Chapter 5

LPG sensing properties of Al, Sn and Cd doped ZnO
and the effect of electron irradiation

Chapter 5 investigates the LPG sensing properties of ZnO nano structured thin films, doped with different doping elements at three different doping concentrations. Three doping elements viz Al, Sn and Cd were used for the comparative study and the doping concentrations were 3, 5 and 7 atomic percentages. All the films used for the study were prepared in identical preparation conditions and were characterized by different characterization techniques. The sensitivity, response time and recovery time of these samples to LPG were determined and compared. Further, the samples doped with 3, 5 and 7 atomic percentage were given high energy electron beam irradiation in two different dosages of irradiation. The sensitivity, response time and recovery time of these samples were also determined and compared with that of the non irradiated samples of same preparation conditions.
5.1 Introduction

Liquefied petroleum gas being the primary fuel of majority of Indian kitchen, sensing it in an easy way has primary concern. It is a flammable mixture of hydrocarbon gases and it mostly contains propane(C$_3$H$_8$) and Butane(C$_4$H$_{10}$) with a density of 0.55 Kg/L. Even if LPG is mostly used for cooking purposes, it is also used as an aerosol, automobile fuel and as a propellant. LPG is heavier than air but lighter than water. Therefore even if it escape from its container it remains on the ground and will be very dangerous. This makes the sensing of presence of LPG in higher concentrations in the atmosphere more important. Majority of sensors used today are metal oxide semiconductor sensors which are comparatively the least expensive and most simple. Metal oxides as thin and thick films are used as sensors but thin films have more advantages as the sensing properties relay on surface morphology of the films[1]. It has been also proved that sensitivity of the films depend on the properties of the grain boundaries[2]. So the study of gas sensing properties of metal oxide films are confined to thin films than thick films or pellets. Metal oxide thin films have been used for gas sensing applications since 1962. Among them the first used was ZnO[3]. ZnO thin film sensors have a high value of sensitivity, which can even sense low concentration such as parts per billion[4-7]. A sensor with a sensitivity of ppb is not easy to fabricate and therefore most of the sensors used for the sensing of pollutant gases, reducing gases or LPG cannot be used in a laboratory for the precise measurement of the concentration of a gas in sub ppm levels.

Among the metal oxide semiconductor sensors, the most used and the most studies are the ZnO sensor. SnO$_2$[8], iron Oxide[9], V$_2$O$_5$[10,11] etc are also being used for gas sensing applications. These metal oxide thin films can be used to sense many
gases including the pollutant gases such as sulfur dioxide, carbon dioxide, oxides of nitrogen, poisonous gases such as carbon monoxide, almost all reducing gases, combustible gases such LPG, biogas and all refining gases. The greatest advantage of these sensors is that a single sensor can be used to sense a number of gases. SILAR method was used for the deposition of the films in the present study because of the simplicity and other advantages of the method over others.

It has been reported that pure and doped ZnO thin films show sensitivity to reducing, combustible and polluting gases. Doping with elements such as Al[12], Cd, Sn[13] etc will increase the sensitivity of the films. Effect of electron irradiation on ethanol sensitivity of Al-ZnO film has been reported recently by the author and co workers[14]. The enhancement in ethanol sensitivity of Al, Sn and Cd doped ZnO thin films due to high energy electron beam irradiation is reported in chapter 4. It was not only the sensitivity but also the response time of the samples were varied by electron irradiation, when the films were used for ethanol sensing.

In the present work, the sensitivity of Al, Sn and Cd doped ZnO thin films to LPG, their response time and recovery time were studied and compared. The effect of high energy electron beam irradiation on sensitivity, response time and recovery time of these samples to LPG was also investigated.

5.2 Materials and methods

The preparation of ZnO thin film with SILAR method is quiet common. This method includes the successive dipping of a pre-cleaned glass substrate in sodium zincate solution and in hot water at nearly boiling temperature[12]. In this method, doping is done by adding an appropriate compound of the dopant into the chemical bath prepared for dipping.
Doping with Al was done by adding calculated amount of Al\(_2\)SO\(_4\) to the sodium zincate bath before dipping. CdCl\(_2\) and SnCl\(_2\) were used for doping to fabricate Cd-ZnO and Sn-ZnO respectively. Cd-ZnO, Sn-ZnO and Al-ZnO films with three different doping concentrations have been prepared; 3 atomic percentage, 5 atomic percentage and 7 atomic percentage. Films of same doping material and concentration were prepared simultaneously in the same cationic solution and water baths using a SILAR dip coating unit to provide identical preparation conditions. All the film were annealed at 450\(^{\circ}\) C for 1 hour. The thickness of all the films used for the present study were measured by gravimetric method and it was found that the films had an average thickness of 0.98 micro meter

Doped ZnO thin films, thus prepared, were placed inside the gas sensing chamber to study the sensitivity of the films to LPG. The variation in resistance of the films in the presence of LPG was observed with Keithley digital multimeter using two probe method. During the process of preparation, there were chemisorbed oxygen at grain boundaries and at film surface, which had trapped the conduction electrons of the film and had resulted in an increase in the resistance of the film. It has been reported that the chemisorbed oxygen exists as O\(_2^-\), O\(^-\) and O\(_2^2-\) depending on the temperature of the surface[15]. As LPG is a mixture of propane (2.17%) and butane (92.82%), the molecules of LPG reacted with these oxygen species and the conduction electrons of the ZnO thin film became free. This led to a decrease in resistance of the film. The gas sensing chamber was maintained at rotary vacuum and was provided with the provision for heating. The temperature of the chamber was controlled with a micro controller. A schematic diagram of LPG sensing unit is given as figure 2.9

Before admitting into the gas sensing chamber, LPG was filled into the pre-heating chamber. There it was heated to 300\(^{\circ}\)C. At a temperature of 300\(^{\circ}\)C and a
pressure of 0.2 m bar, LPG was admitted into the sensing chamber by opening the gas admit valve of the chamber. The resistance of the film reduced considerably, within a time of 1 second, by the admittance of LPG. Closing of gas admit valve cut the flow of LPG into the chamber and the remaining gas in the chamber was removed by the vacuum pump. Then the resistance of the film found increasing and soon it reached the initial value. The time taken by the film to regain its original resistance after the closing of the gas was recorded as the recovery time of the film. The experiment was repeated many times to optimize the response and recovery times. The sensitivity of the films were calculated using the equation

\[
\frac{(R_{\text{air}} - R_{\text{gas}})}{R_{\text{air}}}
\]

A set of Al, Sn and Cd doped ZnO samples were given high energy electron beam irradiation in two different dosage viz 6 K Gray and 8 K Gray. These samples were also put in the gas sensing chamber to study their sensitivity to LPG. The experiment was repeated for the electron irradiated samples also. The sensitivity, response time and recovery time of the samples according to irradiation, doping element and doping concentration were compared and tabulated.

The sensitivity to LPG, response time and recovery time of the samples with an irradiation dosage of 6 K Gray were compared with that of samples with 8 K Gray irradiation.

5.3 Results and discussion

It is well known that oxygen is absorbed on ZnO surface as O\(^{-}\), O\(_2\)\(^{-}\) and O\(_2^2\)\(^{-}\) by capturing electrons[16]. Here in the experiment, LPG acted as a reducing agent and captured the chemisorbed oxygen from the ZnO films. This resulted in increase in number of free electrons on the surface of the thin film and there by an increase in the
conductivity of the film. It was observed that the response time was only 1 second for all films irrespective of doping element and doping concentration. As soon as LPG was removed from the gas chamber, the film regained its initial resistance in a short duration of time called the recovery time.

Table 5.1 compares the response time, recovery time and sensitivity of Al, Sn and Cd doped ZnO thin films to LPG.

The sensitivity of the samples to LPG, according to different doping concentrations were also compared and are tabulated. The results are given in table 5.2. High energy electron beam irradiation increased the surface defects and these defects increased the sensitivity of the films as that observed in the case of ethanol vapour in chapter 4.

The comparison of sensitivity as well as response and recovery times of the films which were undergone electron beam irradiation to the non-irradiated samples were done and recorded. The same was done for Al, Sn and Cd doped ZnO films at three...
different doping concentrations. The comparison of sensitivity, response and recovery times between irradiated and non-irradiated samples of Sn-ZnO, Al-ZnO and Cd-ZnO showed only slight variations in values and all of them followed the same pattern. The comparison table of Al-ZnO is given in table 5.3

<table>
<thead>
<tr>
<th>Doping Concentration</th>
<th>Sensitivity %</th>
<th>Response time (sec)</th>
<th>Recovery time (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>non-irradiated</td>
<td>irradiated</td>
<td>non-irradiated</td>
</tr>
<tr>
<td>3 atomic %</td>
<td>19</td>
<td>35</td>
<td>1</td>
</tr>
<tr>
<td>5 atomic %</td>
<td>33</td>
<td>38</td>
<td>1</td>
</tr>
<tr>
<td>7 atomic %</td>
<td>46</td>
<td>58</td>
<td>1</td>
</tr>
</tbody>
</table>

A graph showing sensitivity of Al-ZnO to LPG according to percentage of doping is given in figure 5.1. Similar graphs of Sn-ZnO and Cd-ZnO are given in figure 5.2 and 5.3 respectively.

![Sensitivity of Al-ZnO to LPG](image)

**Figure 5.1**

Response time of all the samples were found 1 second irrespective of doping concentration, doping element and electron irradiation, but doping as well as irradiation had affected the recovery time of the samples.
A graphical representation of variation of recovery time with doping concentration of the electron irradiated and non-irradiated Al ZnO samples are given in figure 5.4.
Sensitivity and recovery time graphs of Sn-ZnO and Cd-ZnO also followed the same pattern. The corresponding data are given in table 5.1. The samples given 6K Gray irradiation showed no change in sensitivity, response and recovery time from the samples given 8 K Gray irradiation. The corresponding sensitivity data is recorded in table 5.4.

<table>
<thead>
<tr>
<th>Doping</th>
<th>Sensitivity</th>
<th>Recovery time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Non-irradiated</td>
<td>6K Gray irradiated</td>
</tr>
<tr>
<td>Sn</td>
<td>45</td>
<td>60</td>
</tr>
<tr>
<td>Al</td>
<td>32</td>
<td>39</td>
</tr>
<tr>
<td>Cd</td>
<td>30</td>
<td>38</td>
</tr>
</tbody>
</table>

Figure 5.4

Table 5.4: comparison of 5 at % doped ZnO to different dosages of irradiation
5.4 Conclusions

Gas sensing properties of Al-ZnO, Cd-ZnO and Sn-ZnO thin films to LPG were studied and compared.

Al-ZnO, Sn-ZnO and Cd-ZnO thin films prepared by SILAR method were found to have good and fast response to LPG. There was enhancement in sensitivity of Sn-ZnO, Cd-ZnO and Al-ZnO thin films irradiated with high energy electron beam when compared to the sensitivity of non irradiated samples of same configuration.

Response time was found 1 second for all samples, regardless of doping concentration or the dosage of irradiation, but the recovery time of the samples found decreasing due to electron irradiation. A small variation in dosage of irradiation showed no difference in sensitivity, response time and recovery time.
References


