CHAPTER – 5

Response of ITO Thin Film Gas Sensors to

1 Toluene Vapours
2 Benzene Vapours
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### 5.2 BENZENE

#### 5.2.1 INTRODUCTION

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(b) Hazardous effect

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# Chapter 5

## 5.2.2 Experimental Methodology

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References: Benzene
5.1 TOLUENE

5.1.1 Introduction

5.1.1 (i) Need and Importance of Detection of Toluene

(a) Applications

Toluene is an important organic solvent having wide range of applications. It is used in paints, varnishes and shellacs, thinners, nail polish, adhesives and glues, metal cleaners, rust preservatives, fuel systems antifreezes and flame retardants. It also finds applications in production of chemicals, dyes and inks, plastics, medicines, perfumes and detergents [1].

(b) Hazardous effect

It is toxic and has serious clinical implications. Toluene is a significant contributor to indoor air pollution [1]. Toluene is readily absorbed by inhalation or ingestion and tends to be deposited more in tissues that are fatty or have a rich blood supply (e.g. brain, liver, and kidney, fat). After exposure, toluene can pass into the bloodstream. All these prove that there is a dire requirement of a stable, sensitive and selective sensor for the quantitative detection of toluene [2].
(c) Exposure limit

The Occupational Safety and Health Administration (OSHA), USA has set limits for occupational hazards of toluene. The OSHA Permissible Exposure Limits (PELs) for toluene for general, construction and maritime industry is 200 ppm. As per the California OSHA, Cal OSHA PEL, the exposure limits of toluene are provided in Time Weighted Average (TWA) as 10 ppm, and Short Term Exposure Limit (STEL) 150 ppm. National Institute for Occupational Safety and Health (NIOSH) Recommended Exposure Limit (REL) is 100 ppm. The REL was established to prevent changes in muscular coordination, reaction time, mental confusion and irritation of mucous membranes. NIOSH Immediately Dangerous to Life or Health Concentration (IDLH) is 500 ppm. In the “ACGIH” (American Conference of Governmental Industrial Hygienist) Threshold Limit Value (TLV), the TLV for toluene was established to protect against subclinical changes in colour vision and the potential for spontaneous abortion in female workers. Table 5.1.1 (i) indicates the TLV and Explosive limits of Toluene.
Table 5.1.1 (i) TLV and Explosive Limits of Toluene [3]

<p>| | |</p>
<table>
<thead>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Threshold Limit Value</td>
<td>50mL m⁻³, 190mg m⁻³</td>
</tr>
<tr>
<td>Explosive Limits</td>
<td>1.2 -127 %, 6.75 -7.1 %</td>
</tr>
</tbody>
</table>

5.1.1 (ii) Detection

(a) Chemical and physical properties

Fig.5.1.1(i) shows the structure of toluene. The Chemical and Physical Properties of Toluene are as given in Table 5.1.1(ii).

![Structure of Toluene](image)

(b) Review of literature on the detection of Toluene as reported by researchers

One major drawback for N-type SnO₂ based gas sensors is usually their insensitivity for benzene or toluene due to lower oxidation power for a catalyst at the operating temperature of 200-300°C [4]. Nakamura et al [5] have reported that at a constant operating temperature, the change in sensor current
reaches a maximum value at a higher toluene concentration using diamond-based gas sensor fabricated in a layered Pd/i-diamond/p-diamond configuration on highly-doped (p++) silicon (Si) substrate. Yasar Gurbuz et al [4] have reported that at a constant operating temperature, the change in sensor current reaches a maximum value at a higher toluene concentration.

Table 5.1.1 (ii) Chemical & Physical Properties of Toluene [3]

<table>
<thead>
<tr>
<th>CHEMICAL &amp; PHYSICAL PROPERTIES OF TOLUENE</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Formula</td>
<td>C₇H₈ or C₆H₅CH₃</td>
</tr>
<tr>
<td>Molar Mass</td>
<td>92.14 g/mol</td>
</tr>
<tr>
<td>Solubility</td>
<td>Miscible in most organic solvents</td>
</tr>
<tr>
<td>Appearance</td>
<td>Colourless Liquid</td>
</tr>
<tr>
<td>Density</td>
<td>0.8669 g/mL (20°C)</td>
</tr>
<tr>
<td>Melting Point</td>
<td>-93°C, 180 K</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>110.6°C, 383.8 K</td>
</tr>
<tr>
<td>Solubility in Water</td>
<td>0.47 g/L (20-25°C)</td>
</tr>
<tr>
<td>Viscosity</td>
<td>0.590 cP at 20°C</td>
</tr>
<tr>
<td>Threshold Limit Value</td>
<td>50mL m⁻³, 190mg m⁻³</td>
</tr>
<tr>
<td>Main Hazards</td>
<td>Highly Flammable</td>
</tr>
<tr>
<td>Flash Point</td>
<td>4°C (39°C)</td>
</tr>
<tr>
<td>Explosive Limits</td>
<td>1.2 -127, 6.75 -7.1</td>
</tr>
<tr>
<td>Aromatic Compounds</td>
<td>Benzene, Xylene, Naphthalene</td>
</tr>
</tbody>
</table>
Exposure of the films to chloroform, toluene, hexane, and ethanol vapours results in significant and selective increases in electrical resistance, with the response to the vapours having order: toluene > chloroform > hexane >> ethanol have been investigated by Heejoon Ahn et al [11]. Kwang-Su Kim et al [12] have reported measurement of toluene gas at room temperature using a micro fabricated device nano imprinting method. The measured toluene concentrations ranged from 50 ppm to 200 ppm. The transient behaviour of the grafted catalysts during the interaction with toluene has indicated that electrophilic species (O⁻, O₂⁻) are formed as intermediates during the re-oxidation of V⁴⁺ to V⁵⁺ in the presence of gaseous oxygen as reported by Lioubov Kiwi-Minsky et al [13]. Jeffrey Chi-Sheng Wu et al [14] have investigated that the deep oxidation of toluene/air mixture was carried out to test the activity of catalysts. Pt/SDB showed the highest activity among the catalysts and could completely oxidize 90 ppm toluene/air at 150°C and also redox mechanism was proposed to reveal the enhanced kinetic rates. The results suggested that the rate of toluene oxidation might be enhanced due to the fact that
water, one of the products, was expelled from the hydrophobic surface. Feng Wang et al [15] has reported the catalytic performances were similar or better than those in the gas phase oxidation of toluene at reaction temperatures higher than 473 K and under 0.5 – 2.5 MPa. The selectivity of the reaction with respect to mild oxidation products in the presence of V$_2$O$_5$, MoO$_3$, and V$_2$O$_5$-MoO$_3$ could be increased by changing the temperature of catalyst preparation from 400 to 500°C. The selectivity of toluene transformations into benzaldehyde and benzoic acid decreased and into maleic anhydride and deep oxidation products increased as the ability of vanadium-containing catalysts of toluene oxidation to generate the singlet form of molecular oxygen grew reported by Boikov et al [16]. Tomoaki Sato et al [17] reported that the sensing characteristics towards toluene and high concentrations of ethanol were evaluated for a NiO / YSZ-based sensor, aiming at the selective detection of ppb levels of toluene for indoor sensing applications. The application of a SnO$_2$ catalytic cell upstream of a YSZ-based sensor utilizing
NiO-SE resulted in a great improvement of toluene selectivity due to the oxidation of high concentration ethanol (480 ppb).

In recent years, many researchers have devoted themselves to improving the performance of ITO sensor, in order to lower its working temperature and enhance the gas selectivity [6-10]. However there are no reports of use of ITO for quantitative detection of toluene.

(c) Performance criteria to be met

The present work proposes the development of a thin film ITO sensor for the detection of toluene with faster response enhanced sensitivity and selectivity. It is a proven fact that the ITO thin films show better stability.

5.1.2 Experimental Methodology

5.1.2 (i) Fabrication of ITO Toluene Sensors

Indium Tin Oxide (In$_2$O$_3$:10% SnO$_2$) thin films were deposited by the thermal evaporation technique using vacuum coating unit (Hind Hi Vac, Model: 15F6U) with the deposition conditions as described in Table 5.1.2(i)

The fabrication process is as described in chapter 3.
### Table 5.1.2 (i) Deposition Parameters

<table>
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<tr>
<th>Sr. No.</th>
<th>Deposition parameter/condition</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Substrate temperature</td>
<td>623 K</td>
</tr>
<tr>
<td>2</td>
<td>Substrate</td>
<td>Glass</td>
</tr>
<tr>
<td>3</td>
<td>Order of Vacuum</td>
<td>$3 \times 10^{-5}$ Torr</td>
</tr>
<tr>
<td>4</td>
<td>Source to Substrate Distance</td>
<td>0.1 m</td>
</tr>
<tr>
<td>5</td>
<td>Evaporation Boat</td>
<td>Tungsten</td>
</tr>
<tr>
<td>6</td>
<td>Dimension for sensor geometry</td>
<td>5mm x 5mm</td>
</tr>
<tr>
<td>7</td>
<td>Mask</td>
<td>Mica</td>
</tr>
<tr>
<td>8</td>
<td>Evaporation Rate</td>
<td>0.20 to 0.30nm/sec</td>
</tr>
<tr>
<td>9</td>
<td>Thickness of Film</td>
<td>120 to 350nm</td>
</tr>
<tr>
<td>10</td>
<td>Evaporation Time</td>
<td>20 - 25 min</td>
</tr>
<tr>
<td>11</td>
<td>Post Annealing Deposition</td>
<td>At 673 K for 2 hours in 80-90% humidity</td>
</tr>
</tbody>
</table>
| 12      | Sets of Sensors               | #1 : ITO  
# 2 : ITO with diff. thicknesses – 130 nm, 150 nm, 210 nm  
# 3 : Cu/ITO  
# 4 : MnO/ITO  
# 5 : Cr/ITO  
# 6 : Cu/MnO/ITO |

The semiconductor devices thus fabricated were resistive type sensors with geometry as shown in Fig.5.1.2 (i).
Vapour sensing properties of the sensors were characterized in a specially designed measurement system as shown in Fig.5.1.2 (ii). The temperature to the sensor was applied by a current controlled miniature heater using Ni-Cr heating coil, kept outside the chamber and made to touch the back side of the sensor without heating the other parts of the chamber. The sensor temperature measured using a thermocouple placed inside the measurement chamber. Toluene (C\textsubscript{7}H\textsubscript{8}) in liquid form was injected inside the chamber using a calibrated syringe/micro-pipette, where in, it was allowed to evaporate naturally and come in contact with semiconductor sensors kept at elevated temperature. The relative change in
resistance of sensors as given by equation (1) was measured, for different concentrations (ppm) of vapours. After every measurement, the glass chamber was flushed with fresh air.

The relative change in resistance = \( \frac{R_{\text{air}} - R_{\text{gas}}}{R_{\text{gas}}} \times 100(\%) \)  

\[(1)\]
5.1.3 RESULTS AND DISCUSSION

5.1.3 (i) Variation in the electrical resistance of ITO thin film sensor with temperature in the presence of toluene vapours (1000 ppm)

Fig.5.1.3 (i) shows the variation in the surface resistance of ITO thin film sensor $R_{\text{gas}}$ in the presence of toluene vapours.

![Graph showing variation in electrical resistance of ITO sensor with temperature](image)

**Fig.5.1.3 (i)** The electrical resistance of ITO sensor with operating temperature upon exposure to toluene vapours (concentration: 1000 ppm)
The concentration of toluene vapours was 1000 ppm. The background resistance of the sensor in the absence of the test gas was, $R_{\text{air}}$ was found to be almost constant with temperature, within the range of ± 4%. It showed excellent stability against temperature and time variations, which has been reported in chapter 3. This indicates that the toluene vapours have reducing effect on the ITO surface. It also indicates that the redox reaction of toluene vapours on the surface of ITO thin film is maximum at 503 K. As explained in previous chapters the atmospheric oxygen adsorbed on the thin film surface of the oxide semiconductor removes electrons from the conduction band of the surface of the film, creating depletion region, causing the surface conductivity of the film to decrease and hence the resistance to increase. When reducing vapour molecules come in contact with thin film surface, they interact with the surface oxide ions, $O^-$ or $O_2^-$, leading to an inverse charge transference, liberating electrons back to the conduction band of the film surface and thus upon the return of the electrons to the conduction band, the conductivity increases and resistance decreases. This is expressed in a general way as shown in equation (2).

$$ R + O^- \rightarrow RO^- + e^- $$

(2)
The main reactions for the gaseous phase selective catalytic oxidation of toluene are reported by Zhang et al [18] as follows:

\[ C_7H_8(Toluene) + O_2 \rightarrow C_7H_8(Benzaldehyde) + H_2O \]  
\[ C_7H_8O + \frac{1}{2} O_2 \rightarrow C_7H_8O_2(Benzoicacid) \]  
\[ C_7H_8O_2 + \frac{1}{2} O_2 \rightarrow 7O_2 + 3H_2O \]  
\[ C_7H_8O_2 + \frac{3}{2} O_2 \rightarrow C_6H_6 + CO_2 + H_2O \]  
\[ C_7H_8O + 3O_2 \rightarrow C_6H_6 + CO_2 + H_2O \]  
\[ C_6H_5 + \frac{1}{2} O_2 \rightarrow 6CO_2 + 3H_2O \]

It is suggested that among these, reactions (5) and (6) are free radical reactions caused by gaseous phase decomposition and oxidation, and the reaction rate is related to the density of oxygen. Reaction (5) is the catalytic oxidation, and reactions (3) and (4) are catalytic reactions of partial oxidation.

Schmid et al [19] reported another reaction process of toluene as mentioned in equation (8). This equation shows the reaction of total oxidation of utilised analytes.

\[ C_6H_5CH_3 + 18[0] \rightarrow 7CO_2 + 4H_2O \]
In the case of the present study, it seems that upon interaction with the surface oxide ions, the toluene gets oxidized and any of the following chains of reactions are likely.

\[
\begin{align*}
C_7H_8 (\text{toluene}) + 2O^- &\rightarrow C_7H_6O (\text{benzaldehyde}) + H_2O + 2 \text{ e}^- \quad (10) \\
C_7H_6O + 2O^- &\rightarrow C_7H_6O_2 (\text{benzoic acid}) + \text{ e}^- \\
C_7H_6O_2 + O &\rightarrow 7CO_2 + 3H_2O + e^- \\
\text{OR} \\
C_6H_5CH_3 + 3O^- &\rightarrow C_6H_6 (\text{benzene}) + CO_2 + H_2O + e^- \quad (13) \\
C_6H_6 &+ 18O^- \rightarrow 6CO_2 + 3H_2O + 18e^- \quad (14) \\
\text{OR} \\
C_6H_5CH_3 + 18[O^-] & = 7CO_2 + 4H_2O + 18\text{e}^- \quad (15)
\end{align*}
\]

In either case, the reaction results into the liberation of electrons into the conduction band of ITO thin film, increasing the conductivity or decreasing the resistivity of the sensor.
Fig. 5.1.3 (ii) Resistance of ITO thin film sensor $R_{\text{gas}}$ for different concentrations of toluene vapours

Fig. 5.1.3(ii) shows the resistance of the sensor in the presence of the test gas, $R_{\text{gas}}$ for different concentrations in the range from 160 to 1000 ppm. The sensor operating temperature was 503 K.
Fig. 5.1.3 (iii) Relative change in resistance of ITO thin film with change in operating temperature for three different concentrations

Fig. 5.1.3 (iii) shows the relative change in resistance of the ITO sensor with different temperatures when exposed to the three different concentrations of toluene vapours, namely, 333 ppm, 666 ppm and 1000 ppm. As the concentration of toluene vapours increases, the relative change in resistance also increases. As seen from the figure, the relative change in resistance is maximum at 503 K for all three different concentrations, indicating that 503 K is the operating temperature for ITO thin film toluene sensors.
5.1.3 (iv) Response of ITO sensors having different film thicknesses to varied concentrations

Fig.5.1.3 (iv) shows the relative change in resistance of ITO thin film sensors having three different thicknesses with the concentration of toluene. The operating temperature was kept fixed at 503 K. The three sensors of set # 2 contained ITO films with thicknesses, 130 nm, 150 nm and 210 nm. The concentration of toluene vapours was varied from of 166 -1000 ppm. As can be seen from the plot, the relative change in resistance shows almost linear increase with concentration. It also suggests that the thinner films show better response. The reason for this has been explained in Chapter 4, and due to the fact that at higher temperature and for thinner films, the depletion layers extends more deeply into the grains thereby covering more portion of grains, and hence providing more space to accommodate the adsorbing vapours [20].
5.1.3 (v) The effect of various promoting layers on the ITO thin film surface to the detection of toluene

Fig.5.1.3 (v) shows the response of the ITO sensors to toluene vapours when different promoting layers of noble metals and oxides were deposited on the film surface, making the structure of the sensor, as shown in Fig.5.1.3 (v).
Fig. 5.1.3(v) Relative change in resistance of the ITO sensor with & without promoting layers

For this, a set of sensors with thinner films of Cu, MnO and Cr having thickness around 30 nm were deposited at room temperature on the top of the ITO thin film (thickness 210 nm) and the relative change in resistance of the sensors was observed in the presence of the test vapour. The concentration of toluene vapours was 1000 ppm.

As can be seen from the figure, sensors with Cu, MnO and Cr layers on ITO have promoting effects to the detection of toluene. It can be observed from the plot that the sensors with different promoting
layers show maximum relative change in resistance at different operating temperatures. This can be seen from Fig.5.1.3(v). As it reflects from Fig.5.1.3(v), MnO shows maximum relative change in resistance of the film suggesting more sensitivity. It can also be seen that for the sensors with Cu and MnO promoting layers, not only there is the enhancement in the sensitivity but there is also a reduction in the operating temperature. The operating temperature for MnO was 453 K whereas for Cu, it was found to be 473 K. The Cr, Cu, and also MnO promoters work as the electronic sensitizers. They get oxidized upon coming in contact with the oxide surface, increasing the depth of the depletion layer formed on the oxide surface. When the surface is exposed with toluene vapours, the corresponding promoting oxide gets reduced first, liberating free electrons back into the semiconducting oxide. Thus as the number of free electrons increases resistance decreases further also increases. Out of the three promoters, MnO/ITO shows more sensitivity because of the lower work function of Mn (4.1 eV) as compared to Cu (4.53-5.10 eV) and Cr (4.5 eV).
Fig. 5.1.3 (vi) Operating Temperatures of ITO toluene sensors without and with different promoting layers

Fig. 5.1.3 (vii) Relative change in resistance of the ITO sensor with temperature for MnO/ITO sensors

Fig. 5.1.3 (vii) shows the relative change in resistance of the ITO sensor without and with two different thicknesses of MnO, t1 (60 nm)
and $t_2$ (30 nm) on ITO thin film at the operating temperature 453 K.

As seen from Fig. 5.1.3 (viii), more the thickness of MnO, higher is the response. As the ionic radius of Mn is smaller, large number of particles of MnO enhances the depletion layer width further, thus making the surface ready to receive more of toluene molecules.

![Fig. 5.1.3 (viii) Relative change in resistance of the MnO/ITO (of different thicknesses of MnO layer with temperature](image)

Another interesting finding as can be seen from the Fig. 5.1.3 (vii) was that the MnO/ITO sensor shows two maxima, one at 453 K and the other at 493 K. It proves that with MnO/ITO, the oxidation route of toluene is as explained in equation (12) and (13) by first getting oxidized to benzene and then to carbon dioxide and water. At 493 K,
the sensor senses benzene produced as a result of the oxidation process of toluene.

**Fig.5.1.3 (ix)** Transmission electron micrographs of films without and with MnO layer on ITO

Fig.5.1.3 (ix) shows the transmission electron micrographs of ITO thin films without and with MnO. As can be seen from the micrographs, the MnO changes the microstructure of the film, enhancing the
average crystallite size. The crystallite size of ITO sensor without any layer was 14.29 nm, where as for the MnO layer of thickness 30 nm, it was 26.43 nm and MnO layer of thickness 60 nm, the average crystallite size was 50.72 nm. The changed microstructure changes the transduction property of the sensor [21] responsible for the sensitivity of the sensor.

5.1.3 (iv) Response of the MnO/ITO sensor with concentration of toluene vapours in the extended range in 10 – 1000 ppm

In order to actually connect the sensor to an electronic system, the ITO toluene sensor was interfaced with a transducer bridge driving an instrumentation amplifier circuit. The generated voltage due to the change in the resistance of the sensor in the presence of the test gas was measured. Fig.5.1.3 (x) (a) shows the plot of the output voltage from the instrumentation amplifier to various concentrations of toluene, varied from 10 to 200 ppm for the sensor MnO (t1)/ITO. As can be seen from the figure, for the lower range of concentration, i.e from 10 to 200 ppm, the slope of the curve is 0.41 mV/ppm whereas for the range from 300 to 1000 ppm, in Fig.5.1.3 (xiii) (b), the slope is 0.73183 V/ppm. This shows that in the lower concentration of toluene vapours, the relative change in resistance
of the sensor is low. This may be due to the low molecular kinetic energy of toluene in general [25].

![Graph](image1)

**Fig. 5.1.3 (x)** Output voltage from sensor # 4 with toluene concentrations (10 -1000 ppm)
5.1.3 (v) Enhanced performance of Cu/MnO/ITO sensor

In order to further enhance the detection characteristics of MnO/ITO sensors to toluene, a third layer of Cu of thickness around 30 nm was deposited on the top of the MnO/ITO.

\[ \text{y} = 0.09724 - 11.20 \]
\[ R^2 = 1 \]

![Graph](attachment:image.png)

**Fig.5.1.3 (xi)** Variation in the relative change in resistance of the Cu/MnO/ITO sensor with different concentration range (300-1000 ppm).

Fig.5.1.3. (xi) shows the relative change in resistance of the sensor with Cu/MnO/ITO for different operating temperatures to the toluene vapours. It is seen from the graph that with Cu/MnO (t1)/ITO layers, the response was enhanced further. As can be seen
from the figure, the operating temperature got still lowered down and was found to be 373 K. This enhanced performance may be due to the combination of high electronegativity of Cu and low electron work function of MnO.

Fig. 5.1.3 (xi) shows the relative change in resistance of the sensors without and with Cu/MnO (t1)/ITO with different concentrations of toluene vapours. The concentration was varied in the range 300 to 1000 ppm. As can be seen from the figure, the response is linear. For the sensor with Cu/MnO/ITO film, the slope of the plot was found to be 0.09724/ppm, which was FIVE times higher as that against 0.019/ppm for the sensor with only ITO film.

![Graph showing relative change in resistance](image)

**Fig.5.1.3 (xii) Enhanced performance with Cu/MnO/ITO**
Fig. 5.1.3 (xii) Response time of the Cu/MnO/ITO sensor to 1000 ppm toluene vapours (a) Rise time and recovery time of Sensor #6, (b) Dynamic response of #6
Fig. 5.1.3 (xii) (a) shows the static response of the ITO sensor # 6, i.e. Cu/MnO/ITO with respect to time. The rise time i.e. the time required for the output to rise from 10% to 90% of its maximum value was found to be 45 sec where as the recovery time, i.e. the time required for the output to change from the 90% to 10% of its final value, was found to be 52 sec. The response of sensor # 1, i.e. the ITO film was also studied. The rise time of sensor #1 was 90 sec., and the recovery time was found to be 120 sec. The sensor without any promoting layer was very slow as compared to the sensor with Cu/MnO/ITO.

The dynamic response of the sensor # 6 upon successive injections of toluene vapours is shown in Fig. 5.1.3 (xii) (b). A fixed concentration of toluene (1000 ppm) was injected in the test chamber and the resistance of the sensor $R_g$ was measured every 5 sec. When the resistance reached its minimum value, the exhaust was opened. The sensors showed good repeatability.
5.2 BENZENE

5.2.1 INTRODUCTION

5.2.1 (i) Need and importance of Detection of Benzene

(a) Applications

Benzene is mainly produced from crude oil, petrochemical plant and is a colourless, volatile, flammable liquid with a characteristic sweet odour and whose vapours can form explosive mixtures [1]. Benzene is a major industrial chemical with petroleum being the main source from which the compound is derived. It is widely used in chemical processes used to produce products ranging from plastics to pesticides to pharmaceuticals, and manufacturing of chemicals [2].

(b) Hazardous effects

Benzene is a notorious cause of bone marrow failure. Substantial quantities of epidemiologic, clinical, and laboratory data link benzene to a plastic anaemia, acute leukaemia, and bone marrow abnormalities [3]. Acute exposure to relatively high concentrations of benzene (benzol) may result in central nervous system disturbances consistent with solvent exposure, viz., drowsiness, dizziness, headache, tremor,
delirium, ataxia, loss of consciousness, respiratory arrest and death [4].

(c) Exposure Limits

Table 5.2.1 (i)

<table>
<thead>
<tr>
<th>Explosive report</th>
<th>1.2-7.8%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Threshold limit value</td>
<td>10 ppm</td>
</tr>
</tbody>
</table>

5.2.1 (ii) Detection

(a) Chemical, Physical Properties

The structure, the Chemical and Physical properties of Benzene are as shown in table 5.2.1(ii).

Fig. 5.2.1 (ii) Structure of Benzene [5]
Table 5.2.1 (ii) Chemical & Physical properties of Benzene [5]

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar formula</td>
<td>$C_6H_6$</td>
</tr>
<tr>
<td>Molar mass</td>
<td>78.11 g mol$^{-1}$</td>
</tr>
<tr>
<td>Solubility</td>
<td>Colourless liquid</td>
</tr>
<tr>
<td>Appearance</td>
<td>Colourless liquid</td>
</tr>
<tr>
<td>Density</td>
<td>0.8765(20) g/cm$^3$</td>
</tr>
<tr>
<td>Melting point</td>
<td>5.5 °C, 278.7 K</td>
</tr>
<tr>
<td>Boiling point</td>
<td>80.1 °C, 353.3 K</td>
</tr>
<tr>
<td>Solubility in water</td>
<td>Soluble in alcohol, chloroform, $CCl_4$, diethyl ether, acetone</td>
</tr>
<tr>
<td>Viscosity</td>
<td>0.652 cP at 20 °C</td>
</tr>
<tr>
<td>Odour</td>
<td>Characteristic, sweet odour at lower concentrations with a disagreeable, irritating odour at higher concentrations.</td>
</tr>
</tbody>
</table>
(b) **Review of literature on the detection of benzene reported by researchers**

Parreira *et al* [6] studied an efficient method to determine indoor exposition to benzene, toluene, ethyl benzene, xylene, and styrene by Gas Chromatographer analysis with a flame ionization detector (FID) and a solid phase micro extraction sampling device. Reports are there with sensor used for electronic nose applications [7]. Duran *et al* [8] have reported that it is possible to determine contamination of carbon dioxide by benzene at trace levels even in the presence of other pollutants at ppm levels combining a pre-concentrator and a gas sensor array. Horrillo *et al* [9] worked on a semiconductor solid-state multisensor of small size developed as a measuring system.

(c) **Performance criteria to be met**

With promoting layers, people are trying to lower down the operating temperature and maintaining the higher sensitivity. However, sufficient output is not achieved as the lower operating temperature does decrease the sensitivity. So the
objective is to fabricate a device with low operating temperature and high sensitivity and selectivity.

5.2.2 Experimental Methodology

5.2.2 (i) Fabrication of ITO thin film sensor and Measurements

As explained in chapter 3, the direct evaporation technique (Hind Hi Vac, Model: 15F6) was used for the deposition of thin films of ITO thin film benzene sensors.

Fig. 5.2.2 (i) (a and b) shows of the structure and the measurement set-up. A miniature heater prepared of Ni-Cr was kept in the back side of the sensor.

![Diagram](image)
5.2.3 Results and Discussion

5.2.3 (i) Variation in the electrical resistance of the ITO sensor with temperature in presence of Benzene vapours

Fig. 5.2.3 (i) shows the variation in the electrical resistance of ITO thin film sensor $R_{\text{gas}}$ in the presence of benzene vapours.
Fig. 5.2.3 (i) The electrical resistance of ITO sensor $R_{\text{gas}}$ with operating temperature upon exposure to benzene vapours (Concentration 1000 ppm)

The concentration of benzene was 1000 ppm. The background resistance of the sensor in the absence of the test gas, $R_{\text{air}}$, was almost constant with temperature within the range of ± 4%. The graph indicates that the benzene vapours have reducing effect on the ITO surface. As explained earlier, in the absence of the test vapour, atmospheric oxygen gets reduced on the oxide surface of ITO, using electrons from the conduction band of ITO and gets converted to oxide ion, creating a thin depletion region on the
surface. When the same surface comes in contact with benzene vapours, benzene gets oxidized by the surface oxide ions, liberating free electrons back into the conduction band of ITO. This causes a decrease in the surface resistance of ITO sensor. The reactions of benzene in the presence of oxygen are suggested by Fogler and Gurmen [11] as follows:

\[
C_6H_6 + \frac{9}{2}O_2 \rightarrow C_4H_4O_3 + 2CO_2 + 2H_2O \quad (1)
\]

\[
C_4H_4O_3 + 3O_2 \rightarrow 4CO_2 + H_2O \quad (2)
\]

\[
C_6H_6 + \frac{15}{2}O_2 \rightarrow 6CO_2 + 3H_2O \quad (3)
\]

In the present case, the oxidation of benzene on oxide surface can lead to the generation of electrons and can be explained by equation (4).

\[
C_6H_6 + 15\bar{O}^- \rightarrow 6CO_2 + 3H_2O + 15e^- \quad (4)
\]

Figure also indicates that this redox reaction is optimum at 483 K temperature of the ITO sensor, making it an optimum operating temperature for benzene. Upon further increase in the temperature, the resistance increases.
Fig. 5.2.3 (ii) shows the relative change in resistance of the ITO sensor with temperature when exposed to the benzene vapours of different concentrations, namely, 333 ppm, 666 ppm and 1000 ppm.

As can be seen from the figure, as the concentration of benzene vapours increases, the relative change in resistance also increases. The relative change in resistance is maximum at 483 K for all the three different concentrations, indicating that 483 K is the operating temperature for ITO thin film benzene sensors. The redox reaction is temperature dependent and is optimum at 483 K. Upon
further increase in the temperature, the relative change in resistance decreases.

5.2.3 (ii) Response of ITO sensors having different film thicknesses with different concentrations of benzene vapour

![Graph showing relative change in resistance of ITO sensors with benzene concentration](image)

**Fig. 5.2.3 (iii)** Relative change in resistance of the ITO sensor of different thickness with concentration of benzene vapour

Fig. 5.2.3 (iii) shows the relative change in resistance of ITO thin film sensor having three different thicknesses with the concentration of benzene. The thicknesses were 130 nm, 180 nm and 210 nm. The operating temperature was kept fixed at 483 K. The concentration of benzene was varied from of 166-1000 ppm. As it can be seen, the
relative change in resistance shows almost linear increase with concentration. It also suggests that the thinner films show better response. This is in agreement to the previous study for HCHO and toluene sensors.

5.2.3 (iii) The effect of various promoting layers on the ITO thin film surface to the detection of benzene

In order to enhance the performance of the sensor, sets of sensors with thin promoting layers of Cr, MnO, MgO and Cu, deposited on the top of the surface were fabricated and tested for the detection of benzene. The concentration of benzene vapours was 1000 ppm. It can be observed from the Fig.5.2.3 (iv) that sensors with promoting layers show maximum relative change in resistance at different operating temperatures.

In the absence of the test gas and the presence of atmospheric oxygen, these noble metals/oxides get oxidized upon coming in contact with the oxide surface, forming an additional depletion layer on the top or increasing the depth of the depletion layer formed on the oxide surface as shown in Fig.5.2.3 (v) and (vi).
Fig. 5.2.3 (iv) Effect of promoting layers on ITO to the detection of benzene vapours

When such surface is exposed to benzene vapours, benzene reacts with the noble metals/oxide, liberating free electrons. Thus the noble metals/oxides provide additional amount of depletion layer accommodating more benzene molecules and get oxidized on the surface and liberate more number of free electrons. Thus it enhances the response. At the optimum temperature for the corresponding metals, the redox process is maximum and hence at that temperature there is a peak in the relative change in resistance.
Fig. 5.2.3 (v) Chemisorption of Benzene on the film surface

Fig. 5.2.3 (vi) The mechanism of the electronic promoter/sensitizer on the top of the film
It is also observed that the sensor with Cr layer on ITO shows maximum relative change in resistance of the film suggesting more sensitivity. This may be mainly due to the high surface energy of Chromium as against Mn and Cu. It has been reported that the surface energy of Cr is 2.30 J/m$^2$, of Mn is 1.60 J/m$^2$ and of Cu is 1.83 J/m$^2$ [13]. Higher surface energy enhances the surface redox processes.

This was verified by exposing the Cr/ITO sensor to different concentrations of benzene vapour. Chromium has a catalytic effect to benzene vapours. The catalytic oxidation of benzene in the presence of Cr is widely reported [14-16]. As can be seen from the Fig.5.2.3 (v), at the temperature 373 K, the relative change in resistance shows a smaller peak which may be due to the catalytic effect of Chromium at lower temperature. At 483 K, there is another higher peak which may be due to the effect of the formation of chromium oxide and the enhancement of the redox process at that temperature.
Fig. 5.2.3 (vii) Response of Cr/ITO sensor with temperature to different concentration of benzene

Fig.5.2.3 (viii) shows the response of the Cr/ITO sensor to benzene vapours for two different thicknesses of Cr 35 nm and 25 nm. The concentration of Cr in films with different thicknesses was confirmed by EDAX as shown in Fig.5.2.3 (ix). For film with 35 nm thickness, the concentration as reported in EDAX is 0.18 weight % and in the film with 25 nm thickness, the weight % reported is 0.14. The film with 0.18 weight % Cr shows more sensitivity as compared to film with 0.14 weight % and the ITO film without any catalytic layer.
Fig. 5.2.3 (viii) The relative change in resistance of the ITO film with and without Cr layer for various concentrations of benzene vapours.

Fig. 5.2.3 (ix) EDAX of Cr/ITO films (0.18% and 0.14 weight%)
5.2.3 (iv) Selectivity of Benzene sensor with respect to Toluene

As toluene is a derivative of benzene, it is very difficult to obtain selectivity of benzene with respect to toluene. A detailed study of the response of ITO sensor to toluene was carried out in section 1 of this chapter. In continuation of that work, Fig.5.2.3(x) shows the response of Cr/ITO and MnO /ITO sensors to both toluene and benzene, and also that of Cu/ITO to benzene.

It can be seen from the scanning micrographs in Fig.5.2.3. (xi) that the effect of MnO/ITO is different than that of Cr/ITO from ITO without any promoting layer. The surface microstructure with smaller ionic radii of MnO/ITO is more suitable for toluene than that of benzene which has comparatively higher molecular diameter than toluene [17].

As can be seen from Table 5.2.3 (i), the operating temperature for sensors having different promoting layers are quite different for toluene and benzene vapours. The redox process is maximum at different temperatures for films with different promoting layers.
**Fig. 5.2.3 (x) (b) Comparison of response to toluene ad benzene of different sensors**
Fig. 5.2.3 (xi) Scanning electron micrographs of (a) ITO (b) MnO/ITO and (c) Cr/ITO films
Table 5.2.3 (i) Operating temperature of ITO sensors with promoting for benzene and toluene vapours

<table>
<thead>
<tr>
<th>Sensors</th>
<th>Op. Temp.</th>
<th>Cr/ITO Toluene</th>
<th>Cr/ITO Benzene</th>
<th>MnO/ITO Toluene</th>
<th>MnO/ITO Benzene</th>
<th>Cu/ITO Benzene</th>
<th>Cu/MnO/ITO Toluene</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>503 K</td>
<td>483 K</td>
<td>453 K</td>
<td>503 K</td>
<td>483 K</td>
<td>373 K</td>
<td></td>
</tr>
</tbody>
</table>

Toluene is a methyl group. Therefore the molecular kinetic energy of benzene is more than that of toluene. But Benzene requires higher temperature than toluene to get oxidized. It was observed that sensor with Cr/ITO shows optimum operating temperature at 483 K where as the sensor with multiple layers of Cu/MnO/ITO has the operating temperature at 373 K. Cu was used because of its high electro negativity. Fig.5.2.3 (xi) shows a good selectivity for benzene and toluene.
5.2.3 (v) Response of the Cr/ITO sensor in the concentration of range 30 – 1000 ppm of Benzene vapours

In order to actually connect the sensor to the electronic system, the ITO benzene sensor was interfaced with a transducer bridge driving an instrumentation amplifier circuit. The generated voltage due to the change in the resistance of the sensor in the presence of the test gas was measured.
**Fig. 5.2.3 (xiii)** output voltage from the instrumentation amplifier system with benzene concentrations range: 30-1000 ppm

Fig. 5.2.3 (xiii) shows variation in the output voltage from the instrumentation amplifier with the concentrations of benzene in the range of 30 to 1000 ppm for the Cr/ITO sensor. As can be seen from the figure, the response is linear but with different slopes in two different ranges. The response in lower range up to 100 ppm was found more which is due to the fact that with lower concentrations, the amount of H₂O liberated, which affects the performance of the sensor is also less.
5.2.3 (vi) The rise time and recovery time of Cr/ITO sensor

Fig.5.2.3 (xiv) shows the static response of the ITO sensor with Cr/ITO promoter layer with respect to time. The *rise time* i.e. the time required for the output to rise from 10% to 90% of its maximum value was found out to be 38 sec where as the *recovery time*, the time required for the output to change from the 90% to 10% of its final value, was found 53 sec. The rise time for ITO sensor without any promoting layer was found 71 sec and the recovery time was found 51 sec. Thus the Cr/ITO sensor also enhances the speed of response of the sensor.

![Graph showing response time of the Cr/ITO sensor](image)

**Fig.5.2.3 (xiv) Response time of the Cr/ITO sensor**
5.2.3 (vii) The dynamic response of the sensor to cyclic injection of benzene vapours

![Graph showing the dynamic response of Cr/ITO thin film to cyclic exposure of benzene](image)

**Fig.5.2.3 (xv) Response of Cr/ITO thin film to cyclic exposure of benzene**

Fig.5.2.3 (xv) shows the dynamic response of the ITO film sensor to benzene vapours. A fixed concentration of benzene (1000 ppm) was injected in the test chamber and the resistance of the sensor $R_{\text{gas}}$ was measured every 5 sec. Only two cycles are shown in the figure, however the experiment was repeated for several cycles and the sensor showed good repeatability.
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