Gas Sensors Based on Pure and Copper Doped Indium Oxide

Thick film gas sensors based on pure and copper doped indium oxide were fabricated on glass substrates and studied for NO₂ and H₂S gas sensing properties. The copper doping concentration was varied in the range 0.5, 1.5 and 3wt%. The structural properties, surface morphology and compositional analysis of the prepared sensors were done. The optimum operating temperature, response time, recovery time and concentration dependent studies for both test gases were obtained for pure and doped sensors. The detection mechanism for both the test gases to pure and doped sensors was also discussed.

5.1 Introduction

Indium oxide (In₂O₃) is a wide band gap n-type semiconductor with an energy band gap 3.6 eV[1]. The wide band gap renders In₂O₃ with high optical transparency and makes it an important material for different applications. It has been widely used in window heaters, solar cells, and liquid crystal displays [2]. Properties as high transparency in the visible region and high electrical conductivity make In₂O₃ a suitable material for application in solar cells [3, 4], optoelectronic devices [5], liquid crystal displays [6], light emitting diodes [7, 8], photo voltaic devices etc.. Several deposition techniques have been used for the deposition of In₂O₃ films including chemical vapour deposition [9], RF and DC sputtering [10, 11], sol gel [12, 13], spray pyrolysis [14, 15] and electrostatic spray deposition technique [16].
Two crystal structures have been reported for \( \text{In}_2\text{O}_3 \), i.e., the bixbyite structure (rare-earth oxide-structure) which has a body centred cubic structure with space group \( \text{Ia}3 \) and lattice parameter \( a = 10.118 \text{Å} \) (JCPDS 06-0416) and the metastable corundum (\( \text{a-Al}_2\text{O}_3 \)) structure which has a rhombohedral structure with space group \( \text{R}-3c \) and lattice parameters \( a = 5.484 \text{ Å} \) and \( c = 14.508 \text{ Å} \) (JCPDC 22-336). The rare-earth structure can be transformed into the corundum structure at high temperatures (1000°C) and high pressure (65Kbar) [17]. Recently, Yu et al [18] have obtained rh-\( \text{In}_2\text{O}_3 \) nanofibers templated from \( \text{InOOH} \) nanofibers under ambient pressure.

\( \text{In}_2\text{O}_3 \) cubic form is the most stable one and the most used. In the cubic form, the cations form a nearly cubic face-centered lattice in which six out of the eight tetrahedral sites are occupied by oxygen ions. The unit cell of the crystal structure consists of eight such cubes, containing 32 cations and 48 \( \text{O}^2- \) ions. Two nonequivalent cation sites, called “C” and “D”, both with 6-fold oxygen coordination, characterize the structure. The site D is axially symmetric and can be described as a cation surrounded by six oxygen ions at the corners of a distorted cube, leaving free two corners of a diagonal body. For site C the cube is more distorted and the six oxygen ions leave free two corners of a face diagonal (Fig. 5.1) [19]. The density and melting point of bcc-\( \text{In}_2\text{O}_3 \) have been reported to be 7.18 g/cm\(^3\) and 1912°C, respectively [20]. A thermal expansion coefficient of 7.20 ± 0.06 1/K [21], thermal capacity of 99.01 J/Kmol at 300 K [22], permittivity \( (\varepsilon_{\infty}) \) of 4 [23] and refraction index in the visible range of 2.0 ± 0.1 [24] was reported in the literature.
The nearest –neighbor oxygen distribution around each cationic site C and D in the In$_2$O$_3$ bixbyite structure.

In$_2$O$_3$ in stoichiometric form is an insulator and in non-stoichiometric form is an n-type semiconductor material. As the surface conductance mechanism is influenced by the semiconductor metal oxide (SMO) material’s non-stoichiometric composition, the non-stoichiometry of In$_2$O$_3$ will be discussed. The chemical formulas for oxides and inorganic compounds are usually written to indicate that there is a definite ratio of cations to anions in the compound, e.g. M$_a$O$_b$, where a and b are usually small integers determined by the valency of constituents atoms. When the oxide M$_a$O$_b$ does contain M and O atoms in the exact ratio a/b, it is said to have a stoichiometric composition. However numerous metal oxides exhibits marked deviation from stoichiometry. In a compound, non-stoichiometry is equivalent to the presence of point defects in the crystal lattice compared to the stoichiometric conditions and the extent of nonstoichiometry is measured by the net concentration of the corresponding defects. Non-stoichiometry in metal oxides can be of two main types with respect to stoichiometric composition [25].

1) Oxygen deficient (or excess metal) - the main defects can be either oxygen vacancies or interstitial metal ions (excess metal), both of these defects lead to the formation of complimentary free electrons.
Therefore the conductivity is due to the transport of electrons and oxygen deficient oxides are characterized by n-type conductivity.

2) Metal deficient (or excess oxygen) - the predominant defects can be either metal vacancies or interstitial oxygen atoms (excess oxygen). The formation of charged metal ion vacancies leads to the formation of complimentary positive (charge carriers, holes). Therefore the conductivity involves the transport of holes and metal deficient oxides are characterised by p-type conductivity [25].

Generally, In$_2$O$_3$ crystal structure is not ideal since oxygen vacancies are present. In an In$_2$O$_3$ film an oxygen deficiency is observed mainly in the form of oxygen vacancies [26]. These act as doubly charged donors providing electrons to the conduction band. However, it has also been reported that In$_2$O$_3$ films oxygen deficient non-stoichiometry might be due to the presence of excess indium compared to the stoichiometric composition [27]. In this case, the dominant defects are interstitial In$^{3+}$ cations but the possible contributions of these defects to the conductivity are low. Therefore, it can be stated that the main contributors to the conductivity of the oxygen deficient non-stoichiometric In$_2$O$_3$ films are the oxygen vacancies. Oxygen vacancies dominate the conduction mechanism of In$_2$O$_3$. The accurate formula of In$_2$O$_3$ is In$_2$O$_{3-x}$ (V$_O$)$_x$, where V$_O$ is donor-like doubly-charged oxygen vacancy, and $x$ is the oxygen vacancy portion and depends on the oxidation state. Thus, a variety of electrical properties can be obtained (metallic, semiconducting, or insulating behaviour) depending on the stoichiometry, without any further impurity doping.

The electrical properties of In$_2$O$_3$ thin films reported in the literature for semiconducting, or insulating In$_2$O$_3$ have been obtained by different methods [28]. Among them, doping, variation of growth parameter and post
Gas sensors based on pure and copper doped indium oxide are frequently used. Doping In$_2$O$_3$ with Sn is used often to fabricate the ITO films used as transparent conducting electrodes. In order to alter the electrical properties, variation of growth parameters, such as the growth temperature and the content of the process gas, have frequently been used. Adurodija et al. varied substrate temperature and oxygen pressure by means of a pulsed laser deposition process [29]. By increasing the oxygen pressure, the electron density can be reduced by two orders of magnitude. By optimizing the substrate temperature, the electron density can be further reduced by one order of magnitude, while the electron mobility remains nearly constant. Similar results were obtained by Yamada et al. [30]. By varying the He/O$_2$ pressure in a pulsed laser ablation process, the volume resistivity can be increased from $\sim 10^3 \, \Omega \cdot \text{cm}$ up to more than $10^2 \, \Omega \cdot \text{cm}$. One of the other important methods to change the electrical properties is post annealing. Post annealing parameters, such as annealing atmosphere, gas content (normally oxygen content), and annealing temperature, can also change the electrical properties drastically [31-34]. Oxygen gas annealing can significantly increase the film resistivity as well as the internal stress of the film, which can arise at an annealing temperature as low as 100°C [31]. Alam et al. reported that by changing the annealing temperature, the film resistivity can also be altered by more than one order of magnitude [32].

In$_2$O$_3$ in non-stoichiometric form is an n-type semiconductor material suitable for gas sensing applications [35]. During recent years In$_2$O$_3$ became a very interesting material for gas sensor applications, being the best material which allows detection of ozone in the ppb range [36]. In 1993 Takada first reported an O$_3$ sensor using an In$_2$O$_3$ thin film [37]. Since then different deposition techniques, e.g. spray pyrolysis, spin coating, sol-gel method and magnetron sputtering have been used to enhance the sensitivity of In$_2$O$_3$ thin films [38]. The sensitivity of In$_2$O$_3$ can be attributed to the
oxygen vacancies in the films; by controlling the oxygen deficiency, the conductivity of \( \text{In}_2\text{O}_3 \) films can be altered [35]. For the application as a gas sensing material, the electrical properties of this material are very important.

### 5.2 Review of \( \text{In}_2\text{O}_3 \) for Gas Sensing

A short review of \( \text{In}_2\text{O}_3 \) gas sensors for the detection of Ozone (\( \text{O}_3 \)), Hydrogen (\( \text{H}_2 \)), Carbon monoxide (\( \text{CO} \)), Hydrogen Sulphide (\( \text{H}_2\text{S} \)), Nitrogen dioxide (\( \text{NO}_2 \)), Nitric oxide(\( \text{NO} \)) is given in tables below (Table 5.1-5.6).

Table 5.1: Summary of published results on \( \text{O}_3 \) gas sensing characteristics of \( \text{In}_2\text{O}_3 \).

<table>
<thead>
<tr>
<th>Material</th>
<th>Concentration (ppm)</th>
<th>Temperature (°C)</th>
<th>Sensitivity</th>
<th>Year</th>
<th>Method of preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{In}_2\text{O}_3 : \text{MoO}_3 )</td>
<td>1</td>
<td>200</td>
<td>4</td>
<td>1998</td>
<td>Sol-gel [39]</td>
</tr>
<tr>
<td>( \text{In}_2\text{O}_3 : \text{Au} )</td>
<td>0.03</td>
<td>300</td>
<td>40</td>
<td>1999</td>
<td>RF sputtering [40]</td>
</tr>
<tr>
<td>( \text{In}_2\text{O}_3 : \text{Fe}_2\text{O}_3 )</td>
<td>0.1</td>
<td>550</td>
<td>10</td>
<td>2000</td>
<td>Thick film paste [41]</td>
</tr>
<tr>
<td>( \text{In}_2\text{O}_3 : \text{MoO}_3 )</td>
<td>0.2</td>
<td>130</td>
<td>22</td>
<td>2001</td>
<td>Sol-gel [42]</td>
</tr>
<tr>
<td>( \text{In}_2\text{O}_3 : \text{Fe}_2\text{O}_3 )</td>
<td>0.1</td>
<td>135</td>
<td>450</td>
<td>2003</td>
<td>Sol-gel [43]</td>
</tr>
<tr>
<td>( \text{In}_2\text{O}_3 )</td>
<td>1</td>
<td>270</td>
<td>1000</td>
<td>2005</td>
<td>Spray pyrolysis [44]</td>
</tr>
<tr>
<td>( \text{In}_2\text{O}_3 : \text{Fe}_2\text{O}_3 )</td>
<td>0.08</td>
<td>250</td>
<td>28.3</td>
<td>2006</td>
<td>Rheotaxial growth and thermal oxidation (RGTO) deposition [45]</td>
</tr>
<tr>
<td>( \text{In}_2\text{O}_3 ) nanowires</td>
<td>0.280</td>
<td>400</td>
<td>10</td>
<td>2007</td>
<td>Evaporation [46]</td>
</tr>
<tr>
<td>( \text{In}_2\text{O}_3 )</td>
<td>0.200</td>
<td>200</td>
<td>600</td>
<td>2008</td>
<td>Sol-gel [47]</td>
</tr>
</tbody>
</table>

* The sensitivity values presented in this table are taken directly from the respective literature. Their magnitude cannot be compared as different authors have used different formula to calculate sensitivity. The main intent of this table is to highlight the published results on \( \text{In}_2\text{O}_3 \) based gas sensors.
### Table 5.2: Summary of published results on O₃ gas sensing characteristics of In₂O₃

<table>
<thead>
<tr>
<th>Material</th>
<th>Concentration (ppm)</th>
<th>Temperature (°C)</th>
<th>*Sensitivity</th>
<th>Year (reference)</th>
<th>Method of preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>In₂O₃ : Pd</td>
<td>400</td>
<td>220</td>
<td>531</td>
<td>1993</td>
<td>Vacuum evaporated [48]</td>
</tr>
<tr>
<td>In₂O₃</td>
<td>1000</td>
<td>350</td>
<td>88</td>
<td>1998</td>
<td>Spin coating [49]</td>
</tr>
<tr>
<td>In₂O₃ : Ho₂O₃</td>
<td>100</td>
<td>195</td>
<td>4.5</td>
<td>2006</td>
<td>Sol-gel [50]</td>
</tr>
<tr>
<td>In₂O₃ : SnO₂</td>
<td>50</td>
<td>300</td>
<td>2.42</td>
<td>2009</td>
<td>Thick film paste [51]</td>
</tr>
<tr>
<td>In₂O₃ : ZnO</td>
<td>2000</td>
<td>350</td>
<td>7</td>
<td>2011</td>
<td>Vapour deposition [52]</td>
</tr>
</tbody>
</table>

### Table 5.3: Summary of published results on CO gas sensing characteristics of In₂O₃

<table>
<thead>
<tr>
<th>Material</th>
<th>Concentration (ppm)</th>
<th>Temperature (°C)</th>
<th>*Sensitivity</th>
<th>Year (reference)</th>
<th>Method of preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>In₂O₃</td>
<td>1000</td>
<td>350</td>
<td>44</td>
<td>1998</td>
<td>Spin coating [49]</td>
</tr>
<tr>
<td>In₂O₃ : Ho₂O₃</td>
<td>100</td>
<td>195</td>
<td>47</td>
<td>2006</td>
<td>Sol-gel [50]</td>
</tr>
<tr>
<td>In₂O₃ : SnO₂</td>
<td>1000</td>
<td>300</td>
<td>7.5</td>
<td>2008</td>
<td>Sol-gel [53]</td>
</tr>
<tr>
<td>In₂O₃</td>
<td>50</td>
<td>250</td>
<td>4</td>
<td>2008</td>
<td>Sol-gel [54]</td>
</tr>
<tr>
<td>In₂O₃ : SnO₂</td>
<td>50</td>
<td>300</td>
<td>1.56</td>
<td>2009</td>
<td>Thick film paste [51]</td>
</tr>
<tr>
<td>In₂O₃ : Hollow spheres</td>
<td>10</td>
<td>400</td>
<td>3.81</td>
<td>2009</td>
<td>Thick film paste [55]</td>
</tr>
<tr>
<td>In₂O₃ : nanofibers</td>
<td>100</td>
<td>300</td>
<td>5</td>
<td>2010</td>
<td>Electrospinning [56]</td>
</tr>
<tr>
<td>In₂O₃ : Zn nanowires</td>
<td>400</td>
<td>300</td>
<td>22</td>
<td>2012</td>
<td>Vapour deposition [52]</td>
</tr>
</tbody>
</table>

### Table 5.4: Summary of published results on H₂S gas sensing characteristics of In₂O₃

<table>
<thead>
<tr>
<th>Material</th>
<th>Concentration (ppm)</th>
<th>Temperature (°C)</th>
<th>*Sensitivity</th>
<th>Year (reference)</th>
<th>Method of preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>In₂O₃ : Ho₂O₃</td>
<td>10</td>
<td>195</td>
<td>1061</td>
<td>2006</td>
<td>Sol-gel [50]</td>
</tr>
<tr>
<td>In₂O₃</td>
<td>50</td>
<td>269</td>
<td>125</td>
<td>2006</td>
<td>Thick film paste [57]</td>
</tr>
<tr>
<td>In₂O₃ whiskers</td>
<td>10</td>
<td>Room temperature</td>
<td>30</td>
<td>2008</td>
<td>Thin film [58]</td>
</tr>
<tr>
<td>In₂O₃ : SnO₂</td>
<td>10</td>
<td>300</td>
<td>4.98</td>
<td>2009</td>
<td>Thick film paste [51]</td>
</tr>
<tr>
<td>In₂O₃ : nanotubes</td>
<td>20</td>
<td>Room temperature</td>
<td>166</td>
<td>2010</td>
<td>Electrospinning [59]</td>
</tr>
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</table>
Table 5.5: Summary of published results on NO₂ gas sensing characteristics of In₂O₃

<table>
<thead>
<tr>
<th>Material</th>
<th>Concentration (ppm)</th>
<th>Temperature (°C)</th>
<th>Sensitivity</th>
<th>Year (reference)</th>
<th>Method of preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>In₂O₃ : SnO₂</td>
<td>250</td>
<td>250</td>
<td>7.5</td>
<td>1988</td>
<td>RF magnetron sputtering [60]</td>
</tr>
<tr>
<td>In₂O₃</td>
<td>1</td>
<td>150</td>
<td>60</td>
<td>1997</td>
<td>Sol-gel [61]</td>
</tr>
<tr>
<td>In₂O₃ : MoO₃</td>
<td>1</td>
<td>250</td>
<td>23</td>
<td>1998</td>
<td>Sol-gel [39]</td>
</tr>
<tr>
<td>In₂O₃</td>
<td>0.7</td>
<td>250</td>
<td>10</td>
<td>2000</td>
<td>Sol-gel [62]</td>
</tr>
<tr>
<td>In₂O₃</td>
<td>0.7</td>
<td>250</td>
<td>7</td>
<td>2000</td>
<td>High vacuum thermal evaporation [62]</td>
</tr>
<tr>
<td>In₂O₃-NiO</td>
<td>1 ppm</td>
<td>150</td>
<td>40</td>
<td>2000</td>
<td>Sol-gel [63]</td>
</tr>
<tr>
<td>In₂O₃</td>
<td>10 ppm</td>
<td>350</td>
<td>212</td>
<td>2000</td>
<td>R.F sputtering [64]</td>
</tr>
<tr>
<td>In₂O₃ : Au</td>
<td>10 ppm</td>
<td>350</td>
<td>14.26</td>
<td>2001</td>
<td>R.F sputtering [65]</td>
</tr>
<tr>
<td>In₂O₃</td>
<td>0.500</td>
<td>54</td>
<td>1000</td>
<td>2002</td>
<td>Laser ablation [66]</td>
</tr>
<tr>
<td>In₂O₃ : Fe₂O₃</td>
<td>5</td>
<td>100</td>
<td>600</td>
<td>2003</td>
<td>Sol-gel [43]</td>
</tr>
<tr>
<td>In₂O₃ : SnO₂</td>
<td>5</td>
<td>250</td>
<td>175</td>
<td>2006</td>
<td>Sol-gel [67]</td>
</tr>
<tr>
<td>In₂O₃ : Gd₂O₃</td>
<td>100</td>
<td>195</td>
<td>79</td>
<td>2006</td>
<td>Sol-gel [50]</td>
</tr>
<tr>
<td>In₂O₃ : Fe₂O₃</td>
<td>0.5</td>
<td>135</td>
<td>75</td>
<td>2007</td>
<td>Sol-gel [68]</td>
</tr>
<tr>
<td>In₂O₃ nanowires</td>
<td>1</td>
<td>250</td>
<td>2.57</td>
<td>2008</td>
<td>Thick film paste [69]</td>
</tr>
<tr>
<td>In₂O₃</td>
<td>10</td>
<td>250</td>
<td>154</td>
<td>2010</td>
<td>Thick film paste [70]</td>
</tr>
<tr>
<td>In₂O₃ nanoribbon</td>
<td>5</td>
<td>200</td>
<td>70</td>
<td>2012</td>
<td>Electrospinning method [71]</td>
</tr>
<tr>
<td>In₂O₃</td>
<td>6</td>
<td>200</td>
<td>61</td>
<td>2012</td>
<td>AC electrophoresis deposition [72]</td>
</tr>
<tr>
<td>In₂O₃</td>
<td>0.050</td>
<td>Room temperature</td>
<td>32</td>
<td>2012</td>
<td>Thick film paste [73]</td>
</tr>
<tr>
<td>In₂O₃ microspheres</td>
<td>5</td>
<td>250</td>
<td>1.5</td>
<td>2013</td>
<td>Thick film paste [74]</td>
</tr>
<tr>
<td>In₂O₃ microspheres</td>
<td>0.500</td>
<td>150</td>
<td>74</td>
<td>2013</td>
<td>Thick film paste [75]</td>
</tr>
</tbody>
</table>
Table 5.6: Summary of published results on NO gas sensing characteristics of In$_2$O$_3$

<table>
<thead>
<tr>
<th>Material</th>
<th>Concentration (ppm)</th>
<th>Temperature (°C)</th>
<th>Sensitivity</th>
<th>Year (reference)</th>
<th>Method of preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>In$_2$O$_3$:Se</td>
<td>3</td>
<td>150</td>
<td>8</td>
<td>1999</td>
<td>Thermal evaporation [76]</td>
</tr>
<tr>
<td>In$_2$O$_3$</td>
<td>0.500</td>
<td>54</td>
<td>100</td>
<td>2002</td>
<td>Laser ablation [66]</td>
</tr>
<tr>
<td>In$_2$O$_3$</td>
<td>100</td>
<td>150</td>
<td>1000</td>
<td>2008</td>
<td>Metal organic chemical vapor deposition [77]</td>
</tr>
<tr>
<td>In$_2$O$_3$</td>
<td>10</td>
<td>150</td>
<td>25</td>
<td>2010</td>
<td>Thick film paste [78]</td>
</tr>
<tr>
<td>In$_2$O$_3$:Au</td>
<td>25</td>
<td>500</td>
<td>25</td>
<td>2010</td>
<td>RF Sputtering [79]</td>
</tr>
</tbody>
</table>

In addition to the detection of above gases, In$_2$O$_3$ based gas sensors are used for the detection of alcohol vapour [80], ethanol [53, 81-83], ammonia [84,85], methanol [86], humidity [87], propane [88], Acetone [89], formaldehyde [89,90], toluene [89, 91, 92], Heptanes [89].

5.3 Motivation of the Work

Compared to other semiconducting metal oxides like ZnO, WO$_3$, SnO$_2$, In$_2$O$_3$ is a comparatively new candidate for gas sensing studies. The literature review shows that in pure form itself the material is a very good sensor for the detection of many gases and vapour. In the present work the gas sensing properties of pure and doped In$_2$O$_3$ thick film sensor to the test gases NO$_2$ and H$_2$S is studied. In our studies the dopant used for enhancing the gas sensing property of pure In$_2$O$_3$ sensor is copper. The effect of copper doping on the gas sensing properties of In$_2$O$_3$ had not studied yet. This chapter deals with the preparation of nanopowders, fabrication of gas sensor, characterization and...
gas sensing properties of pure and copper doped In$_2$O$_3$ sensor. The structural properties, surface morphology and compositional analysis of obtained materials were characterized with XRD, Raman Spectroscopy, SEM and EDS. Sensors were evaluated at different working temperature under one concentration of the target gas in air to find the optimum working temperature. Sensor response to different concentration of target gas is studied at this optimum temperature. The mechanism involved in the detection of pure and copper doped tungsten oxide to both NO$_2$ and H$_2$S gas is also discussed.

5.4 Gas Sensor Fabrication

99.999% pure In$_2$O$_3$ powder was purchased from Sigma Aldrich. The powder was thoroughly powdered in mortar. For the preparation of pure In$_2$O$_3$ sensors the mortar powdered In$_2$O$_3$ powder was used. Copper doping in In$_2$O$_3$ was done by powder impregnation method. Depending upon the wt% of copper doping, known amount of copper acetate monohydrate was dissolved in water. The required ml of dissolved copper acetate solution is added drop wise into pre determined amount of In$_2$O$_3$ powder. The resultant mixture was thoroughly stirred continuously for two days. It was then dried at 100°C overnight. The copper doping concentration was varied from 0.5, 1.5 and 3wt%. For fabrication of thick film sensor the powder was dispersed in methanol, coated on substrate and annealed at an ~ temperature of 600°C overnight. The films thus prepared had an approximate thickness of 20µm.

5.5 Structural and Spectroscopic Characterization

5.5.1 XRD Characterization

The crystalline structure and particle size of the 600°C annealed pure and copper doped In$_2$O$_3$ thick film sensor were examined by X-ray diffraction measurement (XRD, Bruker AXS D8 Advance). Fig. 5.2 shows
the XRD spectra of pure and copper doped In$_2$O$_3$ annealed at 600°C overnight. The 0.5, 1.5 and 3 wt% copper doped In$_2$O$_3$ sensors are denoted as I + 0.5wt% Cu, I + 1.5wt% Cu and I + 3wt% Cu respectively. The XRD spectrum revealed the cubic bixbyite phase with preferred (222) orientation (JCPDS CAS No. 06-0416). Therefore the thick film sensor of pure and doped In$_2$O$_3$ obtained after annealing at 600°C was crystalline in nature. No additional peaks were observed due to copper doping. A small shift for (222) peak was observed towards lower theta side, probably due to copper doping. The intensity of all the major peaks was found to decrease with copper doping.

![Fig. 5.2 XRD patterns of pure and copper doped In$_2$O$_3$ thick film sensor annealed at 600°C](image)

The crystallite size (D) was calculated from peak broadening using the Scherrer approximation, which is defined as

$$D = \frac{0.9 \lambda}{B \cos \theta}$$  \hspace{1cm} (5.1)

Where $\lambda$ is the wavelength of the X-ray (1.5418 Å), $B$ is the full width at half maximum (FWHM, radian) and $\theta$ is the Bragg angle (degree). The particle size was estimated individually from the FWHM of each plane and the average of all the planes were taken to obtain the average particle size.
The average particle size of the pure In$_2$O$_3$, 0.5wt%, 1.5wt%, 3wt% copper doped thick film sensor were found to be 24nm, 23nm, 24nm and 25nm respectively. Hence the pure and copper doped sensor obtained after annealing was identified by XRD as nanocrystalline in nature.

5.5.2 Scanning Electron Microscopy

Fig. 5.3 shows the SEM image of pure and copper doped In$_2$O$_3$ thick film sensor annealed at 600°C overnight. Highly textured films were obtained after annealing at 600°C.

![SEM images of pure and copper doped In$_2$O$_3$ thick film sensor](image_url)
Separate particles are not visualized in the SEM images. Mainly particle agglomeration was found in the thick film sensors. Particles with not much definite shape are found in the SEM images for both pure and copper doped In$_2$O$_3$ sensors. Copper addition did not show any effect on the surface morphology or particle size of the sensor elements as confirmed by the XRD results.

**5.5.3 EDS**

The EDS spectrum of 600$^\circ$C annealed pure In$_2$O$_3$ thick film sensor obtained is shown in fig. 5.4. Spectrum reveals presence of indium and oxygen elements only. Fig. 5.5 shows the EDS spectrum of 3wt% copper doped In$_2$O$_3$ thick film sensor. Spectrum gives clear evidence for presence of copper in the doped samples.

![Fig. 5. 4 EDS spectrum of 600$^\circ$C annealed pure In$_2$O$_3$ thick film sensor.](image-url)
Fig. 5.5 EDS spectrum of 600°C annealed 3wt% copper doped In$_2$O$_3$ thick film sensor.

5.5.4 Raman Spectroscopy

Fig. 5.6 Raman spectra of 600°C annealed pure and copper doped In$_2$O$_3$ thick film sensor

Raman spectroscopy was used to further investigate the local chemical structure of the In$_2$O$_3$ based sensor films. The Raman spectrum of pure and
Gas sensors based on pure and copper doped indium oxide

copper doped In₂O₃ thick film sensor is shown in fig. 5.6. The 0.5, 1.5 and 3wt% copper doped In₂O₃ sensors are denoted as I + 0.5wt% Cu, I + 1.5wt% Cu and I + 3wt% Cu respectively. Peaks are observed at 308, 367, 497, and 630 cm⁻¹ and these are in general agreement with those values previously reported in the literature [92, 93]. The peak at 308 cm⁻¹ corresponds to the δ(InO₆) bending vibration of InO₆ octahedra. The 367 cm⁻¹ peak can be assigned to the stretching vibrations of In–O–In linkages, while peaks at 497 and 630 cm⁻¹ can be attributed to octahedral stretching vibrations ν(InO₆). Significant decrease in intensity of all the main peaks was observed in the copper doped sensors.

5.6 Gas Sensors Based on Pristine In₂O₃

5.6.1 Nitrogen Dioxide Detection

Response of the thick film sensor towards a low concentration of 7 ppm was studied in the temperature range of 50 to 200°C. The sensor response of sensor was measured as ratio of resistance \( \frac{R_{\text{gas}}}{R_{\text{air}}} \), here \( R_{\text{gas}} \) is resistance of the sensor in presence of gas and \( R_{\text{air}} \) is the resistance of the sensor before the introduction of gas. Fig. 5.7 (a) to (g) shows response of In₂O₃ thick film sensor at different temperatures towards the concentration of 7 ppm. The response time is taken as the time taken by the sensor to reach 90% of maximum value and recovery time is taken as the time taken by the sensor to reach 10% of base value (value before the introduction of gas) in all the measurements.
Fig. 5.7 Response of In$_2$O$_3$ thick film sensor towards 7 ppm of NO$_2$ gas at (a) 50$^\circ$C, (b) 75$^\circ$C, (c) 100$^\circ$C, (d) 125$^\circ$C, (e) 150$^\circ$C, (f) 175$^\circ$C, (g) 200$^\circ$C.
Gas sensors base on pure and copper doped indium oxide

Fig. 5.8 (a) shows the sensitivity of thick film In$_2$O$_3$ sensor to 7 ppm NO$_2$ gas at various temperatures. Here the sensitivity value is taken as the maximum response value corresponding to respective temperature in fig. 5.7 (a) to (g). The sensor showed maximum sensitivity of 2.82 at 100$^\circ$C. The sensitivity decreases beyond this temperature. As the temperature increases beyond 150$^\circ$C the sensor resistance is not stable and this causes increased disturbance in the measurement. Fig. 5.7 (g) shows that at working temperature of 200$^\circ$C the disturbance is very high indicating that thick film sensor cannot operate satisfactorily at this temperature.

![Graphs showing sensitivity, response time, and recovery time of In$_2$O$_3$ thick film sensor towards 7 ppm of NO$_2$ gas at different temperatures.]

Fig. 5.8 (a) Sensitivity (b) Response time (c) Recovery time of In$_2$O$_3$ thick film sensor towards 7 ppm of NO$_2$ gas at different temperatures
Considering the maximum sensitivity, response and recovery time, 100°C is considered as the optimum temperature for the gas sensing measurement. Fig. 5.8 (b) and (c) shows the response and recovery time of the In$_2$O$_3$ thick film sensor at different temperature. At the optimum temperature of 100°C the response and recovery time was found to be 40 seconds and 12.27 minutes respectively. The response time at this temperature is found to be relatively high and the recovery time is found to be relatively low.

Concentration dependent studies were performed at this optimum temperature. Fig. 5.9 (a) & (b) shows the concentration dependent studies performed. Fig. 5.10 shows the sensitivity of the sensor to different concentration. The maximum concentration studied with the set up was 57 ppm with a sensitivity of 43.5 and minimum concentration was 1.79 ppm with a sensitivity of 1.1.

![Fig. 5.9 (a) & (b) Response of In$_2$O$_3$ thick film sensor towards different concentrations of NO$_2$ at 100°C](image)
Gas sensors base on pure and copper doped indium oxide

Fig. 5.10 Sensitivity of In$_2$O$_3$ thick film sensor towards different concentrations of NO$_2$ at 100°C

6.2 Hydrogen Sulphide Detection

The sensor response in case of reducing H$_2$S gas was calculated as ratio of $\frac{R_{\text{air}}}{R_{\text{gas}}}$, here $R_{\text{air}}$ is resistance of thick film sensor before introduction of gas and $R_{\text{gas}}$ is resistance of sensor in presence of gas. The temperature dependent measurements were found to be not satisfactory in terms of response and recovery times and hence only room temperature measurements were done. Fig. 5.11 (a) and (b) shows the concentration dependent measurements performed at room temperature.

Fig. 5.11 (a) & (b) Response of In$_2$O$_3$ thick film sensor towards different concentrations of H$_2$S at room temperature.
Since the recovery time for H$_2$S sensing was very high for the pure In$_2$O$_3$ thick film sensors the maximum concentration studied was limited to 57 ppm.

The lowest measured concentration was 3.57 ppm with a sensitivity of 1.1. For 57 ppm concentration the sensor measured a sensitivity of 95. The sensitivity of the sensor to different concentrations studied is shown in fig. 5.12 (a). The response and recovery time of the pure In$_2$O$_3$ thick film sensor to different concentrations studied is shown in fig. 5.12 (b) and (c).

![Graphs showing sensitivity, response time, and recovery time](image)

Fig. 5.12 (a) Sensitivity (b) Response time (c) Recovery time of In$_2$O$_3$ thick film sensor towards different concentrations of H$_2$S gas at room temperature

**5.7 Gas Sensors Based on 0.5wt% Copper Doped In$_2$O$_3$**

**5.7.1 Nitrogen Dioxide Detection**

Response of the sensor towards a concentration of 7 ppm of NO$_2$ gas was studied in the temperature range of 50 to 200°C. Fig. 5.13 (a) to (g) shows response of sensor at different temperatures towards this concentration.
Gas sensors based on pure and copper doped indium oxide

Fig. 5.13  Response of 0.5 wt% copper doped In$_2$O$_3$ thick film sensor towards 7 ppm of NO$_2$ gas at (a) 50°C, (b) 75°C, (c) 100°C, (d) 125°C, (e) 150°C, (f) 175°C, (g) 200°C.
The sensitivity of sensor at different temperatures towards the concentration of 7 ppm is shown in fig. 5.14 (a). Temperature dependent gas sensing measurements shows that 100°C is the optimum operating temperature of the 0.5wt% copper doped In$_2$O$_3$ sensor. Beyond this temperature the sensitivity decreases. The response of the sensor at this temperature is 7.29. The response and recovery time of the sensor to different temperatures are shown in fig. 5.14 (b) and (c) respectively. At optimum temperature of 100°C the 0.5wt% copper doped sensor had a response time of 9 seconds and recovery time of 8.03 minutes. Response and recovery time recorded at this temperature are relatively small.

Fig. 5.14 (a) Sensitivity (b) Response time (c) Recovery time of 0.5 wt% copper doped In$_2$O$_3$ thick film sensor towards 7 ppm of NO$_2$ gas at different temperatures
Concentration dependent studies performed at optimum temperature of 100°C are shown in fig. 5.15. The lowest measurable concentration was found to be 1.79 ppm with a sensitivity of 1.16. The highest measured concentration with the set up was 28.58 ppm with a sensitivity of 35.4. The sensitivity of the sensor to different concentrations of the NO₂ gas studied is shown in fig. 5.16.

![Graph showing response to different concentrations of NO₂](image1)

**Fig. 5.15** Response of 0.5wt% copper doped In₂O₃ thick film sensor towards different concentrations of NO₂ at 100°C.

![Graph showing sensitivity vs concentration](image2)

**Fig. 5.16** Sensitivity of 0.5wt% copper doped In₂O₃ thick film sensor towards different concentrations of NO₂ at 100°C.
5.7.2 Hydrogen Sulphide Detection

Sensor response towards different concentrations of H$_2$S gas measured at room temperature is shown in fig. 5.17 (a) and (b). Only room temperature measurements were performed. The temperature dependent gas sensing measurements were found to be unsatisfactory in this case also.

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

Fig. 5.17 (a) & (b) Response of 0.5wt% copper doped In$_2$O$_3$ thick film sensor towards different concentrations of H$_2$S at room temperature.

The sensitivity of 0.5wt% copper doped In$_2$O$_3$ thick film sensor to the concentration studied is shown in fig. 5.18 (a). Due to the large recovery time of the sensor the concentration dependent studies were limited to 28.58 ppm. The response and recovery times of the sensor to the concentration studied are shown in fig. 5.18 (b) and (c).
Gas sensors based on pure and copper doped indium oxide

Fig. 5.18 (a) Sensitivity (b) Response time (c) Recovery time of 0.5wt% copper doped In$_2$O$_3$ thick film sensor towards different concentrations of H$_2$S gas at room temperature

5.8 Gas Sensors Based on 1.5wt% Copper Doped In$_2$O$_3$

5.8.1 Nitrogen Dioxide Detection

Response of sensor towards a concentration of 7 ppm of NO$_2$ gas studied in the temperature range of 50 to 200$^\circ$C is presented in the figures 5.19 (a) to (g).
Fig. 5.19 Response of 1.5 wt% copper doped In$_2$O$_3$ thick film sensor towards 7 ppm of NO$_2$ gas at (a) 50$^\circ$C (b) 75$^\circ$C (c) 100$^\circ$C (d) 125$^\circ$C (e) 150$^\circ$C (f) 175$^\circ$C (g) 200$^\circ$C
Sensitivity of sensor at different temperatures towards this concentration of 7 ppm is shown in fig. 5.20 (a). At 50 and 75°C the recovery time is very large and hence the measurement was discontinued. Temperature dependent gas sensing behaviour shows that optimum operating temperature for 1.5wt% copper doped In$_2$O$_3$ sensor is 100°C with a response of 8.72. The response and recovery times at this temperature were 9 seconds and 6 minutes respectively. Response and recovery times of sensor at different temperatures for the 7 ppm concentration are shown in fig. 5.20 (b) and (c). Response and recovery times of the sensor at this temperature show a relatively small value.

Fig. 5.20 (a) Sensitivity (b) Response time (c) Recovery time of 1.5 wt% copper doped In$_2$O$_3$ thick film sensor towards 7 ppm of NO$_2$ gas at different temperatures
The concentration dependent studies conducted at his optimum temperature of 100°C show that lowest measured concentration is 1.79 ppm with a sensitivity of 1.21. The highest measured concentration with the set up was 28.58 ppm with a sensitivity of 38.74. Fig. 5.21 (a) and (b) shows response of sensor towards different concentration at the optimal temperature of 100°C. Fig. 5.22 shows sensitivity towards different concentrations at 100°C.

Fig. 5.21 (a) and (b) Response of 1.5wt% copper doped In$_2$O$_3$ thick film sensor towards different concentrations of NO$_2$ at 100°C.

Fig. 5.22 Sensitivity of 1.5wt% copper doped In$_2$O$_3$ thick film sensor towards different concentrations of NO$_2$ at 100°C.
5.8.2 Hydrogen Sulphide Detection

Response of 1.5wt% copper doped In$_2$O$_3$ sensor towards different concentration of H$_2$S gas measured at room temperature is shown in fig.5.23 (a), (b), (c) and (d).

![Fig. 5.23 (a) (b) (c) and (d) Response of 1.5wt% copper doped In$_2$O$_3$ thick film sensor towards different concentrations of H$_2$S at room temperature.](image)

Sensitivity of sensor to different concentrations of H$_2$S gas at room temperature is shown in fig. 5.24 (a). The minimum measured concentration was found to be 3.57 ppm with a sensitivity of 1.15. The maximum...
concentration studied with the set up was 286 ppm with a sensitivity of 1055. The response and recovery time of the sensor to different concentrations at room temperature is shown in fig. 5.24 (b) and (c).

![Graphs showing sensitivity, response time, and recovery time of the sensor.]

Fig. 5.24 (a) Sensitivity (b) Response time (c) Recovery time of 1.5 wt% copper doped In$_2$O$_3$ thick film sensor towards different concentrations of H$_2$S gas at room temperature.

5.9 Gas Sensors Based on 3wt% Copper Doped In$_2$O$_3$

5.9.1 Nitrogen Dioxide Detection

Response of sensor towards a concentration of 7ppm of NO$_2$ gas was studied in temperature range of 50 to 200$^\circ$C. Fig. 5.25 (a) to (g) shows response of sensor at different temperatures towards this concentration.
Gas sensors based on pure and copper doped indium oxide.

Fig. 5.25 Response of 3wt% copper doped In$_2$O$_3$ thick film sensor towards 7 ppm of NO$_2$ gas at (a) 50°C (b) 75°C (c) 100°C (d) 125°C (e) 150°C (f) 175°C (g) 200°C.

Development of semiconductor metal oxide gas sensors for the detection of NO$_2$ and H$_2$S gases.
Sensitivity of sensor at different temperatures towards a concentration of 7 ppm is shown in fig. 5.26 (a). The corresponding response and recovery time of 3wt% copper doped In$_2$O$_3$ sensor at different operating temperatures is shown in fig. 5.26 (b) and (c) respectively. Due to very large recovery time the measurement was discontinued at 50°C. Maximum sensitivity was achieved at an operating temperature of 100°C with a response of 8.83. The response and recovery times at this optimum temperature was found to be 6 seconds and 4 minutes respectively. Marked improvement in sensitivity, response and recovery time were obtained at this temperature.

![Graphs showing sensitivity, response time, and recovery time](image)

Fig. 5.26 (a) Sensitivity (b) Response time (c) Recovery time of 3wt% copper doped In$_2$O$_3$ thick film sensor towards 7 ppm of NO$_2$ gas at different temperatures
The concentration dependent studies at this temperature are shown in fig. 5.27 (a) and (b). The lowest measured concentration was 1.79 ppm with a response of 1.32 and maximum measured concentration with the set up was 28.58 ppm with a response of 41.32. Fig. 5.28 shows the sensitivity towards different concentration at 100°C.

Fig. 5.27 (a) & (b) Response of 3wt% copper doped In$_2$O$_3$ thick film sensor towards different concentrations of NO$_2$ at 100°C.

Fig. 5.28 Sensitivity of 3wt% copper doped In$_2$O$_3$ thick film sensor towards different concentrations of NO$_2$ at 100°C.
5.9.2 Hydrogen Sulphide Detection

Response of 3wt% copper doped In$_2$O$_3$ sensor towards different concentrations of H$_2$S gas measured at room temperature is shown in fig. 5.29 (a), (b), (c) and (d).

Fig. 5.29 (a), (b), (c) & (d) Response of 3wt% copper doped In$_2$O$_3$ thick film sensor towards different concentrations of H$_2$S at room temperature.

Sensitivity of sensor to different concentrations of H$_2$S gas at room temperature is shown in fig. 5.30 (a). The minimum measured concentration was 3.57 ppm with a sensitivity of 1.32. The maximum concentration
Gas sensors based on pure and copper doped indium oxide studied with the setup was 286 ppm with a sensitivity of 3986. The response and recovery time of the sensor to different concentrations at room temperature is shown in fig. 5.30 (b) and (c).

![Graphs showing sensitivity, response time, and recovery time](image)

Fig. 5.30 (a) Sensitivity (b) Response time (c) Recovery time of 3wt% copper doped In$_2$O$_3$ thick film sensor towards different concentrations of H$_2$S gas at room temperature

5.10 Discussion of the Results

It is well known that when an n-type semiconductor metal oxide is exposed to air, oxygen molecules can adsorb on the surface of the particles and form O$_2^-$, O$, O^{2-}$ ions by capturing electrons from the conduction band,
which in turn produces an electron-depleted space-charge layer in the surface region. As the dimensions of nanoparticles are sufficiently reduced, they can be completely depleted and the response to gases increases [94, 95].

5.10.1 NO₂ Detection Mechanism

The detection of NO₂ in air at low temperatures can be explained by the high chemical activity of NO₂. It has been proven by means of different characterization techniques that NO₂ oxidizes nonstoichiometric oxides like SnO₂ and TiO₂ [96]. Generally, changes in sensor resistances can be associated with surface chemisorption processes and explained in terms of an electron-transfer between the semiconductor and adsorbed gases [97]. The resistance of In₂O₃ films increases after exposure to the oxidizing gas NO₂ and it returns to the initial value when the NO₂ gas is removed. It is well known that n-type semiconductors have higher resistance in an NO₂ environment as compared to that in vacuum [98]. This is because if an electronegative molecule [98, 99] such as oxygen or NOₓ, (NO and NO₂) is approaching the semiconductor surface and its electron affinity χ is larger than the semiconductor work function Φ, the molecule will tend to pick up an electron from the semiconductor conduction band and become chemisorbed at the surface. With further adsorption the surface becomes more negatively charged while a positive space-charge layer forms behind it. In this process, the energy band at the surface bends upwards, and the work function increases. The net result of the chemisorption of the acceptor-type gas such as NO₂ on the n-type semiconductor surface is an increase in electron depletion region and hence a decrease in electron concentration in the conduction band near the semiconductor surface, and hence a decrease in the conductance close to the surface.
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Adsorption of electron acceptor gaseous species like O₂, NO₂ will lead to band bending \((q\Delta V_s)\) due to the formation of surface depletion layer (surface charge region) with a thickness \(d\), because of the free charge carrier capture at the surface as discussed in section 3.10 of chapter 3. So, due to the chemisorption of acceptor gases, the influence of the following factors should be discussed: (1) nature and density of active surface states \(S\), sites for the gas adsorption. (2) possibility of electron transfer from semiconductor to the adsorbates resulting the formation of chemisorbed surface species.

In solid-state chemistry the association of active surface states with the surface defects—reducing states, such as metal cations in low oxidation states, or oxygen vacancies, or F-centers—is postulated. Earlier works done by Gurlo et al [100,101], Ivanovskaya et al.[102], Sasaki et al. [103] and De Wit [104] with the help of the combined ESR and XPS investigation established the forming of non-stoichiometric, \(\text{In}_2\text{O}_3\_x\) upon annealing with a high concentration electronic (F-centers) and ‘hole’ centers (\(\text{In}^{2+}\)) in the sensitive layers. These earlier works concluded that F centers and hole centers can appear as active surface states for the adsorption of oxidizing gases and make easier electron transfer to adsorbates leading to the formation of chemisorbed surface species or depletion layers.

According to Solovjeva et al. [105] high mobility of electrons in \(\text{In}_2\text{O}_3\) at low temperature is provided by easy electron exchange process between \(\text{In}^{2+}\) and \(\text{In}^+\) ions. The formation of \(\text{In}^{3+}\) in \(\text{In}_2\text{O}_3\) lattice takes place in oxygen deficiency:

\[
\text{In}_2\text{O}_3 \rightarrow \text{In}^{3+}_{2-x} \text{In}^{2+}_x \text{O}_{3-x} [\text{F}]_x + \frac{1}{2} x \text{O}_2 \tag{5.2}
\]

\(\text{In}^+\) ions in \(\text{In}_2\text{O}_3\) lattice may appear as a result of the process.
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\[ 2 \text{In}^{2+} \leftrightarrow \text{In}^+ + \text{In}^{3+} \quad (5.3) \]

Additional electrons which have to be introduced into the oxide lattice by oxygen vacancies formation or interstitial metal atoms ionization in order to maintain the overall neutrality of the crystal, should be associated with neighboring lattice metal ions [106] reducing them, \( \text{In}^{3+} \) to \( \text{In}^{2+} \). So, basically three types of defects have to be considered, i.e., \( \text{In}^{2+} \) lattice ions, interstitial \( \text{In} \), most likely \( \text{In}^{3+} \), and oxygen vacancies (\( \text{V}_o \)). Partially reduced cations (i.e. \( \text{In}^{2+} \) and \( \text{In}^+ \) in \( \text{In}_2\text{O}_3 \)) play the role of \( \text{NO}_2 \) chemisorption centers at comparatively low temperature [63]. The general scheme for \( \text{NO}_2 \) detection at \( \text{In}_2\text{O}_3 \) surface is given by

\[ \text{NO}_2\text{gas} + (Z)_s \leftrightarrow (ZO)_s + \text{NO gas} \quad (5.4) \]

Here \( Z \) is the chemisorptions sites, sites being \( \text{In}^{2+} \) and \( \text{F}^-\)centers. The surface species denoted as \( (ZO)_s \) are \( (\text{In}^{3+} - \text{O}^-)_s \) and \( (\text{V}_o\text{-O}^-)_s \) [42]. From the above equations it can be understood that the highest activity regarding \( \text{NO}_2 \) is observed for systems with the most pronounced deviation from stoichiometry. The increase of non stoichiometry is also expected to increase the surface concentration of adsorbed oxygen since more adsorption sites are available for the atmospheric oxygen to adsorb on the surface of \( \text{In}_2\text{O}_3 \).

The properties of electron transfer in polycrystalline layers strongly depend on the grain boundaries [107], which contain a high density of surface states. These states can trap or scatter free carriers, generate potential barriers or severely deplete the grains of free carriers and determine the material conductivity. The smallest particles have the highest density of surface defects, which could negatively influence the transport properties [108]. So we can say that the transport of electrons, which is determined by the microstructure of the sensing element such as the grain size of
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semiconductor particles, also determine the In$_2$O$_3$ resistance in air and NO$_2$. Hence we can conclude that the material’s structure also play fundamental role in its NO$_2$ response.

Gurlo et al. [61] studied the effect of grain sizes on the NO$_2$ gas sensing behavior of In$_2$O$_3$. They studied the particle size in the range of 5-100nm. The highest sensitivity was obtained for sensors with small grain size in the range of 5-20nm. Another grain size related sensitivity work on indium oxide for NO$_2$ gas sensing by the same group reported that the sensitivity increased very much for grain sizes below 30nm. They related the results with that of grain size dependent sensitivity shown by tungsten oxide reported by Tamaki et al. [109]. Singh et al. [81] studied the size dependent gas sensing properties of In$_2$O$_3$ nanoparticle layers in the range of 8-30nm. They reported as the size becomes larger than 15nm, electrical conduction is controlled by the interface between particles and is not dependent upon particle size. In our pure and copper doped sensor the particle size is in the range of 23-25nm. Considering the above grain size related works and results we assume that in our sensors the conduction is in the grain boundary control.

Enhanced NO$_2$ gas sensing properties of copper doped In$_2$O$_3$ gas sensors is discussed below. Studies on SnO$_2$ have shown that the copper atoms in Cu-doped tin oxide can form donor-like sites (Cu$^+$ centers), which possess much better stability than the intrinsic donors (oxygen vacancies) in pure tin oxides [110]. In other studies [111,112] the Cu impurity was considered as an acceptor like one which is attributed to the CuO doping [113]. CuO is a p-type semiconductor and can form heterojunctions with n-SnO$_2$ which results in acceptor like behaviour of the compounds. The copper impurity in the SnO$_2$ film can create both interstitial point defects and
film inhomogeneity on account of CuO formation. We consider the similar effects in In₂O₃ due to copper doping.

The resistance in air of the pure In₂O₃ sensor increased considerably by copper doping. Similar increase in resistance in air was obtained for pure tin oxide sensors when doped with copper [114-117]. This increase in resistance of tin oxide in pure air is attributed due to formation of p-n heterojunctions (p-CuO and n-SnO₂), which induces an electron-depleted space charge layer at the surface of tin oxide [118-121]. In our copper doped gas sensors CuO and In₂O₃ are p and n-type semiconductors, respectively, having a strong electronic interaction due to which the CuO–In₂O₃ surface consists of numerous p–n junctions causing very high resistance of films in air. From the measured resistance value for pure (100kΩ) and copper doped In₂O₃ (0.5wt% copper doped- 2.4MΩ) at room temperature, it can be seen that copper doped sensors show very high resistance. Hence we consider that doping with Cu leads to the formation of CuO which acts as acceptor type impurity.

Two possible mechanisms can be assumed for the enhancement effect in gas sensing. The first mechanism proposed for improvement in sensor performance due to copper doping is due to cuprous ions Cu⁺, which coexist with cupric ions Cu²⁺ [122]. A similar effect is reported for copper doped tin oxide sensor by Ghimbeu et al [116]. The local oxygen deficiency, when annealing, may trigger the occurrence of the following reaction:

\[ 2\text{CuO} \rightarrow \text{Cu}_2\text{O} + \frac{1}{2} \text{O}_2 \uparrow \]  

which reduces some Cu²⁺ to Cu⁺ and thus, Cu²⁺ and Cu⁺ coexist. When NO₂ gas molecules are brought in contact with the sensing element, NO₂ is adsorbed on active centers, Cu⁺. Hence NO₂ gets reduced to NO₂⁻ radicals.
Gas sensors based on pure and copper-doped indium oxide

Meanwhile, Cu\(^+\) gets oxidized to Cu\(^{2+}\). The highly active NO\(_2\) combines with preadsorbed O\(^-\) or O\(_2\)\(^-\) removing electrons further from the conduction band of In\(_2\)O\(_3\) further increasing the resistance of the In\(_2\)O\(_3\). The reaction proceeds as follows.

\[
\begin{align*}
\text{NO}_2(g) + e^- &\rightarrow \text{NO}_2^-(\text{ads}) \\
\text{NO}_2(g) + \text{O}_2^-(\text{ads}) + 2e^- &\rightarrow \text{NO}_2^-(\text{ads}) + 2\text{O}^-(\text{ads}) \\
\text{NO}_2^-(\text{ads}) + \text{O}_2^-(\text{ads}) &\rightarrow 2\text{O}^-(\text{ads}) + \text{NO}_2
\end{align*}
\]

(5.6)  
(5.7)  
(5.8)

Another possibility for the enhanced sensitivity is an increase in In\(^{2+}\) centers due to copper doping. Earlier Ivanovskaya et al. [63] and Bogdanov et al. [123] proved with the help of ESR measurements that the number of In\(^{2+}\) centers increased with nickel (Ni) doping and this resulted in enhanced sensitivity. Thus we assume that the presence of Cu\(^+\) ions along with ‘hole’ center (In\(^{2+}\)) and oxygen vacancies act as additional adsorption sites for the gas which increases the sensitivity.

In our gas sensing measurement results we found that the sensitivity of 0.5wt% copper-doped In\(_2\)O\(_3\) increased to 7.29 (fig. 5.31). On increasing the doping level to 1.5wt% and 3wt% we found that the sensitivity achieves saturation level (S = 8.72 for 1.5wt%, S = 8.83 for 3wt%). With copper addition the copper forms copper oxide on the surface of In\(_2\)O\(_3\). As the concentration of doping increases more CuO–In\(_2\)O\(_3\) heterojunctions are formed that does not enhance the sensitivity of the sensor to NO\(_2\) much. If the doping concentration is increased (more than 3wt%) further high covering of In\(_2\)O\(_3\) surface by CuO occurs resulting in very little change in sensitivity. Or else it can also be explained that when the doping concentration increases the number of In\(^{2+}\) ions produced will also attain a
saturation level and hence the sensitivity also attain saturation. It is also found that the response time as well as the recovery time of the copper doped In$_2$O$_3$ sensor decreases with copper doping. The improved response as well as recovery time performance of doped In$_2$O$_3$ over pure In$_2$O$_3$ is due to the catalytic interaction of copper ion with the gas species to be detected.

![Graph showing sensitivity at different copper doping % to 7 ppm NO$_2$ gas at respective optimum temperature.](image)

Fig. 5.31 Sensitivity at different copper doping % to 7 ppm NO$_2$ gas at respective optimum temperature

5.10.2 H$_2$S Detection Mechanism

H$_2$S gas detection studies were performed only at room temperature, since the temperature dependent studies were not satisfactory. The sensors were not able to recover its base resistance value or it took long recovery time especially hours for the recovery, hence only room temperature measurements were performed. On exposure to H$_2$S gas the resistance of pure as well as copper doped sensors was found to decrease and hence the conductivity was found to increase. The different mechanism associated with the gas sensing process is discussed below.
For most of the In$_2$O$_3$ gas sensors, the sensing mechanism was proposed as the adsorption and desorption of the gas molecules on the surface of the sensing materials, which can cause the change in resistance [57, 58, 124 - 126]. Oxygen vacancy created at high temperature annealing can induce non-stoichiometry on the surface of In$_2$O$_3$. Atmospheric oxygen can get adsorbed on to this surface site. The oxygen adsorbed on the surface directly influences the conductance of the In$_2$O$_3$ based sensors as shown in figure 5.32. When the In$_2$O$_3$ thick film sensor was exposed to H$_2$S gas, the strong reducing gas might react with adsorbed oxygen ions on the surface and put back the electrons into In$_2$O$_3$ semiconductor, resulting in the increase of conductance of In$_2$O$_3$. The reaction may proceed as follows (ad) represents adsorbed species and (g) represents gas.

\[
O_2(g) + e^- \leftrightarrow O_2^-(ad) \quad (5.9)
\]

\[
O_2^-(ad) + e^- \leftrightarrow O_2^{2-} (ad) \quad (5.10)
\]

\[
H_2S(g) + O_2^{x-}(ad) \leftrightarrow H_2S(ad) + O_2(g) + xe^- \quad (5.11)
\]

\[
2H_2S(ad) + 3O_2^{x-}(ad) \leftrightarrow 2SO_2(g) + 2H_2O(g) + 3xe^- \quad (5.12)
\]

The net reaction is

\[
2H_2S(g) + 3O_2^{x-}(ad) \leftrightarrow 2H_2O(g) + 2SO_2(g) + 3xe^- \quad (5.13)
\]

According to this mechanism a high concentration of surface adsorbed oxygen ions would favour the forward reaction.
Another mechanism involves the sulfuration of the sensing materials as shown in previous studies for zinc oxide and tin oxide [127,128]. Xu et al. [129] proposed that at relatively low temperature range (25–160 °C) the dominant mechanism is the sulfuration of In$_2$O$_3$ and at relatively high temperature range (160–300 °C) the surface adsorption and the sulfuration both contribute to the responses of the sensors. According to their studies at room temperature, In$_2$O$_3$ might undergo partial sulfuration when exposed to H$_2$S and In$_2$O$_3$ transformed into well-conducting In$_2$S$_3$ [130] as follows:

\[
\begin{align*}
\text{In}_2\text{O}_3(s) + 3\text{H}_2\text{S (g)} & \rightarrow \text{In}_2\text{S}_3(s) + 3\text{H}_2\text{O (g)} \\
\text{In}_2\text{S}_3(s) + 9/2 \text{O}_2(g) & \rightarrow \text{In}_2\text{O}_3(s) + 3\text{SO}_2(g)
\end{align*}
\]

The above two are the possible gas sensing mechanism in pure In$_2$O$_3$ sensor. The recovery kinetics was significantly slow. In pure In$_2$O$_3$, the following reactions are necessary in series for the recovery: (1) desorption of SO$_2$ and H$_2$O (2) diffusion of oxygen to the sensing surface (3) adsorption of ambient oxygen gas (4) ionization to negative charge of surface oxygen (O$_2^-$ ads). When reducing gases are detected using n-type oxide semiconductor gas
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sensors, the recovery values are usually longer than the response values [49, 53, 131, 132, 133]. This can be explained by the markedly slower serial surface reactions to form $O_2^{−}_{\text{ads}}$ during the recovery, compared to the oxidation reaction of reducing gas by $O_2^{−}_{\text{ads}}$.

Enhanced sensitivity as well as improved response and recovery characteristics was observed when indium was doped with copper. This can be explained in term of similar sensitivity increase when tin oxide was doped with copper [117]. Morrison [134] proposed two mechanisms of catalyst control on gas sensors: the spillover mechanism and the Fermi level energy control mechanism. In the spillover mechanism the surface catalyst dissociates the gas molecule, and reactive atoms formed are spilled over on the semiconductor surface and influence the conductivity. The Fermi level mechanism assumes that the $H_2S$ converts the Cu or CuO into CuS which has a relatively high conductivity and the response is greatly improved.

It is assumed that in copper doped $In_2O_3$ sensors copper doping results in the formation of p-n junctions causing very high resistance of films in air. The p-n junction is formed at the interface between CuO and $In_2O_3$. While oxygen-deficient $In_2O_3$ shows n-type conductivity by electrons, oxygen-excess CuO shows p-type conductivity by holes. The CuO grains residing between In$_2$O$_3$ grains, forms a network of p-n junctions as shown in fig. 5.33(a). Since CuO and $In_2O_3$ are p- and n-type semiconductors, respectively, a p-n junction forms at each interface between CuO and $In_2O_3$ grains, which induces an electron depleted space charge layer at the surface of In$_2$O$_3$. The schematic band diagram of the typical n-p-n-p, In$_2$O$_3$-CuO-In$_2$O$_3$-CuO and band structure in the vicinity of the In$_2$O-CuO interface can be drawn as shown in fig. 5.33 (b) & (c). The formation of depletion region due to p-type CuO and n-type In$_2$O$_3$ tends to reduce the effective thickness of the
underlying In\textsubscript{2}O\textsubscript{3} layer through where the charge carriers can flow. Moreover diffusion of some amount of copper into In\textsubscript{2}O\textsubscript{3}, and the formation of electronic barriers at the In\textsubscript{2}O\textsubscript{3}-CuO intergranular region in the bulk of the film cannot be precluded. Copper is known to diffuse extensively and can draw oxygen from In\textsubscript{2}O\textsubscript{3} to create intergranular (In\textsubscript{2}O\textsubscript{3}- CuO) barriers. The combined effect of the depletion layer at the interface, and the inter diffusion of copper are therefore expected to yield a high value of the resistance of film in air.

Fig. 5.33 Schematic diagram of CuO/In\textsubscript{2}O\textsubscript{3} sensing mechanism.

(a). In\textsubscript{2}O\textsubscript{3} particles surrounded by CuO  
(b). Band structure for CuO- In\textsubscript{2}O\textsubscript{3} contact  
(c). Potential barrier diagram of n- In\textsubscript{2}O\textsubscript{3}/p-CuO/n- In\textsubscript{2}O\textsubscript{3}/p-CuO  
(d). Potential barrier diagram of n- In\textsubscript{2}O\textsubscript{3}/metallic-CuS/n-In\textsubscript{2}O\textsubscript{3}  
(e). Potential barrier appeared again
Generally CuO layer can be formed on the surface of In$_2$O$_3$ in two ways either as a continuous layer, or dispersed in the form of dotted islands. The schematic representation for both the sensor is shown in figure 5.34

![Figure 5.34 Cross-sectional views of In$_2$O$_3$- CuO sensor (a) continuous layer (b) CuO dispersed in the form of dotted islands](image)

According to the representation fig. 5.34(b) represents a higher resistance than in fig. 5.34(a). This is because in addition to the depletion region and the inter diffusion of Cu into In$_2$O$_3$, oxygen adsorbs on the uncovered In$_2$O$_3$ surface between the CuO and captures electrons from the conduction band to remain as O$_2^-$ ions until desorbed at high temperature or in the presence of reducing gas. The oxygen adsorption increases the extent of depletion region between the CuO dots as shown in fig 5.34 (b). Thereby the measured resistance in air for In$_2$O$_3$-CuO sensor is expected to increase further [34]. In pure In$_2$O$_3$ the resistance was found to be 100kΩ and in 0.5wt% copper doped sensors the resistance was found to be in the range of 2.4MΩ. Due to this huge variation in resistance we expect that in our copper doped sensors copper forms islands on the surface of In$_2$O$_3$. Moreover sintered gas sensors are composed of a mixture of CuO and In$_2$O$_3$ and thus CuO is dispersed here and there in a sensor.
However, if the above CuO layer is exposed to H$_2$S the CuO is converted to copper sulphide (CuS) which is a good electronic conductor as in the following equations.

$$\text{CuO} + \text{H}_2\text{S} \rightarrow \text{CuS} + \text{H}_2\text{O} \quad (5.16)$$

The formation of CuS at room temperature is reported earlier by Kong and Li [135]. CuS is known to be highly conducting in nature and thus the n-p-n heterostructure as well as charge depletion layer will be destroyed and transformed to a metal-n-type semiconductor configuration. A typical metal-n-semiconductor band picture can be drawn in fig. 5.33(d). Since the work function of CuS is lower than that of In$_2$O$_3$ the band bending is as shown. This particular situation arises because at equilibrium there is a flow of electrons from the lower work function species, i.e., CuS, to higher work function species, i.e., In$_2$O$_3$. This results in the band bending downwards which facilitates the easy flow of electrons from CuS to In$_2$O$_3$ and vice versa, since there is no barrier between them as shown in fig. 5.33(d). This flow of electrons results in a decrease in electrical resistance. This configuration is similar to a metal-semiconductor contact for an ohmic junction where there is an unimpeded conduction of electrons in either direction. This theory explains quite convincingly the decrease in resistance on exposure of CuO/In$_2$O$_3$ sensor element to reducing gases like H$_2$S and the increase in resistance back to the original value once this H$_2$S atmosphere ceases to exist. So, the potential barrier appears again, as seen in fig. 5.33(e). The formation of CuS on the surface of tin oxide has been confirmed with the help of X-ray diffraction [136], X-ray photoelectron spectroscopy [137] and Raman spectroscopy [138] measurements in earlier works.
Besides the above described mechanism the uncovered In$_2$O$_3$ surfaces between the dispersed CuO are also exposed to H$_2$S simultaneously. The conversion of CuO to metallic CuS shifts the extent of depletion region towards the p-type CuO and increases the effective thickness of In$_2$O$_3$ layer. Cu present in the form of CuO is known to initiate hydrogen spillover because it chemisorbs hydrogen rather weakly [139] and the hydrogen atoms on its surface are highly mobile [140]. The hydrogen after spillover quickly interacts with the adsorbed oxygen and removes it from the uncovered In$_2$O$_3$ surface between the dispersed CuO islands. This removal of oxygen leaves behind the excess free electrons that are available for conduction. The resultant of all these reaction is increased sensitivity of copper doped In$_2$O$_3$ sensors to H$_2$S at room temperature.

Due to the effect of very large recovery time the concentration dependent study for pure and 0.5wt% copper doped sensors were limited in the range of 3.57 ppm to 28.58 ppm. In our copper doped sensors as shown in table 5.8 the 0.5wt% sensor was found to have a maximum sensitivity to the lower concentrations (3.57 to 17.85 ppm) studied but had very poor dynamics characteristics (response and recovery times). In our measurements we found that as the concentration of copper increased the dynamic characteristics also exhibited good values. The response and recovery time was found to be very low for the 3wt% copper doped sensors.

It is assumed that in 1.5 and 3wt% copper more CuO-In$_2$O$_3$ junctions are formed. Hence there is less uncovered In$_2$O$_3$ surface left between the dispersed CuO islands and less interaction of H$_2$S with In$_2$O$_3$. The presence of more CuO-In$_2$O$_3$ junctions results in the formation of more CuS. The
conversion time required for CuS to CuO is very less and results in very low recovery time for higher concentration copper doped In$_2$O$_3$ sensors. The rate of conversion of CuS to CuO is very fast. The very large recovery time for pure In$_2$O$_3$ and 0.5 wt% copper doped In$_2$O$_3$ sensors are assigned due to the formation of less CuO-In$_2$O$_3$ junction and hence more interaction between In$_2$O$_3$ and H$_2$S resulting in high recovery time. The similar effect also takes place with response time also.

Concentration dependent studies done on 1.5 and 3wt% copper doped sensors prove that as the gas concentration increased the 3wt% doped sensors showed increased sensitivity than 1.5wt% doped sensors. In the case of 3wt% copper doped sensors for higher concentration (286ppm) studied the sensitivity was as high as 3985, where as for the 1.5wt% the sensitivity was 1055 for the same concentration studied. This increased sensitivity is assigned due to the presence of more CuO-In$_2$O$_3$, p-n-p-n, junctions. When the concentration of H$_2$S increases more CuO-In$_2$O$_3$ will break resulting in the formation of more CuS and hence increased sensitivity. In 1.5 and 3wt% copper doped In$_2$O$_3$ sensors the resistance is higher than 0.5wt% in air. Hence at low H$_2$S concentration there is less breakage of CuO-In$_2$O$_3$ junctions in 1.5 and 3 wt% copper doped sensors than 0.5wt% doped sensor resulting in lower sensitivity at low concentration.

5.11 Conclusion

99.999% pure In$_2$O$_3$ powders were purchased and thoroughly mortar powdered to prepare the pure In$_2$O$_3$ sensor. Copper doped In$_2$O$_3$ was prepared by powder impregnation method. Required amount of copper acetate monohydrate dissolved in water was added to In$_2$O$_3$ powder, the
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mixture was thoroughly stirred for two days, dried at 100°C to obtain the copper doped In₂O₃ powder. Pure and copper doped In₂O₃ sensor was prepared by dispersing the prepared powder in methanol and drop coating on to glass substrates. The sensor was annealed at 600°C overnight before performing the gas sensing measurements. The main conclusions drawn from the above presented experimental data on pure and copper doped In₂O₃ sensors are:

Crystalline structure of pure and copper doped In₂O₃ sensor was revealed as cubic bixbyite structure. Average crystallite size is not affected by the addition of copper. The crystallite size for pure In₂O₃, 0.5wt%, 1.5wt%, and 3wt% copper doped In₂O₃ thick film sensor was found to be 24nm, 23nm, 24nm and 25nm respectively.

The XRD spectrum revealed the cubic bixbyite phase with preferred (222) orientation. No separate peaks were obtained in XRD data due to copper doping. The intensity of all the main reflections was found to decrease with copper doping. A small shift for the (222) peak was observed towards the lower theta side due to copper doping.

The surface morphology and elemental composition were characterized by scanning electron microscopy and energy dispersive X-ray analysis. Separate particles were not visualized in the SEM images. Mainly particle agglomeration with not much definite shape was found in both pure and copper doped In₂O₃ thick film sensors. Copper addition did not show any effect on the surface morphology or particle size of the sensor elements as confirmed by the XRD results. The presence of copper in the doped sensors was confirmed by EDS analysis.
The temperature dependent gas sensing property of pure and copper doped In$_2$O$_3$ sensor was investigated in order to find the optimal sensor operating temperature and sensor response to NO$_2$ test gas.

Copper addition was found to enhance the gas sensing properties In$_2$O$_3$ sensor. Two possible mechanisms are suggested for enhanced gas sensing. One is the increase in In$^{2+}$ centers that occur due to copper addition. Another mechanism is due to cuprous ions Cu$^+$, which coexists with cupric ions Cu$^{2+}$ that can enhance the gas sensing property of doped sensors.

Optimum operating temperature for pure and copper doped In$_2$O$_3$ sensor was 100°C. The response and recovery time was found to decrease with copper doping.

The table below presents the sensitivity of the sensors obtained, along with their optimum operating temperature, response and recovery time for the studied concentration of 7ppm NO$_2$ gas.

<table>
<thead>
<tr>
<th>Sensor</th>
<th>Sensitivity</th>
<th>Optimum temperature</th>
<th>Response time (sec)</th>
<th>Recovery time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure In$_2$O$_3$</td>
<td>2.82</td>
<td>100°C</td>
<td>40</td>
<td>12.3</td>
</tr>
<tr>
<td>In$_2$O$_3$ + 0.5wt% Copper</td>
<td>7.29</td>
<td>100°C</td>
<td>13</td>
<td>8.03</td>
</tr>
<tr>
<td>In$_2$O$_3$ + 1.5wt% copper</td>
<td>8.72</td>
<td>100°C</td>
<td>9</td>
<td>6</td>
</tr>
<tr>
<td>In$_2$O$_3$ + 3wt% Copper</td>
<td>8.73</td>
<td>100°C</td>
<td>6</td>
<td>4</td>
</tr>
</tbody>
</table>

The H$_2$S gas sensing property of pure and copper doped In$_2$O$_3$ sensor was performed at room temperature. The temperature dependent studies were not satisfactory. Copper addition was found to enhance the H$_2$S gas sensing property of In$_2$O$_3$. It is attributed to p-n heterojunction
formed by CuO-In$_2$O$_3$. In presence of H$_2$S gas CuO gets converted to metallic CuS which is very conducting and hence enhance the sensor performance.

Gas sensing behaviour of pure and copper doped In$_2$O$_3$ sensor to a few concentration of H$_2$S gas is tabulated below.

Table 5.8: Summary of H$_2$S gas sensing results of pure and copper doped In$_2$O$_3$ thick film sensor

<table>
<thead>
<tr>
<th>Sensors</th>
<th>Concentration</th>
<th>Sensitivity</th>
<th>Response time(sec)</th>
<th>Recovery time(min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure In$_2$O$_3$</td>
<td>3.57</td>
<td>1.1</td>
<td>46</td>
<td>3.98</td>
</tr>
<tr>
<td></td>
<td>7.14</td>
<td>1.35</td>
<td>57</td>
<td>8.55</td>
</tr>
<tr>
<td></td>
<td>10.71</td>
<td>1.98</td>
<td>70</td>
<td>42.9</td>
</tr>
<tr>
<td></td>
<td>17.85</td>
<td>7.25</td>
<td>85</td>
<td>78.62</td>
</tr>
<tr>
<td>In$_2$O$_3$ + 0.5wt% copper</td>
<td>3.57</td>
<td>1.35</td>
<td>20</td>
<td>5.93</td>
</tr>
<tr>
<td></td>
<td>7.14</td>
<td>2.79</td>
<td>14</td>
<td>16.13</td>
</tr>
<tr>
<td></td>
<td>10.71</td>
<td>68</td>
<td>12</td>
<td>87.95</td>
</tr>
<tr>
<td></td>
<td>17.85</td>
<td>125</td>
<td>6</td>
<td>153</td>
</tr>
<tr>
<td>In$_2$O$_3$ + 1.5wt% copper</td>
<td>3.57</td>
<td>1.15</td>
<td>24</td>
<td>3.28</td>
</tr>
<tr>
<td></td>
<td>7.14</td>
<td>4.2</td>
<td>9</td>
<td>4.65</td>
</tr>
<tr>
<td></td>
<td>10.71</td>
<td>7.11</td>
<td>7</td>
<td>5.53</td>
</tr>
<tr>
<td></td>
<td>17.85</td>
<td>11.65</td>
<td>7</td>
<td>10.02</td>
</tr>
<tr>
<td>In$_2$O$_3$ + 3wt% copper</td>
<td>3.57</td>
<td>1.32</td>
<td>8</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>7.14</td>
<td>4.67</td>
<td>6</td>
<td>0.63</td>
</tr>
<tr>
<td></td>
<td>10.71</td>
<td>7.58</td>
<td>6</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td>17.85</td>
<td>14.44</td>
<td>5</td>
<td>2.57</td>
</tr>
</tbody>
</table>

Concentration dependent studies for NO$_2$ gas at optimum operating temperature for pure and copper doped In$_2$O$_3$ thick film sensors were studied. The room temperature concentration dependent studies for H$_2$S gas were also studied.
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References


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