CHAPTER -7
ETHANOL GAS SENSOR

7.1 Introduction

Gas sensors are devices that interact with a gas to initiate the measurement of its concentration. The gas sensor then provides output to a gas instrument to display the measurements. Common gases measured by gas sensors include ammonia, aerosols, arsine, bromine, carbon dioxide, carbon monoxide, chlorine, chlorine dioxide, Diborane, dust, fluorine, germane, halocarbons or refrigerants, hydrocarbons, hydrogen, hydrogen chloride, hydrogen cyanide, hydrogen fluoride, hydrogen selenide, hydrogen sulfide, mercury vapor, nitrogen dioxide, nitrogen oxides, nitric oxide, organic solvents, oxygen, ozone, phosphine, silane, sulfurdioxide, and water vapour.

Important measurement specifications to consider when looking for gas sensors include the response time, the distance, and the flow rate. The response time is the amount of time required from the initial contact with the gas to the sensors processing of the signal. Distance is the maximum distance from the leak or gas source that the sensor can detect gases. The flow rate is the necessary flow rate of air or gas across the gas sensor to produce a signal.

Gas sensors can output a measurement of the gases detected in a number of ways. These include percent lower explosive limit (LEL), percent volume, trace, leakage, consumption, density, and signature or spectra. The lower explosive limit or lower flammable limit (LFL) of a combustible gas is defined as the smallest amount of the gas that will support a self-propagating flame when mixed with air (or oxygen).
and ignited. In gas-detection systems, the amount of gas present is specified in terms of % LEL: 0% LEL being a combustible gas-free atmosphere and 100% LEL being an atmosphere in which the gas is at its lower flammable limit. The relationship between % LEL and % by volume differs from gas to gas. Also called volume percent or percent by volume, percent volume is typically only used for mixtures of liquids. Percent by volume is simply the volume of the solute divided by the sum of the volumes of the other components multiplied by 100%. Trace gas sensor is given in units of concentration: parts per million (ppm). Leakage is given as a flow rate like ml/min. Consumption may also be called respiration, given in units of ml/L/hr. Density measurements are given in units of density: mg/m$^3$. A signature or spectra measurement is a spectral signature of the gases present; the output is often a chromatogram. Common outputs from gas sensors include analog voltage, pulse signals, analog currents and switch or relays. Operating parameters to consider for gas sensors include operating temperature and operating humidity. Gas monitoring devices are in demand for a rapidly growing range of applications.

Metal oxide-based chemical sensors have been used extremely for the detection of toxic pollutant gases, combustible gases and organic vapours. The main advantage of chemical sensors is long life, small in size, low power consumption and easy fabrication. Many reports have demonstrated that the gas sensing properties of the semi-conducting sensors are greatly affected by the addition of metal oxides and noble metals [1-6]. Metallic oxides are generally used as sensor material. Semiconducting metal oxide sensors have been extensively studied due to their simplicity and sensitivity to the ambient conditions [7-9].
Zinc oxide (ZnO), an n-type metal oxide semiconductor sensing material with a wide band gap ($E_g = 3.37$ Ev at 300 K), has been under extensive research owing to its high chemical stability, low cost, and good flexibility in fabrication. It has pronounced gas sensitivity to such gases as NH$_3$, O$_3$, NO$_2$, CO, H$_2$, ethanol and other species [10-12]. Recent years have witnessed great interests to improve the gas sensitivity as well as selectivity and to decrease the working temperature. Most of the studies up to now are focused on sintered particle or thin-film based devices, but reports on the gas sensing properties of one-dimensional zinc oxide nanomaterials are rare. Several groups have recently proposed that the nanowires or nanoribbons of semiconducting oxides are very promising sensors, and some of their results have shown that the devices based on one-dimensional nanostructures have great potential in overcoming the fundamental limitations of traditional semiconductor oxide sensors based on sintered particles or thick-films such as low sensitivity, poor stability and high working temperature [13-16].

### 7.2 Gas sensor Design

The ZnO doped with Mn has potential application in opto electronic devices like LED, PV solar cells as window layer and in gas sensors. The gas sensor properties were estimated at the facility available in Bishop Hebers College, Tiruchirappalli. The instrument involves a design capable of permitting a known gas inside a chamber allowing it to be present for a period of time and letting out afterwards. The ethanol sensing behaviour of the electrodes were tested by measuring the resistivity of the sample with ($R_g$) and without gas ($R_a$). The gas sensitivity is evaluated by the expression
\[ S_G = \frac{R_a}{R_g} - 1 \text{ or } \frac{R_a - R_g}{R_g} \]

The schematic diagram of the experimental set up is shown in Fig. 7.1. The ZnO doped with Mn thin films prepared using SILAR were mounted one sample at a time in the sensor element holder inside the air tight chamber mounted with a platinum heater with provision for gas inlet and outlet. The sensor temperature was measured by the Ni-Cr thermocouple with an accuracy of \( \pm 1^\circ \text{C} \) using a temperature controller. The test gas diluted in air was admitted inside the chamber using a mass flow controller. An electric fan was installed in the container which improves the gas and air flow. The resistances of the samples were measured using a Keithly meter in the presence of test gas and air.
7.3 Ethanol Gas Sensing:

Ethanol vapours on the sensor element being dominant in this temperature range, the sensitivity characteristic of the sensor is associated with a modification of the ZnO surface by the electron transfer mechanism. ZnO is an n–type semiconductor, in which adsorbed oxygen reacts with the test gas releasing electrons to the conduction band by which the conductivity increases. As in the case of ethanol vapour it is well known that there are two oxidation states of ethanol.

\[ \text{C}_2\text{H}_5\text{OH} + \frac{1}{2} \text{O}_2 \rightarrow \text{CH}_3\text{CHO} + \text{H}_2\text{O} \quad \ldots \ldots \quad (7.2) \]

\[ \text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O} \quad \ldots \ldots \quad (7.3) \]

The equation (7.2) represents oxidation by the dehydrogenation to CH$_3$CHO intermediate and equation (7.3) oxidation by the dehydration to C$_2$H$_4$\cite{17-19}. But the selectivity for the two reactions is initiated by the acid-base properties of the oxide surface. The dehydrogenation process is more probable and is favoured on the acid surface. A number of experiments have been carried out for the stability of the sensor with time.

7.4 Results and Discussion:

The typical gas sensing response obtained for the undoped and 1 % to 3 % preliminary results of the gas sensor for ethanol gas with the sensing element as SILAR grown Mn doped ZnO are presented here. Mn doped samples were shown in Fig. 7.2. It is observed that the gas sensing response is oscillatory. The region where saturation in response is observed is used for evaluating the sensing performance and its recovery rate. It is observed that Mn incorporation of 1% in solution is most
sensitive. The typical temperature of post annealing of the samples was 350 °C for 30 minutes. The gas sensing at room temperature were performed.
Fig. 7.2 The typical sensor response of Mn doped ZnO thin films (annealed at 350 °C for 30 minutes) with time (min) at room temperature for ethanol.
7.5 Conclusion:

The Gas sensors revealed a saturation region between 3 to 5 seconds and recovery region in 16 to 20 seconds. The studies revealed that the results of sensing are promising and further improvements in gas sensing properties are possible by carrying out more studies. The studies include, raising the temperature of the sensing surface to an optimum value, and improving the conductivity by vaccum annealing, ion implantation and etching. The viability of constructing a thin films gas sensor for ethanol and other gases are being explored with the SILAR grown metal oxide sensing elements particularly Mn doped ZnO.
References


