SnO$_2$ thin film gas sensor: Effect of variation of applied voltage

Publication:

Chapter 4

SnO$_2$ thin film gas sensor: Effect of variation of applied voltage

4.0 Introduction .................................................................................................................. 141
4.1 Experimental procedure for preparation of SnO$_2$ thin film ................................. 142
4.2 Characterizations of SnO$_2$ thin film ......................................................................... 143
  4.2.1 Structural properties of SnO$_2$ thin film .............................................................. 144
    4.2.1.1 X-ray diffraction (XRD) analysis ................................................................. 144
    4.2.1.2 Surface morphology of the films by SEM ................................................... 145
    4.2.1.3 Elemental analysis by EDAX ...................................................................... 146
    4.2.1.4 Microstructural property by TEM ............................................................... 146
    4.2.1.5 Thickness measurements .............................................................................. 148
  4.2.2 Optical properties of the SnO$_2$ thin film by UV-visible spectroscopy ... 148
  4.2.3 Electrical properties of SnO$_2$ thin film sensor .................................................. 149
    4.2.3.1 I-V characteristics ...................................................................................... 149
    4.2.3.2 Electrical conductivity .................................................................................. 150
    4.2.3.3 Thermoelectric power (TEP) measurements .............................................. 151
4.3 Effect of variation of applied voltage on gas sensing performance of SnO$_2$
  thin film.......................................................................................................................... 152
  4.3.1 Variation of gas response of SnO$_2$ thin film with operating temperature 152
  4.3.2 Variation in gas response with H$_2$ gas concentration ...................................... 154
  4.3.3 Selectivity of SnO$_2$ thin film for H$_2$ gas against other gases ....................... 155
  4.3.4 Response and recovery time .............................................................................. 156
  4.3.5 Gas sensing mechanism ..................................................................................... 157
4.4 Conclusions ................................................................................................................. 158

References ....................................................................................................................... 160
Figure captions

Fig. 4.1: Flow chart for preparation of SnO₂ thin film.
Fig. 4.2: X-ray diffraction pattern of SnO₂ thin film.
Fig. 4.3: SEM images of SnO₂ thin film at three different magnifications of (a) 15,000× and (b) 20,000×
Fig. 4.4: EDAX spectra of SnO₂ thin film.
Fig. 4.5: (a-c) TEM images of SnO₂ at different spots and (d) corresponding SAED pattern.
Fig. 4.6: The variation of relative absorbance (αt) with wavelength (λ).
Fig. 4.7: Plot of (αhν)² versus hν for SnO₂ thin film.
Fig. 4.8: I-V characteristics of the SnO₂ thin film.
Fig. 4.9: Variation of conductivity with temperature.
Fig. 4.10: Variation of thermo emf verses temperature difference.
Fig. 4.11: Variation of gas response to H₂ with operating temperature.
Fig. 4.12: Gas response with H₂ gas concentration at 150 °C.
Fig. 4.13: Selectivity of sensor for various gases.
Fig. 4.14: Response and recovery profile of SnO₂ thin film sensor.
Fig. 4.15: Variation of response and recovery time with concentration of H₂.

Table captions

Table 4.1: Comparison of observed ‘d’ values, obtained from XRD data, with the standard d values, from JCPDS card No. 21-1250.
Table 4.2: d values obtained from XRD and TEM.
Table 4.3: Gas response and selectivity in % of SnO₂ thin film for different gases at 150°C operating temperature.
4.0 Introduction

In last two decades there exists a worldwide strong interest in realizing inexpensive oxide thin films to be used, for example, in solar cells, as gas sensor devices or as coating to heat glass windows. Gas sensors have a great influence in many areas such as environmental monitoring, domestic safety, public security, automotive applications, space crafts, houses and sensor networks. It has some advantages over other possible materials such as SnO$_2$, In$_2$O$_3$, ZnO or Cd$_2$SnO$_4$ due to its unique combination of interesting properties: non-toxicity, good electrical, optical and piezoelectric behaviour and its low price. Tin oxide (SnO$_2$) is a versatile material having applications in the areas like transparent electrodes in photoelectric conversion devices namely amorphous silicon solar cells, liquid crystal display, gas sensor and many more [1-3], mainly due to its outstanding properties.

Hydrogen is mainly used for energy generations in the near future due to the fact that fuel cell electricity generators are clean, quiet and more efficient than any other known technology. It is therefore straightforward that in all these applications safety measures should be of highest concern due to the explosive properties of hydrogen. To this end, there is an emerging scientific interest in developing solid state hydrogen sensors based on different operation principles [4], as catalytic-type chemiresistive [5], thermoelectric [6] and micromechanical gas sensors [7]. Recent works have shown that SnO$_2$ is a promising material for applications as sensors towards various gases. Moon et al [8] reported SnO$_2$ exhibiting good response towards CO. Patil and co-workers [9] synthesized SnO$_2$ which gives gas response towards H$_2$ gas. While Jain et al [10] reported Ni-doped to be sensitive towards LPG. Most of the researchers have focused on detection of LPG, H$_2$S, H$_2$ and NH$_3$ because of their toxicity, their relation with atmospheric composition or to their high levels in some environments.

Spray pyrolysis technique (SPT) is useful alternative to the traditional methods for obtaining thin films of pure SnO$_2$. It is of particular interest because of its simplicity, low cost and minimal waste production. In this technique, a solution consisting of the ions of required compound is sprayed on a heated substrate and their pyrolysis results in
deposition of the compound in thin film form. The chemical reactants are selected such that the products other than the desired compound are volatile at the temperature of deposition [11].

The work on SnO$_2$ [12-14], demonstrated the possibility to synthesize high quality c-axis orientated nanostructures by a simple spray pyrolysis deposition method using tin chloride aqueous solutions as a single precursor. It was found that size and shape of SnO$_2$ nanostructures prepared by spray pyrolysis strongly depend on the SnCl$_2$ concentration, deposition time, growth temperature and the substrate properties. In solution systems of wet-growth methods, the morphology of grown SnO$_2$ crystals has been controlled by the reaction conditions and the presence of various additives. In order to obtain the desired crystals size and shape of SnO$_2$ product by solution-based methods, so-called surfactant or capping molecules are added to the solution. They can manipulate the growth kinetics and determine the final morphologies being adsorbed to the certain crystal planes. For instance, hexamine [15] and oleic acid [16] promotes the growth resulting in thinner and high-aspect ratio rods. Additives such as sodium dodecyl sulfate (SDS) [17], triethanolamine (TEA) [17], citric acid [18] retard the growth along the c-axis direction resulting in a disk-like structures or platy forms.

In the present chapter, we report polycrystalline SnO$_2$ thin film prepared by spray pyrolysis technique using tin chloride pentahydrate as precursor and citric acid as a surfactant and the gas sensing characteristics were obtained by measuring the sensor response as a function of various controlling factors like operating temperature, operating voltages (1V, 5V, 10V 15V, 20V and 25V) and concentration of gases. To our best knowledge this is the first report on preparation of polycrystalline SnO$_2$ thin film from citric acid and tin chloride solution system.

4.1 Experimental procedure for preparation of SnO$_2$ thin film

SnO$_2$ thin film was deposited by spray pyrolysis technique (SPT) onto ultrasonically cleaned glass substrate using tin chloride pentahydrate as precursor and citric acid as a surfactant. The surfactants added to the spraying solutions increases the stability of those solutions, and the uniformity of the deposited film. The solution of SnCl$_4$·5H$_2$O (0.1M)
was prepared in de-ionized water and methanol in a volume ratio of 1:1. Citric acid [HOOC-CH$_2$-C(OH)(COOH)CH$_2$-COOH.2H$_2$O] (0.1 M) was dissolved in double distilled water. Both the solutions were mixed under constant stirring to get the clear and homogeneous precursor solution. The solution was sprayed continuously through a glass nozzle of 0.1 mm inner diameter onto substrate kept at 350 °C. The deposition parameters like spray rate 5 ml/min. was adjusted using air as a carrier gas, nozzle to substrate distance (25 cm) were kept constant, and to and fro frequency of the nozzle (18 cycles min$^{-1}$) were kept constant at the optimized values indicated in brackets.

**Fig. 4.1:** Flow chart for preparation of SnO$_2$ thin film.

### 4.2 Characterizations of SnO$_2$ thin film

The X-ray diffraction pattern was recorded on diffractometer using CuK$_\alpha$ radiation with a wavelength $\lambda = 1.5418$ Å at 2θ values between 20° and 80°. The average crystallite size (D) was estimated using the Scherrer equation [19] as follows:
\[ D = \frac{0.9\lambda}{\beta \cos \theta} \]  

(1)

where \( \lambda \), \( \beta \) and \( \theta \) are the X-ray wavelength, the full width at half maximum (FWHM) of the diffraction peak, and Bragg's diffraction angle, respectively.

A JEOL 2300 model (Japan) was used to examine the surface morphology of the sample by scanning electron microscopy (SEM) and the percentage of constituent elements was evaluated by the energy dispersive analysis by X-rays (EDAX). TEM analysis was carried out with a Philips CM-200 transmission electron microscope (point resolution 2.8 Å).

4.2.1 **Structural properties of SnO\(_2\) thin film**

4.2.1.1 **X-ray diffraction (XRD) analysis**

![X-ray diffraction pattern of SnO\(_2\) thin film.](image)

**Fig. 4.2:** X-ray diffraction pattern of SnO\(_2\) thin film.

The X-ray diffraction pattern of the SnO\(_2\) thin film is shown in Fig. 4.2. It shows well defined diffraction peaks, indicating formation of polycrystalline phases. The diffraction peak indexing, done by matching with the Joint committee on powder diffraction standard (JCPDS) (no. 21-1250), clearly revealed formation of the SnO\(_2\) phases with tetragonal structure. The average crystallite size was determined using Scherrer equation
which was observed to be 33 nm. The $d_{hkl}$ experimental value for the film was compared with the standard values in Table 4.1.

Table 4.1: Comparison of observed ‘d’ values, obtained from XRD data, with the standard d values, from JCPDS card No. 21-1250.

<table>
<thead>
<tr>
<th>$\theta$</th>
<th>$d$- values</th>
<th>FWHM</th>
<th>Crystallite size (nm)</th>
<th>$d$-values</th>
<th>$h \ k \ l$</th>
</tr>
</thead>
<tbody>
<tr>
<td>26.60</td>
<td>3.3608</td>
<td>0.103</td>
<td>38</td>
<td>3.3510</td>
<td>(110)</td>
</tr>
<tr>
<td>33.90</td>
<td>2.6498</td>
<td>0.111</td>
<td>37</td>
<td>2.6440</td>
<td>(101)</td>
</tr>
<tr>
<td>38.00</td>
<td>2.3720</td>
<td>0.109</td>
<td>37</td>
<td>2.3620</td>
<td>(200)</td>
</tr>
<tr>
<td>51.80</td>
<td>1.7667</td>
<td>0.132</td>
<td>29</td>
<td>1.7650</td>
<td>(211)</td>
</tr>
<tr>
<td>54.80</td>
<td>1.6767</td>
<td>0.130</td>
<td>28</td>
<td>1.6750</td>
<td>(220)</td>
</tr>
<tr>
<td>61.90</td>
<td>1.5000</td>
<td>0.159</td>
<td>32</td>
<td>1.4980</td>
<td>(310)</td>
</tr>
<tr>
<td>66.00</td>
<td>1.4181</td>
<td>0.125</td>
<td>27</td>
<td>1.4150</td>
<td>(301)</td>
</tr>
</tbody>
</table>

4.2.1.2 Surface morphology of the film by scanning electron microscop (SEM)

![SEM images of SnO$_2$ thin film at different magnifications of (a) 15,000× and (b) 20,000×](image)

Fig. 4.3: SEM images of SnO$_2$ thin film at different magnifications of (a) 15,000× and (b) 20,000×

Fig. 4.3 shows SEM images of the SnO$_2$ thin film on glass substrates at two different magnifications. It exhibit uniform and granular morphology, covering the entire substrate area. The average particle size SEM image is found to be ~65 nm.
4.2.1.3 Elemental analysis by EDAX

The EDAX analysis was used to examine the composition of the deposited materials. Fig. 4.4 shows the EDAX spectra for SnO$_2$ thin film composition. It is seen that the major peaks are of tin and oxygen and no other impurity. Stoichiometric mass % of Sn and O in SnO$_2$ are 78.77 and 21.23, respectively. The mass % of Sn and O in our sample are 83.64 and 16.36 which is not as per the stoichiometric proportion and observed to be the oxygen deficient, leading to the semiconducting nature of SnO$_2$.

Fig. 4.4: EDAX spectra of SnO$_2$ thin film.

4.2.1.4 Microstructural property by TEM

Fig. 4.5(a-c) shows TEM micrographs of the SnO$_2$ powder obtained by scratching the thin films. The TEM images confirm the nanometric size of the particles in the range of 30-48 nm. The TEM micrograph of powders also shows a well distribution of nano-particles in powders.

A selected area electron diffraction (SAED) pattern of nano-particles in powder sample is shown in Fig. 4.5(d). The electron diffraction patterns of nano-particles represent a collection of halo-rings and discrete spots, and confirm poly-crystalline structure of the prepared nano-particles. Six fringe patterns corresponding to planes:
(110), (101), (200), (211), (220) and (310) are consistent with the peaks observed in XRD patterns. The ring to the centre distance of each ring is measured as 3.70, 4.31, 4.36, 5.94, 6.29 and 8.06 nm and expressed in terms of nm$^{-1}$. The reciprocal of these values gives the interplanar distance, d [20]. Details are given in Table 4.2.

Fig. 4.5: (a-c) TEM images of SnO$_2$ at different spots and (d) corresponding SAED pattern.
Table 4.2: $d$ values obtained from XRD and TEM.

<table>
<thead>
<tr>
<th>Reported d values (Å)</th>
<th>XRD d values (Å)</th>
<th>Electron diffraction (TEM)</th>
<th>Planes (hkl)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Reciprocal of $d$ values $\delta_{hkl}$ (nm$^{-1}$)</td>
<td>$d$ values $d_{hkl}$ Å</td>
</tr>
<tr>
<td>3.3510</td>
<td>3.3608</td>
<td>3.70</td>
<td>2.7027</td>
</tr>
<tr>
<td>2.6440</td>
<td>2.6498</td>
<td>4.31</td>
<td>2.3201</td>
</tr>
<tr>
<td>2.3620</td>
<td>2.3720</td>
<td>4.36</td>
<td>2.2935</td>
</tr>
<tr>
<td>1.7650</td>
<td>1.7667</td>
<td>5.94</td>
<td>1.6835</td>
</tr>
<tr>
<td>1.6750</td>
<td>1.6767</td>
<td>6.29</td>
<td>1.5898</td>
</tr>
<tr>
<td>1.4980</td>
<td>1.5000</td>
<td>8.06</td>
<td>1.2406</td>
</tr>
</tbody>
</table>

4.2.1.5 Thickness measurements

The film thickness was measured by a weight difference method [21, 22] in which weight of the sample deposited, area and densities were considered. The thickness, sample weight and sample area are related as

$$t = \frac{M}{A \rho}$$

where $M$ is the weight of the sample deposited in g, $A$ the area of the sample in cm$^2$ and $\rho$ the materials density in gm cm$^{-3}$. The obtained value for thickness of the film was 580 nm.

4.2.2 Optical properties of the SnO$_2$ thin film by UV-vis spectroscopy

The optical density ($\alpha t$) of the film was recorded in the wavelength range 300 to 700 nm. Fig. 4.6 shows the variation of relative absorbance ($\alpha t$) with wavelength ($\lambda$) for SnO$_2$ thin film. Absorption coefficient is of the order of $10^4$ cm$^{-1}$. In order to confirm the nature of the film's optical transition as direct allowed or direct forbidden, the optical data was analyzed using the classical relation [23]:

$$\alpha \nu = A (\nu - E_g)^n,$$

where $A$ is a constant depending upon the type of the transition that prevails. Specifically, for an allowed, direct allowed transition $n$ is 1/2. Fig. 4.7 shows the variation of $(\alpha \nu)^2$ versus $\nu$, which is a straight line, indicating that direct transition is the dominant
transition involved. The energy gap is obtained by extrapolating the linear portion of the $(\alpha h\nu)^2$ versus $h\nu$ plot to $\alpha = 0$. The band gap energy is found to be 3.6 eV.

Fig. 4.6: The variation of relative absorbance ($\alpha t$) with wavelength ($\lambda$).

Fig. 4.7: Plot of $(\alpha h\nu)^2$ versus $h\nu$ for SnO$_2$ thin film.

4.2.3 Electrical properties of SnO$_2$ thin film sensor

4.2.3.1 I-V characteristics

Fig. 4.8 represents I-V characteristics of the SnO$_2$ thin film at room temperature. It was clear from the I-V characteristics that the contacts fabricated on the film were Ohmic
in nature [9]. The current was measured while the bias voltage increased from 0 to 25 V and decreased to zero. The measurement was repeated with negative bias voltage. Every current value measured during voltage increase nearly coincided with that measured during voltage decrease.

![Graph of I-V characteristics of the SnO\textsubscript{2} thin film.](image)

**Fig. 4.8:** I-V characteristics of the SnO\textsubscript{2} thin film.

### 4.2.3.2 Electrical conductivity

Fig. 4.9 represents the variation of conductivity with temperature of SnO\textsubscript{2} thin film. It is clear from the graphs that the conductivity is varying with temperature. Film composition plays a major role in the electrical conductivity of transparent conducting SnO\textsubscript{2} thin films. The composition of films was obtained from EDAX analysis as shown in Fig. 4.4. The average mass percentage of tin and oxygen was 83.64 and 16.36 respectively. This indicates that the film was oxygen deficient in nature. It is a known fact that the oxygen deficiency gives rise to electrical conductivity in transparent conducting oxides.
4.2.3.3 Thermoelectric power (TEP) measurements

The graph of thermo emf with temperature difference is as shown in Fig. 4.10. In order to decide the type of charge carrier, thermoelectric power measurement was taken. The thermoelectric power is the ratio of thermally generated voltage to the temperature difference in the semiconductor, which gives the information about charge carriers in the deposited material. In thermoelectric power measurements, the open circuit thermo-voltage generated by film sample when a temperature gradient is applied across a length of a sample is measured. The type of conductivity exhibited by spray deposited SnO$_2$ thin film is determined by thermoelectric power (TEP) measurement. The TEP depends on the location of Fermi energy level in the material and the type of scattering mechanism. These variations are found to be non-linear with n-type conduction. The non-linearity indicates non-degeneracy of the material whose thermoelectric power is proportional to $n^{th}$ power of absolute temperature [24, 25].
From Fig. 4.10, it is seen that as temperature increases, thermo emf also increases. The sign of emf decides the type of charge carrier. The polarity of thermally generated voltage was positive indicating that the films exhibit n-type conductivity.

4.3 Effect of variation of applied voltage on gas sensing performance of SnO₂ thin film

Gas response (S) is defined as the ratio of change in conductance of the sample on exposure to a test gas to the conductance in air [26, 27].

$$S = \frac{I_g - I_a}{I_a} = \frac{\Delta I}{I_a}$$

(4)

where $I_a$ is the value of initial equilibrium conductance of the sensing material in presence of air and $I_g$ is the conductance of the sensing material in the presence of the target and $\Delta I$ the change in resistance. The sensor was examined under different gases such as LPG, H₂, CO, CO₂, NH₃, O₂, Cl₂ and ethanol.

4.3.1 Variation of gas response of SnO₂ thin film with operating temperature

Fig. 4.11 shows the variation of gas response of SnO₂ thin film sensor to 300 ppm H₂ gas with operating temperature. It is seen that for temperatures lower and higher than 150 °C, the sensor response is less indicating 150 °C to be an optimum temperature to have high sensing response at different operating voltages (1V, 5V, 10V, 15V, 20V, 25V). The
gas response for SnO$_2$ sample is found to be better than that reported in literature [28, 29]. The operating voltage is also one of the main factors that influence the gas response to H$_2$ gas. The operating voltage is necessary for driving electrons in gas sensing film. However, when the operating voltage is too high, the response to H$_2$ gas will be decreased. The decrease of the gas response can be explained as follows: An increase in operating voltage results in increase in electron concentration in the film and at grain boundaries. I-V characteristic (Fig. 4.8) shows the current in the sensor is a non-linear increase with an increasing operating voltage. The increase of current indicates increasing electric charge in the film. Since there is electrostatic repulsion between electronic excess negative charges in the film and gaseous H$_2$ molecules, the amount of H$_2$ adsorption quantities in the film decreases. As a consequence, a decrease in response to H$_2$ gas of the gas sensing film is observed and shows higher gas response at 150 °C for all operating voltages.

![Graph showing variation of response to H$_2$ gas with operating temperature.](image)

**Fig. 4.11:** Variation of response to H$_2$ gas with operating temperature.
4.3.2 Variation in gas response with H\textsubscript{2} gas concentration

To test the H\textsubscript{2} gas concentration characteristics, the sensor was exposed to H\textsubscript{2} gas of different concentrations at a constant operating temperature. The gas response to H\textsubscript{2} in concentration range (100-1000 ppm) is shown in Fig. 4.12 at 150 °C operating temperature and six operating voltages (1V, 5V, 10V, 15V, 20V, 25V). It indicates that the sensor has good response to H\textsubscript{2} at the operating voltage 5V. For all the operating voltages, the gas response values were observed to increase continuously with increasing the gas concentration up to 1000 ppm at 150 °C. The rate of increase in gas response was relatively larger up to 300 ppm, smaller during 300-1000 ppm and then saturates after 300 ppm. Thus the active region of the sensor would be between 100-300 ppm. At lower gas concentration, the monolayer of gas molecules would be expected to be formed on the surface which would interact with the surface more actively giving larger sensitivities [30]. There would be multilayer of gas molecules on the sensor surface at the higher gas concentration resulting in saturation in gas response.

![Fig. 4.12: Gas response with H\textsubscript{2} gas concentration at 150 °C.](image-url)
4.3.3 Selectivity of SnO$_2$ thin film for various gases

Selectivity can be defined as the ability of a sensor to respond to a certain gas in the presence of different gases [31]. Percent selectivity [32] of one gas over others is defined as the ratio of the maximum response of target gas (e.g. H$_2$) to the maximum response of other gas at optimum temperature of target gas,

\[
\% \text{ Selectivity} = \left( \frac{S_{\text{other gas}}}{S_{\text{Target gas}}} \right) \times 100
\]  

(5)

Fig. 4.13 depicts the selectivity of SnO$_2$ thin film sensor for H$_2$ (300 ppm) at 150 °C and at the operating voltage 5V. The sensor showed the high response for H$_2$ gas among the following gases: LPG, NH$_3$, CO, CO$_2$, C$_2$H$_5$OH, H$_2$S, O$_2$ and Cl$_2$.

![Selectivity of sensor for various gases.](image)

**Fig. 4.13:** Selectivity of sensor for various gases.

Table 4.3 shows the gas response and corresponding selectivity of gases against H$_2$ at 250°C. The selectivity of H$_2$ is considered as 100 %.

It is observed from Table 4.3 and Fig. 4.13 that SnO$_2$ thin film is sensitive to H$_2$ and it has relatively good selectivity against other interfering gases. This is the main feature of SnO$_2$ thin film sensor.
Table 4.3: Gas response and selectivity in % of SnO\textsubscript{2} thin film for different gases at 150 °C operating temperature.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Gas response</th>
<th>Selectivity in %</th>
</tr>
</thead>
<tbody>
<tr>
<td>LPG</td>
<td>5</td>
<td>2.67</td>
</tr>
<tr>
<td>Ethanol</td>
<td>12</td>
<td>6.43</td>
</tr>
<tr>
<td>CO</td>
<td>10</td>
<td>5.35</td>
</tr>
<tr>
<td>H\textsubscript{2}</td>
<td>186.6</td>
<td>100</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>16</td>
<td>8.57</td>
</tr>
<tr>
<td>Cl\textsubscript{2}</td>
<td>0.9</td>
<td>0.48</td>
</tr>
<tr>
<td>NH\textsubscript{3}</td>
<td>0.1</td>
<td>0</td>
</tr>
<tr>
<td>H\textsubscript{2}S</td>
<td>56</td>
<td>30.01</td>
</tr>
<tr>
<td>O\textsubscript{2}</td>
<td>0.6</td>
<td>0.32</td>
</tr>
</tbody>
</table>

4.3.4 Response and recovery time

The response/recovery time is an important parameter used for characterizing a sensor. It is defined as the time required to reach 90% of the final change in current, when the gas is turned on and off respectively. The gas response verses time is shown in Fig. 4.14 for 300 ppm of H\textsubscript{2}. From the plot, it is seen that the response time is 90 s and the recovery time is 130 s.

![Fig. 4.14: Response and recovery profile of SnO\textsubscript{2} thin film sensor.](image-url)
Fig. 4.15: Variation of response and recovery time with concentration of H$_2$.

Fig. 4.15 shows the response and recovery time verses H$_2$ gas concentration. It is revealed that response time decreased from 160 s to 56 s when H$_2$ concentration is increased from 100 ppm to 1000 ppm. This may be due to the presence of sufficient gas molecules at the interface for reaction to occur. From the graph, it is found that for higher concentrations of H$_2$, the recovery time was long. This may be due to the reaction products are not leaving from the interface immediately after the reaction.

4.3.5 Gas sensing mechanism

The gas sensing mechanism of an n-type tin oxide is based on electrical conduction results from point defects, such as oxygen vacancies and interstitial tin atoms (i.e. non-stoichiometric composition), that acts as donor [33-35]. When exposed to air, freshly prepared tin oxide particles adsorb oxygen atoms on the surface [36]:

\[
\begin{align*}
O_{2(gas)} & \leftrightarrow O_{2(ads)} \quad (6) \\
O_{2(ads)} + e^- & \leftrightarrow O^-_{2(ads)} \quad (7) \\
O_{2(ads)} + e^- & \leftrightarrow 2O^-_{(ads)} \quad (8)
\end{align*}
\]
Thus the oxygen atoms pick up the electrons from the conduction band of the tin oxide and are adsorbed on the particle surface as \( O^- \) and also other oxygen adsorbates such as \( O^{2-} \) and \( O_2^- \) are also to cover the surface.

Under \( H_2 \) exposure, a surface reaction reduces the coverage of oxygen, causing returning electrons to \( SnO_2 \) [9] by the following reactions:

\[
2H_2(gas) + O_2^{-}(ads) \leftrightarrow 2H_2O_{(vap)} + e^- \tag{9}
\]

\[
H_2(gas) + O^{-}_{(ads)} \leftrightarrow H_2O_{(vap)} + e^- \tag{10}
\]

The extra electrons released in this process enhance the surface conductance of the thin film. The model proposed above, explains the gas sensing mechanism of the \( SnO_2 \) thin film sensor qualitatively. But it does not explain the increase in the gas response with rise in operating temperature (Fig. 4.11). In this connection, the microstructure, particularly the size and distribution of surface porosity may also have a significant role. This is so because the surface \( SnO_2 \) thin film may provide suitable chemisorption sites, and hence can influence the extent as well as the kinetics of the oxidation reaction (Eq. 8) between the sensor surface and the surrounding gas ambient. The minimum operating temperature found in the present work is only 150 °C. At such a low temperature, the reaction region is mostly limited to the sensor surface (Fig. 4.5) or at the most up to the gas-solid interface. Therefore, it is suggested that uniform granular distribution would cause high response at such a low temperature as has been observed in the present work.

**4.4 Conclusions**

From the results, following statements can be made for the sensing performance of the \( SnO_2 \) thin film sensor.

i) Polycrystalline \( SnO_2 \) thin film could be prepared by simple and inexpensive spray pyrolysis technique (SPT) using tin chloride pentahydrate as precursor and citric acid as a surfactant.

ii) \( SnO_2 \) thin film was characterized by XRD, SEM, EDAX, TEM and UV-spectroscopy to study their structural, microstructural and optical properties.
iii) SnO$_2$ thin film sensor shows a high response to H$_2$ gas in a wide concentration range at operating temperature 150 °C and at an operating voltage 5V.

iv) The sensor showed good selectivity to H$_2$ gas against LPG, NH$_3$, C$_2$H$_5$OH, CO, CO$_2$ and Cl$_2$ gases.

v) The polycrystalline SnO$_2$ thin film exhibits rapid response–recovery which is one of the main features of this sensor.

vi) The results obtained by SPT are promising for the preparation of sensitive and low cost hydrogen sensor operating at low temperature.
References


***