CHAPTER VII
ETHANOL SENSING BEHAVIOUR OF DELAFOSSITE OXIDES

Semiconducting metal oxide (SMO) sensors are one of the most widely studied groups of gas sensors for detecting oxidizing and reducing gas. During the past few decades, SMO gas sensors have become a prime technology in several domestic, commercial, and industrial gas sensing systems. Among the available gas sensing methods, the SMO gas sensor devices have several unique advantages such as low cost, small size, simplicity in measurement, durability, ease of fabrication, and low detection limits (< ppm levels) [1-7]. In addition, most SMO based sensors tend to be long-lasting and somewhat resistant to poisoning. For these reasons, they have rapidly grown in popularity and also becoming the most extensively used gas sensors available these days.

Several materials are fabricated to enhance the sensing characteristics of the SMO gas sensors. Various SMO mixed with different dopants, catalysts, adhesives, binders, volatile fillers, electrodes and few more have been studied [8-17]. In addition to the variations in the composition of the SMO materials, their film deposition methods provide another variable for sensor design. These deposition methods include pyrolysis, oxidation of metallic films, reactive sputtering, chemical vapour deposition (CVD), laser ablation, electron-beam evaporation techniques etc. [18-27].

There are many reports in delafossite oxide compounds that exhibit p-type conductivity and display good carrier flow [28, 29]. The delafossite compounds are classified as a ternary oxides group with chemical formula $A^+B^{3+}O_2$ [29, 30]. The
A-site cations are composed of Cu, Ag, Pd, or Pt transition-metal ions maintained in a monovalent state. The B-site cations mostly consist of trivalent transition metals, group III metal elements, group 13 metal elements, or rare earth. Its ABO$_2$ structure is formed by alternative stacking layers of O-A-O dumbbell and BO$_2$ edge-shared octahedral along the c-axis. The A$^+$ cation is linearly connected to O$^{2-}$ anion in c-axis and the [BO$_2$] octahedra are formed by sharing of edge BO$_2$. The trivalent B$^{3+}$ ions occupy in the middle of the octahedral block.

Among the delafossites, the most promising sensors are based on the inclusion Cu as one of the cations in the structure. This delafossite displays p-type conduction resulting from unsaturated bonds by the non-stoichiometry of the materials due to Cu deficiency in Cu layer and excess O interstitials. The unsaturated bonds of delafossite can accept electrons and modify the conduction process which is suitable for sensing mechanism in gas sensors. More reports have been already documented, stating that the Cu-based delafossite can be used for ozone, ethanol and acetone sensing [31-34]. However, in the present study, prepared delafossites samples were engaged as sensing element in detecting ethanol vapour alone.

7.1. SENSORS FOR VOCs

Volatile organic compounds (VOCs) are chemical by products emitted from industries and accumulated little by little in our living atmosphere. These VOCs not only cause environmental pollution but also directly affect human health. For example, alcohols and aromatic hydrocarbons are potentially hazardous to human health due to their capabilities to stimulate the mucous membranes and upper respiratory tracts. Formaldehyde (HCHO) is highly toxic even at low concentration.
Despite their toxicity and hazard, VOCs are still used in industries as intermediates to produce other chemicals and as solvents in research laboratories. Therefore, the development of gas sensors for early detection of VOCs is necessary.

Metal oxide based chemical sensors have been used extensively for the detection of toxic pollutant gases, combustible gases and organic vapours. The main advantages of chemical sensors are their low price, small size, high sensitivity, and low power consumption. Ethanol, also called ethyl alcohol, pure alcohol, grain alcohol, or drinking alcohol, is a volatile, flammable, colourless liquid. Prolonged heavy consumption of alcohol can cause significant permanent damage to the brain and other organs. But ethanol is one of the most commonly used and wide spread alcohols, and thus there is a need to develop sensors for its detection. Ethanol gas sensors can be applied in many fields, such as the control of fermentation processes [35], safety testing of food packaging, and can also be fixed on vehicle steering wheels to monitor drunken driving [36, 37]. Thus gas sensing devices are in demand in environmental monitoring and also to avoid the toxic gas leakages and endangering the human body.

7.2 METAL OXIDE SEMICONDUCTOR SENSORS

Recently, gas sensors based on the semiconducting metal-oxides such as SnO\textsubscript{2} and ZnO [38-42] have been found to be very useful for detecting ethanol vapour. Semiconductors are used as gas sensors based on the principle of the variability of electrical conductivity of metal oxides when exposed to these gases. Thus metal oxide semiconductor (MOS) sensor technology is based on the change in resistance of a sensitive metal oxide layer which is induced by the interaction between a surface and
ambient gases. Metal oxide semiconductors demonstrate good detection sensitivity, robustness and the ability to withstand high temperatures and the technique is commonly used to monitor a variety of toxic and inflammable gases in a variety of air pollution monitoring systems, the food industry, medical diagnosis equipment and gas leak alarms.

7.3 CHARACTERISTICS OF GAS SENSORS

In order to characterize sensor performance, a set of parameters is used [43]. The most important parameters and their definitions are listed below.

- **Sensitivity** is a change of measured signal per analyte concentration unit, i.e., the slope of a calibration graph.
- **Selectivity** refers to characteristics that determine whether a sensor can respond selectively to a group of analytes or even specifically to a single analyte.
- **Stability** is the ability of a sensor to provide reproducible results for a certain period of time. This includes retaining the sensitivity, selectivity, response, and recovery time.
- The **detection limit** is the lowest concentration of the analyte that can be detected by the sensor under given conditions, particularly at a given temperature.
- **Dynamic range** is the analyte concentration range between the detection limit and the highest limiting concentration.
- **Resolution** is the lowest concentration difference that can be distinguished by the sensor.
- **Response time** is the time required for the sensor to respond to a step concentration change from zero to a certain concentration value.
Recovery time is the time it takes for the sensor signal to return to its initial value after a step concentration change from a certain value to zero.

- Working temperature is usually the temperature that corresponds to maximum sensitivity.
- The life cycle is the period of time over which the sensor will continuously operate.

All of these parameters are used to characterize the suitability of a particular sensor element. An ideal chemical sensor would possess high sensitivity, dynamic range, selectivity and stability and also low detection limit, good linearity, small hysteresis and response time. Researchers usually make efforts to approach only some of these ideal characteristics, disregarding the others. In the case of environmental monitoring applications, when the concentrations of pollutants normally change slowly, the detection limit requirements can be much higher, but the response time of a few minutes can be acceptable. Typically, the important parameters in sensor development are sensitivity, selectivity, and stability called as the ‘3S’. However, in this chapter discussions are mostly on sensitivity parameter together with response and recovery time.

Normally, the gas sensor based on MOS has an optimum operating temperature at high temperature about 250-350 °C. When the MOS is heated at lower temperature about 100-200 °C, oxygen molecules in the atmosphere are adsorbed on its surface and form oxygen ion molecules by attracting an electron from the conduction band of MOS as per the reaction kinetics represented in Eq. (7.1):

$$\text{O}_2(\text{gas}) + e^- \leftrightarrow \text{O}_2(\text{ads}) \quad (7.1)$$
At higher temperatures, the oxygen ion molecules are dissociated into oxygen ion atoms with singly or doubly negative electric charges by attracting an electron again from the conduction band as shown in Eq. (7.2) and (7.3):

$$\frac{1}{2} \text{O}_2 + e^- \xrightleftharpoons[\text{k}_\text{oxy}]{\text{ads}} O^- (\text{ads}) \quad (7.2)$$

$$\frac{1}{2} \text{O}_2 + 2e^- \xrightleftharpoons[\text{k}_\text{oxy}]{\text{ads}} \text{O}^{2-} (\text{ads}) \quad (7.3)$$

where $k_{\text{oxy}}$ is the reaction rate constant. The oxygen ions on the surface of MOS are extremely active with the target gas molecule and give up the electrons from the surface back to the conduction band of MOS. In general, a chemical reaction between gas molecule and oxygen ions can be represented as in Eq. (7.4):

$$X + \text{O}^{b-} \xrightarrow[\text{ads}]{\text{k}_\text{gas}} X' + be^- \quad (7.4)$$

where, ‘X’ and ‘X’’ is target gas and out gas, respectively. The ‘b’ value is the number of electrons and ‘$k_{\text{gas}}$’ is the reaction rate constant of the gas reaction. The chemical reaction causes a change of the carrier concentration in the conductivity and thus, change of sensor resistance. Thus, when SMO based sensor is exposed to a reductive gas at a moderate temperature, the gas reacts with surface oxygen species of the film, which decreases the surface concentration of oxygen ions and increases the electron concentration. This eventually increases the conductivity of the films. However, the charge state modification takes place only at the grain boundary or porous surface. The change of sensor resistance depends on the type of charge carriers in MOSs.
For thin film semiconductor metal oxide based gas sensors, the porosity of the sensing layer is an important parameter [44-47]. Gas diffusion through the pores can cause changes in electrical properties of the film, making the gas detection easier. Although most metal oxide semiconductors sensitive to gas concentration are n-type semiconductors, there are also a few kinds of p-type semiconductors that could be used as sensing materials. The enhancement of the gas response via the control of the acceptor density has rarely been investigated for p-type oxide semiconductors. The reaction between reducing analyte gas and negatively charged oxygen on the surface of p-type oxide semiconductors decreases the near-surface hole concentration via the electron–hole recombination reaction, which increases the resistance of the sensor [48]. Several sensors have been fabricated during the last decade to selectively detect various VOC components like ethanol, acetone, hydrocarbon, and LPG.

7.4 WORKING PRINCIPLE OF SMO GAS SENSORS

Despite the simplicity of SMO measurements for use as gas sensors, the detection mechanism is complex and not yet fully understood. This complexity is due to the various parameters that affect the function of the solid state gas sensors. These include the adsorption ability, electro physical and chemical properties, thermodynamic stability, as well as the adsorption/desorption properties of the surface [49-58]. However, it is believed that gas sensing by SMO devices involves two major key functions as receptor and transducer [59, 60]. The former involves the recognition of a target gas through a gas-solid interface which induces an electronic change of the oxide surface, while the latter is based on the transduction of the surface phenomenon into an electrical resistance change of the sensor [59]. When a sensor is heated to a high temperature in the absence of oxygen, free electrons easily flow through the
grain boundaries of the SMO film. In an oxygen atmosphere, oxygen is adsorbed onto the SMO surface, forming a potential barrier at the grain boundaries. The interaction of atmospheric oxygen with the SMO surface forms charged oxygen species, which trap electrons from the bulk of the material. The layer of charged oxygen at the surface repels other electrons from interacting with the bulk of the film, creating a region depleted of electrons which result in an increased potential barrier at the grain boundaries. This impedes the flow of electrons and thus increases the resistance.

Metal oxides exhibit various electro-physical features, ranging from insulators to wide band-gap semiconductors [61-73]. The non-transition metal oxides contain elements with one oxidation state because they require a large amount of energy to make other oxidation states that would bind to the oxygen ion ligand [61]. In contrast, because of the various oxidation states that might form on transition metal oxides compared to non-transition metal oxides, the surface properties and the types of chemisorptions that occur on the surface are important and have been widely studied [61, 62, 64]. This variation in the oxidation states causes significant changes in the surface chemistry response towards oxygen and other target gaseous molecules [49].

The electrical conductance of the sensor is determined by the amount of electrons in its conduction band. The more the amount of electrons in the conduction band, the higher the conductivity of the sensor. The oxygen vacancy in the film acts as an electron donor to provide electrons to the conduction band of the material. When the sensor is exposed to air, oxygen molecules adsorb on the surface of the film to form various oxygen species (O$_2^-$, O$^-$ and O$_2^{2-}$) by capturing electrons from the conduction band. The oxygen species adsorbed on the surface of film form a rather
thick depletion region. If the surrounding test gas molecules do not adsorb at all or only physically adsorb on the surface of the film, there are no electron exchange between the film and the test gas molecules. Hence the conductivity of the film remains the same level as without the test gas surroundings. When the gas molecules chemically adsorb on the film at a moderate temperature, some electrons will transfer across the interface between them and result in a varying conductivity.

Furthermore, oxidative and reductive gas surroundings have opposite behaviours. When the desired concentration of gases is introduced, many possible processes can occur. The gases may react with the oxygen adsorbed on the surface or with the semiconductor surface, or with both. For an n-type semiconductor, the resistivity increases due to electron capture by an oxidizing gas and decreases with the presence of a reducing gas owing to electron transfer into the conduction band, while the opposite holds for a p-type semiconductor [74]. Explaining each and every possible process involved is very difficult from the theoretical point of view.

The gas sensing properties are usually characterized in terms of dynamic change of resistance and gas-sensing response. The gas sensing response of n-type semiconductor based gas sensor to a reducing gas is normally defined as the ratio of the resistance change ($\Delta R$) due to gas introduction to the resistance when the gas is present ($R_g$), while the response to an oxidizing gas is defined as the ratio of the resistance change ($\Delta R$) to the resistance in air ($R_a$). For p-type semiconductor gas sensor, the definitions are reversed [74].
7.5 EXPERIMENTAL SETUP AND PROCEDURE

Despite the fact that the testing setups of SMO sensors tend to differ, their overall principle remains the same. Generally, the metal oxide semiconductor (MOS) gas sensors work on the basis of the change of the electrical properties of the sensors, which results from the absorption of the tested gas on the surface of the sensors. Fig. 7.1 shows the schematic of SMO gas sensor device used to study sensing characteristics of the studied delafossite structured thin films that act as sensing elements. The sensor set-up mainly consists of a testing chamber filled with target gas, power supplies, heaters and an electrometer for resistance measurement. The testing chamber consists of SMO sensor platform with provision to monitor the sensor temperature and to measure its resistance variation. Before admitting the test gas, high vacuum in the order of $10^{-3}$ Torr was created.

![Fig. 7.1 Schematic diagram of a gas sensing system](image-url)
For measuring the sensitivity of the sensor, deposited SMO films on glass substrates were mounted on a sensor platform attached with a standard heater. The temperature was controlled by an automatic temperature controller and monitored using a precision thermometer. Initially, the sensitivity of the sensor and its variation was detected at 30 °C. After keeping the sensor at the desired temperature, the adequate voltage was applied across the electrical contacts of the sensor. A predefined amount of ethanol was taken for a particular ppm level in a beaker and placed above the heater to make it as ethanol vapour. A high sensitive electrometer was connected to the testing circuit to monitor and record the resistance variation of the sensor against time.

Metal oxide gas sensing mechanism is based on the interaction between the surface of sensing material and gas molecules which alter the resistance of metal oxide. Initially, when metal oxide was exposed to the air at room temperature, the oxygen molecules are chemisorbed on the surface of metal oxide surface to form active oxygen species (O$_2^-$), which is also known as electron acceptors. A layer of negatively charge oxygen species will be formed on the surface of the metal oxide. It happens to both n-type and p-type oxide based materials.

When chemisorptions accumulate the O$_2^-$ species on the surface of the films, holes accumulate in the near surface region. It contributes to the major hole carriers in films. The negatively charge oxygen species will transfer the electrons from the surface towards the hole accumulating layer and reduce the holes density resulting in an increase in resistance when reducing gas such as ethanol contact with the films.
Therefore when the sensor is exposed to ethanol vapour, the film surface adsorbs the gas molecules and thus raising the electrical resistance. The experiment was repeated again for two different substrate temperatures namely 100 and 200 °C. Fig. 7.2 illustrates the experimental setup utilized for the present study, in which an electron beam evaporation unit is engaged as the test chamber.

Fig. 7.2 Experimental gas sensing setup

7.5 RESULTS AND DISCUSSIONS

In spite of the technological advancements, a greatly growing demand exists for sensors that detect and monitor gases in environmental and biological systems. However, the equipment is often bulky, with typical fixed-site stations for the analysis and such systems are very costly. Thus, there is growing requirement for the development of compact, portable, affordable and high sensitive sensors. In addition,
sensing element’s role is prime and therefore it should have unique requirements. The semiconductor metal oxide-based gas sensors have all these unique requirements, so it has attracted great attention in the past several decades.

A variety of metal oxides have been investigated for ethanol sensing and the most representative sensor materials are SnO$_2$ and ZnO [75-78]. In addition, additives, such as SiO$_2$, Mn$_3$O$_4$, and WO$_3$, can also be added to SnO$_2$ and ZnO semiconducting oxides for having better sensing behaviour [79-81]. Although there are several fundamental technologies exploited in semiconductor metal oxide-based ethanol sensors, the most promising sensors are based on the Cu-based delafossite structures. This is because of its quick response to a surface reactive mechanism that modifies its electrical parameter.

In the present work, delafossite oxides of ABO$_2$ (A = Cu, B = Al, Fe, Cr, Mn) have been prepared using the spray pyrolysis technique and prior to gas sensing study, they were engaged for DC electrical conductivity measurements. Based on the study, CuCrO$_2$ and CuMnO$_2$ have better conductivity even at low temperatures, which is one of the suitable requisite for the fabrication of gas sensors. However, the room temperature electrical conductivities of the spray deposited rhombohedral delafossites, CuAlO$_2$ and CuFeO$_2$ are moderate ($\sim$10$^{-5}$ mho/cm) their expected sensitivity to ethanol gas is usually weak. Hence, reported sensing features are very rare for CuAlO$_2$ [82] and only a few reports for CuFeO$_2$, related to alcohol sensing [83].

After understanding the structural, optical and electrical properties of the prepared films, the ethanol gas sensing behaviour of the optimized films are tested.
Respective sensing film is kept at room temperature and the film resistance at that instant is taken as initial/base resistance of the sensor element. The room temperature electrical resistance of the study materials is listed in Table 7.1.

**Table 7.1 Room temperature resistance of the optimized study materials**

<table>
<thead>
<tr>
<th>Study materials</th>
<th>Room temp. Resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO</td>
<td>800 MΩ</td>
</tr>
<tr>
<td>CuAlO₂</td>
<td>300000 MΩ</td>
</tr>
<tr>
<td>CuFeO₂</td>
<td>2000 MΩ</td>
</tr>
<tr>
<td>CuCrO₂</td>
<td>22 MΩ</td>
</tr>
<tr>
<td>CuMnO₂</td>
<td>66.926 KΩ</td>
</tr>
</tbody>
</table>

It is well known that for gas sensing characterization, sensor element chosen should have high electrical conductivity. The other one requirements of the gas sensors are low power consumption because the sensors need to work reliably and continuously. A low resistance material has lower driving power when it is used as a sensor. As evident from Table 7.1, most of the study materials show the high resistance of the order of meg-ohm and are therefore not suitable as sensing element in sensor devices. However, among the material chosen, the room temperature resistance of CuMnO₂ and CuCrO₂ films are comparatively less and therefore engaged in a gas sensor using as the sensor element.

The sensing property of oxide-based sensors under ethanol is investigated by allowing ethanol vapour after removing the dry air from the test container. The concentration of ethanol vapour in the test chamber can be calculated using the ideal gas equation (Eq. 7.5) at standard temperature and pressure. According to the gas equation:

\[ PV = NkT \]  

(7.5)
where ‘P’ is the standard pressure (760 mm of Hg), ‘V’ is the volume of the test chamber (64000 cc) and ‘k’ is the Boltzmann constant. Using these constants, N can be estimated. Using the known value of ‘N’, a number of particles constitute one ppm is calculated. In the present study, gas sensing measurement was conducted by exposing the sensor to a constant 300 ppm of ethanol gas.

It is well-known that the response of any metal oxide based semiconducting gas sensor is greatly influenced by its operating temperature. Generally high thermal energies are required to overcome the energy barrier on the surface of the metal oxide to allow the gas molecule interactions to occur [84]. In order to determine the optimal operating temperature for the sensors with CuMnO$_2$ and CuCrO$_2$ as sensing element, the concentration of ethanol vapour was kept at a constant value of 300 ppm. The change in resistance of the sensor before and after admittance of the ethanol gas with time is noted for three different temperatures, RT, 100 and 200 °C.

For polycrystalline substances, grain boundaries contribute most of the resistance. It may also be considered that the surface conductivity of a semiconducting oxide film depends on the electron concentration near the surface, which in turn is affected by the nature of the chemisorbed species. In this study, the reason for the change in the resistance may be due to the oxidation of ethanol vapours upon coming in contact with the film surface, which liberates free electrons and H$_2$O. The atmospheric oxygen chemisorbs on the surface of the film as O$_2$ or O$^-$, removing an electron from the conduction band of the semiconductor film, developing a depletion region on the surface. Ethanol vapours react with the chemisorbed oxygen and re-inject the carrier, thereby changing the resistance of the study material.
The possibility of a reaction of ethanol with the sensing layers can be explained as two oxidation states (Eq. 7.6 and 7.7) [19]:

\[
\begin{align*}
C_2H_5OH_{(g)} + [O] & \rightarrow CH_3CHO + H_2O \text{ (the dehydrogenation to acetaldehyde)} \quad (7.6) \\
C_2H_5OH_{(g)} + [O] & \rightarrow C_2H_4 + H_2O \text{ (the dehydration to ethylene)} \quad (7.7)
\end{align*}
\]

in which [O] represents the surface oxygen ions.

The first reaction is a process initiating the oxidation by the dehydrogenation to CH₃CHO intermediate, and the second reaction is initiated by the dehydration to C₂H₄. But the selectivity for the two reactions is initiated by the acid–base properties of the oxide surface. The dehydrogenation process is more probable on the oxide surface with basic properties, while the dehydration is favoured on the acid surface [85]. The intermediate products, acetaldehyde and ethylene, are subsequently reduced to CO₂ and H₂O. At higher temperature, the depletion region created by the chemisorptions of oxygen on the surface extends more deeply, providing larger scope for more gaseous elements to be adsorbed, thereby giving a better response. Also, the hydroxyl group desorbs at higher temperatures [86]. Thus for lower temperature operation (<150°C), the surface of the sensor does not get completely desorbed, which causes a smaller change in resistance.

The delafossite structured study materials are p-type semiconductors. The oxide surface of a p-type semiconductor is readily covered with chemisorbed oxygen, even at low oxygen partial pressure and even at temperatures up to 500 °C [87]. Thus at the sensing temperature, the adsorption of negatively charged oxygen can generate the holes for conduction.
\[
\frac{1}{2} \text{O}_2(\text{g}) \leftrightarrow \text{O}^- (\text{ads}) + \text{h}^+
\] (7.8)

The following gas-sensing reactions might be considered according to the charges of the adsorbed oxygen species under the assumption of full oxidation of \(\text{C}_2\text{H}_5\text{OH}\).

\[
\text{C}_2\text{H}_5\text{OH}(\text{g}) + 6\text{O}^- (\text{ads}) + 6\text{h}^+ \rightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{g})
\] (7.9)

That is, the oxidation reaction with reducing gases increases the resistivity of the surface regions of the p-type nanostructures, which in turn increases the sensor resistance [88]. Thus in the charge accumulation model of p-type semiconductors [89–91], the conduction occurs along the conductive surface.

The sensitivity can be calculated by noting the changes in resistance of the sensing element using the expression [92]:

\[
\text{Sensitivity} = \left[ \frac{\text{R}_{\text{gas}} - \text{R}_{\text{air}}}{\text{R}_{\text{air}}} \right] \times 100 \%
\] (7.10)

where ‘\(\text{R}_{\text{gas}}\)’ is the resistance of the sensor when it is exposed to the gas and ‘\(\text{R}_{\text{air}}\)’ is the resistance of the sensor when exposed to ambient air. The response time is defined as the time taken for the sensor to attain 90 % of the maximum change in resistance on exposure to the test gas and the recovery time is defined as the time taken by the sensor to get back to 10 % of the value of its resistance at the time of maximum resistance. The response and recovery times of the sensor towards constant 300 ppm ethanol were also studied.
7.5.1 Sensing Behaviour of CuMnO₂ Thin Films

The optimized CuMnO₂ thin film was initially mounted in the test chamber and the resistance was noted. On inclusion of the ethanol vapour, the resistance value and hence the sensitivity of the sensor increases, which was noted at regular interval of time. Fig. 7.3 shows the sensitivity variation of the ethanol gas sensor with time for the CuMnO₂ sensing element for three different temperatures. When the CuMnO₂ sensor is exposed to ethanol vapour at different operating temperatures, the ethanol molecules reacts with the thin film surface resulting in the increase of resistance with time.

![Fig. 7.3 Sensitivity variations of the CuMnO₂ ethanol gas sensor](image)

The sensitivity and the response–recovery behaviour is an important characteristic that determines the performance of gas sensors. Moreover, the sensing
element can be reusable as it returns to its original state by modifying its surface state in a short while, when the air is admitted. At RT, when the sensor is exposed to ethanol source, the response time is 990 s with a moderate sensitivity of 47.9 % and once the ethanol gas is removed, the response decreases slowly and tries to reach the initial value, however not attained even the time exceeds above half an hour. Observed response and recovery times signify the initiated change in surface states of the sensing element is poor.

When the operating temperature of the sensor is increased to 100 °C, the sensitivity of the sensor is 57.39 % and the response time is 670 s. However, the recovery is very slow on exposing the sensing element to air. Since the sensing element was not responsive, the recovery time is too large to measure it. Compared to the previous operating temperature of the sensor element, the response time is quite improved but the existing poor recovery suggests that the sensing elements are not reusable.

When the operating temperature of the sensor is further increased to 200 °C, the response increases rapidly and reaches the maximum sensitivity of 70.87 %. Once the ethanol source is removed, the response decreases quickly to the baseline compared to the one observed in previous operating temperatures. The response time of the sensor is 505 s and its recovery indicates a quick response–recovery characteristics compared to other operating temperatures of the sensor. Sluggish recovery of the sensor is typical of the oxide-based sensors, possibly due to slow desorption rate of C₂H₅OH from the CuMnO₂ surface [93].
Hence, the operating temperature of the sensor has a part to play in the sensitivity and response time of the sensor. Among the three different operating temperatures, CuMnO$_2$ sensors exhibited the highest sensitivity at 200 °C, accompanied by a quick response and recovery.

The characteristic feature of MOS gas sensor is its fast response in detecting gas, however, it requires a very long recovery time after the exposure of the target gas [94, 95]. Usually, it takes few minutes to recover back to the baseline level after the target gas is removed [96]. The reason for having a long recovery time of MOS gas sensing is due to the desorption rate. During the presence of target gas, the molecules of target gas interact with the detecting surface of MOS gas sensor, and then the chemisorptions take place at the detecting surface of the metal-oxide, this chemisorptions reaction will result in chemical electrode effects and changes the sensor resistance value. But during the removal of the target gas, there are still some gas molecules remain at the detecting surface of MOS gas sensor, and it takes a long period of time for all these molecules to desorbs from the detecting surface of MOS gas sensor. As a consequence, it causes long recovery time for MOS gas sensor after the exposure of the target gas.

7.5.2 Sensing Behaviour of CuCrO$_2$ Thin Films

The sensing properties of CuCrO$_2$ sensors were studied by exposing them to 300 ppm of ethanol. In general, the O-H bond in C$_2$H$_5$OH dissociates and yields ethoxide which donates an electron to the CuCrO$_2$ surface. The surface slowly accumulates the adsorbed C$_2$H$_5$OH which results in a prolonged changing trend in resistance during the exposure of the target gas. As a result, in the present study, it is believed that the adsorption kinetics of C$_2$H$_5$OH is slower at the room temperature compared to higher operating temperatures (100 and 200 °C).
The sensitivity and the response–recovery behaviour of CuCrO₂ gas sensors were recorded and its variation with time is shown in Fig. 7.4.

![Graph](image)

**Fig. 7.4 Sensitivity variations of the CuCrO₂ ethanol gas sensors**

When the sensor element is exposed to ethanol source at room temperature, the response time is 790 s with a moderate sensitivity of 40 % and once the ethanol source is removed, the response decreases slowly to the baseline and the recovery time is almost more than an hour. This may be due to the delay in changing its surface state and therefore the usability of the sensor is very remote. When the operating temperature of the sensor is 100 °C, the response time decreases to 518 s with improved sensitivity of 63.11 %. When the testing chamber was flushed with air, the response decreases slowly to the baseline and the recovery time is hard to detect. This time delay in changing its surface state shows the sensors poor irreversibility.
On further increased the operating temperature of the sensor to 200 °C, the corresponding response increases rapidly and reaches its steady value with a much improved sensitivity of 73.6 %. Once the ethanol source is removed by admitting air, the response decreases more or less quickly to the baseline compared to the other operating temperatures of the sensor element. The reaction kinetics is fast enough for surface saturation by the adsorbed species which leads the resistance of the sensors to reach a minimum value within a reasonable time. The response time for the sensor is 509 s and the recovery time a few minutes indicates a fast response–recovery characteristic compared to the other operating temperatures of the sensor. Among the three different test temperatures, CuCrO₂ sensor exhibits the highest sensitivity at 200 °C.

Exhibited higher sensitivity of this sensor can be ascribed to the grain size effect. Smaller grains have enhanced surface to volume ratio and the formation of depletion regions comparable in size with the grains dimensions, enabling a more efficient interaction towards ethanol vapour [97, 98]. In addition, when the grains are smaller than the theoretical penetration length of the depletion region, the energy bands are almost flat throughout the whole grain and the conductivity is fully controlled by the intra-crystallite conductivity, which is the most sensitive areas of the gas molecules interactions with the surface [98]. The sensitivity of a metal oxide gas sensor is mainly determined by the efficient interactions between the target analyte and the surface area of the materials. The greater surface area to volume ratio of the materials enhances the interaction between adsorbed analyte and the sensor surface, boosting the sensitivity of a sensor [99].
According to the reported literature, the porous structure of sensing material can bring inveterate enhancement in the gas sensing properties [100], since it provides a large active area to interact with the gas, and allow the gas to diffuse agilely [101]. Also, it is obvious that more roughness is favourable for gas sensing application because of its more trapping situation. The CuMnO$_2$ and CuCrO$_2$ gas sensor samples had the highest roughness values compared to the other study materials which can entrap the gas species and hence promote the sensitivity to ethanol vapour.

7.6 CONCLUSION

Since semiconductor metal oxide gas sensors have attracted many researchers, the emphasis has been given in the present study to the delafossite type ABO$_2$ thin film structures. The response of the sensor and its dependence to the preparation and measuring conditions were optimized and compared. The increase of resistance on exposing the sensor to ethanol gas is due to the transfer of electrons from the surface towards the hole accumulating layers thereby reduces the hole density and conductivity. As CuMnO$_2$ and CuCrO$_2$ sensor elements have a remarkable conductivity at room temperature, they prove themselves the most promising candidates suitable for gas sensing applications. Sensors were tested in three different temperature environments (RT, 100 & 200 °C) for the constant 300 ppm level of ethanol gas. Among the tested operating temperatures, 200 °C was the favourable condition that improved the gas sensing characteristics with moderate response time and partial irreversibility. Spray pyrolysed films usually have high porosity and rough surface that result in larger surface area rendering them very attractive to use as efficient gas sensors with more sensitivity. The study thus promotes the materials CuMnO$_2$ and CuCrO$_2$ thin film as good candidate for ethanol gas sensing than the alternatives CuO, CuFeO$_2$ and CuAlO$_2$. 

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