Detection of H$_2$S gas at lower operating temperature using sprayed nanostructured In$_2$O$_3$ thin films

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Abstract. Nanostructured indium oxide (In$_2$O$_3$) thin films were prepared by spray pyrolysis (SP) technique. X-ray diffraction (XRD) was used to investigate the structural properties and field emission scanning electron microscopy (FESEM) was used to confirm surface morphology of In$_2$O$_3$ films. Measurement of electrical conductivity and gas sensing performance were conducted using static gas sensing system. Gas sensing performance was studied at different operating temperature in the range of 25–150 $^\circ$C for the gas concentration of 500 ppm. The maximum sensitivity ($S = 79\%$) to H$_2$S was found at lower temperature of 50 $^\circ$C. The quick response (4 s) and fast recovery (8 s) are the main features of this film.

Keywords. Nanostructured In$_2$O$_3$; thin films; spray pyrolysis; H$_2$S gas sensor; low temperature.

1. Introduction

Hydrogen sulphide (H$_2$S) is a toxic and inflammable gas, produced in sewage plants, coal mines and oil and natural gas industries. It is used in large amounts in various chemical industries, research laboratories and as a process gas in the production of heavy water (Kaur et al 2008). Presently, the atmospheric pollution has become a global burning issue. Gases from automobiles and industrial exhausts are polluting the environment. In particular, indium oxide is promising material for detection of various substances, e.g. LPG, H$_2$, CO$_2$, NH$_3$, C$_2$H$_5$OH, CH$_3$OH, Cl$_2$ and H$_2$S. Furthermore, nanostructured materials present new opportunities for enhancing the properties and performance of gas sensors and are recognized as essential for achieving high gas sensitivity.

Indium oxide thin film is a technologically important transparent conducting oxide (TCO) material (Riveros et al 2006). In$_2$O$_3$ is used in different fields like: photovoltaic devices, transparent windows in liquid crystal displays, sensors, anti-reflection coatings (Chopra et al 1983) and electrochromic devices (Sharma et al 2009). Thin films of In$_2$O$_3$ can be prepared by a variety of techniques such as chemical vapour deposition (Kane and Schweitzer 1975) spray pyrolysis (Manifacier et al 1979) vacuum evaporation (Murali et al 2002) and magnetron sputtering (Haines and Bube 1978).

Among these techniques, spray pyrolysis technique compete with others due to its low cost, suitable properties and process well suited to large scale production. It has several advantages in producing nanocrystalline thin films suitable for the gas sensors, such as, relatively homogeneous composition, easy control of film thickness and fine and porous microstructure. In this work, nanocrystalline In$_2$O$_3$ thin films with different spraying time of the solution were prepared by spray pyrolysis technique. Crystal structure and grain sizes were studied from X-ray diffraction and FESEM. These nanocrystalline In$_2$O$_3$ thin films were tested for sensing different conventional gases and were observed to be most sensitive to H$_2$S at 50 $^\circ$C.

2. Experimental

2.1 Preparation of nanocrystalline In$_2$O$_3$ thin films

Indium oxide thin films were prepared using spray pyrolysis technique. The films of various thicknesses were deposited by varying deposition time of solution between 10 and 40 min. The solution was prepared by dissolving indium trichloride (InCl$_3$) [Alfa Aesar] in deionized water and adding 1–3 drops of concentrated HCl to clean the precipitate so as to get desired solution concentration (0.025 M). The spray produced by nozzle was sprayed onto the glass substrates heated at 250 ± 5 $^\circ$C. Various parameters such as solution concentration (0.025 M), spray rate (5 mL/min), nozzle to and fro frequency (16 cycles/min), nozzle to substrate distance (30 cm), etc were optimized to obtain good quality films. This resulted in the formation of well adherent, transparent and uniform indium oxide thin films. The films with different deposition time of: 10, 20, 30 and 40 min were obtained and referred to as S1, S2, S3 and S4, respectively in text. The samples were fired at 500 $^\circ$C for 1 h.
2.2 Chemical reaction

The indium oxide formulation can be represented as:

\[ 2\text{InCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{In}_2\text{O}_3 + 6\text{HCl} \text{ (gas)} \uparrow \quad (1) \]

2.3 Sensing system for measurement of gas sensitivity

The gas sensing studies were carried out using a static gas chamber to sense H_2S gas in air ambient. The nanostructured SnO_2 thin films were used as the sensing elements. Cr–Al thermocouple is mounted to measure the temperature. The output of thermocouple is connected to temperature indicator. Gas inlet valve fitted at one of the ports of base plate. Gas concentration inside the static system is achieved by injecting a known volume of test gas in gas injecting syringe. Constant voltage is applied to the sensor and current can be measured by picoammeter.

2.4 Characterization of thin films

The nanostructured In_2O_3 thin films were characterized by X-ray diffraction (Miniflex Model, Rigaku, Japan) using CuKα radiation with a wavelength, λ = 1.5418 Å. The microstructure of the films was analysed using a field emission scanning electron microscope (FE–SEM, JEOL, JED 6300). Thermoelectric power measurement was carried out using TEP set up. Electrical and gas-sensing properties were measured using a static gas sensing system. The sensor performance on exposure of LPG, carbon dioxide, hydrogen, ammonia, ethanol, chlorine and H_2S was examined.

3. Results and discussion

3.1 Measurement of films thickness

Film thickness was measured by using a micro-gravimetrical method (Sartale and Lokhande 2001). The films were deposited on clean glass slides whose mass was previously determined. After the deposition, the substrate was again weighed, determining the quantity of deposited indium oxide. Measuring the surface area of the deposited film, taking account of indium oxide specific weight of the film, thickness was determined using the relation:

\[ T = \frac{M_{\text{In}_2\text{O}_3}}{A \cdot \rho \cdot 10^4}, \]

where \( A \) is the surface area of the film (cm\(^2\)), \( M_{\text{In}_2\text{O}_3} \) the quantity of the deposited tin oxide and \( \rho \) the specific weight of indium oxide. Measurements of film thickness with deposition spray time are given in table 1.

### Table 1. Variation of activation energy and thickness with spray time (thickness).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Spray time</th>
<th>Thickness (nm)</th>
<th>Activation energy (eV) (temperature range 40–150°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>153</td>
<td>0.561</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>169</td>
<td>0.515</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>172</td>
<td>0.461</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>189</td>
<td>0.369</td>
</tr>
</tbody>
</table>

3.2 Thermoelectric power measurements

The \( p \)- or \( n \)-type semiconductivity of the thin films of In_2O_3 were confirmed by measuring the thermoelectric power of the thin film samples. The In_2O_3 were observed to be the \( n \)-type material.

3.3 Structural properties

The structural characterization of deposited films was made by X-ray diffraction (XRD) technique with monochromatic CuKα radiation, \( \lambda = 1.5418 \) Å. The XRD patterns were

![XRD of In_2O_3(30 min)](image)

Figure 1. X-ray diffractogram of most sensitive indium oxide thin film.
Nanostructured $\text{In}_2\text{O}_3$ thin films as low temperature $\text{H}_2\text{S}$ sensor

recorded in 2θ interval from 20 up to 80° with a step of 0.05°. Figure 1 shows X-ray diffractogram of nanocrystalline indium oxide thin film. The observed peaks: (211), (222), (400), (440), (620) and (622) are very well matching with JCPDS data of indium oxide (JCPDS data card no. 44-1087) possessing cubic structure. It is seen from the figure that the films exhibited strong orientation along (222). The average crystalline size calculated from Scherrer’s formula was found to be 23 nm.

3.4 Microstructure study

The surface topography of the films was analysed using a field emission scanning electron microscopy as shown in figure 2(a and b).

The morphology of the particles was roughly spherical in shape. The average particle size was about 36 nm. Larger particles may be due to the agglomeration of smaller crystallites as shown in the low magnification image as in figure 2(a and b) shows the high magnification image, indicating the sphere associated with smaller crystallites.

3.5 Electrical properties

3.5a I–V characteristics: Figure 3 shows I–V characteristics of samples S1, S2, S3 and S4 observed to be nearly symmetrical in nature indicating ohmic nature of contacts. The non-linear I–V characteristics may be due to semiconducting nature of the thin film samples.

3.5b Electrical conductivity: Figure 4 shows variation of log (conductivity) with an operating temperature. The conductivity of each sample is observed to be increasing with an increase in temperature. The increase in conductivity with increase in temperature could be attributed to negative temperature coefficient of resistance and semiconducting nature of nanocrystalline $\text{In}_2\text{O}_3$. It is reported (Sharma and Garg 1990; Mandouh and Mandouh 1995) that there is variation of activation energy with thickness. As the thickness of the film increases the activation energy goes on decreasing. The activation energy calculated from slopes of line for 10, 20, 30 and 40 min thin films were found to be 0.561, 0.515, 0.461 and 0.369 eV, respectively.

3.6 Gas sensing performance

3.6a Sensitivity: It is defined as the change in conductance of the sample on exposure to gas to the original conductance. It is given by the relation:

$$S(\%) = \frac{G_a - G_g}{G_a} \times 100 \quad \text{(3)}$$

where $G_a$ is the conductance of sensor in air and $G_g$ the conductance of sensor in presence of gas.

Figure 5 shows variation of sensitivity with operating temperature of samples S1, S2, S3 and S4 on exposure to...
500 ppm H$_2$S. It is clear from figure 5 that the H$_2$S sensitivity of sample S3 is higher ($S = 79\%$) at 50°C as compared to those of S1, S2 and S4. It is well known that the sensitivity of the metal–oxide semiconductor sensors is mainly determined by the interactions between a target gas and the surface of the sensors. Due to the greater surface area of nanostructured materials, its interaction with the adsorbed gases is stronger, leading to higher gas response.

3.6b Selectivity: The response of the sensor to a specific gas in the mixture of gases is the selectivity.

Selectivity of nanocrystalline indium oxide thin film sensors is measured at an operating temperature of 50°C. Figure 6 depicts bar diagram to indicate H$_2$S selective ability of the sensor. It is clear from the figure that the responses of all samples to LPG, CO$_2$, H$_2$, NH$_3$, C$_2$H$_5$OH, CH$_3$OH and Cl$_2$ gases are lower as compared to their response to H$_2$S. Nanocrystalline indium oxide thin films are, therefore, highly selective to H$_2$S.

3.6c Response and recovery of sensor: The time taken by the sensor to attain the 80% of maximum change in resistance on exposure to the gas is response time. The time taken by the sensor to roll back to 80% of its original resistance is the recovery time.

The response and recovery of the nanostructured indium oxide thin film (S3) sensor on exposure of 500 ppm of H$_2$S at 50°C are represented in figure 7. The response is quick (4 s) and recovery is fast (8 s).
Nanostructured In$_2$O$_3$ thin films as low temperature H$_2$S sensor

3.7 Discussion

The gas-sensing mechanism of In$_2$O$_3$-based thin films belongs to the surface controlled type, which is based on the change in conductance of the semiconductor. The oxygen adsorbed on the surface directly influences the conductance of the In$_2$O$_3$-based sensors as shown in figure 8.

The amount of oxygen adsorbed on thin film surface depends on the operating temperature, particle size and specific surface area of sensor. The state of oxygen on the surface of In$_2$O$_3$ thin film undergoes the following reaction:

\begin{equation}
O_2 (\text{gas}) \rightarrow O_2 (\text{ads}),
\end{equation}

\begin{equation}
O_2 (\text{ads}) + e^- \rightarrow O_2^- (\text{ads}),
\end{equation}

\begin{equation}
O^- + e^- \rightarrow O^{2-} (\text{ads}).
\end{equation}

The oxygen species capture electrons from the material, which results in the concentration changes of holes or electrons in the In$_2$O$_3$ semiconductor. When the In$_2$O$_3$ thin film is exposed to H$_2$S gas, the reductive gas reacts with the oxygen adsorbed on the thick film surface. Then, the electrons are released back into the semiconductor, resulting in the change in the electrical conductance of In$_2$O$_3$ thin films. It can be expressed in the following reaction:

\begin{equation}
\text{H}_2\text{S} + 3\text{O} \rightarrow \text{H}_2\text{O} + \text{SO}_2 + 6e^-.
\end{equation}

In$_2$O$_3$ thin film when exposed to H$_2$S gas, conductivity would be very low in air and very high on exposure to H$_2$S gas and therefore, the gas response would be highest for In$_2$O$_3$ thin film. For the In$_2$O$_3$ thin film, the low gas response at low operating temperature can be attributed to the low thermal energy of the gas molecules, which is not enough to react with the surface adsorbed oxygen species. As a result, the reaction rate between them is essentially low and low gas response is observed. On the other hand, the reduction in response after the optimum operating temperature may be due to the difficulty in exothermic gas adsorption at higher temperature and as a result, the initial resistance of thin film would decrease and the overall change in resistance on exposure to gas would be smaller leading to lower response to the target gas (Patil et al 2010, 2012). Uniform and optimum dispersion of an additive dominates the depletion of electrons from semiconductor. Oxygen adsorbing on additive (misfits) removes electrons from the additive and additive in turn removes the electron from the nearby surface region of the semiconductor and could control the conductivity.

4. Conclusions

(I) Nanostructured indium oxide thin films could be prepared by simple and inexpensive spray pyrolysis technique.
(II) The structural and microstructural properties confirm that the as-prepared indium oxide thin films are nanostructured in nature.

(III) The indium oxide thin film of (sample \( S_3 = 30 \) min spray time) was most sensitive to \( \text{H}_2\text{S} \) gas and exhibit the response of \( S = 79\% \) to the gas concentration of 500 ppm at the temperature of \( 50^\circ\text{C} \).

(IV) The sensor has good selectivity to \( \text{H}_2\text{S} \) against LPG, \( \text{CO}_2 \), \( \text{H}_2 \), \( \text{NH}_3 \), ethanol, methanol and \( \text{Cl}_2 \).

(V) The nanostructured indium oxide thin films exhibit rapid response–recovery.

(VI) Low operating temperature, highly selective and rapid response–recovery are the main features of this sensor.

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