CHAPTER–VII

STUDIES ON SENSING PROPERTIES TO ETHANOL GAS

7.1 Introduction

Gas sensors play important role in detecting, monitoring and controlling the presence of hazardous and poisonous gases in the atmosphere at very low concentrations. Semiconductor gas sensors having porous or nano structured matrix are highly sensitive and reliable, having a performance/price ratio comparable to that of microelectronic components. Polycrystalline metal oxide based gas sensors are commercially important for detecting reducible gases such as hydrogen, methane, butane and carbon monoxide with high sensitivities. It is a well known physico-chemical property that the gas adsorption onto the surface of a semiconductor can influence its electrical conductivity. In fact, conductivity of the semiconductor gas sensor changes by many orders of magnitude with respect to initial value in the presence of hazardous gas concentrations up to few ppm in air at ambient pressure.

SnO$_2$ gas sensors have a high sensitivity, the porosity and the crystallite size have proven to be very important factors in improving the sensitivity and response/recovery time of these sensors. In particular, the gas-sensing properties of SnO$_2$ based gad jet have been found to increase many fold by decreasing the crystallite size to about and below 10 nm for both pristine and doped SnO$_2$ materials [1, 2]. The adsorbed gases create space-charge layers on the surface of the crystallites, which generate an electric field that bends the energy band to create a barrier for carrier transport through the film. Decreasing the size of crystallites below 10 nm makes the thickness of this space-charge layer comparable to the size of the grain, which drives the transport toward a “neck-controlled” regime or even a total carrier depleted grain regime with further decrease in the crystallite size. Considering these physic-chemical phenomena, reducing
the SnO$_2$ grain size and narrowing its size distribution through a new or modified process will therefore greatly increase the sensitivity of the gas sensors.

It has been known that absorption or desorption of a gas molecule on the surface of a metal oxide changes the conductivity of the material, this phenomenon being first demonstrated using zinc oxide thin film layers. The sensitivity of a surface to a gas can be as low as parts per billion (ppb) [3-6]. It is highly desirable that metal oxide semiconductor sensors have a large surface area, so as to adsorb as much of the target analyte as possible on the surface, giving a stronger and more measurable response (especially at low concentrations). Indium tin oxide (ITO) electrode is used to fabricate a novel disposable biosensor combined with flow injection analysis for the rapid determination of H$_2$O$_2$. The application of indium tin oxide (ITO) electrodes has attracted increasing interest recently due to their prominent characteristics such as excellent optical transparency, high electrical conductivity, wide electrochemical working window, excellent substrate adhesion, and stable electrochemical and physical properties [7-10].

The products of the ethanol dehydrogenation reaction depend upon the ensemble size of SnO$_2$ [11]. Isolated SnO$_2$ (110) catalyze only the dehydrogenation to acetaldehyde, whereas multiple Cu ensembles show high yields of ethyl acetate in addition to acetaldehyde for surface. Many reactive gases know metal oxides of gas sensors for their sensitivity but they are also ill famed for their cross-sensitivity. A well recognized way for distinguishing gases is using the fact that different kinds of gases tend to react with different case at the sensor surface and that these therefore give rise to differently shaped gas sensitivity/surface temperature characteristics [12].
7.2 Preparation and sensing properties of semiconductor oxide gas sensors

The preparation of In$_2$O$_3$, SnO$_2$ and ITO sensing elements and the experimental set-up used for measuring the resistance radiation and sensitivity to ethanol gas are presented in this section.

7.2.1 Sensing element preparation

For the measurement of gas sensitivity, the sensing elements based on SnO$_2$–In$_2$O$_3$ nanocrystalline powders were fabricated in a conventional way [13]. The powders were pressed into pellets under a pressure of 15 MPa and gold lead was mounted on both sides of the pellet to form the sensing element. The element was enclosed in a quartz tube, which was heated to a certain temperature in a tubular furnace. A constant current was applied across the element. The steady-state resistance of the element was measured in air and in the presence of a target gas in air. The ethanol sensitivity (response magnitude) was defined as the ratio of the sensor resistance in air ($R_{\text{air}}$) to that in an air–gas mixture ($R_{\text{gas}}$), while ethanol sensitivity was defined as the ratio of the sensor resistance in an air–gas mixture ($R_{\text{gas}}$) to that in air.

7.2.2 Experimental setup for sensor data collection

The gas sensing chamber (Fig. 7.1) used for gas sensitivity analysis of the prepared In$_2$O$_3$, SnO$_2$ and ITO powders consists of a steel base with three port holes at the base for inletting of more than one gas at the same time. This helps us to generate the exact gaseous mixing ambient conditions inside the chamber. Above the steel base there is a raised sample holder made of copper which is placed over a heating coil to increase the temperature of the sample. The sample placed above the sample holder is connected by two probes which are further connected in series with a programmable D.C. power supply and a digital multimeter. The thermocouple as shown in the diagram keeps track of the rise in temperature of the sensing material.
(though not required in the present study as it was done at room temperature). The whole system is covered by a glass chamber fitted with rubber tube at its base to ensure complete vacuum in the chamber through suction by a high capacity vacuum pump. The chamber and the electrical measuring systems are well developed for controlled variations of the inner atmospheric temperature and pressure for controlled gas sensing analysis and the resistance variations as shown in Fig. 7.2.

The tin oxide (SnO$_2$) is a well-known n-type semiconducting oxide that has been widely used for reducing gases in an operating temperature range of 273–443 K. This oxide material has high reactivity towards reducing gases at relatively low operating temperature, easy ad-sorption of oxygen on its surface because of its natural non-stoichiometry, stable phase and many more desirable attributes such as cheapness and simplicity. For monolayer coverage the C–O bond cleavage process was favored. This appears to be in contradiction to the experimental results discussed above where ethoxide and acetaldehyde production was observed.

### 7.2.3 Sensitivity measuring procedure

From each sensor response curve, four different features were extracted for each sample. The first feature extraction is the conductance change, defined as

$$
\Delta R = R_{\text{gas}} - R_0
$$

(7.1)

The second feature extraction is the relative response ($\Delta R/R_0$). Sensitivity of a sensor was defined as the ratio of the change in conductance of a sample on exposure to the test gas to the conductance in air.

$$
\text{Sensitivity} = \frac{(R_x - R_a)}{R_a}
$$

(7.2)
where $R_g$ and $R_a$ are conductance of a sample in the presence and absence of a test gas respectively and $\Delta G$ is the change in conductance.

As one of the important parameters of gas sensors, sensitivity has been attracting more and more attention and much effort has been made to enhance the sensitivity of gas sensors. There is not a uniform definition for gas sensor sensitivity now. Usually, sensitivity (S) can be defined as $R_a/R_g$ for reducing gases or $R_g/R_a$ for oxidizing gases, where $R_a$ stands for the resistance of gas sensors in the reference gas (usually the air) and $R_g$ stands for the resistance in the reference gas containing target gases. Both $R_a$ and $R_g$ have a significant relationship with the surface reaction(s) taking place.

A static measuring system is employed, when includes an air tight chamber, the sensor element and the temperature sensor. The test gas is injected inside the chamber through a needle valve. The electrical characteristics of the sensors are observed by changing its temperature in air ambient and this response is considered as a reference response for the calculation of sensitivity. After admittance of the test gas in predefined amount the resistance of the sensor is measured once again for various sensor temperatures. The gas concentration in ppm can be estimated from the gas law,

$$P \frac{NkT}{V}$$  \hspace{1cm} (7.3)

Where $P$ – pressure, $V$-volume of the chamber, $N$-Number of particles $k$ – Boltzmann constant and $T$ – temperature of the chamber. Electrical measurements in the temp range 30-500 °C in air ambient chamber is evacuated to a base pressure of $10^{-2}$ torr using rotary pump. Resistance of the sensor is measured for different amount of ethanol vapour in air ambient. The sensitivity factor of the pellet sensor is calculated using the formula,
\[
\frac{\Delta R}{R_{\text{gas}}} = \frac{R_{\text{air}} - R_{\text{gas}}}{R_{\text{gas}}}
\]  
(7.4)

Where \(R_{\text{gas}}\) – value of the sample resistance in the presence of the test gas

\(R_{\text{air}}\) – sample resistance in dry air.

The density of electrons with sufficient energy to cross the energy barrier is given by the Boltzmann equation

\[n_s = N_d \exp\left(-\frac{qV_s}{kT}\right)\]  
(7.5)

where \(N_d\) = donaor density \(qV_s\) = barrier energy between grains \(V_s\) = the barrier potential, which increases as the concentration of adsorbed oxygen ions increases.

\[PV = NkT\]  
(7.6)

\[N = \frac{PV}{kT}\]  
(7.7)

### 7.3 Studies on In\(_2\)O\(_3\) gas sensors

The prepared sensing elements using these oxide powders were tested for their resistivity changes with ethanol gas concentration. The response and recovery properties were also studied and presented here.

#### 7.3.1 Sensing properties of ethanol gas

It can be seen that by increasing the ethanol concentration from 100 to 500 ppm the resistance of In\(_2\)O\(_3\) nanoparticle was considerably increased. In the present study, simple straightforward and economical combustion technique was employed to prepare In\(_2\)O\(_3\) nanoparticles and sensor devices. In general the gas sensing ability of metal oxide-based sensor depends on the surface reactions. As the powders prepared here having uniformly distributed nano grains, the as prepared powder showed good sensitivity for 400 ppm ethanol concentration as shown in Fig. 7.3. The response
reaches a maximum at 300 sec and then recovers in about 100-150 sec. Fig. 7.4 shows the variation of sensitivity and response time with the particle size of the In$_2$O$_3$ powders heated at different temperatures as explained in Chapter IV. It can be observed that sensitivity is high for the powder with smaller particle size. At the same time response time found increasing when the particle is larger [14]. The existence of ethanol gas causes a transfer of electronic charge at the surface and primarily depends on both gas concentration and temperature [15]. Since In$_2$O$_3$ nanoparticles are $n$-type semiconductor with oxygen vacancies which generally provides donor states, the conductivity of the In$_2$O$_3$ nanoparticles is directed by steady concentration of adsorbed oxygen ions and determined by chemical dynamics including oxidation and diffusion [16]. The surface of In$_2$O$_3$ reacts very quickly with the negatively charged oxygen adsorbates resulting in water and free electrons. As a result, the sensitivity of the In$_2$O$_3$ nanoparticles increases and remains constant as observed at the starting time (sec).

### 7.3.2 Sensing mechanism in In$_2$O$_3$

Atmospheric oxygen gets adsorbed on the surface, removes a carrier (electron) from the conduction band of $n$-type semiconductor gas sensors, becomes $O^{-2}$ or $O^{-}$ species. This phenomenon reduces the overall conductance. The reducing agents, such as hydrogen, carbon monoxide, ammonia and hydrocarbon gases will react with chemiadsorbed oxygen. This process will reinject the carrier and increase the sensor conductance. It is well known that the electrical conductivity in indium oxide is due to non-stoichiometric composition as a result of oxygen deficiency. The conductivity is of $n$-type. When the indium oxide sensor element surface is placed in an air ambient, the oxygen molecules are adsorbed at the surface resulting in the formation of $O^{2-}$,
$O^-, O^{2-}$ ions, thus decreasing the concentration of the number of charge carriers near the surface giving rise to a depletion region. When exposed to reducing gases like ammonia and ethanol vapor, mutual interaction between the reactant i.e. reducing gas and oxygen species, results in oxidation of reducing gas at the surface. This oxidation phenomenon helps in the removal of oxygen ion from indium oxide surface resulting in decrease in the barrier height between the grains, thus increasing the conductance. During the chemisorption at higher temperature 400 K, oxygen is adsorbed in ionic form as shown in the following reactions

$$O_2 + e^- = O^{2-} \quad (7.8)$$

$$O^{2-} + e^- = 2O^- \quad (7.9)$$

Above 400 K, the reactivity of $O^{-2}$ species is high. The formation of $O^{-2}$ species is also possible as follows $O^{- \text{ads}} + e^- = O^{-2}$. $O^{-2}$ ions are not adsorbed because these species are not stable and are usually trapped by oxygen vacancies. The present investigation aims to fabricate chemical gas sensing device with good sensitivity that can operate at low temperature.

### 7.4 SnO$_2$ gas sensor

Tin oxide is an excellent and a widely used material for gas sensor applications because of its high sensitivity, good chemical inertness, its inexpensive nature, high material stability and relatively low operating temperature with a fast response time though poor selectivity to hazardous gases, since it is sensitive to almost all the gases. The selectivity can be achieved by doping with noble metals, modifying the fabrication technologies and altering other physical parameters. It is an oxygen deficient n-type semiconductor and crystallizes in a rutile structure. It is commonly used as a gas sensor-particularly for reducing gases in industrial and domestic purposes. The tin oxide detects the reducing gases CO, H$_2$, N$_2$ and H$_2$S.
7.4.1 Gas Sensing Properties of SnO\textsubscript{2}

The maximum sensitivity was obtained for a particular concentration of the gas and is strongly influenced by the nature of the particle size. It was of interest to understand the sensing mechanism that influences the response characteristics of the SnO\textsubscript{2} sensor. The observed increase in the sensitivity \( \frac{R_a}{R_g} \) could be related either due to a large resistance in air \( (R_a) \), and a substantial change in resistance in the presence of the ethanol gas concentration, resulting in low value of \( R_g \). The sensitivity variation with time is shown in Fig 7.5 for an ethanol concentration of 400 ppm. Sensitivity is about 18. For an enhanced performance, it is desired that both the changes occur effectively. When the particle size is in the nano range (10-20 nm), the surface area is enhanced and correspondingly contact with ethanol is increased. This reduces the resistance largely. The increase in the value of \( R_a \) is due to the enhanced activation of the chemisorbed oxygen on the surface of SnO\textsubscript{2} powdered particles thereby decreasing the concentration of free charge carriers. The chemisorbed activity is expected to vary according to the equations

\[
O_2(g) \rightarrow O_2(ads) + e^- \quad T \geq 500k \rightarrow O_2^-(ads) \quad (7.10)
\]

\[
O_2^-(ads) + e^- \quad T \geq 500k \rightarrow 2O_2^-(ads) \quad (7.11)
\]

The stabilization is achieved when an equilibrium concentration of adsorbed species is obtained. However decrease in resistance \( (R_g) \) with the interaction of sensing gas ethanol concentration was more for the nano grained SnO\textsubscript{2} sensor in comparison to the bulk SnO\textsubscript{2} particles, indicating the effectiveness of the presence of nanoscale materials. Response time of the sensor is also found to decrease with presence of large quantity of ethanol gas and also smaller grain size. Response time
for pure SnO$_2$ is found to be about 450s whereas for the nano grained SnO$_2$ powder prepared in the present study, with ethanol concentration, the response time reduces to 250s as can be observed from Fig. 7.6.

7.4.2 Sensing mechanism in SnO$_2$

It is well known that the resistance of SnO$_2$ changes according to various reducing gas environments. In air atmosphere, oxygen is adsorbed onto SnO$_2$ surface by capturing electrons from the conduction band and remains as O$_2^-$, O$^-$ or O$_2^{2-}$ ions until they desorb at higher temperature. These adsorbed oxygen species induce a subsequent potential barrier at the grain boundaries and a resistive depletion layer is formed which determines most of the sensor resistance. When a flammable gas is introduced, the adsorbed oxygen is removed by oxidation of the gas and the captured electrons are injected into the conduction band. This results in a reduction of the potential barrier height and decrease in resistance of the sensor. It was of interest to understand the sensing mechanism that influences the response characteristics of the SnO$_2$ sensor. The observed increase in the sensitivity ($\frac{R_a}{R_g}$) could be related either due to a large resistance in air ($R_a$), and a substantial change in resistance in the presence of the ethanol gas concentration, resulting in low value of $R_g$. For an enhanced performance, it is desired that both the changes occur effectively.

The stabilization is achieved when an equilibrium concentration of adsorbed species is obtained. Figure shows the variation in the sensor resistance ($R_g$) under is presence of ethanol gas concentration from 100 ppm to 500 ppm. The corresponding variation in $R_g$ is found to be decrease continuously with increase in temperature for both the sensors. However decrease in resistance ($R_g$) with the interaction of sensing
gas ethanol concentration was more for the SnO\textsubscript{2} sensor in comparison to the bulk SnO\textsubscript{2} particles, indicating the effectiveness of the presence of nanoscale materials. Response time of the sensor is also found to decrease with the presence of sensors. Response time for bulk SnO\textsubscript{2} is found to be 200s to 300s whereas with the nano grained SnO\textsubscript{2} powder prepared in the present study the response time reduces to about 150s to 200s.

The observed increase in the sensitivity \( \left( \frac{R_a}{R_g} \right) \) could be related either due to a large resistance in air \( (R_a) \) or a very small resistance \( (R_g) \) in the presence of ethanol gas, and for an enhanced performance it is desirable that both the changes occur accordingly. The increase in \( R_a \) value is dependent on the nature of the concentration being on the SnO\textsubscript{2} powdered particles. The difference between the work function of ethanol concentration and SnO\textsubscript{2} powdered particle is expected to play a crucial role in defining the resistance, \( R_a \) value. The transformation of SnO\textsubscript{2} powdered particle resistance with ethanol concentration is due to reduction in the concentration of conduction electron present in the sensing SnO\textsubscript{2} particle via Fermi energy exchange control mechanism. It results in an increase in the value of \( R_a \) for SnO\textsubscript{2} and its variation with ethanol concentrations. The dissociated atoms spill over onto the surface of underneath sensing SnO\textsubscript{2} particle and interact with the adsorbed oxygen. The interaction leads to the release of trapped electrons thereby, increasing the concentration of electron in the conduction band of SnO\textsubscript{2} nanoparticles. Therefore, the resistance \( (R_g) \) of the prepared sensor structure decreases in the presence of reducing ethanol concentration.
7.5 In$_2$O$_3$:Sn based Gas Sensors

Gas sensing elements were prepared with ITO powders prepared using various Sn% of 5, 10, 15, 20 and 50. The sensing ability to ethanol concentration, sensitivity and response characteristics are studied and presented here.

7.5.1 Gas sensing properties of In$_2$O$_3$:Sn powders

In order to study the influence of Sn% doping to ethanol concentration, 100 to 500 ppm of ethanol gas concentrations were used to measure the sensitivity. Fig. 7.7 shows the change of sensitivity with Sn% doping. Sensitivity is found to be maximum for 400 ppm of ethanol. Further, sensitivity is found increasing with enhanced Sn doping, which reaches a maximum for 50% doping. This is due to the obvious reason that SnO$_2$ is usually more sensitive to reducing gases than In$_2$O$_3$.

Fig. 7.8 shows the response curves for different Sn% doped In$_2$O$_3$:Sn powders. The response time is found to be nearly the same, about 300 sec for all the powders. The recovery time is fast showing the highly reversible nature of all the powders prepared in the present study. Sensing mechanism can be proposed as given in sections 7.3.2 and 7.4.2 for In$_2$O$_3$ and SnO$_2$ sensing elements respectively.

7.6 Conclusion

In$_2$O$_3$, SnO$_2$ and In$_2$O$_3$:Sn powders prepared by the sol-gel combustion synthesis were studied for their sensitivity to various ethanol gas concentration. The sensitivity is reasonable for In$_2$O$_3$ and SnO$_2$ powders for various concentrations of ethanol, but showing high sensitivity to 400 ppm specifically. Doping of Sn into In$_2$O$_3$ showed good improvement in sensitivity, which is found continuously increasing with enhanced concentration. The sensors show good response and recovery time in
seconds. These improved results can be due to the larger surface area and uniform size distribution of the oxide powders prepared in the present study using the sol-gel combustion synthesis process.
References

Fig 7.1 Schematic diagram of the gas sensing chamber used for sensing Characteristics measurements
Fig 7.2 Experimental setup of the gas sensing unit used for sensor characteristics measurements
Fig. 7.3 Sensitivity analysis of as-prepared In$_2$O$_3$ powder
400 ppm ethanol concentration

Fig. 7.4 Variation of sensitivity and response time vs Particle size
of In$_2$O$_3$ powder
Fig 7.5 Sensitivity of SnO$_2$ powder to 400 ppm ethanol

Fig 7.6 Variation of sensitivity and response time with SnO$_2$ particle size for 400 ppm ethanol concentration
Fig 7.7 Sensitivity of indium tin oxide with different ethanol concentration
Fig. 7.8 Sensitivity vs response time graph of ITO (a) 95:05, (b) 90:10, (c) 85:15, (d) 80:20 and (e) 50:50 sensing element for 400 ppm ethanol concentration