Chapter: 5

Synthesis and gas sensing performance of pure and modified \((\text{Sn}_{0.3}\text{Ti}_{0.7})\text{O}_2\) thick film resistors

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Synthesis and gas sensing performance of pure and modified (Sn$_{0.3}$Ti$_{0.7}$)O$_2$ thick film resistors

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5.1 Introduction

Gas sensors are used for monitoring and controlling of industrial processes, analysis of gas compositions, for surveillance and many other applications. The development of gas sensor devices with optimized gas response and selectivity has been gaining prominence in recent years [1]. There has been a sustained and successful effort to make use of this change for purposes of gas detection. Hydrogen sulfide is a toxic gas, often produced in coal, coal oil and natural gas manufacturing. Therefore, reliable sensors with low cost, low energy consumption, having high gas response, selectivity, and operable in a sub ppm range of H₂S are in high demand for environmental safety and industrial control purposes.

Among the metal oxides, tin dioxide and titanium dioxide, due to their chemical and electrical properties, are particularly appealing both for basic research and for a wide variety of possible applications [2]. Tin dioxide is the most common material in gas sensing [3], but it is widely used as transparent conductor and in heterogeneous catalysis. Titanium dioxide is used as a photo catalyst in solar cells, as an optical coating, in gas sensing, etc. Tin dioxide and titanium dioxide are both wide-gap semiconductors, showing several similarities in structural as well as in electronic properties.

One of the most active fields in the sensor research is the exploration of new materials that enable enhanced gas-sensing properties of all the materials currently examined, semiconducting oxides, for example, SnO₂ and TiO₂. These materials are of strong interest, largely because their physical properties are important for promising application as a gas sensor [4-7]. The gas-sensing property for the SnO₂-based sensors [8] is found to be affected dominantly or even controlled by their surfaces. Above 400-500°C (oxygen losses), the low temperature SnO₂-sensors suffer from a structure instability and poor selectivity [9], while that for the TiO₂-based sensors by their bulk constituents as well and are suited to work at high temperature (1000-1200°C) [10-11]. Since the two oxides have distinct gas-sensing behaviors, a combination of them would presumably initiate a new system [12], which might have the gas sensing properties that are not present in either of their bulk oxides was reported in literature [13-15]. The (Sn₀.₃Ti₀.₇)O₂ material could be more selective and stable.
The goal of this chapter was to synthesis the ST$_{30}$ material and used to study the structure and morphology of the powder. Prepared films were used to study the electrical properties and their changes in contact with different gases. SEM, XRD, TGA and DTA measurements were adopted to analyze the morphology, the crystalline structure, crystallite size and thermal stability. Finally, electrical properties and gas sensing properties have been studied.

5.2 Experimental work

5.2.1 Preparation of material

AR grade SnCl$_2$ · 2H$_2$O and TiCl$_3$ (15% HCl) were used for the preparation of ST$_{30}$ powder. Tin (II) dichloride dihydrate (SnCl$_2$.2H$_2$O) (0.3M) was dissolved in distilled water. Further Titanium chloride III (TiCl$_3$) (0.7M), containing 15% HCl was introduced drop wise into the solution with constant stirring followed by slowly heating it in air at 80°C. For stoichiometry, the whole process was carried out by maintaining the solution under soft stirring at the temperature of 50°C. The prepared powder was sintered at 1000°C for 10 h. Then this powder ground in an agate pastle-mortor to ensure sufficiently fine particle size [15-18].

5.2.2 Preparation of thick films

The thixotropic paste was formulated by mixing the fine powder of ST$_{30}$ with a solution of ethyl cellulose (a temporary binder) in a mixture of organic solvents such as butyl cellulose, butyl carbitol acetate and terpineol. The ratio of the inorganic to organic part was kept at 75:25 in formulating the paste. This paste was screen printed on a glass substrate in a desired pattern to prepare thick films [19-21]. The films were fired at 550°C for 30 min. in an air atmosphere to remove the residual.

5.2.3 Modification of thick films

The CuO-modified (Sn$_{0.3}$Ti$_{0.7}$)O$_2$ thick films were obtained by dipping them in a 0.01M aqueous solution of copper chloride (CuCl$_2$) for different intervals of dipping time of 05,10 and 20 min. These films were dried at 80°C, followed by firing at 550°C for 30 min. The films so prepared are termed as ‘cupricated’ films [22-24].

5.2.4 Thickness measurement

The gas sensing performance is based on the phenomena of adsorption. Adsorption is the surface phenomena. In thick films the surface structure is also
responsible for its gas sensing ability. As the thick film exhibits the properties of bulk material, the larger the thickness the better the gas sensing performance could be. So the thickness of the film was calculated to optimize the physical parameters of the film. The thickness (t) of the film was calculated using a weight-difference method.

$$t = \frac{m}{\rho \times A} \quad \ldots (5.1)$$

Where, m is the mass of the film deposited on the substrate in gm, ‘A’ the surface area of the film in cm$^2$ and ‘$\rho$’ is the density of the material. Average thickness of the film was observed to be 75µm. The reproducibility of the film thickness was achieved by maintaining the proper rheology and thixotropy of the paste.

### 5.3 Structural properties

#### 5.3.1 X-ray diffraction studies (XRD)

Fig. 5.1 shows the X-ray diffraction patterns of ST$_{30}$ thick film. X-ray diffraction analysis at room temperature was carried out to recognize the crystalline phase of ST$_{30}$ powder. ST$_{30}$ film exhibited a rutile TiO$_2$ single phase. It has been possible to observe that the ST$_{30}$ peak positions well matched with JCPDS data of rutile TiO$_2$ (JCPDS No.: 76-0649), allowing us to indirectly verify that the synthesis of the material correctly occurred. The prepared sample shows single phase of the ST$_{30}$ film at calcinations temperature 1000°C. This temperature is lower than that required to prepare the material by the solid-state reaction (1500°C) [25]. The sharpness of the peaks indicates the polycrystalline nature of the film material.

![XRD pattern of pure ST$_{30}$ film.](image)
Table 5.1 shows the X-ray diffraction analysis of the pure ST$_{30}$ film. The d values were in good agreement with those in the JCPDS for TiO$_2$ (rutile) possessing tetragonal structure. The average crystallite size was calculated using Debye-Scherrer formula [26] for various identified diffraction peaks and which has been found to be nearly 41 nm.

**Table 5.1: X-ray diffraction analysis data of sample pure ST$_{30}$.**

<table>
<thead>
<tr>
<th>20 (degree)</th>
<th>d spacing (Å)</th>
<th>FWHM</th>
<th>Peak intensity in %</th>
<th>Crystallite size (nm)</th>
<th>hkl plane</th>
</tr>
</thead>
<tbody>
<tr>
<td>27.40</td>
<td>3.252</td>
<td>0.278</td>
<td>100</td>
<td>42</td>
<td>110</td>
</tr>
<tr>
<td>35.87</td>
<td>2.501</td>
<td>0.272</td>
<td>53.1</td>
<td>36</td>
<td>101</td>
</tr>
<tr>
<td>39.17</td>
<td>2.298</td>
<td>0.334</td>
<td>11.6</td>
<td>34</td>
<td>200</td>
</tr>
<tr>
<td>41.09</td>
<td>2.194</td>
<td>0.280</td>
<td>23.2</td>
<td>42</td>
<td>111</td>
</tr>
<tr>
<td>43.89</td>
<td>2.060</td>
<td>0.354</td>
<td>9.8</td>
<td>32</td>
<td>210</td>
</tr>
<tr>
<td>54.10</td>
<td>1.693</td>
<td>0.330</td>
<td>62.9</td>
<td>40</td>
<td>211</td>
</tr>
<tr>
<td>56.47</td>
<td>1.628</td>
<td>0.274</td>
<td>21.8</td>
<td>48</td>
<td>220</td>
</tr>
<tr>
<td>62.32</td>
<td>1.487</td>
<td>0.355</td>
<td>9.1</td>
<td>49</td>
<td>002</td>
</tr>
<tr>
<td>63.88</td>
<td>1.445</td>
<td>0.363</td>
<td>10.2</td>
<td>35</td>
<td>310</td>
</tr>
<tr>
<td>68.79</td>
<td>1.363</td>
<td>0.291</td>
<td>22.9</td>
<td>49</td>
<td>301</td>
</tr>
<tr>
<td>69.42</td>
<td>1.352</td>
<td>0.290</td>
<td>11.3</td>
<td>49</td>
<td>112</td>
</tr>
<tr>
<td>76.27</td>
<td>1.247</td>
<td>0.301</td>
<td>4.6</td>
<td>48</td>
<td>202</td>
</tr>
</tbody>
</table>

**5.3.2 Scanning Electron Microscopy (SEM)**

**5.3.2.1 Pure ST$_{30}$ film**

To study the surface morphology of the film and to identify the constituents of the film SEM-EDAX analysis was carried out.

![SEM image of pure ST$_{30}$ film.](image)
Fig. 5.2 depicts a SEM image of a pure ST$_{30}$ thick film fired at 550$^\circ$C. The film consists of voids and a wide range of particles with particle sizes ranging from 200 to 840 nm distributed non-uniformly.

5.3.2.2 Cupricated ST$_{30}$ films

Figs. 5.3(a-c) depict SEM images of cupricated ST$_{30}$ thick films for the dipping time interval of 05, 10 and 20 min. fired at 550$^\circ$C, respectively. The micrograph shows a number of small particles distributed uniformly between the larger grains around the ST$_{30}$ film, which may be attributed to the presence of CuO. The change in dipping time of the film changes the particle sizes. The particle sizes ranging from 151 to 350nm (Fig. 5.3(a)), 145 to 220nm (Fig. 5.3(b)), and 175 to 500 nm (Fig. 5.3(c)) were observed. The micrograph (10 min dipping) appears to consist of a number of small particles distributed uniformly between the larger grains of the ST$_{30}$ film. The smaller particle may be attributed to the presence of CuO. The film seems to be highly porous with a large effective area for oxygen adsorption.

Table 5.2 shows variation of specific surface area (SSA) with dipping time of the films. It is observed that the specific surface area of the ST$_{30}$ material varies with dipping time of the film. SSA value is increasing with dipping time, reaches to maximum for 10 min dipping time and then decreases with further increase of dipping time interval. This tendency is in agreement with the decrease of the ST$_{30}$ particle size. The larger surface area may benefit the contact between base material and catalysts, and can adsorb larger numbers of oxygen species as well as increase gas response of the film.

Table 5.2: Variation of specific surface area with dipping time of ST$_{30}$ films

<table>
<thead>
<tr>
<th>Samples</th>
<th>Av. Particle Size, d nm (SEM)</th>
<th>Specific Surface Area (SSA) m$^2$/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure ST$_{30}$ film</td>
<td>520</td>
<td>5.77</td>
</tr>
<tr>
<td>Cupricated ST$_{30}$ (05min) film</td>
<td>240</td>
<td>12.50</td>
</tr>
<tr>
<td>Cupricated ST$_{30}$ (10min) film</td>
<td>200</td>
<td>15.00</td>
</tr>
<tr>
<td>Cupricated ST$_{30}$ (20min) film</td>
<td>337</td>
<td>8.90</td>
</tr>
</tbody>
</table>
**Fig. 5.3:** SEM images of cupricated ST$_{30}$: (a) 05min, (b) 10min and (c) 20 min films.
5.3.3 Elemental Analysis

Fig. 5.4(a) and in Fig 5.4(b) depicts the EDAX spectra of pure ST$_{30}$ and cupricated ST$_{30}$ films.

![EDAX spectra of pure ST$_{30}$ film](image1)

(a)

![EDAX spectra of cupricated ST$_{30}$ film](image2)

(b)

Fig. 5.4: EDAX spectra of: (a) pure ST$_{30}$ and (b) cupricated ST$_{30}$ films.

Table 5.3 shows elemental composition of pure and cupricated ST$_{30}$ films. In elemental analysis study, by EDAX, the major peaks observed were of tin, titania and oxygen in pure film and in cupricated films the major peaks of tin, titania, oxygen and copper were observed. It is clear from the table that the weight percentage of copper increased with dipping time. The film with the dipping time of 10 min was observed to be more oxygen deficient (23.37 wt %). This oxygen deficiency may make the sample possible to adsorb a large amount of oxygen species favorable for higher gas response.
5.3.4 Texture coefficient (Tc)

The surface to volume ratio is one of the important parameter in gas sensing which affects the rate of adsorption of the gas on the surface of the film. The structure of the film and orientation of the plane of the crystal that interact with the gas are also responsible for gas sensing ability of the sensing element. So the texture coefficient (Tc) of the film was determined using Eq.5.2. It has been observed that the preferred orientation is the (110) plane for ST10 sample. Texture coefficient of the film was found to be 3.52 for (110) plane.

Texture coefficient of (hkl) plane,

\[ Tc(hkl) = \frac{I(hkl)/Io(hkl)}{\frac{1}{N} \times \sum I(hkl)/Io(hkl)} \]  

\[ \cdots \text{(5.2)} \]

Where, N - No. of planes of XRD

Table 5.3: Elemental composition of pure and cupricated ST$_{30}$ Thick Films

<table>
<thead>
<tr>
<th>Samples</th>
<th>Wt. % of</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sn</td>
</tr>
<tr>
<td>Pure ST$_{30}$ film</td>
<td>20.59</td>
</tr>
<tr>
<td>Cupricated ST$_{30}$ (05 min) film</td>
<td>22.29</td>
</tr>
<tr>
<td>Cupricated ST$_{30}$ (10 min) film</td>
<td>22.50</td>
</tr>
<tr>
<td>Cupricated ST$_{30}$ (20 min) film</td>
<td>21.57</td>
</tr>
</tbody>
</table>

5.4 Optical properties by UV –Vis –NIR spectrophotometer

As report says that the best suitable MOS material for gas sensing applications should have the band gap above 2.5 eV. The optical properties of the synthesized material were studied to find the band gap of the material. Fig. 5.5 shows the variation of absorbance with wavelength of ST$_{30}$ sample. From the figure we can find that absorption band is observed in the UV region between 200 nm and 450 nm at curve. The optical energy band gap is to be 3.35 eV, using the relationship [28, 29].

\[ Eg = \frac{h \times c}{\lambda} \]  

\[ \cdots \text{(5.3)} \]

h – Planck’s constant, \( h = 4.135 \times 10^{-15} \) (eV·s), c - speed of light (m/s), c = 3\times10^8 (m/s), \( \lambda \) - wavelength (nm).
5.5 Thermal properties by TGA) / DTA

Fig. 5.6 shows the TGA/DTA profiles of pure ST$_{30}$ sample. About 4.703 mg of powders were used for the test. Weight loss of ST$_{30}$ material was observed to be nearly 1%. The small weight loss may be contributing to larger stability of the prepared material.

The DTA showed the endothermic nature of reactions for pure ST$_{30}$. The heat absorbed by the samples may be due to the non-stoichiometry of ST$_{30}$ and its oxygen deficiency.

Fig. 5.6: TGA/DTA of pure ST$_{30}$ film.
5.6 Electrical properties

5.6.1 I-V characteristics

Fig. 5.7 shows the I-V characteristics of pure and cupricated ST$_{30}$ thick films in air atmosphere. The nature of the graph observed was linear. Which again indicates that the contacts made for the practical observation was ohmic in nature.

![I-V characteristics graph](image)

Fig. 5.7: I-V characteristics of pure and cupricated ST$_{30}$ films.

5.6.2 Temperature coefficient of resistance (TCR)

The material was tested for its variation in resistive property with the variation in temperature. Fig. 5.8 shows the variation in the resistance of the film in air (Ra) and gas (Rg) of pure and cupricated (10 min.) with operating temperature. The resistance of the sample is observed to be decreasing with an increase in temperature. The decrease in resistance with increase in temperature could be attributed to negative temperature coefficient of resistance.

![Resistance vs. Operating Temp. graph](image)

Fig. 5.8: Variation of resistance of the film with operating temperature.
The TCR of the film is calculated by using Eq. 5.5 and found to be negative.

\[ R_T = R_0[1 + \alpha T] \quad \ldots (5.4) \]

\[ \text{TCR}(\alpha) = \frac{\text{slope}}{R_o} \quad ^{\circ}C \quad \ldots (5.5) \]

Table 5.4 depicts the TCR values for pure and cupricated films. TCR value of modified film observed is less than that of the pure film. This reveals that the modified film is more semiconducting in nature than the pure film.

Table 5.4: Variation of temperature coefficient of resistance

<table>
<thead>
<tr>
<th>Samples</th>
<th>TCR(\alpha) (1/\circ C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure (a)</td>
<td>-0.00263</td>
</tr>
<tr>
<td>Pure (g)</td>
<td>-0.00377</td>
</tr>
<tr>
<td>Mod.(g)</td>
<td>-0.00893</td>
</tr>
</tbody>
</table>

5.6.3 Electrical conductivity

The temperature dependence of electrical conductivity of ST\textsubscript{10} thick film was carried out on the static gas sensing system in the temperature 323-723 k. The observations were carried by testing the film through several heating and cooling cycles repeatedly. Successive heating and cooling cycles resulted in the stabilization of the surface resistance of the film. During every cycle, the samples were heated up to 723 k and cooled them to room temperature. All data were recorded during cooling.

Fig. 5.9 shows the variation of conductivity with temperature for the pure and cupricated samples. The legends suffixed ‘a’ are the graphs for samples tested in air atmosphere, while the legends suffixed ‘g’ represent the graphs for the conductivities in the presence of H\textsubscript{2}S gas. The graph shows the nonlinear variation of conductivity with temperature for all samples. This shows the semiconducting nature of the films. The conductivity of particular cupricated sample, upon exposure of gas, was larger than that in air. The conductivity of the sample cupricated for 10 min was largest of all. The conductivities of cupricated ST\textsubscript{30} samples were larger than that of pure ST\textsubscript{30} at particular temperature in the presence of gas or in air.
Activation energy is calculated from the slope of the graph of log(conductivity) versus $1/T$ (Fig. 5.9). Table 5.5 shows the variation of activation energy with dipping time of the film. It was observed that the activation energy of most sensitive film (0.140 eV) (10 min.) is less than the pure film (0.242 eV) at 200°C. This reveals that the surface cuprication of the films improves the gas response of the film; since less amount of energy is required to change the one stable state to other state of sensor.

Table 5.5: Variation of activation energy with dipping time of ST$_{30}$ films

<table>
<thead>
<tr>
<th>Samples</th>
<th>Activation energy(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure ST$_{30}$ film</td>
<td>0.242</td>
</tr>
<tr>
<td>Cupricated ST$_{30}$ (05min) film</td>
<td>0.172</td>
</tr>
<tr>
<td>Cupricated ST$_{30}$ (10min) film</td>
<td>0.140</td>
</tr>
<tr>
<td>Cupricated ST$_{30}$ (20min) film</td>
<td>0.148</td>
</tr>
</tbody>
</table>

5.7 Gas sensing properties

5.7.1 Pure ST$_{30}$ film

5.7.1.1 Gas response with operating temperature

The film were tested to various gases at different operating temperatures and showed maximum response to CO$_2$. Fig. 5.10 shows variations in response to CO$_2$ gas with operating temperature of the pure ST$_{30}$ film fired at 550°C. The gas response values of pure thick films were determined at various operating temperatures ranging from 100 to 450°C for CO$_2$ gas. The response increases with increasing the operating temperature, attains its maximum at 300°C and then decreases with a further increase in
operating temperature. It has been noted that the optimum operating temperature of pure film is 300°C.

**Fig. 5.10:** Variations in response to CO$_2$ gas with operating temperature of pure ST$_{30}$ film.

### 5.7.1.2 Selectivity

The observations of the gas sensing performance of the film to various gases were compared to study the selectivity of the film. The percent selectivity of the film for the CO$_2$ gas over others target gases is presented here. The percent selectivity was calculated using following formula:

\[
\text{% Selectivity} = \frac{S_{\text{other gas}}}{S_{\text{target gas}}} \times 100 \quad \text{…. (5.6)}
\]

**Fig. 5.11** shows the bar diagram indicating of the % selectivity of the pure ST$_{30}$ sensor operated at 300°C to CO$_2$ gas against other gases. It is evident that the pure sensor is highly selective to CO$_2$ at 300°C gas against the other gases.

**Fig. 5.11:** % Selectivity of pure ST$_{30}$ film to CO$_2$ against other gases.
5.7.2 Cupricated ST\textsubscript{30} films

5.7.2.1 Gas response with operating temperature

Figs. 5.12 shows variations in response to H\textsubscript{2}S gas with operating temperature of the cupricated ST\textsubscript{30} thick films for the dipping time interval of 05, 10 and 20 min. fired at 550°C. The gas response values of surface cupricated ST\textsubscript{30} films were determined at various operating temperatures ranging from 100 to 450°C to H\textsubscript{2}S gas.

![Graph showing variations in response to H\textsubscript{2}S gas with operating temperature of cupricated ST\textsubscript{30} films.]

The modified film suppresses gas response of CO\textsubscript{2} gas of pure film and enhances the response to H\textsubscript{2}S gas. The film dipped for 10 min. was most sensitive H\textsubscript{2}S gas. The response to H\textsubscript{2}S gas was increasing with the increase in the operating temperature. It attained its maximum (at 200°C) and on further increase in operating temperature the response observed was decreased. It is clear that the optimum operating temperature of cupricated film is 200°C.

5.7.2.2 Gas response to different gas concentrations

Fig. 5.13 exhibits response to H\textsubscript{2}S gas for various gas concentrations ranging from 100 to 1000 ppm at 200°C operating temperature of cupricated ST\textsubscript{30} film. It observed that gas response increases linearly from 100-400 ppm after that, film shows nearly constant response. This may be due to the masking of sensor surface and not responding further increasing gas concentration. So sensor would be used in active region (100-400 ppm).
5.7.2.3 Variation of gas response with dipping time

The variation of the gas response of the cupricated films treated for different intervals of dipping time was studied. From Fig. 5.14 it is clear that the response to H$_2$S goes on increasing with an increase in the dipping time interval. H$_2$S gas response attains its maximum at 10min dipping and decreases with further dipping increase in dipping time.

5.7.2.4 Selectivity

The selectivity of the modified film is presented in Fig. 5.15. The bar diagram depicts the % selectivity of the cupricated (10 min) ST$_{30}$ film operated at 200°C to H$_2$S gas against other gases. From the graph it is clear that the cupricated sensor was highly selective to H$_2$S gas at 200°C. The response to all other tested gases was very small as compare to response to the H$_2$S gas.
5.7.3 Response and recovery time of sensors

5.7.3.1 Pure ST$_{30}$ film

The response and recovery time observed are presented in Fig. 5.16. The response time to optimized concentration of H$_2$S gas of pure ST$_{30}$ film was 6 s and recovery time was 50 s at operating temperature 300°C.

5.7.3.2 Cupricated ST$_{30}$ film

Fig. 5.17 shows the response and recovery of cupricated (10 min) ST$_{30}$ film to H$_2$S gas at 200°C. The response time of the film was 4 s and recovery time was 43 s at operating temperature 200°C. This indicates that surface cuprication of the film reduces the response and recovery time of the sensor. The small response and recovery time are the remarkable features of the cupricated ST$_{30}$. 

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**Fig. 5.15:** % Selectivity of cupricated (10 min) ST$_{30}$ film.

**Fig. 5.16:** Response and recovery of pure ST$_{30}$ film at 300°C.
5.7.4 Long-time stability of sensor

5.7.4.1 Pure ST$_{30}$ film

The changes over long operation times in the gas response of are very important, when one sensor is used. These changes determine the frequency at which calibration checks should be carried out and the frequency at which the sensors may have to be replaced. They can only be determined over long periods of time. **Fig. 5.18** depicts long time stability of pure ST$_{30}$ film. The response of the sensor was studied over a long period nearly 2 month. It was observed that the response of this sensor was found to be nearly constant for one month only and there after it decreases. So this pure film sensor could work over a month only.
5.7.4.2 Cupricated ST\textsubscript{30} film

The response of modified sensor was checked every after 5 days and the response found to be constant over long period of 2 month. **Fig. 5.19** shows the long time stability of cupricated ST\textsubscript{30} sensor. These sensors could work over a long period of time.

![Cupricated ST\textsubscript{30} film](image)

**Fig. 5.19:** Long time stability of cupricated (10 min) ST\textsubscript{30} film.

5.8 Error measurement:

In order to confirm the reliability of reproducing the same result of the film response to the target gas, the film was repeatedly tested for the same target gas keeping all parameters constant. The variations in the observations were used to identify the % deviation from the average reading of the gas response.

The standard deviation, \( \sigma \), is calculated from the squares of the deviations from the mean using the following formula:

\[
\sigma = \sqrt{\frac{(x_1 - \bar{x})^2 + (x_2 - \bar{x})^2 + \ldots + (x_n - \bar{x})^2}{n-1}}
\]  

.... (5.7)

**Table 5.6** shows Measurement of % error in gas response of ST\textsubscript{30} film of pure and most gas sensitive modified ST\textsubscript{30} film.

**Table 5.6:** Measurement of % error in gas response

<table>
<thead>
<tr>
<th>Samples</th>
<th>Temp. (°C)</th>
<th>Gas response</th>
<th>Standard Deviation (( \sigma ))</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure ST\textsubscript{30} film</td>
<td>300</td>
<td>13.20</td>
<td>0.79</td>
<td>6</td>
</tr>
</tbody>
</table>
From above table, it is clear that the cupricated film shows less deviation from the mean value of gas response as compare to gas response of pure film.

### 5.9 Summary Table

<table>
<thead>
<tr>
<th>Samples</th>
<th>Optimum operating conditions</th>
<th>Gas sensing performance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dipping Time</td>
<td>Temp. (°C)</td>
</tr>
<tr>
<td>Pure ST&lt;sub&gt;30&lt;/sub&gt; film</td>
<td>--</td>
<td>300</td>
</tr>
<tr>
<td>Cupricated ST&lt;sub&gt;30&lt;/sub&gt; film</td>
<td>10min</td>
<td>200</td>
</tr>
</tbody>
</table>

ST<sub>30</sub>: (Sn<sub>0.3</sub>Ti<sub>0.7</sub>)O<sub>2</sub>, Conc.: concentration, Max.: Maximum, Res.: Response, Rec.: Recovery.

### 5.10 Discussion

The mechanism of H<sub>2</sub>S gas diffusion through porous ST<sub>30</sub> film is presented in Fig.5.20. This sensor shows a better performance at a relatively low temperature. Also a higher sensor response has been found at 400 ppm H<sub>2</sub>S concentration and an operating temperature of 200°C. These results of varying sensor response with varying surface morphology can be easily explained with the activation energy of the sensors. As the sensing mechanism depends on the chemical reaction taking place on surface of the sensing material and every chemical reaction depends on the activation energy. Higher activation energy lowers the electronic conduction of the sensor. The activation energy was found lowest in case of 10 min dipping time of the film and a relatively higher sensor response has been found accordingly.
**Fig. 5.20:** Mechanism of H₂S gas diffusion through porous thick film.

When reducing gas molecules like CO₂ react with negatively charged oxygen adsorbates, the trapped electrons are given back to conduction band of ST₃₀. The energy released during decomposition of adsorbed CO₂ molecules would be sufficient for electrons to jump up into conduction band of ST₃₀, causing an increase in the conductivity of sensor.

For oxidation of CO₂, some amount of activation energy has to be provided thermally. An increase in operating temperature surely increases the thermal energy so as to stimulate the oxidation of CO₂. The reducing gas (CO₂) donates electrons to ST₃₀. Therefore, the resistance decreases, or the conductance increases. This is the reason why the gas response increases with operating temperature. The point at which the gas response reaches maximum is the actual thermal energy needed for the reaction to proceed. However, the response decreases at higher operating temperatures, as the oxygen adsorbates are desorbed from the surface of sensor [27]. Also, at high temperatures the carrier concentration increases due to intrinsic thermal excitation and the Debye length decreases. This may be one of the reasons for the decreased gas response at high temperatures.

**5.11 Conclusions**

1) The thick films of pure ST₃₀ were sensitive to CO₂ gas at 300°C.
2) The thick films of pure and cupricated ST₃₀ was observed to be semiconducting in nature and showed a negative temperature coefficient of resistance.
3) The cuprication alters morphology and shifts response of the films towards H₂S gas at temperature (200°C).
4) Copper oxide could form the misfits on the surface of ST₃₀ film. Larger the misfits on the surface, larger would be the number of oxygen ions adsorbed on the surface leading to high resistance.
5) Average crystallite size from XRD of ST₃₀ film was found to be 41 nm.
6) Response and recovery time of cupricated film was 4 s and 43 s respectively.
7) The optical energy band gap of the sample was found to be 3.35 eV.
8) The texture coefficient (Tc) of the film was found to be 3.52.
9) Error measurement of gas response of modified film was observed to be 1%, which less than the pure film response (6%).
References


