Chapter: 8

Synthesis and gas sensing performance of pure SnO$_2$ and TiO$_2$ thick film resistors
Chapter: 8

Synthesis and gas sensing performance of pure SnO$_2$ and TiO$_2$ thick film resistors

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.1 Introduction</td>
<td>221</td>
</tr>
<tr>
<td>8.2 Experimental work</td>
<td>221</td>
</tr>
<tr>
<td>8.2.1 Preparation of material</td>
<td>221</td>
</tr>
<tr>
<td>8.2.2 Preparation of thick films</td>
<td>221</td>
</tr>
<tr>
<td>8.2.3 Thickness measurements</td>
<td>221</td>
</tr>
<tr>
<td>8.3 Structural properties</td>
<td>222</td>
</tr>
<tr>
<td>8.3.1 X-ray diffraction studies (XRD)</td>
<td>222</td>
</tr>
<tr>
<td>8.3.2 Scanning Electron Microscopy (SEM).</td>
<td>223</td>
</tr>
<tr>
<td>8.3.2.1 Pure SnO$_2$ film</td>
<td>223</td>
</tr>
<tr>
<td>8.3.2.2 Pure TiO$_2$ film</td>
<td>223</td>
</tr>
<tr>
<td>8.4 Gas sensing properties</td>
<td>224</td>
</tr>
<tr>
<td>8.4.1 Pure SnO$_2$ film</td>
<td>224</td>
</tr>
<tr>
<td>8.4.1.1 Gas response with operating temperature</td>
<td>224</td>
</tr>
<tr>
<td>8.4.1.2 Selectivity</td>
<td>225</td>
</tr>
<tr>
<td>8.4.2 Pure TiO$_2$ film</td>
<td>225</td>
</tr>
<tr>
<td>8.4.2.1 Gas response with operating temperature</td>
<td>225</td>
</tr>
<tr>
<td>8.4.2.2 Selectivity</td>
<td>226</td>
</tr>
<tr>
<td>8.5 Summary Table</td>
<td>226</td>
</tr>
<tr>
<td>8.6 Discussion</td>
<td>227</td>
</tr>
<tr>
<td>8.7 Conclusions</td>
<td>227</td>
</tr>
<tr>
<td>References</td>
<td>228</td>
</tr>
</tbody>
</table>
Figure captions:

Fig. 8.1: XRD of: (a) SnO$_2$ and (b) TiO$_2$ films.
Fig. 8.2: SEM image of pure SnO$_2$ film.
Fig. 8.3: SEM image of pure TiO$_2$ film.
Fig. 8.4: Gas response of pure SnO$_2$ film.
Fig. 8.5: Selectivity of pure SnO$_2$ film.
Fig. 8.6: Gas response of pure TiO$_2$ film.
Fig. 8.7: Selectivity of pure TiO$_2$ film.
8.1 Introduction

The air is a mixture of gases. Depending on the environment, it may contain various chemical pollutants, e.g. SOx, NOx, NH3, H2S, CO or volatile organic compounds. Some of these pollutants are either explosive (like methane) or highly toxic (like carbon monoxide). The others cause disturbances in a human or animal body. Living in the contemporary industrialized world requires the protection against the influence of these hazardous substances, what induces the need for continuous monitoring of the specified compounds. First successful semiconductive sensors were made of metal oxides, i.e. SnO2, TiO2, ZnO, Fe2O3, Al2O3, and Y2O3. Eventually the tin dioxide became the dominating gas sensitive material. SnO2 based sensors are the best-understood type among the oxide-based gas sensors. Highly selective and sensitive SnO2 and TiO2 sensors are not available yet [1].

8.2 Experimental work

8.2.1 Preparation of material

Tin (II) dichloride dihydrate (SnCl2.2H2O) ((99.8 %, Aldrich) was dissolved in distilled water followed by slow heating to obtain SnO2 base material. TiO2 base material was prepared using Titanium chloride III (TiCl3), containing 15% HCl (99.8 %, Aldrich) with slow heating at 80°C. These powders were calcinated at 1000°C for 6 h to obtain crystalline base material SnO2 and TiO2 [3-5]. Then this powder ground in the agate pastle–mortor to ensure sufficiently fine particle size.

8.2.2 Preparation of thick films

The thixotropic paste was formulated by mixing the fine powder of (Sn0.3Ti0.7)O2 with temporary binder as a mixture of organic solvents. The ratio of the inorganic to organic part was kept at 75:25 in formulating the paste. This paste was screen printed [6-8] on a glass substrate in a desired pattern (1.5cm x 0.5cm) to prepare thick films. The films were fired at 550°C for 30 min. in an air atmosphere to remove the residual.

8.2.3 Thickness measurement

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

\[ t = \frac{m}{\rho \times A} \] .... (8.1)
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 deposited 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.

8.3 Structural Properties

8.3.1 X-ray diffraction studies (XRD)

To identify the structure and phase purity of the prepared sample, X-ray diffraction analysis (XRD) measurement was performed. XRD analysis of these powders were carried out in the 20-80 deg. (2\( \theta \)) range using Cu-K\( \alpha \) (with \( \lambda = 1.54 \) Å, 40 kV, 30 mA) radiation.

The X-ray diffraction patterns of SnO\(_2\) and TiO\(_2\) thick films are shown Fig.8.1 (a) and (b). XRD analysis at room temperature was carried out to recognize the crystalline phase of SnO\(_2\) and TiO\(_2\) powder. It shows well defined broad diffraction peaks, indicating formation of polycrystalline phases. The diffraction peak indexing, done by matching with the Joint committee on powder diffraction standard (JCPDS) (no. 72-1147) clearly revealed the formation of the SnO\(_2\) phases with tetragonal rutile structure. In prepared TiO\(_2\) material, a mixed phase of rutile and anatase was observed [9]. The peaks are very well matched with JCPDS data (Rutile: 76-0649 and Anatase: 84-1286). The sharpness of the peaks indicates the polycrystalline nature of the film material.

![X-ray diffraction patterns of SnO\(_2\) and TiO\(_2\) thick films](image)
8.3.2 Scanning Electron Microscopy (SEM)

8.3.2.1 Pure SnO$_2$ film

Fig. 8.2 is a SEM image of pure SnO$_2$ thick film fired at 550°C. SnO$_2$ film consists of voids and a wide range of particles with particle sizes ranging from 175 to 600 nm.

Fig. 8.3 is a SEM image of pure TiO$_2$ thick film fired at 550°C. TiO$_2$ consists of particles of 350 to 960 nm distributed non-uniformly.
8.4 Gas sensing properties

8.4.1 Pure SnO₂ film

8.4.1.1 Gas response with operating temperature

Fig. 8.4 shows variations in response to H₂S gas with operating temperature of the pure SnO₂ thick films fired at 550°C. The gas response values of pure (pure) was determined at various operating temperatures ranging from 100 to 450°C to H₂S gas. Pure SnO₂ films showed maximum response to H₂S (S=27.7) for 400 ppm at 350°C. The response goes on with increasing the operating temperature, attains its maximum at 350°C and then decreases with a further increase in operating temperature. It is clear that the optimum operating temperature of pure film is 350°C.
8.4.1.2 Selectivity of SnO\textsubscript{2} film

Selectivity or specificity is defined as the ability of a sensor respond to a certain (target) gas in the presence of other gases. Percent selectivity of one gas over others is defined as the ratio of the maximum response of target gas to the maximum response of other gas at optimum temperature of target gas,

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

Fig. 8.5 shows the bar diagram indicating the selectivity of the pure SnO\textsubscript{2} sensor operated at 350°C to H\textsubscript{2}S gas against other gases. It was observed that both films showed the lack of selectivity.

![Selectivity of pure SnO\textsubscript{2} film.](image)

8.4.2 Pure TiO\textsubscript{2} film

8.4.2.1 Gas response with operating temperature

Fig. 8.6 shows variations in response to H\textsubscript{2}S gas with operating temperature of the pure TiO\textsubscript{2} thick films fired at 550°C. The gas response values of pure (pure) was determined at various operating temperatures ranging from 100 to 450°C to H\textsubscript{2}S gas. Pure TiO\textsubscript{2} film showed gas response to H\textsubscript{2}S (S=19.50) for 800ppm at 350°C. The response goes on increasing with the operating temperature, attains its maximum at 350°C and then decreases with a further increase in operating temperature. It is clear that the optimum operating temperature of pure film is 350°C.
8.4.2.2 Selectivity of TiO\textsubscript{2} film

Fig. 8.7 shows the bar diagram indicating the selectivity of the pure TiO\textsubscript{2} sensor operated at 350°C to H\textsubscript{2}S gas against other gases. It was observed that both films showed the lack of selectivity.

8.5 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>Temp. (°C)</td>
<td>Gas conc. (ppm)</td>
</tr>
<tr>
<td>SnO\textsubscript{2} film</td>
<td>350</td>
<td>800</td>
</tr>
<tr>
<td>TiO\textsubscript{2} film</td>
<td>350</td>
<td>800</td>
</tr>
</tbody>
</table>
8.6 Discussion:

The gas sensing mechanism belongs to the surface controlled type which is based on the change of the electrical conductance of the semiconducting material upon exposure to H\textsubscript{2}S vapors. The gas response is a function of grain size, surface state and oxygen adsorption [10]. The surface area generally provides more adsorption-desorption sites and thus the higher gas response. The H\textsubscript{2}S sensing mechanism is based on the change in conductance of SnO\textsubscript{2} and TiO\textsubscript{2} films, which is controlled by H\textsubscript{2}S species and the amount of chemisorbed oxygen on the surface. It is known that atmospheric oxygen molecules are adsorbed on the surface of semiconductor oxide in the form of O\textsuperscript{2–}, O\textsuperscript{−} or O\textsuperscript{2−}. The reaction kinematics may be explained by the following reactions:

\[
\begin{align*}
\text{O}_2\text{(gas)} + e^- & \rightarrow \text{O}_2^-(\text{ads}) \quad \text{.... 8.3} \\
\text{O}_2^-\text{(ads)} + e^- & \rightarrow 2\text{O}_2^-\text{(ads)} \quad \text{.... 8.4}
\end{align*}
\]

The presence of chemical adsorbed oxygen could cause electron depletion in the thick film surface and building up of Schottky surface barrier: consequently, the electrical conductance of the thick film decreased to a minimum. The SnO\textsubscript{2} and TiO\textsubscript{2} films interact with oxygen by transferring the electron from the conductance band to adsorbed oxygen atoms. The reaction to H\textsubscript{2}S can be explained as a reaction of gas with the O\textsuperscript{2−} (ads):

\[
\text{H}_2\text{S} + 3\text{O}_2^-\text{(ads)} \rightarrow \text{H}_2\text{O(g)} + \text{SO}_2\text{(g)} + 3e^- \quad \text{.... 8.5}
\]

With this reaction, many electrons could release to thick film surface. This could make the Schottky surface barrier decrease, with the depletion layer thinner: consequently, the electrical conductance of the film increases. More gas would be adsorbed by the thick film surface: consequently, the gas response was enhanced.

8.7 Conclusions

1) The thick films of SnO\textsubscript{2} were sensitive to H\textsubscript{2}S (S=27.7) gas at 350°C.
2) The thick films of TiO\textsubscript{2} were sensitive to H\textsubscript{2}S (S=19.5) gas at 350°C.
3) Average crystallite size from XRD using Scherrer formula was 35 nm of SnO\textsubscript{2} film.
4) Average crystallite size from XRD using Scherrer formula was 40 nm of TiO\textsubscript{2} film.
5) Selectivity of pure SnO\textsubscript{2} and pure TiO\textsubscript{2} films was found to be poor.
References


