([O]/[Sn]\) is quantitatively analysed by calculating the peak areas of the O 1s and Sn 3d$_{5/2}$ peaks. The areas of XPS peaks have been compensated by the sensitivity factors, 0.78 for O1s and 7.8 for Sn 3d$_{5/2}$ by Kratos (Moulder et al., 1992). The obtained values are 1.92, 1.69, 2.09 and 1.90 for doping concentrations 0.3, 0.6, 0.9 and 1.2 wt%, respectively. However, the value of O 1s level of the spectrum point out the amount of oxygen directly bound to Sn. The components of the oxygen in XPS reflect the presence of mixed oxidation states of SnO$_2$. This finding is consistent with the intermediate value of stoichiometric ratio Sn:O found by EDX. The value of [O] / [Sn] atomic ratio of 1.64 for the maximum sensitivity sample is related with the fact that, it is composed from SnO$_{2-x}$ ($0 < x < 0.5$), and undoubtedly there exist plenty of oxygen vacancies on the film surface with excess adsorbed oxygen, congruent with EDX results (Section 3.6). The convolution of profile is indicative of the presence of different forms of oxygen at the film surface, which influence the accurate determination of the amount of oxygen directly bound to Sn atoms.

### 3.11 Ageing Effects on Sensors

The effects of ageing on the sensitivities of the doped films are studied in detail in comparison to undoped. As gas sensing is a surface process, the changes in surface sites can alter the oxygen adsorption mechanism and thereby the sensitivity of the films. The ageing effect analyses have been done on the films...
stored in ambient atmosphere. They are loaded in the sensor chamber at regular intervals and sensitivities are determined. The analysis has been repeatedly conducted for 8 years. The samples show a decrease in its LPG response after ageing. After a storage period of four years, it is seen that the response time is increased and the resistance variation after exposing to LPG is not smooth. The samples are thereafter annealed at a temperature equal to the deposition temperature before subjecting the ageing sensitivity analysis. It has been observed that the annealed samples almost recovered the previous response time and sensitivity values.

### 3.11.1 Surface Morphology of Aged Films – FESEM

Ageing due to atmospheric contact can influence doped tin oxide sensors by affecting the surface, the bulk or both. To identify the effect, the sensor morphology and microstructures are studied by SEM micrographs and X-ray diffractograms of both virgin and aged sensors.

Figure 3.51 (a), (b) and (c) show the micrographs of virgin, four and eight years aged samples respectively of SnO$_2$:Mg-0.6(325) film, which showed the maximum gas response in 1000 ppm LPG. The surface features are clearly visible in the fresh samples, while aged samples show growing surface modulation dependant on the duration of exposure to atmosphere, in particular humidity, which transformed the surface to form a melt away-like feature on the film. The SEM micrographs of undoped films deposited at 325°C, after eight years of storage is shown in Figure 3.51(d) for comparison. The micrograph shows that the undoped films are also affected by humidity.
To look further into the features on the sensor surface, high resolution FESEM images of the aged films are obtained. The FESEM image of SnO$_2$:Mg-0.6(325) film after storage of 8 years is shown in figure 3.52 with higher magnification. In aged samples, the appearance has been changed and the particles are not distinctly visible in the micrographs, in comparison with fresh samples. A thin coating can be observed over the surface, which partially covered up the surface grains. This feature points out a surface alteration that has happened to the SnO$_2$ film, due to atmospheric interaction.
Figure 3.52 FESEM image of higher magnification for the SnO$_2$:Mg-0.6(325) film, after 8 years of storage.

The films are absolutely adhering on, without a symbol of lift off from the substrate even after prolonged ageing. The images indicate that the formed layer may be very thin of the order of few atomic layers. To confirm this, etching on the surface of the film is carried out by argon-ion impinge at 3.8 KV for 3 min.

Figure 3.53 FESEM image of SnO$_2$:Mg-0.6(325) aged film (a) after etching the surface (b) after annealing at 325°C.

By etching, a layer of nearly 10 nm is removed from the surface. The FESEM image of the etched surface has taken and shown in figure 3.53(a). The particles re-appear as in the fresh film and the voids also appear. This demonstrates that no permanent change has occurred to the lower layers of the film. Annealing of the same set of sample in ambient air at 325°C
regains the morphology as evidenced by FESEM images (figure 3.53(b)) endorsing that the outer layers affected possibly by atmospheric humidity, can be readily get rid of from the surface and makes the crystalline microstructure more sharp and faceted. Small particles, possibly resulted from the residual layer can be observed at the grain surface after annealing of the aged film is shown in figure 3.54 in higher magnification.

![FESEM image of SnO$_2$:Mg-0.6(325) aged film, after annealing at 325°C, with higher magnification](image)

**Figure 3.54** FESEM image of SnO$_2$:Mg-0.6(325) aged film, after annealing at 325°C, with higher magnification

### 3.11.2 X-ray Diffractogram of Aged Film

The X-ray diffractogram of virgin SnO$_2$:Mg-0.6(325) film shown in figure 3.55(a), depicts the tetragonal SnO$_2$ phase. The peaks positions and texture are similar after ageing of eight years (figure 3.55(b). It is concluded that the cassiterite structure has not affected due to ageing except that the back ground noise has increased to a certain extent. This may be as a result of stray reflections emanated from the transformed layer due to ageing.
After ageing, the characteristic peaks (110) and (101) of the sensor film retain their sharp profile without any decline in intensity. It is also to be noted that, for the prominent reflections, the broadening of peaks are not evidenced. Thus from XRD it is confirmed that the crystallinity and the texture remain unaltered.

3.11.3 Effect of Ageing on FTIR Spectra

To elucidate the modification in sensor sample on ageing, the FTIR studies are carried out. In the FTIR spectrum of the above mentioned film (figure 3.56) the broad absorption bands, below 1000 cm\(^{-1}\) corresponds to the different modes of the Sn–O vibrations, and it is intricate to distinguish Sn–O stretching in Sn–OH, Sn–O–Sn, Sn–OOH, and Sn–OH–Sn groups (Nakamoto, 1970). The vibrations observed in the aged sensors at wave number 587 cm\(^{-1}\), are predominantly due to Sn-OH bonds in SnO\(_2\) phase (Lu and Schmidt, 2008). The broad peak at 764 cm\(^{-1}\) is argued as the OH
translational modes or Sn-O-Sn stretching vibrations (Wu et al., 2009). The presence of OH in the samples is confirmed by the $\delta_{\text{OH}}$ vibrations at 875 cm$^{-1}$, which are assigned as the vibrational lattice mode (Amalric, 2001).

Figure 3.56 FTIR of eight years aged SnO$_2$:Mg-0.6(325) film

However the absence of OH mode of vibrations at 3000–3600 cm$^{-1}$, due to the in-plane deformation, suggests the formed layer is marginal. Adsorption that involves direct H$_2$O linkage to SnO$_2$ (i.e., SnO$_2$:H$_2$O) is ruled out due to the absence of peak at 1620 –1640 cm$^{-1}$ (bending vibration of hydroxyl groups of molecular water). The most feasible alternative is that water molecules are adsorbed strongly to less coordinated Sn atoms on the (110) surfaces of cassiterite (SnO$_2$). These H$_2$O molecules undergo reversible dissociation reactions forming a hydroxyl such as SnOH, Sn–(OH)–Sn, or both (Kumar et al., 2011). The extent of H$_2$O molecules dissociated depends on the surface composition, temperature, amount of
humidity and time span. In the present study, FTIR analysis suggests the formation of Sn–OH and Sn–OOH phases, in the long duration stored samples. The presence of hydroxyl (-OH) species, also cause to increase in infrared absorbance and act to remove more free electron charge carriers from the SnO₂ film to produce an increase in the electrical resistance (Ferguson et al., 2009).

3.11.4 Effect of Ageing on the Surface Chemical State - XPS Analysis

The ageing of the film is evidenced by change in surface features as discussed and can expect possibly in composition also. Figure 3.57(a) shows the typical broad-scan XPS spectrum, within the B.E. range of 0 –1200 eV, obtained for the 8 years aged SnO₂:Mg-0.6(325) film.
The spectrum primarily shows the Sn 4d, Sn 3d_{5/2}, Sn 3d_{3/2}, O 1s, peaks at 25.8, 486.3, 495.3, and 531.3 eV respectively, which confirm the presence of Sn and O. But after Ar plasma etching the Sn 3d peaks become stronger (figure 3.57(b)), accompanied by a decrease of C 1s peak. The changes can be associated with the removal of a thin surface layer of the film as a result of etching, substantiated by morphological change detected in the FESEM images, shown earlier in figure 3.50(a).

3.11.4.(a) Surface etching and deconvolution of O1s peak

In the aged morphology before etching, the asymmetry in high-energy side of O 1s peak at 531.3 eV required deconvolution (from the high resolution XPS scan), which resolve that the shoulder corresponds to binding energy 531.6 eV (figure 3.58(a)), corresponds the presence of –OH on the surface.

Figure 3.58 Deconvolution of O 1s peak of the XPS spectra by GL30 fit on Vision processing software (a) before etching, (b) after etching
On etching, the 531.6 eV peak disappears completely and a fresh peak at 530.2 eV arises. The peak at 531.6 eV is assigned to hydroxide and/or oxy-hydroxide since the binding energy position of this deconvoluted peak agrees with that reported for potassium tin hydroxide and zinc oxide (Sladkevich et al, 2009; Satish and Mulla, 2011). XPS depth profiling by argon plasma treatment, most likely expose the inner layers with further oxygen escape under vacuum, gives out a peak at 530.2 eV (figure 3.58(b)). This binding energy corresponds to oxygen deficient SnO$_2$ and formed by the interaction of plasma under oxygen deficient atmosphere.

Usually it is recognised that non-defective SnO$_2$ surface is unreactive towards H$_2$O. But oxygen vacancies at the surface in the SnO$_2$ polycrystalline matrix are known to act as active catalytic sites for the adsorption of molecules. Accordingly, the presence of physisorbed water from atmospheric humidity on the SnO$_2$ surface is usually detected at low temperatures, as the temperature is not sufficient to chemisorb water, where the low coordinated tin ions in the layer interacts by short distance forces and hydroxyl molecules are adsorbed, which set off a change in surface. Thus the humidity interacts on SnO$_2$ or SnO surface to form SnO(OH) or Sn(OH).

\[
2\text{SnO}_2 + \text{H}_2\text{O} + e^- \leftrightarrow 2\text{Sn-O(OH)} + \text{O}^- \quad \text{...............3.3}
\]

OR

\[
2\text{SnO}^- + \text{H}_2\text{O} + e^- \leftrightarrow 2\text{Sn-(OH)} + \text{O}^- \quad \text{...............3.4}
\]

It has also been observed from XPS that the (O) / (Sn) value varied from the average value 1.78 in the bulk to 1.97 at the surface layer. This strengthening of the oxygen ratio on the surface layer of films may be likely
due to adsorption of oxygen ions formed during the hydroxyl formation. By
heating above 250°C, the hydroxyl group on the surface layer starts to
escape by desorbing oxygen ion, to transform back to the SnO₂ or SnO. This
formation is further supported by the fact that the sensor surface acts as
electron acceptor in the hydroxyl presence (Korotchenkov et al., 1999),
whereas donor properties by adsorbed water molecules, in which the former
is evidenced by the increase in resistance observed in the present sensor
samples on ageing.

This conclusion is substantiated by the annealing results of the
samples in atmospheric oxygen, by which the features on the aged film
surface are completely removed through oxidation of Sn-OH to Sn-O or
SnO₂ (Milliron et al., 2000) and the initial sensitivity is regained (section
3.11.6(b)).

3.11.5 Effect of Ageing on Film Resistance

As the ageing period increases, a marginal increase in the sheet
resistance value for the SnO₂:Mg films is observed due to progressive
surface modification by atmospheric humidity, as shown in figure 3.59. As
discussed, the adsorption of hydroxyl groups on SnO₂ is considered to be
the reason which brings about an increase of the resistance. The variation of
the film resistance for long duration storage, Rₜ with storage time, t in
months may be expressed by the relation

\[ Rₜ = r₀ + r₀^{1/2} \ln(t), \]

\[ \text{………………3.5} \]

where r₀, is the initial resistance of the film. It can be evidenced that most of
the sensor resistance variation was observed during the initial months of
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storage. An analogous ageing variation (small duration) in resistance is reported in physical vapor deposited CdSe thin films (Sebastian P. J., 1991). The films when exposed to air, water molecules became physically adsorbed on the film surface. Since physisorption is not a stimulated process no heat of adsorption is involved and attached molecule can be freed easily. The physisorbed species on the surface forms a precursor state bonded to the surface by weak forces to become chemisorbed by capturing free electrons from the conduction band exhibited by the generation of attached surface hydroxyl groups. Thus the surface layer is partially covered by the layer of hydroxyl groups that formed during storage in normal atmosphere and the resistance would show an increase. This hydroxyl layer can be eliminated by heating the film under ambient air and a drop in resistance is confirmed.

![Figure 3.59 Variation in resistance of SnO2:Mg-0.6(325) film with time (on ageing) in humid atmosphere](image)

**Figure 3.59** Variation in resistance of SnO₂:Mg-0.6(325) film with time (on ageing) in humid atmosphere

### 3.11.6 Effect of Ageing on LPG sensing

The effect of ageing on the film sensitivities are studied for 8 years showed a slow decline on ageing. After a storage period of four years, it is
seen that the response time has increased and the resistance variation profile is not smooth as in virgin sensor on exposure to LPG.

3.11.6.(a) Relationship with deposition temperature and Mg concentration

The decrease in LPG sensitivity with ageing for 0.6 wt. % Mg doped film deposited at 285°C, 325°C and 355°C are shown in figure 3.60. A sudden decrease of nearly 15 % in sensitivity has measured in the initial 24 months. Then the fall in sensitivity is small for a storage period up to six years. Thereafter the sensitivity decrease is sluggish. After 8 years of storage the sensitivity of the film declined by 38 % of initial sensitivity and reached a response of 58 % for the 325°C deposited sample.

![Figure 3.60 LPG (1000 ppm) response variation with ageing duration, of 0.6 wt. % Mg doped films deposited at temperatures 285, 325 and 355°C](image)

Table 3.10 shows the variation in LPG sensitivity for virgin films pyrolysed in the temperature range 285 – 355°C, with Mg concentration varying from 0 to 1.2 wt.%, along with the retaining of response after
prolonged ageing periods of one, two, four, six and eight years, as a percentage of respective initial sensitivity.

Table 3.10 LPG response for virgin films and their percentage sensitivity in aged films

<table>
<thead>
<tr>
<th>Deposition Temperature (°C)</th>
<th>Mg concentration (wt.%)</th>
<th>Initial Sensitivity (%)</th>
<th>Retaining of sensitivity after ageing periods (percentage of initial sensitivity) %</th>
<th>1 Yr</th>
<th>2 Yrs</th>
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</table>

The percentage decrease in sensitivity due to ageing is almost uniform irrespective of film deposition condition or initial sensitivity. Nearly 10 % of sensitivity is lost after one year of storage and the rate decreases thereafter. In contrast to the initial sensitivity, the decrease after 6 and 8 years is 26- 38 % and 38- 50 % respectively. This may be due to the fact that, as the gas sensing is mainly a surface process, the changes in surface composition have altered the oxygen adsorption capability and thereby a change in the sensitivity.

3.11.6.(b) Effect of annealing

The 8 year aged samples are then annealed at a temperature equal to its deposition temperature to observe the variation in sensitivity. The
annealed samples almost recover the previous sensitivity magnitude as shown in figure 3.61. Literature shows that the hydroxyl groups begin to desorb at $T > 200–250^\circ\text{C}$ and are practically absent at $T > 350^\circ\text{C}$ (Korotcenkov, 2004) and the recovery of gas response on annealing of the present sensors validate the fact.

![Graph showing LPG sensor response regain with annealing temperature, in eight years aged SnO$_2$:Mg-0.6(325) film](image)

**Figure 3.61** LPG sensor response regain with annealing temperature, in eight years aged SnO$_2$:Mg-0.6(325) film

### 3.11.7 Effect of Ageing on Methane Sensing

The change in sensitivities of the films with ageing to methane is also investigated. The methane sensitivity is also found to decrease with storage period. The percentage lowering in methane sensitivity is almost uniform for the films, irrespective of whether Mg doped or undoped. Table 3.11 shows the decreasing profile of methane sensitivity for the deposited films with ageing period.
Table 3.11 Retaining sensor response towards methane after storage period

<table>
<thead>
<tr>
<th>Deposition Temperature (°C)</th>
<th>Mg concentration (wt. %)</th>
<th>Sensitivity (%) within one month after deposition</th>
<th>Retaining sensitivity after ageing period (%)</th>
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<tr>
<td></td>
<td></td>
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<tr>
<td></td>
<td>1.2</td>
<td>32</td>
<td>27</td>
</tr>
</tbody>
</table>

After one year of storage, undoped film deposited at 285°C, having initial sensitivity 24 %, drops by 21 %, whereas SnO₂:Mg-0.6(325) film, having initial sensitivity 52 % drops by 15 %. After three years of storage, the drop in sensitivity is in the range 38 % to 25 %, and after six years it is in the range 42 % to 33 % respectively for lower response sample to higher response sample. After eight years of storage, the films with least methane response shows 41 % of initial sensitivity, and the film with maximum response shows 57 % of its initial response.

3.12 Sensing Mechanism in Mg Doped Tin Oxide Thin Film

Spray deposited thin films include large number of possible active surface states produced due to the peculiarity of the deposition process. It appears that both sensitisation mechanisms namely electronic (Jiaqiang et
and chemical (Rakesh et al., 2006), reasonably accommodate to the present material. The electronic sensitisation mechanism is valid here, as the change in oxidation state is brought about, and gas reaction may be through space charge area by the dopant atoms. The chemical sensitisation is also relevant as doped material resistance varies with temperature; and sensitivity along with response time varies with particle size and adsorbed oxygen concentration. Accordingly, the LPG sensing by SnO₂:Mg is not conventional and may be attributable to a different sensitisation mechanism.

The surface trap density determines the depletion layer length of metal oxide. This can be indirectly estimated by the measure of the current through the system containing innumerable number of grains and grain boundaries. Therefore, to achieve high gas sensitivity (Madou and Morrison, 1989), the ratio between the average grain size of metal oxide and the depletion layer length is important.

It is interesting to note that, as the doping concentration increases to 0.6 wt%, the sensitivity increases with the deposition temperature, to peak at 325°C and then lessens for higher deposition temperature. This variation follows the TC(110) value, indicative of the direct involvement of this orientation in gas sensing. The decrease in sensitivity above optimal temperature can be attributed to oxygen diffusion into the grains that affects the oxygen vacancy concentration.

Compared to pure SnO₂, greater amount of oxygen is adsorbed in Mg doped SnO₂ thin films. Elemental analysis from EDX clearly shows the presence of both Sn and O in the as-produced doped samples. However, the atomic ratio O:Sn is slightly above 2 (from EDX) and the formation of Sn²⁺ and
Sn\(^{4+}\) states (from XPS) implies that gas adsorption happens even after deposition, even though the phase identification reveals the formation of oxygen deficient SnO\(_2\) phases. The electrical properties of the boundaries between the grains and the surface of a thin film are affected by the adsorption and desorption of gaseous molecules. Oxygen ions can be perceived at the grain boundaries or surface on account of the deficiency in crystalline matrix. Due to the chemisorptions of oxygen, the resistivity of the material increases after deposition. The complexity of intermixing of additives with oxygen deficient SnO\(_2\) together with adsorbed oxygen at the interfaces or surfaces make the gas sensing scheme involved. The decrease in crystallite size follows increase in the number of adsorption sites as well as the surface density of the negatively charged oxygen to cause an increase in sensitivity.

3.13 Summary

For Mg doped SnO\(_2\) films the (110), (101), (200), (211) and (301) peaks with good intensity are obtained at lower temperature of 285°C, where as in earlier report on undoped film, these peaks are obtained at higher temperatures. These films adhere strongly to glass substrates, resist physical abrasion and exhibit high optical visible transparency. The undoped films are highly textured with (211) and (301) reflections where as in Mg doped films (110) and (101) planes show an enhanced growth profile. Increase of Mg doping concentration level up to 0.9 wt. % is helpful in decreasing the crystallite size by certain inhibit process. The growth parameters and physical properties of SnO\(_2\):Mg spray pyrolysed thin films have been effectively investigated. The films are polycrystalline in nature with interlocking garden trowel shaped crystallites observed in the SEM images. Doping of magnesium in SnO\(_2\), results in the modification of
morphological properties by bringing a favourable crystallite orientation to enhance oxygen adsorption. Electrical conductivity is depend on the composition and the morphology of the films and studied in relation to the gas sensing measurement.

In the present investigation there exists less evidence for inclusion of Mg into lattice sites and it is observed that small amount of Mg additions always change the electrical resistance significantly. This is consistent with the fact that the adsorption of a gas into the surface of a semiconducting material can produce a large change in its electrical resistivity. Mg concentration and deposition temperatures influence the crystallite size, shape, texture of microstructure and hence the gas adsorption-desorption mechanism. At the same time, band gap energy and micro strains get influenced by deposition parameters.

An excellent sensitivity of 93 % is achieved for 1000 ppm LPG at an operating temperature of 350°C, where the methane sensitivity at this operating temperature is very poor. But at an elevated temperature of 385°C sensitivity of 53 % is obtained for same ppm of methane.

The analysis of core levels of the prepared films has been undertaken with the help of X-ray photoelectron spectroscopy. The O 1s and Sn 3d peaks show multiple components, which indicate a non uniform bonding environment. The non-stoichiometric O:Sn ratio suggests the presence of oxygen vacancies and the deconvolution of the peaks exhibits primarily two oxidation states.

The sensing performance of 93% shows a significant progress over the published literature. The gas sensing process is strongly related to the
crystallite orientations and grain surface reactions. Gas sensing result is related with the (110) growth, which is technologically advantageous and can be enhanced by varying Mg dopant concentration.

When depositing 0.6 wt% Mg doped SnO₂ at moderate temperature, the composition of the sensor is oxygen deficient SnO₂, accomplished with oxygen adsorption and have shown to detect LPG effectively. The deconvoluted XPS peak at 532.7 eV corresponds to adsorbed oxygen or ‘chemisorbed oxygen’. Oxygen ions can be perceived at the grain boundaries or surface, on account of the inadequacy in the crystalline matrix. It is concluded that, to increase the gas sensitivity of SnO₂ films, the dopants enjoy more oxygen adsorption capability is to be added in appropriate amount. The grain dimensions are influenced both by doping concentration, as well as by substrate temperature. It is also showed that the variation in crystallite size is useful to enhance the sensitivity.

In order to study aging effect of Mg doped SnO₂ sensors, a sequence of measurement has been carried out for the period of eight years. XRD analysis confirmed that the cassiterite structure has not affected due to ageing. Since the sensor gas response is apparently affected by ageing, to elucidate the variation, the surface composition and morphology are studied comprehensively.

FESEM images on aged sensors show that the atmosphere influences the surface. The surface morphology and gas sensing properties are almost regained by annealing the aged films and it is concluded that ageing did not bring about in any permanent change to the sensors. The -OH formation on the surface layers of aged samples by the interaction with atmosphere is
confirmed by the presence of pair of hydroxyl (SnOH and SnO-OH) vibrations at 875 and 764 cm\(^{-1}\) in FTIR spectra.

Change in XPS spectra after etching confirms the alteration in surface composition happened to the aged samples. The deconvoluted O 1s peak of aged sensors at 532.6 eV is assigned to hydroxide and/or oxy-hydroxide. On etching the surface layer, the 532.6 eV peak disappears completely. An increase in sheet resistance on ageing by the hydroxyl presence due to the acceptor properties of the surface layer brings about further support to this fact. The ageing ascribed to hydroxyl adsorption in these films arises mainly because of the non-stoichiometry of the films.

On interaction with reducing gas molecules, the adsorbed oxygen leads to an increase in the number of free electrons in the conduction band and as a result the resistance of the sensor changes. A decrease in LPG sensitivity is observed with ageing. A steady decrease of nearly 10 % in sensitivity happened in the initial 12 months. Then the fall in sensitivity is small for a storage period up to six years and the decrease after 6 and 8 years is 27- 40 % and 38- 53 % respectively for the Mg doping range 0 - 1.2 wt.% and deposition range 285- 355°C.

However the gas sensitivity, adherence and durability of lightly Mg-doped SnO\(_2\) films are extremely appreciable.