Chapter: 6

Synthesis and gas sensing performance of pure and modified 
(Sn$_{0.5}$Ti$_{0.5}$)O$_2$ thick film resistors

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Chapter: 6

Synthesis and gas sensing performance of pure and modified (Sn$_{0.5}$Ti$_{0.5}$)O$_2$ thick film resistors

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6.1 Introduction

Among the metal oxides, tin dioxide and titanium dioxide are important materials because they are potential candidates for a wide range of applications, such as catalyst, gas sensors, adsorption materials and micro-wave dielectric ceramics [1–3]. SnO₂ exists in cassiterite form with a tetragonal rutile structure and lattice constants of a=4.738 and c=3.188 Å, while rutile TiO₂ possesses the lattice parameters a=4.593 and c= 2.959 Å. Due to their similar structure and close lattice parameters, it is possible to obtain solid solutions (SnₓTi₁₋ₓ)O₂ of TiO₂ and SnO₂ under certain processing conditions [4–6].

Conventionally, the solid solution (SnₓTi₁₋ₓ)O₂ can be formed from cassiterite SnO₂ and rutile TiO₂ via solid-state reaction, where mixtures of TiO₂ and SnO₂ were calcined at temperature as high as 1200–1600°C [7]. Such a high temperature inevitably leads to coarsened grains, poor homogeneity and thus undesired properties. It was reported that the solid solution Sn₀.₅Ti₀.₅O₂ was prepared by mechanochemical process from the oxide mixture of SnO₂ and TiO₂ [8]. In mechanochemical process high-energy ball milling with large quantity of SnO₂ and TiO₂ is required. To address these problems, co-precipitation [9], sol-gel [9], wet chemistry route [10] has been developed to prepare (SnₓTi₁₋ₓ)O₂ - based solid solutions. Wet chemistry route is low cost and widely available metal-chloride as the starting materials, low operating temperature.

Since the two oxides have distinct gas-sensing behaviors, a combination of them would presumably initiate a new system [11], which might have the gas sensing properties that are not present in either of their bulk oxides [12-14]. The (Sn₀.₅Ti₀.₅)O₂ material could be more selective and stable. In this chapter, the preparation of a solid solution (Sn₀.₅Ti₀.₅)O₂ via a wet chemistry route is presented. More specifically, we aim at better information on: (i) the structure and morphology of the powder; (ii) electronic properties and their changes in contact with different gases. Scanning Electron microscopy (SEM), X-ray diffraction (XRD) and Thermal gravimetric analysis (TGA) measurements were adopted to analyze the morphology, the crystalline structure, Crystalline size and thermal stability. Finally, electrical properties and gas sensing properties have been performed. (Sn₀.₅Ti₀.₅)O₂ binary oxides hereinafter labeled as ST₅₀.
6.2 Experimental work

6.2.1 Preparation of material

AR grade SnCl₂ · 2H₂O and TiCl₃ (15% HCl) were used for the preparation of ST₅₀ powder. Tin (II) dichloride dihydrate (SnCl₂·2H₂O) (0.5M) was dissolved in distilled water. Further Titanium chloride III (TiCl₃) (0.5M), 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 [15-16].

6.2.2 Preparation of thick films

The thixotropic paste was formulated by mixing the fine powder of ST₅₀ 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 (1.5cm x 0.5cm) to prepare thick films [17-19]. The films were fired at 550°C for 30 min. in air atmosphere to remove the residual.

6.2.3 Modification of thick films

The nano-Cu-modified ST₅₀ thick films were obtained by dipping them in a 0.01M aqueous solution of nano copper solution for different intervals of dipping time of 10, 20 and 30 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 [20-21]. The Cr-modified films were prepared by dipping them in a 0.1M aqueous solution of chromium trioxide (CrO₃) for different interval of dipping time: 10, 20 and 30 min. These films were dried at 80°C, followed by firing at 550°C for 30 min. The films so prepared are termed as ‘chrominated’ films.

6.2.4 Thickness measurement

The thickness (t) of the film was calculated using a weight-difference method.

\[ t = \frac{m}{\rho \times A} \]  \[ \ldots (6.1) \]
Where, \( m \) is the mass of the film deposited on the substrate in gm, ‘A’ the surface area of the film in \( \text{cm}^2 \) and ‘\( \rho \)’ is the density of the material. Average thickness of the film was observed to be 75\( \mu \)m. The reproducibility of the film thickness was achieved by maintaining the proper rheology and thixotropy of the paste.

6.3 Structural properties

6.3.1 X-ray diffraction (XRD)

Fig. 6.1 shows the X-ray diffraction patterns of ST\(_{50}\) thick film. X-ray diffraction analysis at room temperature was carried out to recognize the crystalline phase of ST\(_{50}\) powder calcinated at 1000\(^\circ\)C. It is observed that the ST\(_{50}\) peak positions very well matched with rutile SnO\(_2\) (JCPDS no.: 72-1147). A prepared sample shows single phase of the solid solution ST\(_{50}\) at calcinations temperature 1000\(^\circ\)C.

![XRD pattern of ST\(_{50}\) sample.](image)

Table 6.1 depicts the X-ray diffraction analysis of the ST\(_{20}\) thick film. The d values were in good agreement with those in the JCPDS for SnO\(_2\) (rutile) possessing tetragonal structure. The average crystallite size was calculated using Debye-Scherrer formula [23]. The average crystal size observed about 37 nm.
Table 6.1: X-ray diffraction analysis data of ST$_{50}$ film

<table>
<thead>
<tr>
<th>$2\theta$ (degree)</th>
<th>d spacing (Å)</th>
<th>FWHM</th>
<th>Crystallite Size, D(nm)</th>
<th>hkl plane</th>
</tr>
</thead>
<tbody>
<tr>
<td>26.6</td>
<td>3.34</td>
<td>0.275</td>
<td>41</td>
<td>110</td>
</tr>
<tr>
<td>34.1</td>
<td>2.63</td>
<td>0.227</td>
<td>53</td>
<td>101</td>
</tr>
<tr>
<td>38.1</td>
<td>2.36</td>
<td>0.281</td>
<td>41</td>
<td>200</td>
</tr>
<tr>
<td>38.9</td>
<td>2.13</td>
<td>0.282</td>
<td>41</td>
<td>111</td>
</tr>
<tr>
<td>52.0</td>
<td>1.76</td>
<td>0.277</td>
<td>38</td>
<td>211</td>
</tr>
<tr>
<td>55.0</td>
<td>1.67</td>
<td>0.453</td>
<td>26</td>
<td>220</td>
</tr>
<tr>
<td>58.3</td>
<td>1.58</td>
<td>0.437</td>
<td>27</td>
<td>002</td>
</tr>
<tr>
<td>62.2</td>
<td>1.49</td>
<td>0.441</td>
<td>28</td>
<td>310</td>
</tr>
<tr>
<td>65.2</td>
<td>1.43</td>
<td>0.334</td>
<td>40</td>
<td>112</td>
</tr>
<tr>
<td>66.1</td>
<td>1.37</td>
<td>0.441</td>
<td>28</td>
<td>301</td>
</tr>
<tr>
<td>71.3</td>
<td>1.31</td>
<td>0.476</td>
<td>27</td>
<td>202</td>
</tr>
<tr>
<td>79.1</td>
<td>1.20</td>
<td>0.302</td>
<td>52</td>
<td>321</td>
</tr>
</tbody>
</table>

6.3.2 Scanning Electron Microscopy (SEM)

6.3.2.1 Pure ST$_{50}$ film

Fig. 6.2: SEM image of pure ST$_{50}$ film.

Fig. 6.2 depicts a SEM image of pure ST$_{50}$ thick film fired at 550°C. The film consists of voids and a wide range of particles with particle sizes ranging from 200 to 840 nm distributed non-uniformly.
6.3.2.2 Cupricated ST\textsubscript{50} films

Figs. 6.3(a-c) depict SEM images of cupricated ST\textsubscript{50} films for the dipping time interval of 10, 20 and 30 min. fired at 550\degree C, respectively. The micrograph shows a number of small particles distributed uniformly among the larger grains around the ST\textsubscript{50} 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 350 nm (Fig. 6.3(a)), 145 to 205 nm (Fig. 6.3(b)), and 175 to 500 nm (Fig. 6.3(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\textsubscript{50} film. The smaller particle may be attributed to the presence of CuO.
**Fig. 6.3:** SEM images of Cupricated: (a) ST$_{50}$ (10min), (b) ST$_{50}$ (20min) and (c) ST$_{50}$ (30 min) films.

**Table 6.2** represents the variation in specific surface area (SSA) with the change in dipping time of the films. It is observed that the maximum SSA of the film with dipping time (20 min.) is 17.14m$^2$/g. The larger surface area may enhance the interaction between base material and catalysts, and can adsorb larger numbers of oxygen species as well as increase gas response of the film.

**Table 6.2:** Variation of specific surface area with dipping time of cupricated film

<table>
<thead>
<tr>
<th>Samples</th>
<th>Av. Particle Size (nm) (SEM)</th>
<th>Specific Surface Area (SSA) m$^2$/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure ST$_{50}$ film</td>
<td>520</td>
<td>5.77</td>
</tr>
<tr>
<td>Cupricated ST$_{50}$ film (10min) film</td>
<td>240</td>
<td>12.50</td>
</tr>
<tr>
<td>Cupricated ST$_{50}$ film (20min) film</td>
<td>175</td>
<td>17.14</td>
</tr>
<tr>
<td>Cupricated ST$_{50}$ film (30min) film</td>
<td>337</td>
<td>8.90</td>
</tr>
</tbody>
</table>

**6.3.2.3 Chrominated ST$_{50}$ films**

**Figs. 6.4(a-c)** depict the SEM images of chrominated ST$_{50}$ thick films for the dipping time interval of 10, 20 and 30 min. fired at 550$^\circ$C respectively. The micrograph shows a number of small particles distributed uniformly among the larger grains around the ST$_{50}$, which may be attributed to the presence of Cr$_2$O$_3$. The change in dipping time of the film changes the particle sizes. The particle sizes ranging from 170 to 400nm
(Fig. 6.4(a)), 160 to 270nm (Fig. 6.4(b)), and 195 to 600 nm (Fig. 6.4(c)) were observed. In micrograph (20 min. dipping), it appears that a number of small particles distributed uniformly among the larger grains of the ST_{50}. The film seems to be highly porous with a large surface to volume ratio consequently the large effective area for oxygen adsorption.
**Fig. 6.4:** SEM images of chrominated: (a) ST$_{50}$ (10min), (b) ST$_{50}$ (20min) and (c) ST$_{50}$ (30 min) films.

**Table 6.3** shows variation of specific surface area (SSA) with dipping time of the films. It is observed that the maximum SSA of the film with dipping time (20 min.) is 13.64$\text{m}^2$/g. The larger surface area may increase the interaction between base material and catalysts, and can adsorb larger numbers of oxygen species as well as increase gas response of the film.

**Table 6.3:** Variation of specific surface area with dipping time of chrominated film

<table>
<thead>
<tr>
<th>Samples</th>
<th>Av. Particle Size (nm) (SEM)</th>
<th>Specific Surface Area (SSA) $\text{m}^2$/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure ST$_{50}$ film</td>
<td>520</td>
<td>5.77</td>
</tr>
<tr>
<td>Chrominated ST$_{50}$ (10min)</td>
<td>270</td>
<td>11.11</td>
</tr>
<tr>
<td>Chrominated ST$_{50}$ (20min)</td>
<td>220</td>
<td>13.64</td>
</tr>
<tr>
<td>Chrominated ST$_{50}$ (30min)</td>
<td>310</td>
<td>9.68</td>
</tr>
</tbody>
</table>

**6.3.3 Elemental Analysis**

**6.3.3.1 Pure and Cupricated ST$_{50}$ films**

The quantitative elemental composition, of Sn, Ti, O and Cu associated in the sensor element, was carried out using EDS (JEOL, JED-2300, Germany) and it is presented in **Fig. 6.5(a)** and in **Fig 6.5(b)** for pure film and cupricated film, respectively.
Fig. 6.5 EDAX spectra of: (a) pure and (b) cupricated ST$_{50}$ films.

Table 6.4: Elemental composition of pure and cupricated films

<table>
<thead>
<tr>
<th>Samples</th>
<th>Wt. % of</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sn</td>
<td>Ti</td>
<td>O</td>
<td>Cu</td>
</tr>
<tr>
<td>Pure ST$_{50}$ film</td>
<td>39.20</td>
<td>39.91</td>
<td>20.89</td>
<td>0.00</td>
</tr>
<tr>
<td>Cupricated ST$_{50}$ (10 min) film</td>
<td>40.35</td>
<td>40.76</td>
<td>18.60</td>
<td>0.29</td>
</tr>
<tr>
<td>Cupricated ST$_{50}$ (20 min) film</td>
<td>41.83</td>
<td>42.25</td>
<td>15.11</td>
<td>0.81</td>
</tr>
<tr>
<td>Cupricated ST$_{50}$ (30 min) film</td>
<td>40.49</td>
<td>40.84</td>
<td>17.79</td>
<td>0.88</td>
</tr>
</tbody>
</table>

Table 6.4 shows elemental composition of pure and cupricated ST$_{50}$ films. It is seen that major peaks observed are of tin, titania and oxygen in pure film and tin, titania, oxygen and copper in cupricated films without presence of any impurity. It is
clear from the table that the weight percentage of copper increased with dipping time. The film with the dipping time of 20 min was observed to be more oxygen deficient (15.11 wt %). This oxygen deficiency may make the sample possible to adsorb a large amount of oxygen species favorable for higher gas response.

6.3.3.2 Chrominated ST₅₀ films

The quantitative elemental composition, of Sn, Ti, O and Cr associated in the sensor element, was carried out using EDS (JEOL, JED-2300, Germany) and is represented in Fig. 6.6 of chrominated films. Table 6.5 shows elemental composition of chrominated ST₅₀ films. It is observed that major peaks appeared are of tin, titania, chromium and oxygen. It is clear from the table that the weight percentage of chromium increased with dipping time. The film with the dipping time of 20 min was observed to be more oxygen deficient (14.74 wt %). This oxygen deficiency may make the sample possible to adsorb a large amount of oxygen species favorable for higher gas response.

![EDAX spectra of chrominated ST₅₀ film.](image)

**Table 6.5:** Elemental composition of pure and chrominated films

<table>
<thead>
<tr>
<th>Samples</th>
<th>Wt. % of Sn</th>
<th>Wt. % of Ti</th>
<th>Wt. % of O</th>
<th>Wt. % of Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure ST₅₀ film</td>
<td>39.20</td>
<td>39.91</td>
<td>20.89</td>
<td>0.00</td>
</tr>
<tr>
<td>Chrominated ST₅₀ (10 min)</td>
<td>40.35</td>
<td>40.76</td>
<td>17.92</td>
<td>0.97</td>
</tr>
<tr>
<td>Chrominated ST₅₀ (20 min)</td>
<td>41.83</td>
<td>42.25</td>
<td>14.74</td>
<td>1.18</td>
</tr>
<tr>
<td>Chrominated ST₅₀ (30 min)</td>
<td>40.49</td>
<td>40.84</td>
<td>16.7</td>
<td>1.97</td>
</tr>
</tbody>
</table>
6.3.4 Texture coefficient (Tc)

The texture coefficient (Tc) of the film was determined using equation 6.2. From that, it was observed that Tc approaches to unity for randomly distributed samples whereas Tc is larger than unity for a preferentially oriented (hkl) plane. The lower value of Tc reveals that the films have poor crystallinity. It has been observed that the preferred orientation is the (110) plane for ST50 sample. Texture coefficient of the film was found to be 2.97.

Texture coefficient of (hkl) plane,

$$Tc(hkl) = \frac{1}{N} \times \sum I(hkl)/Io(hkl)$$  \hspace{1cm} (6.2)

Where, N- No. of planes of XRD

6.4 Optical properties by UV –Vis –NIR Spectrum

Fig. 6.7 shows the variation of absorbance with wavelength for ST50 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 energy band gap (Eg) of the prepared powder was determined using the absorption UV-Vis –NIR spectra. The optical energy band gap is found to be 3.74 eV [24, 25].

![Fig. 6.7: Variation of absorbance with wavelength for ST50 sample.](image)
6.5 Thermal properties by TGA / DTA

Fig. 6.8 shows the TGA/DTA profiles of pure ST\textsubscript{50} sample. Thermogravimetric (TGA) analysis of the samples was carried out using a Mettler Toledo Star system-851 under similar conditions in static air. Thermal stability of pure ST\textsubscript{50} was examined by a TGA, using $\alpha$-Al\textsubscript{2}O\textsubscript{3} powder as the reference in air and at a heating rate of 10 °C/min. About 6.612 mg of powders was used for the test. Weight loss of ST\textsubscript{50} material was observed to be nearly 2.5%. The small weight loss may be contributing to its larger stability of the prepared material.

The DTA showed the endothermic nature of reactions for pure ST\textsubscript{50} film. The heat absorbed by the samples may be due to the non-stoichiometry of ST\textsubscript{50} and oxygen deficiency.

6.6 Electrical properties

6.6.1 I-V characteristics

Fig. 6.9 shows the I-V characteristics of pure and cupricated ST\textsubscript{50} thick films in air atmosphere. The linearity in the graphs indicates the ohmic nature of the pressure contacts.
6.6.2 TCR value of pure, cupricated and chrominated ST\textsubscript{50} films

Fig. 6.10 shows the variation of resistance of the film in air (Ra) and gas (Rg) of pure and cupricated (20 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. TCR of the film was calculated using the following equations and found to be negative.

\[
R_T = R_0 [1 + \alpha T] \quad \text{..... (6.3)}
\]

\[
\text{TCR}(\alpha) = \frac{\text{slope}}{R_0} / ^\circ \text{C} \quad \text{.... (6.4)}
\]
**Table 6.6** depicts the TCR values for pure and cupricated films. TCR value of cupricated film is more negative than pure film. This reveals that the cupricated film is more semiconducting than the pure film.

**Table 6.6:** Variation of temperature coefficient of resistance of pure and cupricated film

<table>
<thead>
<tr>
<th>Samples</th>
<th>TCR(α) (1/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure (a)</td>
<td>-0.00296</td>
</tr>
<tr>
<td>Pure (g)</td>
<td>-0.00570</td>
</tr>
<tr>
<td>Mod.(g)</td>
<td>-0.00697</td>
</tr>
</tbody>
</table>

**Fig. 6.11** shows the variation of resistance of the film in air (Ra) and gas (Rg) of pure and chrominated (20 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. The TCR of the film is calculated by using Eq. 6.4 and found to be negative.

**Fig. 6.11:** Variation of resistance of the film with operating temperature of pure and chrominated ST50 films.

**Table 6.7** depicts the TCR values for pure and chrominated films. TCR value of chrominated film is more negative than pure film. This reveals that the chrominated film is more semiconducting than the pure film.
Table 6.7: Variation of temperature coefficient of resistance of pure and chrominated film

<table>
<thead>
<tr>
<th>Samples</th>
<th>TCR(α) (1/oC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure (a)</td>
<td>-0.00335</td>
</tr>
<tr>
<td>Pure (g)</td>
<td>-0.00400</td>
</tr>
<tr>
<td>Mod.(g)</td>
<td>-0.00473</td>
</tr>
</tbody>
</table>

6.6.3 Electrical conductivity

6.6.3.1 Cupricated ST$_{50}$ films

The temperature dependence of electrical conductivity of ST$_{50}$ thick film was carried out on gas sensing system in the temperature 323-723 k. Several heating and cooling cycles were studied for this purpose. Successive heating and cooling cycles resulted in the stabilization of surface resistance. The sample were heated to 723 k and allowed to cool to room temperature. All data were recorded during cooling.

![Graph of electrical conductivity with temperature](image)

**Fig. 6.12**: Variation of electrical conductivity with temperature of pure and cupricated ST$_{50}$ films.

**Fig. 6.12** represents 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$_2$S gas. The conductivity varied nonlinearly with temperature for all samples. Activation energy is calculated from the slope of the graph of log (conductivity) versus (1000/T) k$^{-1}$ (**Fig. 6.12**) for particular samples. The conductivities of cupricated ST$_{50}$ samples were larger than that of pure ST$_{50}$ at particular temperature.
in the presence of gas or in air. The conductivity observed of the cupricated sample for 20 min was largest of all.

**Table 6.8** shows the variation of activation energy with dipping time of the film. It was observed that the activation energy of most sensitive cupricated film (0.196 eV) (20 min.) is less than the pure film (0.241 eV) at 200°C. This reveals that the surface modification of the films improves the gas response of the film; since less amount of energy is require to change the one stable state to other state of sensor.

**Table 6.8:** Variation of activation energy with dipping time of cupricated films

<table>
<thead>
<tr>
<th>Samples</th>
<th>Activation energy(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure ST$_{50}$ film</td>
<td>0.241</td>
</tr>
<tr>
<td>Cupricated ST$_{50}$ (10min) film</td>
<td>0.220</td>
</tr>
<tr>
<td>Cupricated ST$_{50}$ (20min) film</td>
<td>0.196</td>
</tr>
<tr>
<td>Cupricated ST$_{50}$ (30min) film</td>
<td>0.124</td>
</tr>
</tbody>
</table>

**6.6.3.2 Chrominated ST$_{50}$ films**

**Fig. 6.13** represents the variation of conductivity with temperature for the pure and chrominated 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 ethanol gas. The conductivity varied nonlinearly with temperature for all samples. Activation energy is calculated from the slope of the graph of log (conductivity) versus (1000/T) $k^{-1}$ for particular samples. The conductivities of chrominated ST$_{50}$ samples were larger than that of pure ST$_{50}$ at particular temperature in the presence of gas or in air. The conductivity of the chrominated sample observed for 20min was largest of all.

Activation energy is calculated from the slope of the graph of log conductivity versus 1000/T (**Fig. 6.13**). **Table 6.9** shows the variation of activation energy with dipping time of the film. It was observed that the activation energy of most sensitive chrominated film (0.135 eV) (20 min.) is less than the pure film (0.241 eV) at 200°C. This reveals that the surface modification of the films improves the gas response of the film; since less amount of energy is require to change the one stable state to other state of sensor.

**Table 6.9** shows the variation of activation energy with dipping time of chrominated films.
**Fig. 6.13:** Variation of electrical conductivity with temperature of pure and chrominated ST\textsubscript{50} films.

**Table 6.9:** Variation of activation energy with dipping time of chrominated films

<table>
<thead>
<tr>
<th>Samples</th>
<th>Activation energy(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure ST\textsubscript{50} film</td>
<td>0.241</td>
</tr>
<tr>
<td>Chrominated ST\textsubscript{50} (10min) film</td>
<td>0.164</td>
</tr>
<tr>
<td>Chrominated ST\textsubscript{50} (20min) film</td>
<td>0.135</td>
</tr>
<tr>
<td>Chrominated ST\textsubscript{50} (30min) film</td>
<td>0.151</td>
</tr>
</tbody>
</table>

**6.7 Gas sensing properties**

**6.7.1 Pure ST\textsubscript{50} films**

**6.7.1.1 Gas response with operating temperature**

The film were tested to various gases at different operating temperatures and showed maximum response to NH\textsubscript{3}. **Fig. 6.14** shows variations in response to NH\textsubscript{3} gas with operating temperature of the pure ST\textsubscript{50} thick film fired at 550°C. The gas response values of pure were determined at various operating temperatures ranging from 100 to 450°C to NH\textsubscript{3} gas. The response goes on with increasing the operating temperature, attains its maximum at 300°C and then decreases with a further increase in operating temperature. It is clear that the optimum operating temperature of pure film is 300°C.
6.7.1.2 Selectivity

Fig. 6.15 shows the bar diagram indicating the % selectivity of the pure ST$_{50}$ sensor operated at 300°C to NH$_3$ gas against other gases. It is evident that the pure sensor was highly selective to NH$_3$ at 300°C gas against the other gases.

6.7.2 Cupricated ST$_{50}$ films

6.7.2.1 Gas response with operating temperature

Fig. 6.16 shows variations in response to H$_2$S gas with operating temperature of the cupricated ST$_{50}$ thick films for the dipping time interval of 10,20 and 30 min. fired at 550°C. The gas response values of surface cupricated ST$_{50}$ films were determined at various operating temperatures ranging from 100 to 450°C to H$_2$S gas.
Fig. 6.16: Variations in response to H$_2$S gas with operating temperature of cupricated ST$_{50}$ films.

The cupricated film suppresses response of the gases selected at different operating temperatures of pure film and enhances the response to H$_2$S gas. The response goes on increasing with the operating temperature, attains its maximum (at 250°C) and then decreases with a further increase in operating temperature. It is clear that the optimum operating temperature of cupricated film is 250°C.

6.7.2.2 Gas response to different gas concentrations

Fig. 6.17 exhibits the response to H$_2$S gas for various gas concentrations ranging from 50 to 1000 ppm at 250°C operating temperature of cupricated ST$_{50}$ film.

Fig. 6.17: Variation in H$_2$S response with gas concentration of cupricated film.

It observed that gas response increases linearly from 50-200 ppm after that, the response was nearly constant. 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 (50-200 ppm).

6.7.2.3 Variation of gas response with dipping time

Fig. 6.18 shows the variation of the gas response of the cupricated films treated for different intervals of dipping time. 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 10 min and decreases with further dipping.

Fig. 6.18: Variation in H$_2$S gas response with dipping time of cupricated film.

6.7.2.4 Selectivity

Selectivity of the film was calculated using the following formula,

\[
\text{% Selectivity} = \frac{S_{\text{other gas}}}{S_{\text{target gas}}} \times 100
\]

\[\text{\ldots (6.5)}\]

Fig. 6.19: % Selectivity of cupricated (20 min.) film to H$_2$S against other gases at 250°C.
Fig 6.19 shows the selectivity of the sample ST<sub>50</sub> sensor operated at 250°C to H<sub>2</sub>S gas against other gases. It is evident that the cupricated sensor was highly selective to H<sub>2</sub>S gas at 250°C.

6.7.3 Chrominated ST<sub>50</sub> films

6.7.3.1 Gas response with operating temperature

Fig. 6.20 shows variations in response to ethanol gas with operating temperature of the chrominated ST<sub>50</sub> thick films for the dipping time interval of 10, 20 and 30 min. fired at 550°C. The gas response values of surface chrominated ST<sub>50</sub> films were determined at various operating temperatures ranging from 100°C to 450°C to ethanol gas. The chrominated film suppresses response of the gases selected at different operating temperatures of pure film and enhances the response to ethanol gas. The response goes on increasing with the operating temperature, attains its maximum (at 300°C) and then decreases with a further increase in operating temperature. It is clear that the optimum operating temperature of chrominated film is 300°C.

![Variations in response to ethanol gas with operating temperature of chrominated films.](image)

6.7.3.2 Gas response with gas concentration of chrominated film

Fig. 6.21 depicts the response to ethanol gas for various gas concentrations ranging from 100 to 1000 ppm at 300°C operating temperature. It observed that gas response increases linearly from 100-400 ppm after that, the response remains constant. 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).
6.7.3.3 Variation of gas response with dipping time

Fig. 6.22 shows the variation of the gas response of the chrominated films treated for different intervals of dipping time. It is clear that the response to ethanol gas on increasing with an increase in the dipping time interval. H₂S gas response attains its maximum at 20min and decreases with further dipping.

6.7.3.4 Selectivity

Fig. 6.23 shows the bar diagram indicating the % selectivity of the chrominated (20 min.) ST₅₀ sensor operated at 300°C to ethanol gas against other gases. It is evident that the chrominated sensor was highly selective to ethanol gas at 300°C.
6.7.4 Response and recovery time of sensors

6.7.4.1 Pure ST$_{50}$ film

Fig. 6.24 shows the response and recovery time of pure ST$_{50}$ film. The response time of pure ST$_{50}$ film was 5 s and recovery time was 80 s at operating temperature 300°C.

6.7.4.2 Cupricated ST$_{50}$ film

Fig. 6.25 shows the response and recovery time of cupricated (20 min.) ST$_{50}$ film. The response time of the film was 3 s and recovery time was 39 s at operating temperature 250°C. This shows that surface cuprication of the film reduced the response and recovery time of the sensor. The very short response and recovery time are the important features of the cupricated ST$_{50}$ film.
6.7.4.3 Chrominated ST$_{50}$ film

Fig. 6.26 shows the response and recovery time of cupricated (20 min.) ST$_{50}$ film. The response time of the film was 4 s and recovery time was 34 s at operating temperature 300$^\circ$C. The very short response and recovery time are the important features of the chrominated ST$_{50}$.

6.7.5 Long-time stability of sensor

6.7.5.1 Pure ST$_{50}$ film

Fig. 6.27 shows the long time stability of pure ST$_{50}$ film. The film was tested for the long period of 2 month. The response of the sensor was found to be nearly consistent and stable. No major reduction in the gas response was observed.
6.7.5.2 Cupricated ST$_{50}$ films

Fig. 6.28 shows the long time stability of cupricated ST$_{50}$ film. It was observed that due to cuprication of the films the long time stability of gas response of the sensor is found to be improved.

6.7.5.3 Chrominated ST$_{50}$ film

Fig. 6.29 shows the long time stability of chrominated ST$_{50}$ film. It was observed that due to surface modification of the films the long time stability of gas response of the sensor is found to be improved.
6.8 Error measurement:

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

$$\sigma = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n-1}}$$

Table 6.10 shows Measurement of % error in gas response of ST$_{50}$ film of pure and most gas sensitive modified ST$_{50}$ film.

<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$_{50}$ film</td>
<td>300</td>
<td>10.22</td>
<td>0.53</td>
<td>5</td>
</tr>
<tr>
<td>Cupricated ST$_{50}$ film (20min.) film</td>
<td>200</td>
<td>125.4</td>
<td>1.31</td>
<td>1</td>
</tr>
<tr>
<td>Chrominated ST$_{50}$ film (20min.) film</td>
<td>300</td>
<td>17.9</td>
<td>0.69</td>
<td>4</td>
</tr>
</tbody>
</table>

From above table, it is observed that the maximum error is less than 10%. It means the measurement method carried in this work is correct. It is also observed that error decreases with surface modification that indicates the method of surface modification is correct.
6.9 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;50&lt;/sub&gt; film</td>
<td>--</td>
<td>300</td>
</tr>
<tr>
<td>Cupricated ST&lt;sub&gt;50&lt;/sub&gt; film</td>
<td>20 min</td>
<td>250</td>
</tr>
<tr>
<td>Chrominated ST&lt;sub&gt;50&lt;/sub&gt; film</td>
<td>20 min</td>
<td>300</td>
</tr>
</tbody>
</table>

ST<sub>50</sub>(Sn<sub>0.5Ti0.5</sub>)O<sub>2</sub>, Conc.: concentration, Max.: Maximum, Res.: Response, Rec.: Recovery.

6.10 Discussion

i) Pure ST<sub>50</sub> thick film as an ammonia sensor:

It is known that atmospheric oxygen molecules are adsorbed on the surface of ST<sub>50</sub> semiconductor oxide in the forms of O<sup>-2</sup>, O<sup>-1</sup>, and O<sup>-</sup>, thereby decreasing the electronic conduction. Atmospheric oxygen molecules take electrons from the conduction band of sample to be adsorbed as O<sup>-</sup>. The reaction is as follows:

\[
2\text{(O)} - 36e^- + 2\text{NH}_3 \rightarrow 2\text{N}_2 + 6\text{H}_2\text{O} + 6e^- \quad \ldots \quad (6.7)
\]

When reducing gas molecules like NH<sub>3</sub> react with negatively charged oxygen adsorbates, the trapped electrons are given back to conduction band of ST<sub>50</sub>. The energy released during decomposition of adsorbed NH<sub>3</sub> molecules would be sufficient for electrons to jump up into conduction band of ST<sub>50</sub>, causing an increase in the conductivity of sensor.

For oxidation of NH<sub>3</sub>, 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 NH<sub>3</sub>. The reducing gas (NH<sub>3</sub>) donates electrons to ST<sub>50</sub> film. Therefore, the resistance of the film decreases, or the conductance increases. This could be the reason for increase of gas response of the film with operating temperature. As temperature increases, at particular point of maximum response the adequate
required thermal energy is received by the reaction. However, the response decreases at further increase in operating temperatures, as the oxygen adsorbates are desorbed from the surface of sensor [23]. 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 [10].

**ii) Cupricated ST$_{50}$ thick film a H$_2$S gas sensor:**

The ST$_{50}$ film surfaces were modified with CuCl$_2$ using dipping technique. The CuCl$_2$ would be converted into CuO during the firing of the films. These films can be looked upon as the small particles of surface activators (CuO) distributed along the grain boundaries of base material and would occupy the intergrain spaces which develop the new surface sites beneficial for improvement of the gas response and selectivity of a particular gas.

The ionic radius of copper (0.73 Å) is small therefore the segregation of Cu ions would be easier into the base material and could occupy more surface sites. Due to this, there would be large surface to volume ratio. The adsorption-desorption process would therefore be more effective in case of the Cu-activated films.

The Cu activators can create artificial surface states in the midgap region, leading to unusual physical and chemical properties. For example, the adsorption energy can be higher for the misfit regions, and the discontinuity in the adsorption potential can give rise to unusual selectivity effects for MOS semiconducting oxide sensors. More specifically, the electron-electron interaction in the presence of periodically enhanced disorders in these two-dimensional systems can create the adsorbate-adsorbent interaction and the range of adsorption potentials leading to additional sensitivity improvement.

It is also observed from SEM pictures that the grains associated in Cu-activated films are smaller as compared to the grains associated with the pure film. Therefore, the effective surface area in case of activated films would be larger than the pure film. This enables the faster adsorption-desorption process and therefore, faster response and recovery in case of modified films.

When reducing gas such as H$_2$S, comes in contact with the grains of base material, the potential barrier would decrease as a result of oxidative conversion of H$_2$S
gas and desorption of oxygen. The reaction of H₂S with the adsorbed oxygen ions can be represented as:

\[
\text{H}_2\text{S} + 3\text{O}^- \xrightarrow{250\text{oC}} \text{H}_2\text{O} + \text{SO}_2 + 3\text{e}^- \quad \ldots \quad (6.8)
\]

The nonlinearity of the electrical conductivity-temperature profiles of the samples reveals the semiconducting nature of pure and cupricated ST₅₀. The semiconducting nature may be attributed to oxygen deficiencies in ST₅₀.

**iii) Chrominated ST₅₀ thick film an ethanol sensor:**

The surface chrominated ST₅₀ films can be looked upon as the small particles of chromium oxide distributed along the grain boundaries of ST₅₀. CrO₃ on the surface of ST₅₀ film is not thermally stable above its melting temperature (197°C) losing oxygen to give, after series of intermediate stages, Cr₂O₃ [26]. In this investigation, it is a usual procedure, to test the sensors by heating them at the operating temperatures ranging from 50 to 450°C. The first time heating of sensor, above 200°C, would convert CrO₃ into Cr₂O₃. Some amount of CrO₃ may also be reduced into Cr₂O₃ by trapping electrons from the oxygen vacancies in ST₅₀ material.

Adequate dispersion of chromium oxide on the surface of the sensor could produce misfit regions all across the film surface and enhances the oxygen adsorption capability of the sensor. The larger the amount of oxygen adsorbed on the surface, the larger would be the number of electrons abstracted from the film surface, which in turn would increase largely total initial resistance. On exposure of reducing gas such as ethanol on the film surface, it would be oxidized quickly releasing the abstracted electrons. This would decrease the resistance abruptly giving high gas response.

The amount of oxygen adsorbed on the surface of chrominated ST₅₀ films is more since chromium oxide form misfit regions between the grains of ST₅₀ and act as efficient catalysts for oxygenation. The Cr₂O₃ can create artificial surface states in the mid-gap region, leading to unusual physical and chemical properties. For example, the adsorption energy can be higher for the misfit regions, and the discontinuity in the adsorption potential can give rise to unusual selectivity effects for ST₅₀ based semiconducting oxide sensors. More specifically, the electron-electron interaction in the presence of periodically enhanced disorders in these two-dimensional systems can
affect the adsorbate-adsorbent interaction and the range of adsorption potentials leading to additional sensitivity improvement.

When the optimum amount of chromium oxide is incorporated on the surface of the ST\textsubscript{50} film, chromium species would be distributed uniformly throughout the surface (Fig. 6.4(b)). Due to this not only the initial resistance of the film is high but this amount would also be sufficient to promote the catalytic reaction effectively and the overall change in resistance on exposure of the test gas is larger leading to high gas response.

When the amount of chromium oxide on the surface of the film is less than the optimum, the surface dispersion would be poor and amount may not be sufficient to promote the reaction more effectively leading to decreased sensitivity.

The addition of Cr\textsubscript{2}O\textsubscript{3} into ST\textsubscript{50} could not change the grain size of ST\textsubscript{50} significantly but could change the catalytic properties of ST\textsubscript{50} film.

6.11 Conclusions

1) The thick films of pure ST\textsubscript{50} were sensitive to NH\textsubscript{3} gas at 300°C.
2) Surface cuprication and chromination process was employed to modify only the surface of the film and not the bulk portion of the base material ST\textsubscript{50}.
3) Modified films are more semiconducting than the pure film. TCR value of the modified films are more negative than pure film.
4) The cuprication alters morphology and shifts response of the films towards H\textsubscript{2}S gas at temperature (250°C).
5) Cupricated films were found to be more porous film. As porosity increases of the film, the gas response of the film would be increases.
6) The chrominated films shifts response of the films towards ethanol gas at temperature (300°C).
7) Average crystallite size from XRD using Scherrer formula was 37nm of the ST\textsubscript{50} film.
8) Response time and recovery time of pure film was found to be 5 s and 80 s.
9) Response time and recovery time of cupricated film was found to be 3 s and 39 s respectively. Surface modification reduces the response time and recovery time.
10) Response time and recovery time of chrominated film was found to be 4 s and 34 s respectively. Surface modification reduces the response time and recovery time.

11) Pure and modified films showed the good long time stability.

12) Band gap energy of the prepared ST_{50} material was found to be 3.74eV.

13) Texture coefficient of ST_{50} film was found to be 2.97.

14) Error of measurement of gas response of cupricated and a chrominated film was observed to be 1% and 4%, which is less than the pure film (5%).
References


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