# Chapter 1
General introduction and literature survey

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Chapter 1

General introduction and literature survey

1.0 Introduction

Today in the era of science and technology, automation plays very important role. Now days due to advancement in technology, it is possible for human being to access that information which was, once upon a time, inaccessible due to limitations of natural sensory organs. We can say that science and technology has widened the spectrum of sensing ability of the human being. Rapid advances in microelectronics made us available the technical intelligence. Machines became more ‘intelligent’ and more autonomous. There arose a demand for artificial sensing organs that would enable machines to orient themselves independently in the environment. The rapid growth in technology is opening all new doors of new and precise information and this new information is being used for facilitating the life of human being.

The advancement in the field of agriculture, medical science, environmental science, transportation, education, research and industries etc. plays key role in facilitating the life of the human being. This is possible because of advancement in computing technology and sophisticated intelligent instruments which play key role in the development. Getting the minute information, which is the crux behind every activity, was impossible for the human being because of limitations of sensory organs. Today due to highly sophisticated instrument the shortcomings are overcome. The major and important elements of the instrument, which decide the quality of the instrument, are sensor and transducer which are primary units of information perception. The advancement in information technology has necessitated an equally rapid development of various kinds of signal detection and measurement systems. Consequently, sensors as the primary units of information perception have gained significant importance and are extensively incorporated into industrial automated measuring and control systems. Today each and every field such as medical, pollution control, security, industries etc are influenced by this automation. So it is great need to develop highly sensitive, accurate, precise, fast and tailored instrument.
The atmospheric air we live in contains numerous kinds of gaseous species; some of them are vital or useful for our life while many others are hazardous more or less. It includes gases of natural origins and gases of artificial origins such as combustion gases. Today in many situations, maintaining the level of vital gases such as $O_2$ and controlling the hazardous gases below harmful level is very important. For this we must know the concentration of each gas in real time. Gas sensors are being developed as those devices which respond to selected gas and generate adequate output signal (electric, optical etc.) dependent on the gas concentration in real time.

Fig.1.1 shows block diagram of automatic control system. When input interacts with the sensor (which is specific material), it changes its property may be physical, chemical, mechanical, electrical, magnetic etc. in proportion with the input quantity as a response to the input signal.

Transducer is another block, which transforms one physical quantity into another and gives change in its output response in system understandable and usable form. The output of the transducer is then given to signal conditioning element. The signal conditioning element converts output of the transducer in most appropriate form for either displaying, recording or as per requirement of feedback and control system.

The last block is feedback and control unit which is the decision making block of the intelligent instrument. In order to control the desired parameters needed for getting the expected results the appropriate action is taken by this block.

While selecting the automatic control system for specific application one must understand the characteristics and specifications of the system that decides whether system can fulfill the requirements or not.
1.1 Sensors

In a living organism, the receptor of the sensing organ is in direct contact with the environment. Environmental stimuli are transformed into electrical signals conducted by nerve cells (neurons) in the form of potential pulses. Strong stimuli generate a high pulse frequency, i.e. the process is basically some kind of frequency modulation. Conduction is not the only function of neurons. Additionally, signal amplification and signal conditioning is done. In the brain, information is evaluated and, finally, some action is evoked. We see many similarities between living organism and intelligent instruments when we compare how modern sensors and living organism acquire and process signals.

As there is a sensory organ in a living organism, we find a same equivalent component, receptor, which is part of the technical sensor system. The receptor responds to environmental parameters by changing some of its inherent properties. In the adjacent transducer, primary information is transformed into electrical signals.

The most obvious way to make observations is to use the human senses such as seeing, feeling, smelling and hearing etc. This is often quite adequate or may be the only means possible. In many cases, however, sensors are used that have been devised by man to enhance or replace our natural sensors. The process of sensing is often called transduction, being made with transducers.

Sensor is the first block of automatic control system which directly interacts with the input physical quantity and senses the input signal. The quality of output of the instrument depends on the quality of the sensor. The sensor should be highly sensitive and dynamic in nature. Apart from this, a cheap and reliable sensor with small size, measurement simplicity and durability is the need of the instrumentation industry [1-5]. So in order to develop the sensitivity and reliability of the sensor, interest has been increased to study the transduction principle of various elements that can full fill present demand of the industry. Various types of materials, in search of the most suited materials, and their physical and chemical properties are under investigation for developing the good quality sensors demanded by scientific, engineering and industrial sectors. In many cases sensor itself plays role of sensor as well as transducer (Fig. 1.2).
In various types of gas sensor the functioning of the sensor and transduction can be done by various elements with different activities of the sensor. Table 1.1 shows details about the receptor and transduction function in the gas sensor.

![Block diagram of typical gas sensor.](image)

**Fig. 1.2:** Block diagram of typical gas sensor.

**Table 1.1:** Reception and transduction function in typical gas sensors.

<table>
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<th>Receptor (Function)</th>
<th>Transducer (Function)</th>
<th>Signal</th>
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<td>Oxide Surface (Change in work function)</td>
<td>Grain Boundaries (work function dependent resistance)</td>
<td>Resistance Change</td>
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<td>Solid electrolyte (Gas concentration type)</td>
<td>Electrode (Change in electrode potential)</td>
<td>Chemical Cell (comparison between sensing and reference electrode)</td>
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<td>Piezoelectric Crystal(Quartz oscillator)</td>
<td>Adsorbate attached (increase in mass attached)</td>
<td>Quartz oscillator (Mass dependent resonant frequency)</td>
<td>Resonant frequency change</td>
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**1.2 Need of sensors**

It is well known that no automatic control system can exist without the sensor. So, as far as automation is concerned, sensor is inevitable part of every automatic control system. Today atmospheric pollution is one of the burning problems being faced globally. Today in the era of science and technology, the gases generated or consumed by biological or physiological activities (respiration, photosynthesis, diseases, etc.) of our bodies, animal and plants are important for diagnosing the health condition [6]. Similarly, the gases emitted from food material during ageing, rotting or cooking would give important information about the freshness and quality of those origins. In order to control the pollution and maintaining the quality of environment, covering safety, health,
amenity, energy saving, health control and diagnosis large measures are to be taken worldwide. In reality, however, only limited numbers of gas sensors have been developed up to the level of practical use. The vast use of automatic control systems is being done for controlling air pollution, maintaining gas composition for certain reactions, in industries, hospitals etc. These automatic control systems require tailored gas sensor to fulfill the requirements of the system. These sensors are basically required for sensing the existence of particular gas of interest and knowing its quantity in the environment. Further the output of the system is used for controlling either the environment or the system. Gases from auto and industrial exhausts are polluting the environment. The reducing gases such as: CO [7-8], H₂ [9], C₂H₅OH [10], oxygenic gases such as: CO₂ [11-12], NOx [13-14], O₂ [15-17], CH₃OH [18], CH₄ [19], odorous gases such as: NH₃ [20], H₂S [21], explosive gases such as: C₂H₂, C₂H₄, C₃H₆ [22], LPG [23] and, toxic gases such as: CO, H₂S, Cl₂, NO₂ [24] etc. have to be controlled for the healthy survival of the living beings. Thus, there is an increasing concern about minimization of the emission of autointoxication and also to reduce emission of such unburnt hydrocarbons from automobile and industrial exhausts.

In order to detect measure and control these gases, one should know the exact amount and type of gases present in the ambient. Thus the need to monitor and control these gases has led to the research and development of a variety of sensors using different materials and technologies.

1.3 Types of sensors

In general, Sensors are categorized based on various criterions such as the need of electricity for the operation of the sensor and the mode of their operation.

1.3.1 Necessity of electricity for sensors’ functioning

Basically some sensors require electricity for their operation and some sensors do not need the electricity for their operation. Depending upon the basic requirement of electricity for its functioning, sensors are divided in two types:

a. Passive sensors and

b. Active sensors.
1.3.1.1 Passive sensors

This type of sensors requires an external power for its operation. The passive sensors are sometimes called as parametric because their own properties (parameter) change in response to an input signal and the change in the properties (parameter of the sensor) can be subsequently converted into an output electric signal.

1.3.1.2 Active sensor

This type of sensors directly generates an output signal without using any additional energy, in response to the external input signal e.g. thermocouple or a pH meter.

1.3.2 The mode of operation of sensor

According to mode of their operation the sensors are basically categorized in following six types of energy domains [25-29]:

(a) Mechanical, (b) Magnetic, (c) Thermal, (d) Radiant (optical), (e) Electrical, and (f) Chemical.

1.3.2.1 Mechanical sensors

The change in displacement, velocity, pressure, acceleration, and sound intensity are the input signals for mechanical sensors. These types of sensors are particularly used for measuring fluid level, velocity, pressure and acceleration etc.

1.3.2.2 Magnetic sensors

This type of sensor senses the magnetic field. The Hall effect and mobility are used for the magnetic sensors. Magneto-resistive effect, the change in resistance of the materials when subjected to the magnetic field, is used to find the magnetic field strength. Ni-based magnetic sensors are well known [30].

1.3.2.3 Thermal sensors

In this type the sensor response is temperature dependent. These sensors change their properties such as conductivity, radiation-absorption characteristics, and electromotive force, in response, because of the change in the temperature of the surrounding. In thermocouple, e.g., a thermal energy is converted into electrical energy. In such case the temperature between the two junctions of dissimilar metals like Pt-Pd,
Cu-Fe is converted to emf [31]. The sensors in this category are thermocouples, pyrometers, thermistors, and IR detectors etc. Noble metals such as Pt, Pd or RuO$_2$ are used as inbuilt heater materials in sensor technology.

1.3.2.4 Radiant (optical) sensors

These types of sensors sense the optical signals and the output response is proportional to the incident radiation. The photoconductivity, photovoltaic effects are the phenomena used for radiant sensors. The conductivity of film or pellet changes when certain radiations fall on it. The change in conductance is calibrated for the intensity of the radiation. CdS is a very good example of photoconductive materials [32-33].

1.3.2.5 Electrical sensors

In this type the sensors sense the electric signals and the output response is proportional to the input electrical signal. The measurands for these sensors are current, emf, inductance, resistance and, capacitance etc.

1.3.2.6 Chemical sensors

It is the electronic device which senses the content of specific gas in the environment. It produces electric signal as a response proportional to the value of gas adsorbed or deposited on the surface of sensing element due to chemical reaction of the sensor surface and the target gas.

1.4 Literature survey

Since long, vast research has been going on in the field of MOS gas sensor. The continuous efforts are going on to understand the fundamental science behind gas sensing mechanism. Various materials, either in the form of bulk or nano sized along with surface modification by dipping or doping are being tested for highly sensitive and selective gas sensors. The sensors either in the form of thick films or thin films are under investigation to understand the effect of surface morphology on sensing performance. Table 1.2 and Table 1.3 give the detail overview of the literature survey showing existing status of research in the field of MOS gas sensors.
Table 1.2: A summary of literature report showing wide use of metal oxides as a gas sensor.

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<th>Type</th>
<th>Gases</th>
<th>Ref.</th>
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<td>Pd- and Ca-doped iron oxide</td>
<td>Thin Film</td>
<td>Ethanol vapor</td>
<td>[34]</td>
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<tr>
<td>Zn-doped γFe₂O₃</td>
<td>Thick film</td>
<td>Acetone, ethanol</td>
<td>[35]</td>
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<tr>
<td>pure and Pt-loaded nanocrystalline α-Fe₂O₃</td>
<td>Thick film</td>
<td>Acetone</td>
<td>[36]</td>
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<tr>
<td>γFe₂O₃ and Y₂O₃ doped γFe₂O₃</td>
<td>Thick film</td>
<td>Alcohol, C₂H₅, Petrol</td>
<td>[37]</td>
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<tr>
<td>γFe₂O₃</td>
<td>Thick film</td>
<td>Butane</td>
<td>[38]</td>
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<tr>
<td>Ni-doped γFe₂O₃</td>
<td>Thick film</td>
<td>Acetone and Ethanol</td>
<td>[39]</td>
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<tr>
<td>αFe₂O₃ nanorods</td>
<td>Thick film</td>
<td>Acetone</td>
<td>[40]</td>
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<tr>
<td>ZnO</td>
<td>Thick film</td>
<td>Hydrogen and Ethanol</td>
<td>[41]</td>
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<td>VO₂ nanobelts</td>
<td>Thin film</td>
<td>Alcohol, Gasoline</td>
<td>[42]</td>
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<td>αFe₂O₃ nanostructures and αFe₂O₃ nanocubes</td>
<td>Thin film</td>
<td>Ammonia and various flammable and/or toxic volatile organic compounds</td>
<td>[43]</td>
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<td>CuO/ Fe₂O₃ catalysts</td>
<td></td>
<td>CO</td>
<td>[44]</td>
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<td>Fe₂O₃/ZnO core–shell nanorods</td>
<td>Thick film</td>
<td>Ethanol, petroleum</td>
<td>[45]</td>
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<td>Nano-crystalline Cu-doped ZnO</td>
<td>Thin film</td>
<td>CO</td>
<td>[46]</td>
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<td>Ag-doped α-Fe₂O₃ nanoparticles</td>
<td>-</td>
<td>H₂S</td>
<td>[47]</td>
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<td>Pt-doped α-Fe₂O₃</td>
<td>Thick film</td>
<td>H₂S</td>
<td>[48]</td>
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<td>Tin oxide</td>
<td>Thin-film</td>
<td>Acetic acid, Isopropanol, Ethanol</td>
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<td>Tin, Indium, and zinc Oxides</td>
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<td>SnO₂</td>
<td>Thick films</td>
<td>H₂</td>
<td>[51]</td>
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<td>In₂O₃ mixed α-Fe₂O₃ nanorods</td>
<td>Thick films</td>
<td>Ethanol</td>
<td>[52]</td>
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<td>Thin film</td>
<td>O₃, NO₂</td>
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<td>CuO-modified SnO₂</td>
<td>Thick films</td>
<td>H₂S</td>
<td>[54]</td>
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<td>Sc₂O₃–ZrO₂ solid electrolyte and CuO + CuCr₂O₄</td>
<td>Thick films</td>
<td>NO₂</td>
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<tr>
<td>α-Fe₂O₃ ceramic nanofibers</td>
<td></td>
<td>C₂H₅OH vapor</td>
<td>[56]</td>
</tr>
<tr>
<td>α-Fe₂O₃ nanospheres</td>
<td></td>
<td>Ethanol</td>
<td>[57]</td>
</tr>
</tbody>
</table>
Fe₂O₃ modified of nanostructured SnO₂  Thick films  LPG  [58]
Fe₂O₃/ZnO core/shell nanorods  Thick films  Combustible gas  [59]
Zn-doped γ - Fe₂O₃  Acetone  [60]
α-Fe₂O₃  Highly sensitive direct thermoelectric gas sensors  [61]
SnO₂-Sb₂O₃-Pd  Thin film  H₂, NH₃, CH₄, CO, C₂H₅OH  [62]
SnO₂-Ga₂O₃  Thin film  CH₄  [63]
SnO₂-Bi₂O₃  Thin film  CO  [64]
SnO₂-Sulphuric acid  Pellet  CO, NH₃, Ethanol, Acetone, LPG  [65]
SnO₂-CuO  Paste applied on Al₂O₃ tube  H₂S, CO, C₄H₁₀, C₂H₅OH  [66]
ZnO  Thin film  H₂, SF₆, C₄H₁₀, C₂H₅OH  [67]
ZnO-Ru  Pellet  NH₃  [69]
ZnO, ZnO-Pd, Fe, Ru  Thick film  NH₃  [70]

Table 1.3: Various chemical gas sensor materials, additives and the analyzing gas.

<table>
<thead>
<tr>
<th>Base material</th>
<th>Additives</th>
<th>Analyzing gas</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoO₃</td>
<td>Ti</td>
<td>NH₃, CO, NO₂</td>
<td>[71-73]</td>
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<tr>
<td>Nb₂O₅</td>
<td>SnO₂</td>
<td>NH₃, CO, C₂H₅OH, H₂</td>
<td>[74-76]</td>
</tr>
<tr>
<td>NiO</td>
<td>Li, TiOx</td>
<td>H₂, HCHO, CH₄, CH₃COOH, CO, NO₂</td>
<td>[77-79]</td>
</tr>
<tr>
<td>Ta₂O₅</td>
<td>--</td>
<td>Humidity</td>
<td>[80]</td>
</tr>
<tr>
<td>SnO₂</td>
<td>Pt, Cu, Cr₂O₃, Cd, Pd, Fe, Au, In, Ru, Bi₂O₃, CeO₂, TiO₂</td>
<td>CO, H₂S, SO₂, N₂O, CO₂, CH₃OH, C₂H₅OH, NH₃, Cl₂, LPG</td>
<td>[81-86]</td>
</tr>
<tr>
<td>TiO₂</td>
<td>La, Pt, Cr₂O₃, WO₃</td>
<td>CH₃OH, C₂H₅OH, C₃H₇OH, H₂, O₂, NH₃, NO₂</td>
<td>[87-95]</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>Fe₂O₃, SnO₂, TiO₂</td>
<td>NO₂, NH₃, C₂H₅OH, Butylamines, Propanol, Toluene</td>
<td>[96-98]</td>
</tr>
<tr>
<td>ZnO</td>
<td>Al, Sn, Cu, Pd</td>
<td>LPG, NH₃, H₂, CH₄, CO, H₂S</td>
<td>[99-106]</td>
</tr>
</tbody>
</table>
### Table

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>Al, SiO₂/Si</td>
<td>Humidity, CH₄, NH₃</td>
<td>[107-110]</td>
</tr>
<tr>
<td>CuO</td>
<td>SnO₂</td>
<td>H₂S, Ethanol, CO</td>
<td>[111-114]</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>Au, Zn (Pt, Pd, RuO₂)</td>
<td>Methane, propane, Benzene, Toluene, CO, NO₂, Methanol, Acetone</td>
<td>[115-119]</td>
</tr>
<tr>
<td>In₂O₃</td>
<td>MoO₃, Au, Al, SnO₂</td>
<td>O₃, NO₂, H₂, CO, C₃H₈, H₂S, Cl₂, CO₂, SO₂, NH₃, Ethanol, Acetone</td>
<td>[120,121]</td>
</tr>
</tbody>
</table>

Gas sensor technology has advanced remarkably. The development in the field of gas sensor incorporate use of innovative ideas in sensor fabrication, developing adequate material for small size and low power consumption sensors. To achieve the goals of developing the gas sensors as capable as the sensory organ of our body it is essential to thoroughly understand the gas sensing mechanism, new methods of synthesizing new materials for selective sensors, nano-structured materials for sensors and micro fabrications of sensors.

Semiconductor gas sensors are divided into two main groups.
1) Resistor form and 2) MISFET (Metal/Insulator/ Semiconductor/ field effect transistor).

A resistive gas sensor using oxide semiconductor for detecting inflammable gases was reported in 1962 [122]. The interactions of the gas, in gas sensors those have been mostly developed by using receptors which interact with gas reversibly, fall in four categories i.e. equilibrium, steady state, complete reaction and accumulation mode [123]. In early phase of development of gas sensors, Taguchi invented a gas leakage alarm device to protect people from disasters caused by malfunction of gas appliances in domestic use [124]. Further several revisions including the addition of sensitizers (noble metals like Pd) are made in the semiconductor gas sensor. Humidity sensors have also been used for various aspects such as air conditioning, protection of electronic instruments from due formation. The sensors made of porous composites of metal oxides show change in its AC impedance with a change in humidity at elevated temperature. Further electro chemical cell using solid electrolyte to measure standard free energy of formation of metal oxides or activity of oxygen in molten metal concept was used to apply this type of cell to gas phase in 1963 [125]. In chemical reaction of O₂ at sensing at
reference electrodes, EMF is generated in proportion to logarithmic of the ratio of $O_2$ partial pressure at reference electrode.

As far as various metal oxide semiconductor gas sensors are concern various material have been tested with various gas sensing technique for the purpose of their use as practical gas sensors.

### 1.5 Electrochemical sensor

It is based on the detection of electroactive species involved in chemical recognition process and makes use of charge transfer from a solid or liquid sample to an electrode (Fig. 1.3). An electrochemical sensing requires a closed circuit which enables the flow of current to make measurements.

Chemical sensing as a rule is a multistage and multi channel process, which requires a multi disciplinary approach. Chemical sensors are characterized by the parameters such as a sensitivity, selectivity, response and recovery time and saturation. These sensors are classified in a number of ways based on their principle of operation.

![Typical electrochemical sensor](image)

**Fig. 1.3:** Typical electrochemical sensor

Electrochemical sensors are divided into following categories.

#### 1.5.1 Amperometric sensors

Amperometric sensors are the sensors in which the flow of current is measured at a constant applied potential between electrodes. The resulting current is a direct measure of the rate of the electron transfer reaction and it is proportional to the concentration of target analyte. The counter electrode current arises by two oxygen- reduction steps [126]:
\[ \text{O}_2 + 2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2\text{O} + 2\text{OH}^- \] 
\[ \text{H}_2\text{O}_2 - 2e^- \rightarrow 2\text{OH}^- \]

1.5.2 Potentiometric sensors

In potentiometric sensors, the analytical information is obtained in form of the a potential signal, which is proportional (in a logarithmic fashion) to the concentration (activity) of the species generated or consumed in the recognition event. Such devices rely on the use of ion selective electrode to obtain the potential signal. Upon equilibrium at the analyte-electrolyte interface in chemical cell, an electrical potential develops due to “redox” reaction.

Under quasi–thermodynamic equilibrium conditions, the Nernst equation is applicable [127]

\[ E = E_0 + \frac{RT}{nF} \ln \left( \frac{C_0}{C_R} \right) \]

Where \( R, T, n, F, C_0 \) and \( C_R \) are the gas constants (8.314 J mol\(^{-1}\) K\(^{-1}\), temperature (in K), number of electrons transferred, Faraday constant (96,485 C), concentration of oxidant and reduced product, respectively, and \( E_0 \) is the electrode potential at the standard state.

Ion selective electrodes are potentiometric sensors that measure the potential of specific ionic species in the solution. The pH sensor based on a glass membrane is the oldest type of ion selective electrode [128]. The ion selective electrode ideally follows a Nernst equation:

\[ E = K + \left( 2.303 \times \frac{RT}{zF} \right) \text{Loga}_i \]

Where \( E \) is the potential, \( K \) is a constant representing the effect of various sources such as liquid junction potential, \( R \) is universal gas constant, \( T \) is the absolute temperature, \( Z \) is ionic charge, and \( a_i \) is the activity of ion \( i \). The activity of an ion \( i \) in solution is related to its concentration \( C_i \).

1.5.3 Capacitance sensors

A capacitor is electric circuit component which can store electric energy in response to an applied voltage. The component which can store electrical charge in response to applied potential, the capacitance can be expressed as
\[ C = \frac{\varepsilon_0 \varepsilon_r A}{d} \] .......................... (5)

Where \( \varepsilon_0 \) represents the permittivity in vacuum, \( \varepsilon_r \) is the relative permittivity of the dielectric, \( A \) is the area of the electrode, and \( d \) is the distance between two electrodes.

The operating principle of capacitance sensor is that the analyte of interest can change \( \varepsilon_0, A, \) and \( d \), and therefore, by measuring the change in the capacitance the presence of the measurand can be detected [129]. Capacitive sensors based on changes in thickness rely on the formation of depletion layers in the dielectric capacitor. Depletion layer formed between the p- and n-type semiconductors, metal oxide semiconductors, or metal semiconductors have been investigated for this purpose.

1.5.4 Work function sensors

In the solid phase the work function (\( \phi \)) of material is defined as the minimum energy required by an electron to escape from the Fermi level of the bulk material to the vacuum level [130].

\[ \Phi = \varphi = -q\theta - E_F \] .......................... (6)
\[ E_F = -\varphi - q\theta \] .......................... (7)

The Fermi level corresponds to the electrochemical potential of an electron. At a given temperature, the Fermi level is the highest occupied energy level in the band gap. The energy difference between \( E_F \) and vacuum (Volta) energy level (-q\( \theta \)) is the work function (Fig. 1.4).
Fig. 1.4: work function

When an electroactive material is brought into electrical contact with a metallic electrode, charge transfer occurs until the Fermi energies of both materials reach thermal equilibrium and the Fermi levels of the two materials become equal. However their Volta energy levels are different. The difference in their work function is equal to their difference in Volta energy [131]. The redox properties of material can be studied by measuring their work function using Kelvin probe, which consist of vibration capacitor [132]. Using this method, the change in the work function due to the redox reaction of the material can be measured. When the surface of the metal and the electroactive material are held parallel to each other and separated by a dielectric material, there is a potential difference across the surface due to transfer of charge[133]. This potential difference is given by the difference between the work function of the two materials that constitute the Kelvin probe. The extent to which the gases can interact with the surface dipole determines the amount of work function shift.

1.5.5 Field effect transistor sensors

The basic metal oxide semiconductor field effect transistor consists of four terminals, a source, drain, gate, and substrate. The source and drains are highly conducting regions, whereas the gate is a metal region separated from the source and drain by a gate oxide. The most important parameter of a MOSFET is threshold voltage.
(V_T), which is defined as the gate voltage at which there is an onset of inversion layer at the surface of the semiconductor. The carrier concentration of the inversion layer has opposite polarity to that of the carrier concentration in the bulk of the semiconductor. The formation of inversion layer is controlled by applied gate voltage. The net result is that the current between the drain and source is controlled by the voltage that is applied to the gate and the drain-to-source voltage.

The drain current of a MOSFET is given by the following equation [134]

$$I_D = \beta \left( V_{GS} - V_T - \frac{1}{2} V_{DS} \right) V_{DS} \ldots \ldots \ldots (8)$$

where $V_{GS}$ and $V_{DS}$ are the gate-to-source and drain-to-source voltages, respectively; $V_T$ is the threshold voltage of MOSFET; and $\beta$ is the sensitivity parameter determined by dimension of the gate and given by

$$\beta = \mu C_{ox} \frac{W}{L} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (9)$$

where $\mu$ is the mobility of electrons in the channel, $C_{ox}$ is the gate oxide capacitance per unit area, $W$ is the channel’s width, and $L$ is the length of the channel. The threshold voltage ($V_T$) of the MOSFET is given by

$$V_T = \phi_{MS} + 2 \phi_F + \frac{Q_{dep}}{C_{ox}} \ldots \ldots \ldots (10)$$

where $\phi_{MS}$ is a function of the difference between the work function of the gate and the silicon substrate, $Q_{dep}$ is the change in the depletion region, and

$$\phi_F = kT \frac{q}{N_{sub}} \ln \left( \frac{N_{sub}}{n_i} \right) \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (11)$$

where $N_{sub}$ is the doping concentration of the substrate and $n_i$ is the intrinsic carrier concentration.

The theory of operation of these FET based devices and metal insulator semiconductor (MIS) capacitor as a gas sensor was developed by Lundstrom and co-workers [135, 136].

**1.5.6 Schottky diode based sensors**

It consists of a metal-semiconductor junction instead of semiconductor-semiconductor junction as in conventional diodes. It uses the metal-semiconductor junction as the Schottky barrier. Since the barrier height is lower in metal-semiconductor junction than in the conventional p-n junctions, Schottky diodes have lower forward
voltage drop. An n-type semiconductor is normally used in Schottky diodes. Due to the absence of p-type semiconductor region in these diodes, faster switching times are possible since the mobility of electrons is three times that of the holes. These diodes can be used as sensors for various chemicals if the adsorbed analyte changes the electrical characteristics of Schottky diode.

Based on thermoionic field emission conduction mechanism of the Schottky diode, the I-V characteristics of the diode for forward bias voltage greater than $3kT$ is given by \[137\]

$$I = I_{sat} \exp \left( \frac{qV}{nkT} \right) \quad \ldots \ldots \quad (12)$$

where $k$ is Boltzmann constant, $T$ is temperature in Kelvin, $n$ is ideality factor, and $I_{sat}$ is saturation current.

$$I_{sat} = S A^* \exp \left( \frac{-q\phi_b}{kT} \right) \quad \ldots \ldots \quad (13)$$

where $S$ is the area of the junction, $A^*$ is the effective Richardson constant. And $\phi_b$ is the barrier height.

The changes in the I-V characteristics of the Schottky diode in the presence of analyte as a rule are conditioned by the change of the Schottky barrier height. The response can be due either to adsorption of the species of interest at the metal surface affecting interfacial polarization by formation of a dipole layer or to absorption of gases or vapors of interest by semiconductor and their interaction with the semiconductor, which changes the work function and hence the contact potential or built-in voltage of the diode\[138,139\].

### 1.5.7 Catalytic sensors

These sensors are widely known as pellistors, and have been in widespread use for more than in portable, transportable gas alarms. These types of sensors are stable, reliable, accurate, and rugged and have long operating life.

In operation the pellet and consequently the catalyst layer is heated by passing a current through the underlying coil. In the presence of flammable gas or vapor, the hot catalyst allows oxidation to occur in a chemical reaction similar to combustion. The catalyst reaction releases heat, which causes the temperature of the catalyst together with that of its underlying pellet and coil to rise. This rise in temperature results in a change in
the electrical resistance of the coil, and it is this change in electrical resistance which constitutes the signal from the sensor.

The sensor temperature rise can be detected via an increase in coil resistance, typically by incorporating the sensing element in a Wheatstone bridge circuit. A measurement voltage is applied across both arms of the bridge, and the resistance in each arm is matched so that the potential difference measured across the center of the bridge is zero i.e. balancing of the bridge. Any change in the resistance of the platinum wire will now result in a change in this measured voltage.

1.5.8 Conductometric sensors

The basic operation of conductometric sensors is the change in resistance under the effect of reaction (adsorption, chemical reactions, diffusion, catalysis) taking place on the surface of the sensing layer. The chemical species interact with the sensitive layer and thus modulate the electrical conductivity. This can be measured as a change in the current, which is correlated to the concentration of the chemical species.

1.6 Conductometric gas sensors

![Fig. 1.5: Typical structure of conductometric sensor.](image_url)
The operating is based on the fact that their electrical conductivity can be modulated by presence or absence of some chemical species that comes in contact with the device [140]. It consists of two elements, a sensitive conducting layer of sensing material and contact electrodes mounted on substrate. These electrodes are often integrated and embedded in the sensing layer. Fig. 1.5 shows a typical structure of a conductometric sensor.

To make the measurement, a DC voltage is applied to the device and current flowing through is monitored as the response.

The most accepted mechanism, explaining sensitivity of n-type metal oxide-based sensor, includes consideration of the role of the chemisorbed oxygen [141, 142]. Oxygen chemisorption means the formation of $O_2^-$, $O^-$, and $O_2^{2-}$ species on the surface. Among these $O^-$ proved to be more reactive than $O_2^-$, while $O_2^{2-}$ is not stable. So the dominant species is $O^-$ species. The oxygen chemisorptions results in a modification of the space charge region toward depletion. The appearance of reducing gas leads to partial consumption of the adsorbed oxygen coverage, and hence the resistance. The above mechanism suggests the existence of a grain boundary. The relation between the amount of change in resistance to the concentration of a combustible gas can be expressed by a power law equation [141].

$$G = \frac{1}{R} = k C^n \ldots \ldots \ldots (14)$$

where $C$ is the concentration of the analyte and $K$ and $n$ are individual constants, which depend on the mechanism of sensitivity and must be determined empirically by calibration.

To activate reactions of oxygen chemisorptions and surface catalysis, high temperature (> 200°C) is required. For this purpose, metal-oxide gas sensors have incorporated heaters, which are electrically isolated from the sensing layer.

**Advantages**

The main advantages of the conductometric type of sensors are

(i) Easy fabrication
(ii) Simple operation
(iii) Low production cost
(iv) Compact
(v) Durable
as a result they are amenable to being placed in situ in monitoring wells.

1.6.1 Categories of conductometric gas sensor

The two main categories of the conductometric gas sensors are thick and thin film sensors. Their preparation involves different techniques. The different structural properties due to the fabrication and film thickness lead to different sensing properties.

1.6.1.1 Thick film technology

In thick film sensors the film thickness is typically in the range of 2-300 µm. Thick-film technology, based mainly on screen printing, is the most common fabrication technique for such sensors. The layer itself is porous body, so the inner surface also becomes a working surface. Therefore, the gases diffuse into it, leading to good sensitivity. The microstructure of the sensing layer is function of the temperature parameters of grains sintering. The conductance usually is controlled by the contact resistance between the grains.

To prepare thick films, the paste of functional material is formulated and printed onto an insulating surface in a definite pattern [143,144].

The thick film is prepared by screen-printing and then firing process. For thick film technology, paste of the functional material is prepared with the use of some temporary binder (organic binder) [145,146]

A proper permanent binder, glass frit, is used along with the functional material to achieve adhesion of a film to the substrate. The paste is printed on an insulating substrate (e.g. glass plate, alumina), which can stand at higher temperatures, using screen-printing to get the definite pattern. The printed film is dried under an IR lamp to remove the temporary binder and then fired at a higher temperature with a definite time-temperature profile to obtain stability and better adhesion of the film to the substrate.

An important and growing application of sensors fabricated using thick film and related techniques is to the detection and monitoring of gases. The materials most widely preferred for oxygen, flammable gases and toxic gases are semiconducting oxides which present an opportunity for reactions that involve molecular chemistry that is confined to the surface layer of atoms but, the electrical consequences of which are manifested
through a considerable volume of solid. Surface reactions are followed by a change in resistance of entire sample. In other instances surface reactions may modify the conductance only to a depth of the order of micron but the semiconducting oxide in the thick film forms provides a high source to bulk form (e.g. in a porous thick film) and so exhibits enormous conductance sensitivity to atmospheric composition. In either case semiconductor gas sensors function as gas sensitive resistors and thus represent a simple, low cost means of atmospheric monitoring.

The effectiveness of gas sensors prepared from thick films of semiconducting oxides depends on several factors including the nature of the reaction-taking place at the oxide surface, the temperature, the catalytic properties of the surface, the electronic properties of the bulk oxide and the microstructure.

It is possible to prepare semiconducting oxides in the form of thin films for gas sensing. However, thick film technology offers following advantages:

(i) a route to small-scale devices at lower cost than that of the thin film equivalently
(ii) a good control over the thickness and microstructure is possible
(iii) life time expected to be larger
(iv) properties of bulk materials

1.6.1.2 Thin film technology

Thin films as the name suggests are thin in nature. Generally thickness of thin films is less than 5 to 500 nm, in special cases even 1 µm. Since the thickness of the films is less than the average mean free path, the resistance of these films is quite higher than that of the thick films. Thin films are defined as the films having thickness less than the average mean free path of an electron, in the medium [147]. At present, for conductometric sensors, mainly oxide semiconductors or mixed oxide semiconductors are used as base materials [148]. Polymers, thin-film metals, and the carbon nanotubes which exhibit changes in their conductivity when exposed to the analyte, also can be used for fabricating such sensors. Extensive literature is available for variety of polymers [149-151], Metal oxides [152-154] and mixed oxides [155]. Metals are normally substituted into polymers, and the choice of metal governs the sensitivity of the
conductometric sensors. A variety of metallic nanowires have also been reported for gas sensing, such as palladium nanowires for hydrogen sensing [156].

The most common preparation process is thin-film technology based on sputtering, evaporation, chemical vapor deposition, spray pyrolysis, chemical deposition, or laser ablation method of forming the sensing layer. Sensing layers in thin film sensors have more dense structure in comparison with thick film sensors. There are three methods of obtaining thin films.

i. Physical method like vacuum evaporation and sputtering of the material,

ii. Chemical method like electrochemical or chemical vapor deposition (CVD), electroplating, chemical bath deposition, ion plating and,

iii. Spray pyrolysis.

(i) Physical vapor deposition

The two most important methods for deposition of thin films by PVD are vacuum evaporation and sputtering of the material [157, 158].

The objectives of the method are to transfer atoms from the source material (boat or target) to the substrate automatically. In evaporation, the atoms are removed from the source by thermal energy where in sputtering the atoms are dislodged from a solid target (source) surface through the impact of gaseous ions.

In vapor deposition, the source material is kept in filament or a boat and is evaporated in a clean environment (in vacuum = 10^{-6} torr) by passing a current through the resistive filament/boat.

(ii) Chemical vapor deposition (CVD)

It is a process, in which chemically volatile compound of a material to be deposited, with the other reactor, to produce a nonvolatile solid that deposits automatically on the substrate. The advantages of CVD are as follows.

- A large variety of films and coating of metals, semiconductors and compounds possessing high purity and desirable properties.
- Capability of producing films of a varying stoichiometry.
- Suitable for batch and semi-continuous operation.
(iii) Spray pyrolysis

Spray pyrolysis involves spraying of a solution, usually aqueous, containing soluble salts of the constituent atoms of the desired compounds onto heated substrates. The hydrolysis reaction mentioned earlier is normally involved. Whether or not the process can be classified as CVD depends on whether the liquid droplets vaporized before reaching the substrate or react on it after splashing. Several workers have used preheating (temperature, about 200-500°C) of the sprayed droplets to ensure vaporization of the reactants before they undergo a heterogeneous reaction at the substrate. The technique is very simple and is adaptable for mass production for large area coating for industrial applications. Various geometries of spray setups are employed, including an inverted arrangement in which larger droplets and gas phase precipitates are discouraged from reaching the substrate, resulting in films of better quality [159, 160].

1.7 Importance of gas sensors

In the atmosphere, pollution is increasing day-by-day. Therefore, the atmospheric pollution has become a global issue. Gases from auto and industrial exhausts are polluting the environment. These harmful and toxic gases cause serious problems in atmospheric pollution. It is important to detect and monitor such gases. There is a need of gas monitoring for the following three broad categories.

a) For oxygen, in connection with the monitoring of breathable atmospheres and for control of combustion processes (boilers and internal combustion engines). Oxygen concentrations in the region of 20% in the former and 0.5% in the latter need to be monitored.

b) For flammable gases in air in order to protect against the unwanted occurrence of fire or explosion. In this case concentrations to be measured are in the range up to the lower explosive limit, which for most gases, is up to a few percent.

c) For toxic gases in air, where the need is to monitor concentrations around the exposure limits which range from less than 1ppm to several hundred ppm and ambient levels for environmental pollutants such as ozone which range up to around 100 ppb.

The second and third categories are monitored in the industry and in the home with solid-state sensors and in the environment largely by means of optical rather than
solid-state techniques. The measurement of a further, highly significant, component of the atmosphere, namely water vapor, is not considered here except to note that changes in relative humidity can sometimes interfere with the successful monitoring of the three categories of gas mentioned above.

The majority of the well-established types of gas sensor are solid-state devices, which combine rugged construction with sufficiently low purchase costs to allow widespread deployment. In addition, there is a significant sector of the gas sensor market that is served by liquid electrolyte electrochemical cells.

Today we know it very well the effect of the gases in the environment and on the life of living being. The gas may be of vital importance or hazardous, its concentration in the air decides its effect. The concentration of the gas above certain limit (TLV) may cause danger. Table 1.4 and Table 1.5 give the information about the TLV, lower exposure limit and ignition temperature of various gases.

**Table 1.4:** Long and short term exposure limits of some typical toxic gases/vapors

<table>
<thead>
<tr>
<th>Gas/Vapor</th>
<th>Long-Term Exposure Limit, 8 h (ppm)</th>
<th>Short-Term Exposure Limit, 10 min (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂S</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>CO</td>
<td>50</td>
<td>300</td>
</tr>
<tr>
<td>NO₃</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>SO₂</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>200</td>
<td>250</td>
</tr>
<tr>
<td>Cl₂</td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>NH₃</td>
<td>25</td>
<td>35</td>
</tr>
<tr>
<td>HCl</td>
<td>-</td>
<td>5</td>
</tr>
</tbody>
</table>

**Table 1.5:** Lower explosive limit and ignition temperature of some typical combustible gases

<table>
<thead>
<tr>
<th>Gas/Vapor</th>
<th>Lower Exposure Limit (% v/v)</th>
<th>Ignition Temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>4</td>
<td>560</td>
</tr>
<tr>
<td>CO</td>
<td>12.5</td>
<td>605</td>
</tr>
<tr>
<td>CH₄</td>
<td>5</td>
<td>595</td>
</tr>
<tr>
<td>CS₂</td>
<td>1</td>
<td>102</td>
</tr>
<tr>
<td>C₄H₁₀</td>
<td>1.5</td>
<td>365</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>6.7</td>
<td>455</td>
</tr>
</tbody>
</table>
1.8 Principle of gas sensor

Sensing material plays very important role in chemical as well as biological sensor. The multidimensional nature of the interaction between function and composition, preparation method, and end-use conditions of sensing material often makes their rational design for real world very challenging. The chemical sensors can be classified in number of ways, depending on their principle of operation.

Sensor effect deals with the change of various electrophysical characteristics of semiconductor adsorbent when detected particles occur on its surface irrespective of the mechanism of their creation i.e. transformation of the value of adsorption directly into electrical signal which is proportional to the amount of particles adsorbed from surrounding medium or deposited on the surface of operational element of the sensor due to heterogeneous chemical reaction.

![Sketch of an MOS sensor illustrating the detection principle.](image)

**Fig. 1.6:** Sketch of an MOS sensor illustrating the detection principle.

The metal oxide semiconductor sensors are basically categorized into two categories. First one is n-type (Zinc oxide, tin dioxide, titanium dioxide or iron (III)
oxide) which respond to reducing gases. In this oxygen in the air reacts with the surface of the sensor and traps any free electron on the surface or at the grain boundaries of the oxide grains. This produces large resistance in these areas due to the lack of the carriers and resulting potential barriers produced between the grains inhibit the carrier mobility. However if the sensor is introduced to the reducing gas like CH₄, H₂, CO, C₂H₅, or H₂S the resistance drop because the gas reacts with the oxygen and releases an electron. This lowers the potential barrier and allows the electron to flow, thereby increasing the conductivity. And in other category P- type sensor sensors to oxidizing gas like O₂, NO₂ and Cl₂ as these gases remove electrons and produces holes, i.e. producing charge carriers. Equation (1) and (2) describe the reactions occurring at the surface:

\[
\frac{1}{2}O_2 + e^- \rightarrow O^-(s) \text{................. (15)}
\]

\[
R(g) + O^- \rightarrow RO(g) + e^{-}. \text{........... (16)}
\]

where e is electron from the oxide. R (g) is the reducing gas and g and s are surface and the gas respectively [34]. Fig. 1.6 shows the gas sensing mechanism related to gas detection. The resistance of the sensing layer changes when molecules react on the surface.

1.9 Solid-state gas sensor classifications

There are three types of solid-state gas sensor currently in use on a large scale. They are based: (a) on solid electrolyte, (b) on catalytic combustion and, (c) on resistance modulation of semiconducting oxides.

Nowadays, the solid-state gas sensors are being developed because of their small size, low cost and reliability.

1.9.1 Solid electrolyte gas sensors

These sensors work on the principle of electrochemistry or ionic conductivity of the solid electrolyte materials in the presence of gas. Solid electrolytes are materials that allow the conduction of ions but not the conduction of electrons. In common with liquid electrolytes they support the function of electrochemical cells, in which chemical reactions are only allowed to proceed to completion if separate paths are provided for the flow of ions (through the electrolyte) and electrons (through an electronic conductor).
The essential function of the solid electrolyte is to separate two regions of distinct activity of the species to be monitored and to allow high mobility of ions of that species between the two regions. The function of the sensor is addressed through measurement of potential, current or charge passed and to this end it is necessary for the ionic conductivity of the electrolyte to be high and for other modes of electrical conductivity to tend to zero.

1.9.2 Catalytic combustion gas sensors

These sensors contain sensor material with catalyst. When combustible gas is exposed to the sensor, it reacts with catalyst and burns fuel gas, which increases the resistance. The increase in resistance is then correlated with concentration of the combustible fuel gas.

Potentially explosive mixture of methane, or other flammable gases, with air can be monitored by means of catalytic active solid-state sensor developed. The device, often referred to as the “Pellistor”, is essentially a catalytic micro calorimeter. It consists of catalytic surface constructed around a temperature sensor and a heater, which maintains the catalyst at a sufficiently high temperature to ensure rapid combustion of any flammable gas molecules present. Usually heating and temperature measurement functions are combined: a platinum coil is embedded in a refractory bead of alumina, which is maintained at 500°C by a current through the wire. The sensor detects gas concentrations by monitoring changes in the resistance of the wire resulting from temperature increase of produced by combustion.

The response of the catalytic pellistor is not selective but depends on the product of the inflammable gas concentration and its heat of combustion as well as the rate of diffusion of the inflammable gas to the sensor. The sensor thus offers a different response to the different gases at a single concentration, expressed on a volume percentage basis but gives an approximately universal measure of all flammable gases expressed as a percentage of the lower explosive limit. This measure of the “explosiveness” of an atmosphere is often of more practical significance than the identification of the individual components of the atmosphere.

The pellistor is useful for monitoring a wide range of flammable gases but its utility is limited to a measurement range of approximately 0.05 to 5% by volume of
flammable gas in the air. Recent developments in the technology of catalytic gas sensors have focused on reducing the power required by the unit by making it smaller. Another approach to the reduction in the power requirements of the catalytic gas sensor is to operate in an intermittently powered mode.

1.9.3 Semiconducting oxide gas sensor

Semiconductor gas sensors utilizing SnO₂ and ZnO have been studied extensively since they were first proposed by Seiyama [161]. These metal oxide semiconductor based gas sensors can detect various gases by using the conductivity changes of their surfaces due to the adsorption and desorption of gases.

These sensors are based on the semiconducting oxides and on the principle of adsorption phenomenon. The electrical property of the surface is changed due to the adsorption of foreign species on the surface of the semiconducting material.

A gas sensor, in particular, is designed to transform chemical information (concentration) of a particular gas present in the designated space into an electrical signal or optical signal. The sensor must be compact enough to be installed in a commodity appliance and cheap enough to be available for citizens. So instead using the gas sensors based on intrinsic properties such as molecular weight or optical absorption, gas sensors usually adopt indirect methods. These indirect methods utilize functional properties of the material and/ or devices. Semiconductors, ionic conductors (solid electrolyte), piezo electric crystals, catalytic combustion catalysts, optical fibers and other functional materials have been introduced into gas sensor. Table 1.6 gives the detailed information about the classification of the gas sensors.

<table>
<thead>
<tr>
<th>Type</th>
<th>Device structure</th>
<th>Responding property</th>
<th>Sensing materials</th>
<th>Target gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Semiconductor</td>
<td>Resistor (Block, Film)</td>
<td>Resistance</td>
<td>SnO₂, WO₃, metal porphyrines</td>
<td>Inflammable gases, CO, H₂O, NH₃, NO₂, O₃, NO</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>TiO₂ (high temperature operation)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Gas sensitive gate-MISFET</td>
<td>Threshold voltage</td>
<td>Pd gate, WO₃, semiconductor gate</td>
<td>H₂, NH₃, NO₂</td>
</tr>
<tr>
<td>Solid electrolyte type</td>
<td>Gas concentration cell</td>
<td>EMF</td>
<td>Stabilized zirconia K$_2$CO$_3$ NASICON</td>
<td>O$_2$(A/F) CO$_2$ Na Vapor</td>
</tr>
<tr>
<td>------------------------</td>
<td>------------------------</td>
<td>-----</td>
<td>----------------------------------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>Auxiliary phase attached gas cell (type III)</td>
<td>Electrolytic cell + gas diffusion layer(hole)</td>
<td>Electrolytic current</td>
<td>Stabilized zirconia</td>
<td>NO$_2$ CO$_2$</td>
</tr>
<tr>
<td>Electrolytic cell + gas diffusion layer(hole)</td>
<td>Mixed potential</td>
<td>Sb$_2$O$_5$.nH$_2$O (H$^+$ Conductor)</td>
<td>H$_2$, CO</td>
<td></td>
</tr>
<tr>
<td>Mixed gas cell(open circuit)</td>
<td>Short circuit current</td>
<td>Ion exchange membrane (H$^+$ or OH$^-$ conductor)</td>
<td>CO</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Dielectric material</th>
<th>Resistor</th>
<th>AC resistance (due to capacitance change)</th>
<th>Some organic polymers WO$_3$- CuO composites</th>
</tr>
</thead>
<tbody>
<tr>
<td>Insulator</td>
<td>Resistor</td>
<td>AC resistance (due to ionic conductance change)</td>
<td>Mg Cr$_2$O$_4$-TiO$_2$ composites</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Organic polymers</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Piezoelectric crystal</td>
<td>Adsorbent coated quartz oscillator</td>
<td>Resonant frequency</td>
<td>Various adsorbents</td>
</tr>
<tr>
<td></td>
<td>Adsorbent coated SAW device</td>
<td>Delay time</td>
<td></td>
</tr>
<tr>
<td>Optical fiber</td>
<td>Gas sensitive wave guide</td>
<td>Light absorption</td>
<td>WO$_3$ wave guide</td>
</tr>
<tr>
<td></td>
<td>Optical fiber + gas reaction layer</td>
<td>Light absorption, Fluorescent Light (emission, extinction)</td>
<td>Reaction layer Dye metal complex, protein</td>
</tr>
<tr>
<td>Catalytic combustion</td>
<td>Catalyst bead + Pt coil (imbedded)</td>
<td>Resistance of Pt coil (change due to heat of combustion)</td>
<td>Pt supported alumina bead</td>
</tr>
</tbody>
</table>
The choice of type and technique of sensor used, in each specific case, depends upon the nature of analytical problem to be solved.

1.10 Fundamental aspects of gas sensor

As per conclusion from the results of several experiments conducted for understanding and clarifying fundamental aspects of resistor gas sensor using semiconducting oxides it is concluded that the gas sensing phenomenon can basically be reduced into a combination of three basic factors and they are [162]:

1.10.1 Receptor function

It concerns the ability of the oxide surface to interact with the target gas. If the sensor is made of neat oxide, the surface oxygen, especially adsorbed oxygen, of the oxide acts as a receptor. In air, oxygen is adsorbed on the oxide grains as negatively charged ions, inducing the surface space charge layer depletive of electrons or increasing the work function of grains. When the target gas comes in contact, adsorbed oxygen is consumed and decreased down to a steady state level, resulting in corresponding work function. When surface is loaded with foreign receptor like PdO, it acts as a receptor stronger than the adsorbed oxygen, eventually giving rise to a far larger decrease in work function upon exposure to gas.

![Fig. 1.7: Model for gas sensing mechanism.](image)

1.10.2 Transducer function

It concerns the ability to convert the change in work function of grains into electrical resistance. The function has been explained by assuming Schottky barriers for
transport of electron through grain boundaries. The resistance changes with the change in barrier height and so with the change in the work function.

The resistance and gas sensitivity of the device hardly depend on the grain size (diameter-D) when D is larger than a critical value (Dc), which corresponds to twice the thickness (Ls) of surface space charge layer of the oxide, where as the two quantities increase sharply with decreasing D, when D is smaller than Dc. Recent experiments have suggested the possibilities of the participation of tunneling effect for transfer through grain boundaries [46].

When reaction rate is too large compared with the diffusion rate of the gas molecules, gas molecules are mostly consumed in the shallow region of the sensing body and cannot reach the grains located at inner side, leaving them unutilized for the gas sensing and thus resulting in the loss of sensing response.

1.10.3 Utility function

It is defined as ratio of the sensor response (resistance ratio) at given m to the ideal one at m=0. The utility factor decreases sharply with increase in m when m is larger than 3.

\[ m = L \left( \frac{k}{D_k} \right)^{1/2} \]  \hspace{1cm} (17)

L is thickness of the film, k rate constant of surface reaction and Dk Knudsen diffusion constant.

Where \[ D_k = \left( \frac{4r}{3} \right) \left( \frac{2RT}{\pi M} \right)^{1/2} \]  \hspace{1cm} (18)

This where r is pour radius, M is molecular mass of target gas and RT has its usual meaning. Thus r and L are micro-structural parameters which affect utility factor. It is important that utility factor can go down to zero as L or k/Dk is large.

It is also possible to estimate roughly the effect of operating temperature (T) on sensor response. As a rate constant of chemical reaction, k increases exponentially with increasing temperature T, whereas Dk is proportional to square root of T thus ratio K/Dk and then m also increases almost exponentially with increasing T. This means that under conditions of fixed micro-structural parameters, utility factor eventually goes down to zero as T is raised.
1.11 **Role of material used in sensor**

The semiconducting material used in the gas sensor can play different roles in the mechanism of gas detection. The gas sensing material used can play the following roles in gas sensing and detection.

1.11.1 **Operational element material**

In some gas sensors, the semiconducting material of the film directly interacts with the target gas and results in creating adequate output response corresponding to the change in input.

1.11.2 **Catalyst for accelerating reaction**

In some cases, the use of the catalyst is done by modifying the film with catalyst material to boost the reaction rate and causing enhancement in the output response.

1.12 **Effect of additives on sensing mechanism**

Suitable additives, such as Pd, Pt, metal oxide etc. can be used for enhancing the sensing properties. It can improve the sensitivity, faster response and recovery time. The additive can either increase the concentration of the reactants at the surface or lower the activation energy for the reaction, or both.

The effect of additives can be explained by three models: (i) catalytic effect, (ii) Spill-over effect, and (iii) Fermi energy control.

1.12.1 **Catalytic effect**

In the catalytic effect, the metal cluster present at the surface of the film facilitates the reaction between reactive gas (R) and the atmospheric oxygen. Therefore this process has no effect on the resistance of the film.

1.12.2 **Spill-over effect**

In this case, the metallic clusters catalyze reaction and reaction products subsequently spill over from the cluster on to the metal oxide support. Catalyst particles on the surface are able to activate certain gas molecules, e.g. dissociation of oxygen or hydrogen. The spill-over effect can accelerate the reaction, resulting in shorter response time and higher sensitivities [163].
1.12.3 Fermi energy control

In this effect the sensor signal is determined mainly by the electronic contact of the semiconductor with the catalyst, which results in alignment of the Fermi energy of the metal oxide with the additives [164]. This is similar to the Schottky barrier at metal-semiconductor interface. Oxygen species at the surface of the catalyst trap electrons from the metal oxide. Since the density of the electrons in the bulk changes by this process, a depletion layer is created and band bending occurs. The metallic particles become partially oxidized in the ambient gas atmosphere, and the stoichiometry of the catalyst depends on the composition of ambient air. Thus, the position of Fermi level of oxidized catalyst depends on its composition. At equilibrium, the Fermi level of the catalyst and the semiconductor are at the same height. Since the gas reacts with the metal-oxide via the catalyst, the chosen catalyst can strongly change the selectivity.

1.13 Basic characteristics of chemiresistive sensor

The electrical resistance of a chemiresistive sensor changes drastically (increase or decrease) when exposed to the molecules of analyzing gas. Increase or decrease in resistance depends on the nature of sensor material (n-type or p-type) and the gas (reducing or oxidizing). A typical response curve is variation of resistance of sensor with time in exposition and withdrawal of analyzing gas. The response curve is characterized by following five parameters.

i) Gas response (Sensitivity)

The gas response (sensitivity) of the sensor can be defined in many ways. The often used term is the ratio of resistance in air to that in gas i.e. \( S = \frac{R_{\text{air}}}{R_{\text{gas}}} \). A high value of \( S \) for particular gas indicates that the material is very good sensor. The main specification of sensor namely, the sensitivity (\( S \)) is defined very often by equation:

\[
S = \frac{\text{Electrical output (o/p)}}{\text{Chemical input (i/p) to be sensed}} \quad \ldots \ldots \quad (19)
\]

This can be obtained from sensitivity curve (e.g. sensitivity verses gas concentration). If this curve is a straight line (i.e. response is linear) then the slope of the straight line will be same as the sensitivity given by equation (19). However, in case it is
not linear (as will invariably happen near saturation limits or even at other measurand values if sensing process changes e.g. sensing reaction in case of gas sensor), one may have to take equation (19) to define static sensitivity. In this case the dynamic (or incremental) sensitivity $S_{\text{dynamic}}$ is given by equation 20:

$$S_{\text{dy}} = \left[ \frac{\Delta (o/p)}{\Delta (i/p)} \right] \text{ at operating condition} \ldots \ldots \ldots \ldots \quad (20)$$

**Fig. 1.8:** Schematic response-curve of a chemiresistive gas sensor.

Further, one may assume the sensor to be sufficiently linear in its operating range and can take $S_{\text{static}} = S_{\text{dynamic}} = S$ as an approximation. In case of some sensors like resistive gas sensors or thermistors the resistance (o/p parameter) may change from sample to sample even without changing i/p. In such case, it is customary to take the output normalized to i/p (e.g. change in the resistance of the sensor sample divided by initial resistance of that sample without gas input).

This creates a problem in surveying the literature on resistive gas sensors. The different normalization like (i) $R_g / R_a$, (ii) $(R_a-R_g) / R_g = \Delta R / R_g$, (iii) $\Delta R / R_g$, (iv) $(G_g - G_a) / G_a = \Delta G / G_a$ etc. (where, $R_a$ and $R_g$ are the resistances of sample in air and air+gas respectively, $G_a$ and $G_g$ are the conductances of sample in air and air + gas respectively) are used in the literature for studying the gas sensing performance of the materials. It has become customary to call such o/p parameter itself as sensitivity of
resistive gas sensor. But unless original value of resistance (along with definition used, as indicated above) is given, it becomes impossible to compare the sensor parameters (e.g. sensitivity).

We have adopted last definition for normalization i.e.

\[
\text{Gas response (S)} = \frac{(Gg - Ga)}{Ga} = \frac{\Delta G}{Ga} \quad \text{............................ (21)}
\]

It can be seen that \(\Delta G/Ga = \Delta R/Rg\) is the normalized resistance. The sensitivity has also been defined in literature as,

\[
S = \frac{(S)}{(\text{Gas concentration})} \sim \frac{\Delta(S)}{(\Delta \text{Gas conc.})} = \frac{\Delta G}{Ga} / (\Delta \text{Gas conc.}) \text{........................................ (22)}
\]

\[\text{ii) Selectivity}\]

Usually most chemiresistive sensors exhibit significantly high value of sensitivity for many gases under similar operating conditions. Thus the selectivity or specificity of a gas towards an analyzing gas is expressed in terms of dimensions that compare the concentration of the corresponding interfering gas that produces the same sensor signal.

This factor is obtained by:

\[
\text{Selectivity} = \frac{\text{Sensitivity of the sensor for interfering gas}}{\text{Sensitivity towards desired gas}}
\]

\[\text{iii) Response time:}\]

The response time is the time interval over which resistance attains a fixed percentage (usually 90\%) of final value when the sensor is exposed to full scale concentration of the gas (Fig. 1.8).

\[\text{iv) Recovery time}\]

This is the time interval, over which the sensor resistance reduces to 10\% of the saturation value when the sensor is exposed to full-scale concentration of the gas and then placed in the clean air. A good sensor should have small recovery time so that the sensor can be used over again and again.
v) Long term stability

This is the ability of the sensor to maintain its properties when operated continuously for long duration in hostile environment. The good sensors are expected to work for several years without showing drift in any of the above parameters.

1.14 General requirements to all types of operational elements of sensors: Needs for good sensor

1.14.1 Optimization of chemical sensors

For manufacturing quality electronic device optimizing the parameters of the device is very important. The field of chemical sensor is in search of optimal sensing materials and design of adequate theoretical model that may promote optimization of chemical sensors. According to earlier view of problem of gas sensor design, almost any metal oxide can serve as the basis for solid state gas sensor. For this one needs only to prepare this material as sufficiently fine dispersed porous substance with properties controlled by surface states [165].

The term optimization here means achieving either necessary or the best available values of sensitivity, selectivity and response time of chemical sensors at given operating conditions.

In order to achieve the best sensor result we should understand and consider the requirements such as

(i) High response to target agent
(ii) Low cross sensitivity
(iii) Fast and reversible interaction with analytes
(iv) Low sensitivity of the signal to a change in air humidity
(v) Absence of long term drift
(vi) Short time to operational status
(vii) Effective low cost technology
(viii) High reproducibility
(ix) Uniform and strong binding to the surface of the substrate
(x) Easy connection to control unit.
Apart from this, materials for chemical sensors have to possess specific combination of physical and chemical properties, and not every chemical can fulfill these requirements.

**Semiconductor element**

(i) should have substantial chemical durability,

(ii) should not form stable chemical compounds with the particles absorbed.

(iii) should possess sufficient thermal and mechanical strength.

Metal-oxide semiconductors, such as ZnO, SnO₂, TiO₂ and others suit above requirements the best as well as broad band dope semiconductors exhibit very high adsorption sensitivity.

Chemical sensors are gaining importance because of increase in the number of chemical industries, agro based industries and the extensive use of automobiles exhausting hazardous gases. In this domain, the gas sensors are developed with different materials and technologies for improving the performance. In this domain of sensors, the adsorption of gas molecules decides the performance of the sensors, which also gives a measure of the gas concentration. Humidity, gas and chemical species are the measurands of chemical sensors. In order for selecting the functional material for gas sensor one should think over the needs of the good sensor

1.14.2 Improving the sensitivity of conductometric gas sensor

The sensitivity of conductometric metal oxide sensors can be improved using different approaches based on the tools of material engineering such as (1) Bulk doping, (2) Surface modification, (3) Structure optimization etc [166].

1.14.3 Improving selectivity

The selectivity can be improved by selecting or preparing proper materials [166]. The incorporation of catalyst results in improvements of surface reaction selectivity. An applied filter selectivity removes the undesired components.

To improve the stability, a material science approach, i.e. the use of chemically stable materials, seems to be most efficient.
Main considerations for stable conductometric sensors are

(i) Careful selection of sensitive layer
(ii) Film coating technique
(iii) Bias potential
(iv) Measurement scheme

1.15 Chemical properties of material required for chemical sensor applications

1.15.1 Adsorption ability

Earlier research has shown that for effective chemisorptions, sensor material should have particular combination of adsorption/ desorption parameters for oxygen and detecting gases [167, 168]. It is known that the smaller the activation energy of chemisorptions and higher the activation energy of the desorption, the greater is the gas sensing effect of adsorption type sensors [169]. At the same time one has to take into account that at excessively large activation energy of adsorbed species, the desorption might lead to a considerable increase of recovery time after changing the surrounding atmosphere, which is not acceptable for practical applications. That is why for chemisorptions-type of chemical sensors materials with optimal activation energy of desorption for the given work temperature is needed.

1.15.2 Electronic, electro-physical and chemical properties

Metal oxides exhibit a very wide range of electro-physical properties their electrical behavior ranges from the best insulator (Al₂O₃ and MgO) through wide band gap and narrow band gap semiconductors (TiO₂, SnO₂ and Ti₂O₃) to metals (V₂O₃ and ReO₃) and superconductors (SrTiO₃). The range of electronic structure is so wide that the metal oxide compounds have been divided into two categories (1) transition metal oxides (Fe₂O₃, NiO, Cr₂O₃, etc.) and (2) non transition metal oxides which includes (a) pre-transition metal oxides(Al₂O₃) and (b) post-transition metal oxides (ZnO, SnO₂, etc.)

The big difference between the transition and non transition metal oxides is that the transition metal oxides are more sensitive to a change of external conditions.

Sensing material should be characterized by high chemical stability. This property means the absence of corrosion during interaction with the gases and solutions, i.e. an opportunity to work in corrosive media.
1.15.3 Catalytic activity

In many chemical sensors, the sensitivity is determined by the effectiveness of catalytic reaction with the gas being detected at the surface of the sensing material. Therefore, high catalytic reactivity of the surface, and especially selectivity of this reaction to detected gas, is important advantages for a sensor material. As a result, control of catalytic activity of a material is often the main method used in preliminary evaluation of the material’s suitability as a gas sensor, and in determining temperature. It is necessary to note that the maximum catalytic activity to different gases may be observed at different temperatures. This is in fact a favorable property for gas-sensing materials, because by changing the operating temperature the selectivity of the gas sensor may be influenced. However, in spite of the obvious correlation between chemical sensing and heterogeneous catalysis, the choice of the material for gas sensor application is not determined just by catalytic activity. Catalytic activity is an important parameter but not a determining one.

1.15.4 Thermodynamic stability

Materials for chemical that must work at high temperatures have to possess high thermodynamic stability. The better a material’s thermodynamic stability, the higher will be the temperature at which chemical sensor incorporating this material will work, especially in the presence of reducing gases. Sensors materials with high thermodynamic stability should also have better temporal stability. This condition can be attained by suppressing grain-size increase during use. In this case, the opportunity to use materials with small crystallite exists, which is necessary to achieve both high sensitivity and good rate of response. Both high heat of formation and high melting point temperature characterizes such materials. The more reactive materials are those with more negative heat of oxide formation. There is possibility that surface phases formed may have thermodynamic stability different from those of bulk oxides, but it is also important to remember that surface reaction of this kind extensive migration of atoms, a process that may have high activation energy [170]. Such reactions are therefore more likely at high temperature.
1.15.5 Crystallographic structure:

The most important determinants of crystal structure are the stoichiometry or relative numbers of the different types of atoms present, and the co-ordination of ions, i.e. the number of ions of one type surrounding other and their geometric arrangements. Commonly metal oxide consists of several structural units, which may be triangular, tetrahedral, octahedral, or cubic. A considerable crystal structure suggests that metal-ion coordination numbers and geometry show reasonably systematic features that carry over among different structure types. The six fold octahedral coordination is the most common metal ion geometry in the metal oxides used for chemical sensors [171].

Another important parameter is point defects i.e. the degree of deviation of the chemical composition from the ideal chemical formula. The structure of point defects, especially in transition- metal oxides, has been extensively studied for many years [172-174].

1.15.6 Long term stability

Well designed chemical sensors should provide long-term use regardless of the operating conditions. In general, it is required that, any gas sensing device should exhibit stable and reproducible signals for a period of at least 2-3 years. Therefore, high temporal stability of bulk and surface properties of sensing material, even in corrosive media, is very important for sensor applications. The main reasons for long-term instability of solid state gas sensors are following:

(i) A change in metal oxide parameters caused by
   (a) a change in crystallite size- A consequence of insufficient pre-aging by temperature;
   (b) irreversible reactions with the gas phase i.e. reduction during interaction, or reaction with active gases such as SO$_2$, Cl$_2$, etc. that create new phases; and
   (c) reaction with substrate.

(ii) A change in metallization(sensor heating) elements, contacts for metal oxides

(iii) Instability of the wire contacts

(iv) Interaction with an unsuitable sensor casing.

An additional source of temporal drift might be the ionic drift, which can modify electrophysical and surface properties of metal oxides [175].
1.16 Factors determining sensing properties

Gas sensing property is surface effect; it is because change in the concentration of conduction electrons in metal oxide semiconductor is result of surface chemical reaction, such as, adsorption, reduction, re-oxidation and/or catalysis taking place during interaction with analyte gas [168].

The parameters that dictate sensing properties of metal oxides can be divided broadly two categories. 1) Geometrical factors 2) Physico-chemical Properties

1.16.1 Geometrical factors

The resistance of the sensor depends on following factors:

(i) Contact resistance between electrodes and grains
(ii) Intergranular (grain boundary) contact
(iii) Bulk resistance (due to grains and agglomerated grains)

So grain size, crystallographic orientations of the planes porosity and agglomeration of the grains plays very important role in sensitivity of the sensor.

![Diagram showing different components in a granular metal-oxide semiconductor](https://via.placeholder.com/150)

**Fig. 1.9:** A schematic showing the contribution of different components in a granular metal-oxide semiconductor.
Geometrical Factors: the dependence of gas sensitivity on geometrical factors is an issue involving many parameters [176]. As shown in Fig. 1.9 the resistance of the sensor depends on various parameters mentioned above.

i) Grain size effect

It is practically observed in case of sintered SnO$_2$ that the gas sensitivity depends strongly on the crystallite size D in the range of 4-27nm. The sensitivity was nearly independent of the grain size; for D< 20nm, it decreased with decreasing grain size; for D< 10 nm this increase was remarkable [177].

ii) Crystallographic Plane Effect

Different crystallographic orientations have different atomic arrangements and, therefore different electronic properties, such as, surface state density, adsorption/desorption energies. In addition to the grain size, the crystallographic orientation of the plane, particularly for the case of D>>2L, strongly affects the gas sensing properties. This leads to the different chemisorption characteristics of the crystal surfaces [177].

iii) Agglomeration of grains and porosity effect

The effect of grain size and its crystallographic orientation will be pronounced only if the analyte gas has sufficient permeability in the granular network of the sensor. If the grains tend to agglomerate and get densely packed, the porosity would decrease in the permeability of the gas. This would lead to a reduced gas concentration at the surface of the grains, which in turn, would decrease the sensitivity. Thus it is essential that while decreasing the grain size, efforts must be put in to minimize the agglomeration and maximize the porosity so that the sensitivity can be enhanced.

1.16.2 Physico-chemical properties

In addition to geometric properties, the physico-chemical properties exert a great influence on metal oxide gas sensing characteristics. The physico-chemical properties can be influenced by the following parameter:

- Chemical and phase composition
- Physical properties of the additives
- Uncontrolled impurities
As simple metal oxide cannot be used as perfect gas sensor, so to overcome the deficiencies of chemiresistor gas sensor can be overcome [178, 179] by

- Use of additives
- Increases in operating temperature
- Use of binary oxides
- Use of complex multi-component oxides

1.17 Adsorption

The adsorption of the molecules at the solid surface is very interesting phenomena. This process depends on the surface of solid molecules i.e. if the solid surface is small then this process will be slow. So, before the study of the adsorption process, we shall discuss the formation of surface and its role in adsorption process.

The adsorption is of two types: (i) Physisorption and (ii) Chemisorption.

i) Physisorption

The adsorption occurs at the surface of solids. It is due to Van-der-walls force. When this force is exerted between the atoms or molecules there is physical attraction without chemical alteration of the molecules, this is termed as physical adsorption or physisorption.

ii) Chemisorption

When covalent bonds between atoms are broken, each surface atom possesses one or more free valencies. The adsorption occurs due to the molecule’s interaction with these free valencies. This may be regarded as a chemical reaction because there is rearrangement, sometimes drastic, of electrons within the molecule. This type of adsorption is called as chemical adsorption or chemisorption.

![Imbalance of force at the surface.](image)

Fig. 1.10: Imbalance of force at the surface.
Due to fracture of covalent solid, there are unsaturated covalent bonds at the surface. In this process, covalent bonds between atoms are broken and so each surface atom must possess one or more free valencies. The number and types of valencies depends on the bonding between atoms in the bulk solid. The atom on the new surface is slightly displaced from its original position in that it does not have its full complement of neighbors and its coordination number is smaller than the atoms within the bulk of solid as shown in Fig. 1.10. This figure shows that there is an imbalance of forces at surface, and that surface atoms suffer a net force acting inwards. This gives rise to the phenomenon of surface energy, which is related to surface tension in liquid.

A sensing element normally comprising a semiconducting material presenting a high surface-to-bulk ratio is deployed and printed on insulating substrate between two metallic electrodes. Reactions involving gas molecules can take place at the semiconductor surface to change the density of charge carriers available. Hence, the conductance of the device changes progressively with changing atmospheric composition.

Semiconducting oxides are employed to detect the minor concentration of potentially hazardous gases. The central surface reaction controlling most gas responses of semiconducting oxides operating in air at temperature in the range 300-500°C involves the changes in the concentration of surface oxygen species such as $\text{O}^-$ or $\text{O}^2-$ (Fig. 1.11).

**Fig. 1.11:** Charge exchange associated with the chemisorption of oxygen at a semiconductor surface and the potential distribution across a grain junction.
The formation of such ions by oxygen adsorption at the gas/solid interface abstracts electrons from the bulk of the solid; the oxygen can thus be thought of as a trap for electrons from the bulk.

1.18 Features of gases

**Hydrogen sulfide** (H$_2$S) the most dangerous gas, is classified as a chemical asphyxiant because it chemically interacts immediately with blood’s hemoglobin and blocks oxygen from being carried to body’s vital organs and tissues. It is produced from the anaerobic decomposition of organic materials such as manure. Its characteristic rotten-egg smell is easy to be detected at low concentrations. At higher concentrations, H$_2$S will paralyze the sense of smell giving someone a false sense of security and it will cause instant paralysis and death when the concentration exceeds TLV value. From the safety point of view, in situ detection and monitoring of H$_2$S is very important in petrochemical and coal manufacturing industries [180].

**Carbon monoxide** (CO) is a colorless toxic gas, with no odor, making it undetectable to humans. It is produced due to the incomplete combustion of fuels. It is commonly found in the emission in the emission of automobile exhaust. The gas has been shown to bind irreversibly to the iron center of hemoglobin, the oxygen transport molecule in blood. The irreversible binding means that oxygen can no longer be absorbed, which causes damage to human body by a reduction in cellular respiration and high levels of CO exposure results in death.

**Ammonia** (NH$_3$) is a colorless gas with a characteristic pungent odor. Ammonia contributes significantly to the nutritional needs of terrestrial organisms by serving as a precursor to food and fertilizers. Ammonia, either directly or indirectly, is also a building block for the synthesis of many pharmaceuticals. It is also used in cleaning products [181]. Despite its usefulness, ammonia is both caustic and hazardous to human especially when its concentration exceeds TLV value of 25 ppm. An ability to monitor and control these environments is highly desirable.

**Carbon dioxide** (CO$_2$) is a colorless, odorless non-flammable gas and is the most prominent greenhouse gas in Earth’s atmosphere with contribution of 76% in the Earth’s atmosphere besides methane (13%), nitrous oxide (6%) and fluorocarbon (5%) [182]. It is recycled through the atmosphere by the process photosynthesis, which makes human life
Photosynthesis is the process of green plants and other organisms transforming light energy into chemical energy. Light Energy is trapped and used to convert carbon dioxide, water and other minerals into oxygen and energy rich organic compounds. Carbon dioxide is emitted into the air as human exhales, burns fossil fuels for energy and deforest the planet. Every year humans add over 30 billion tons of carbon dioxide in the atmosphere by these processes and it is up 30% since 1750.

Chlorine is widely used in many industrial processes and it is very harmful when emitting into environment. Although chlorine can be detected by gas chromatography, chemical detecting tubes and electrochemical sensors using metal chlorides, the detecting process is very complicated for gas chromatography and chemical detecting tubes, and the electrochemical sensors could not detect dilute chlorine gas [183-185].

Ethanol vapor is one of the most popular gases in industry and our daily life, so it is important to detect and control ethanol vapor. A more positive application of an ethanol vapor sensor may be a breath alcohol checker to monitor ethanol vapor in human breath, which is said to be well correlated with the ethanol concentration in the drunk driver’s blood [186, 187].

Hydrogen is an energy carrier has widespread application. It is exclusively utilized in industrial fields as fuels. It is colorless and odorless gas. It leakage cannot be noticed easily. This gas is potentially hazardous because of explosion possibility.

Liquefied natural gas (LNG) and liquefied petroleum gas (LPG) are highly inflammable gases. They are explosively utilized in industrial and domestic fields as fuels. They are referred as town or cooking gases. Cooking gas consists chiefly of butane (55-vol %) [188], a colorless and odorless gas. It is usually mixed with compounds of sulfur (methyl mercaptan and ethyl mercaptan) having foul smell, so that its leakage can be noticed easily. These gases are potentially hazardous because explosion accidents might be caused when they leak out by mistake. It has been reported that, at the concentration up to noticeable leakage, it is very much more than the lower explosive limit (LEL) of the gas in air. So, there is a great demand and emerged challenges [189] for monitoring them for the purpose of control and safety applications in domestic and industrial fields.
1.19 Metal oxide semiconductor (MOS) materials

A brief literature survey is being presented on various metal-oxides sensors.

**Aluminum oxide** (Al$_2$O$_3$): Aluminum oxide is found to be an excellent sensing material for humidity, apart from other gases, such as, CH$_4$, NH$_3$. Humidity sensors are usually made of porous Al$_2$O$_3$, which is prepared by electrochemical anodization of aluminum thin films. These humidity sensors, however, were found to saturate on exposure to a very high humidity level as well as after a prolonged exposure. These sensors, however, can be easily regenerated by heating them above 100 °C [190]. In addition, nonporous alumina has been found to be a good room temperature operating ammonia sensors.

**Bismuth-oxide** (Bi$_2$O$_3$): Bismuth-oxide has been found sensitive to many gases, such as, H$_2$, CO$_2$, NO and O$_2$. Bi$_2$O$_3$ is being used as a smoke sensor [191] as smoke mainly consists of CO and CO$_2$. The negative point of this sensor is that the operating temperature is very high (450°C). It has been observed that by adding Sb, the operating temperature of Bi$_2$O$_3$ sensor drops down to 200°C. Recently, it has been demonstrated that addition of Fe and Ag lead to stabilization of α-Bi$_2$O$_3$ phase, Cu addition leads to α-Bi$_2$O$_3$ phase and, In and Ni addition stabilize Bi$_2$O$_{2.33}$ structure. Among these, Bi$_2$O$_{2.33}$ structure was found to be highly selective for NO [191].

**Cadmium oxide** (CdO): Sensor based on pure CdO has not been reported so far. However, the ethanol sensing properties of ZnFe$_2$O$_4$ has been found to be drastically improved by adding CdO. This is because; addition of CdO stabilizes Zn$_{0.8}$Cd$_{0.2}$Fe$_2$O$_4$, which adsorbs more oxygen, compared to the ZnFe$_2$O$_4$ [192]. The improved characteristics include: (i) High ethanol sensitivity with a linear behavior in the concentration range from 100 to 1000 ppm; (ii) excellent selectivity to ethanol against other common gases which may co-exist with ethanol, such as petrol, H$_2$, CO, LPG and other hydrocarbon gases; (iii) good stability and durability of the performance; and (iv) almost instant response and recovery behavior.

**Ceria** (CeO$_2$): CeO$_2$ has been found to be a good sensor for the oxygen because of its chemical stability and high diffusion coefficient of oxygen vacancies. It has been observed that CeO$_2$ can be easily reduced into a non-stoichiometric compound. Therefore adding CeO$_2$ (particularly in the form of nanoparticles) with
TiO$_2$ acts as an effective catalyst for the oxygen sensitivity of TiO$_2$. Doping SnO$_2$ by CeO$_2$ was found to be sensitive to H$_2$S at room temperature [193].

**Chromium oxide** (Cr$_2$O$_3$): Cr$_2$O$_3$ is found to be sensitive to H$_2$ and CH$_4$. TiO$_2$ doped Cr$_2$O$_3$ is reported to be sensitive to NO$_2$, O$_2$ and humidity. Recently, sensors based on (Cr$_{2-x}$ Ti$_x$)O, (x=0.05-0.4) has been commercialized by Capteur Sensors [194].

**Cobalt oxide**: Cobalt oxide occurs in two different forms i.e. CoO and Co$_3$O$_4$. Both have a cubic lattice. Co$_3$O$_4$ is a spinell with CO$^{2+}$ and CO$^{3+}$ ions being simultaneously present but at different lattice sites in the crystal. Co$_3$O$_4$ is antiferromagnetic. CoO has an energy band gap of 2.2-2.8 eV, whereas Co$_3$O$_4$ has 1.4-1.8 eV. Both cobalt oxides are normally non-stoichiometric with an excess of oxygen, which makes them p-type semiconductors. Co$_3$O$_4$ has been found to be sensitive to a range of gases NH$_3$, CO, CH$_4$, C$_3$H$_8$, NO$_2$ and Cl. Co$_3$O$_4$ thin films sense NH$_3$ even at room temperature [195].

**Copper oxide** (CuO): CuO is a p-type semiconductor and is known to be sensitive to NO$_2$, H$_2$S and CO. However, CuO is mainly used as additives in n-type metal-oxides, which either form a composite or a random network of hetero-junctions. In particular, CuO-doped SnO$_2$ is found to be highly selective for H$_2$S. CuO has also been used as a catalytic membrane to improve selectivity for CO and ethanol [196].

**Iron oxide**: In Fe-O system, three different polymorphic forms, FeO, Fe$_2$O$_4$ and Fe$_2$O$_3$ exist. Also, Fe$_2$O$_3$ has two typical modifications: α-Fe$_2$O$_3$ (hematite, corundum-type hexagonal lattice, a = 5.035 Å and c = 13.750 Å) and γ-Fe$_2$O$_3$ (maghaemite). α-Fe$_2$O$_3$ has a complex defect structure in which three type's defects species, namely, oxygen vacancies, Fe$^{3+}$ interstitials and Fe$^{2+}$ interstitials are present. The presence of these defects give rise to semiconducting properties. Loss of oxygen leaves behind extra electrons and produces an n-type semiconductor; while extra oxygen (entering the lattice as O$_2$) creates a deficit of electrons (i.e. introduces electronic holes), which produces p-type behavior. Thus, in α-Fe$_2$O$_3$ a transition from n- to p-type response or vice versa can be induced by the change in the gas concentration, by appropriate dopant and/or by the operating temperature.
Fe$_2$O$_3$ is known to show high sensitivity towards organic gases [197]. Various metal oxides have been doped into Fe$_2$O$_3$ to make it selective for a particular gas. It has been demonstrated that ZnO doped Fe$_2$O$_3$ works as a selective NH$_3$ sensor working at room temperature [198]. When doped with Pt, Pd or RuO$_2$, Fe$_2$O$_3$ sensor detects acetone, which finds utility in medical diagnostics [197]. Au or Zn doped Fe$_2$O$_3$ is reported to sense CO and NO$_2$ [199]. The α-Fe$_2$O$_3$ is known to be a good sensing element for H$_2$.

**Gallium oxide** (Ga$_2$O$_3$): Ga$_2$O$_3$ thin films are widely used as oxygen sensors operated at very high temperatures (∼1000°C) owing to its very stable semiconductor character well above this temperature. When Ga$_2$O$_3$ is doped with other oxides, such as, Ta$_2$O$_5$, WO$_3$, NiO, and SnO$_2$, it exhibits good sensitivity towards many gases (NO, NH$_3$, CO and CH$_4$) [200] The Ga$_2$O$_3$ sensor has several advantages: (i) The base resistance of the sensor is established quickly at high operating temperatures, which does not show any drift on prolonged use, (ii) It does not show any cross sensitivity with humidity, (iii) It is stable in atmosphere with low oxygen partial pressures, implying its suitability in burner control units (exhaust gas), (iv) Its response and recovery are very fast owing to high operating temperatures. However, high power consumption is its main disadvantage.

**Indium oxide** (In$_2$O$_3$): In$_2$O$_3$ is found to be very suitable for detection of low concentrations of oxidizing gases like O$_3$ and NO$_2$ [201]. It has been observed that MoO$_3$ doping significantly enhances selectivity of In$_2$O$_3$ for NO$_2$. However, there are reports of gas sensing to other toxic gases, such as, H$_2$S, Cl$_2$, and NH$_3$ [202].

**Molybdenum trioxide** (MoO$_3$): MoO$_3$ is an n-type semiconductor with a band gap of 3.2 eV. MoO$_3$ has two weak properties pertaining to the gas sensing applications: (i) A low melting point (795 °C), and hence low evaporating temperatures. This property restricts the operation of MoO$_3$ sensors to low temperatures, however such temperatures may not indeed be the optimal operating temperature for a particular gas species. (ii) MoO$_3$ has a very high room temperature resistivity (10$^{10}$ Ωcm), making it difficult material to realize as a good sensor and integrate with electronics. Nevertheless, MoO$_3$ is a well-known catalyst for the oxidation of
hydrocarbons and conversion of harmful NO₂ to nitrogen, and currently is being investigated for gas sensing properties [203]. It has been found that by coating a thin layer of Ti over MoO₃ films, its sensitivity for NH₃ enhances considerably [204].

**Niobium oxide** (Nb₂O₅): Nb₂O₅ thin film has attracted attention as a dielectric material for solid-type electrolytic capacitors owing to its higher dielectric constant and durability. Nb₂O₅ is an n-type semiconductor and is gaining popularity for detection of NH₃ [205].

**Nickel oxide** (NiO): NiO is a p-type semiconductor with a wide band gap of 4.2 eV. NiO finds a wide range of applications due to its good chemical stability as well as excellent optical and electrical properties. NiO is being considered as one of the promising potential electrode materials for supercapacitors as well as for many other applications such as catalyst, electrochromic films, p-type transparent film and fuel cell electrodes. Recent works have shown that NiO is also an attractive functional gas-sensing layer for application both in thermoelectric and chemiresistive-type gas sensors. A novel thermoelectric hydrogen gas sensor using NiO film as a thermoelectric material and Pt film as a catalyst have been proposed in the literature [206].

**Tantalum oxide** (Ta₂O₅): Nb₂O₅ is not a popular material for gas sensors. However, Ta₂O₅ is reported to be a good humidity sensor [207]. Interestingly it has been observed that by using an overlayer of Nb₂O₅ improves significant sensitivity and response time of InₓOᵧNₓ films to CO, H₂, and CH₄. Thus there is a need to investigate the role of Nb₂O₅, as a promoter in gas sensors.

**Tin dioxide** (SnO₂): SnO₂ is the most widely used materials for detection of various gases [208-214]. At first glance it appears that SnO₂ is an extremely versatile material for gas sensors. However, this is not the case as SnO₂ responds to reducing species, e.g. H₂S, H₂,CO, Hydrocarbons etc, as well as to oxidizing gases like NOₓ, and O₃, making it a highly non-selective material. An interaction with reducing gases leads to decrease in its electrical resistance; while oxidizing gases cause an increase in the resistance. Thus, from the response curve of a SnO₂ sensor it is difficult to distinguish between different gases with the same sign of electrochemical potential. In general, the poor selectivity of metal-oxide gas sensors is a major concern.
**Titanium dioxide** (TiO$_2$): TiO$_2$, like many other transition metal oxides, is a high resistive n-type semiconductor with rather poor conductivity to be adopted for sensing oxidative gases. To overcome this disadvantage, the electronic structure should be altered into p-type by the addition of foreign atoms. A few works that show how the addition of Cr to TiO$_2$ alters the electronic conductivity from n to p-type have appeared, opening the development of novel gas sensors. The p-type materials obtained under appropriate conditions responded with a sharp decrease in its resistance upon exposure to diluted NO$_2$. The advantages of TiO$_2$ are that it is a highly stable material at high temperatures and harsh environments and, has thermal expansion coefficient matching with alumina [215], making it suitable for the fabrication of thin film based sensors.

**Tungsten oxide** (WO$_3$): WO$_3$ is an n-type semiconductor and shows good response to both NH$_3$ and NO$_x$. These two gases are characterized by opposite resistance changes in the film which makes it possible to detect NH$_3$ and NO selectively, if only one of the two gases is present in the ambient. Unlike SnO$_2$, the surface of WO$_3$ is not sufficiently covered with adsorbed O$_2$ and requires catalyst or promoters to obtain adequate sensitivity. In the past, several workers have reported WO$_3$ films doped with different elements including Au, Mo, Mg, Re etc, to selectively detect different toxic gases [216-220]. Doping of WO$_3$ thick films with Cu has been shown to enhance NH$_3$ sensitivity [219,220]. Surface modifications of WO$_3$ films with Au and Pt were also found to enhance sensitivity towards NH$_3$ [221]. Thin films of tungsten oxide covered by Pt over layer have been studied for NH$_3$ detection [222].

**Vanadium oxides** (V$_2$O$_5$): V$_2$O$_5$ has been extensively used as a catalyst in oxidation reactions. This feature also makes V$_2$O$_5$ as a good promoter in enhancing the sensitivity of TiO$_2$, MoO$_3$ and ZnO sensors [223].

**Zinc oxide** (ZnO): ZnO is a remarkable material with a wide variety of optical, electrical and piezoelectric applications. As discussed in the Introduction, ZnO is the first metal-oxide gas sensing material, and has been investigated widely [224]. It is sensitive to many gases, such as, trimethylamine, hydrogen, oxygen, ethanol and NH$_3$ at moderate temperature, with good stability. A NH$_3$ selective sensor working at room temperature is reported when Fe$_2$O$_3$ is doped in ZnO [198].
In recent studies, nanostructured ZnO in the form of wires, tapes, particles, etc. have been found to exhibit improved sensitivity to different gases owing to a larger surface to volume ratio [224].

1.20 Objectives of the present study

In this study Fe₂O₃ has been studied for its gas sensing properties. Earlier literature says that Fe₂O₃ can not be used as base material for gas sensing application. But the contrast is also available in literature. It is reported that by modifying the material, using nano structured form of Fe₂O₃ and controlling the physical structure the film, Fe₂O₃ can be the promising material for commercial gas sensor application.

The major objectives of the present research work are:

i. To prepare thick films of Fe₂O₃ material.

ii. To fabricate static gas sensing system and to test the films for their gas sensing performance.

iii. To modify the films using additives and to study the effect of the additives on gas sensing performance.

iv. To study the effect of surface to volume ratio on adsorption-desorption mechanism, synthesize nano Fe₂O₃, prepare thick films of nano material and study their gas sensing performance.

v. To modify the film structure, prepare thin films of Fe₂O₃ using spray pyrolysis technique and study their gas sensing performance.

vi. To study the effect of annealing temperature on film structure, phases of the material and on gas sensing performance.

vii. To characterize the material, thick films, and thin films by various analytical techniques such as XRD, SEM, AFM, TEM, UV-VIS spectroscopy and TGA.
1.21 Definition of the problem

With comprehensive and critical survey of the literature, it is decided to study on “Studies on gas sensing performance of pure and modified Fe$_2$O$_3$ thick film resistors”.

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References


[41] Li-Jian Bie, Xiao-Na Yan, Jing Yin, Yue-Qin Duan, Zhi-Hao Yuan, *Sensors and Actuators B* 126 (2007) 604.


[44] Tao Cheng, Zhiyong Fang, Qixiu Hu, Kaidong Han, Xiaozhi Yang, Youjin Zhang, *Catalysis Communications* 8 (2007) 1167.


[59] Shufeng Si, Chunhui Li, Xun Wang, Qing Peng, Yadong Li, 


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