**CuO- SnO$_2$ nanocomposites thin films for the fast detection of H$_2$S gas**

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**Abstract**

CuO-SnO$_2$ nanocomposites thin films were prepared by spray pyrolysis method onto the heated glass substrate at 250 °C. The films were fired at 500 °C. As prepared thin films were studied using XRD and SEM. The gas sensing performance of different composition of CuO-SnO$_2$ was studied on exposure of different gases for 10 ppm. sensor shows quick response (3 s) and fast recovery (6 s) time. The results are discussed and interpreted.

**Keywords:** Spray Pyrolysis, CuO-SnO$_2$ nanocomposites, H$_2$S gas sensing, quick response, fast recovery

1. **Introduction**

The semiconductor-based chemical sensors own their popularity to their small size, simple operation, high sensitivity, selectivity, and relatively simple associated electronics. The metal oxide-sensing layer (SnO$_2$ or CuO) has been fabricated in different physical forms such as thin film, thick films, and bulk pellets. However, the thin film form is expected to be most effective, because sensing is basically a surface phenomenon of film [1].

Monitoring of H$_2$S is crucial in laboratories and industrial areas. Hence a sensor with fast detection and high gas response is desired. It was demonstrated that the cations with a low electro- negativity value are best suited for SnO$_2$ doping with regard to hydrogen sulfide detection. However, it was found by Yamazoe and co-workers, that doping of tin dioxide with copper that is intermediate in electro negativity, gives rise to the outstanding sensitivity [2].

This paper deals with the preparation of composite thin films of SnO$_2$ and CuO. These films were studied using different analytical techniques. These CuO-SnO$_2$ nanocomposites thin films were tested for sensing different gases and was observed to be most sensitive to H$_2$S at 250 °C.
2. Experimental details

2.1. Preparation of pure CuO - SnO₂ nanocomposites thin films

The starting material used for the preparation of CuO-SnO₂ nanocomposites thin films were copper chloride dehydrate (CuCl₂.2H₂O Purified Loba Chemie) and tin chloride dehydrate (SnCl₂.2H₂O Purified Merk ). Copper chloride dehydrate and tin chloride dehydrate were mixed at various volume ratio such as 30:70, 50:50 and 70:30 as indicated in Table 1. To stabilize the starting solution, a few droplets of hydrochloric acid (HCl) were added. The temperature of the substrate is maintained at a constant value by using a temperature controlled hot plate. The deposition parameters like substrate temperature (250 °C), rate of spraying solution (7 mL/min.), nozzle to substrate distance (30 cm), quantity of the solution sprayed (30 ml), pressure of carrier gas, and to and fro movement of the nozzle were kept constant. The as prepared CuO- SnO₂ nanocomposites thin films samples (S1, S2, and S3) were annealed at 500 °C for 1 h.

Table 1 Amounts of spraying solutions and reactant

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>CuCl₂.2H₂O (cm³)</th>
<th>SnCl₂.2H₂O (cm³)</th>
<th>Reactants</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>30</td>
<td>70</td>
<td>CuO:SnO₂</td>
</tr>
<tr>
<td>S2</td>
<td>50</td>
<td>50</td>
<td>CuO:SnO₂</td>
</tr>
<tr>
<td>S3</td>
<td>70</td>
<td>30</td>
<td>CuO:SnO₂</td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1. Structural analysis

Fig. 1 shows the X-ray diffractogram of CuO-SnO₂ nanocomposites thin film. The structural properties of the films were investigated using XRD. The 2θ values were varied from 20 to 80. The calculated average crystallite size was found to be 14 nm respectively.

Fig. 1. X-ray diffractogram of CuO-SnO₂ nanocomposites thin film (most sensitive sample (S2))
3.2. Surface Morphology

![SEM image of CuO-SnO₂ nanocomposites thin film](image)

**Fig. 2.** SEM image CuO-SnO₂ nanocomposites thin film (most sensitive sample (S2))

SEM imaged of CuO-SnO₂ nanocomposites was represented in Fig. 2. Grain size observed to be in the range of 23 - 33 nm.

3.3. Elemental composition using (EDAX)

Stoichiometrically expected at % of Sn, Cu and O is: 20, 20 and 60. Observed at % pure CuO - SnO₂ nanocomposites thin films were given in Table 2. It is clear from table 2, that as prepared CuO - SnO₂ nanocomposites thin films were observed to be nonstoichiometric in nature.

**Table 2** Quantitative elemental analysis as prepared CuO-SnO₂ nanocomposites thin film

<table>
<thead>
<tr>
<th>Element</th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mass %</td>
<td>at %</td>
<td>mass %</td>
</tr>
<tr>
<td>O</td>
<td>27.19</td>
<td>72.36</td>
<td>67.96</td>
</tr>
<tr>
<td>Sn</td>
<td>67.96</td>
<td>24.38</td>
<td>60.03</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>

4. Gas sensing performance of the sensors

4.1. Gas response:

![Graph](image)
Fig. 3 represents the response characteristics of the CuO-SnO\textsubscript{2} nanocomposite thin films as a function of operating temperature. Among all the films, the sample (S2) film shows the maximum response (7599) at 250 °C to 10 ppm of H\textsubscript{2}S.

4.2. Response and recovery of the sensor

The response and recovery of the CuO-SnO\textsubscript{2} nanocomposites thin film (S2) sensor on exposure of 10 ppm of H\textsubscript{2}S at 250 °C are represented in Fig. 4. The response is quick (3 s) and recovery is fast (6 s). The high oxidizing ability of adsorbed oxygen species on the surface nanoparticles and high volatility of desorbed by-products explain the quick response to H\textsubscript{2}S and fast recovery.

![Graph showing response and recovery of the sensor](image)

**Fig. 4.** Response and recovery of the sensor for most sensitive sample (S2).

**Conclusion:**

CuO-SnO\textsubscript{2} nanocomposites thin films were prepared by simple spray pyrolysis technique. The structural and microstructural properties confirm that the as-prepared CuO-SnO\textsubscript{2} nanocomposites thin films are nanostructured in nature. The CuO-SnO\textsubscript{2} thin film of (Sample S4) was most sensitive to H\textsubscript{2}S gas and exhibit the response of S = 7499 to the gas concentration as 100 ppm at the temperature of 250 °C. The CuO-SnO\textsubscript{2} nanocomposites thin films exhibit rapid response–recovery which is one of the main features of this sensor.

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Reference: