1
Introduction

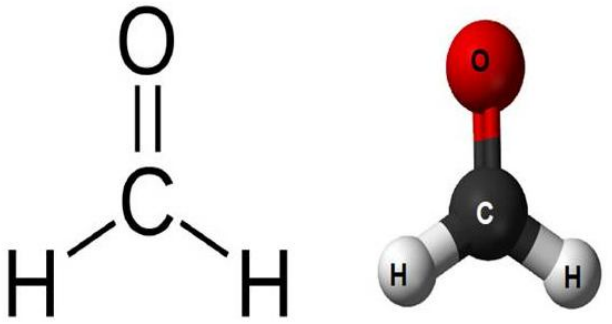
1.1 Formaldehyde gases in indoor air

At present, most people spend more than 80% of their daily time in an indoor environment and various research articles showed that they are suffering from various acute health issues such as sick building syndrome (SBS) [Kawamura et al., 2005], headache, nausea, asthma, irritation of the eyes, nose and throat due to the exposure of volatile organic compounds (VOCs) originating from indoor household products [Chen et al., 2015]. VOCs are gases that are produced in the air either by thermal or chemical decomposition of many everyday products used in our daily life, such as plastic, carpets, beauty and skin care products, antiseptics, glues, adhesives, paper, plywood-based furniture and so on [Allouch et al., 2013]. In indoor air, the common VOCs are methanol, ethanol, trichloroethylene, acetone, benzene, formaldehyde, etc. [Chung et al., 2013]. Among them, formaldehyde (HCHO) is considered one of the most dangerous indoor air pollutants, which is colorless and strong-pungent smelling gas. It was already reported by several research articles that formaldehyde has adverse health effects for human beings due its long-time exposure at home above a certain limit, and as per the Occupational Safety and Health Administration (OSHA), the allowed safe exposure limit of formaldehyde is around 0.75 ppm [Castro-Hurtado et al., 2013] [Zhang et al., 2017]. Various types of health issues, such as irritation of the eyes, nose and throat occurs above the exposure limit of 0.4 –1 ppm of formaldehyde. Moreover, after exposure of formaldehyde with high concentration (> 3 ppm) our body is induced with cytotoxic effects (cell and tissue damage). Furthermore, it was also reported that due to prolonged exposure to formaldehyde at levels of 6 ppm, human has been affected by various chronic diseases such as nasopharyngeal cancer, pulmonary damage and leukaemia [Kawamura et al., 2005]. These facts have attracted massive attention for measuring the presence of formaldehyde in indoor environments to save both humans and as well as the environment.



Fig. 1.1 : Daily time spent by people in the outdoor and indoor environments.

Formaldehyde



Formaldehyde	HCHO
Density	815 kg/m³
Molecular Weight/ Molar Mass	30.031 g/mol
37 wt.% solution in water	Formalin

Figure 1.2: Formaldehyde bond, density, molecular weight and commercial formalin source.

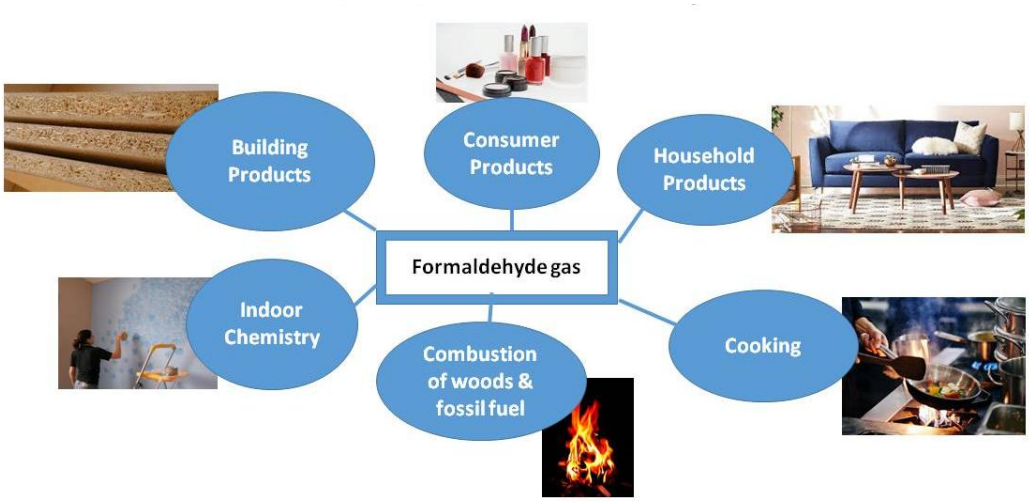


Figure 1.3: Various sources of formaldehyde in the indoor environment.



Figure 1.4: Various health issues due to exposure to formaldehyde in indoor areas.

Moreover, formaldehyde gas is readily soluble in water, known as formalin (37 wt.% of formaldehyde gas in water). Formalin has disinfectant properties, and hence, it is used as a

tissue fixative in many laboratories and hospitals. It is also used as an embalming liquid in laboratories to preserve biological species for a long time. Last few years, it has been reported by several newspapers and research articles that formalin solution has been used by some dishonest fish sellers as a preservative during the transportation of fish to the local market. Due to the disinfectant properties of formalin, it is used on freshly caught fish to avoid their spoilage so that it look fresh (Figure 1.5). However, due to the ingestion of formalin-treated fish, people face various health problems such as inflammation of the mouth and nose, vomiting, abdominal pain, etc., as shown in figure 1.6. Food Safety and Standards Authority of India (FSSAI) sets the daily maximum consumption limit of formaldehyde via food products, which is 30 mg per Kg to 100 mg per Kg body weight [Bianchi et al., 2007]. Hence, there is an urgent requirement for a real-time portable formaldehyde gas monitoring system to measure the presence of formaldehyde in food products.



Figure 1.5: Formalin is generally used as an embalming fluid, but nowadays, it is also used in fish to enhance their shelf-life during transportation to market.



Figure 1.6: Health effects due to ingestion of formalin-treated fish.

1.2 Literature Review on formaldehyde sensing

A gas sensor is a transducer which converts the concentration of various gases into an electrical signal to build a system for the real-life world. From the last 50 years, gas sensors have been used to detect various gases in the air which, includes inorganic (NO_2, NO, NH_3, H_2, CO_2, etc.) gases and organic (methanol, ethanol, acetone, toluene, benzene, formaldehyde etc.) vapors. To detect various concentrations of gases, different types of gas sensors are used, and their working principles are based on various principles such as gas chromatographic, catalytic, infrared (NDIR), electrochemical, chemiresistive, field-effect transistor (FET), acoustic and so on. Among the various types of sensor mechanisms used in gas sensor technology, chemiresistive types sensors mechanism are mostly used for the development of portable gas sensing systems to detect formaldehyde gases.

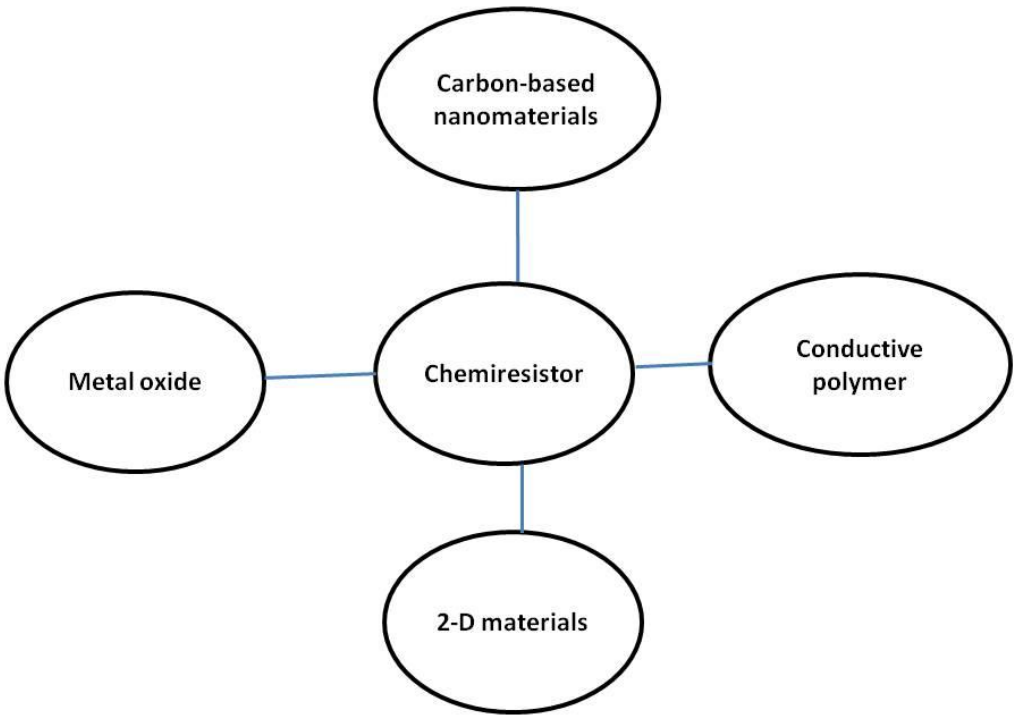


Figure 1.7: Classification of the chemiresitive gas sensors.

1.2.1 Chemiresistive gas sensors

Chemiresistors are conducting materials and in the presence of reducing (CO, H_2S, HCHO etc.) or oxidizing gases (NO_2), the resistance has been changed due to chemical interaction between the analyte and the sensing material [Barsan et al., 2001b]. In 1985, Wohltjen first coined the term chemiresistor and the most common chemiresistive materials are metal-oxide semiconductors (SnO_2, ZnO, NiO, WO_3 etc.) [Eranna et al., 2004], conductive polymers, 2D materials (MoS_2, WS_2, SnS_2 etc.) [Jung, 2014] [Kumar et al., 2019], carbon-based nanomaterials like graphene [Ye et al., 2016] [Li et al., 2015a] and carbon nanotubes [Li et al., 2017a][Lu et al., 2011] etc. Last few decades, researchers are doing extensive work to develop formaldehyde sensors using various metal oxides semiconductor (MOS) materials such as SnO_2 [Li et al., 2011a][Xu et al., 2014], ZnO [Pearton et al., 2005][Özgür et al., 2005], NiO [Lee et al., 2007][Dirksen et al., 2001], WO_3 [Deng et al., 2012][Sukunta et al., 2018], TiO_2 [Lin et al., 2011], and so on [Eranna et al., 2004]. In the early 1960s, Naoyoshi Taguchi found that in the presence of reducing or oxidizing gases the resistance of tin dioxide (SnO_2) has been changed and after doing a lot of research and experiments, for the first time, he developed a commercial version of thick film gas sensors. To date, thick film metal oxide semiconductors based gas sensors are using various industrial and real-time gas monitoring systems due to some inherent properties such as low production cost, high response with good reliability [Das et al., 2014]. Recently, among the various chemiresistive materials, metal oxide semiconductor (MOS) based sensor has been used in portable gas detection system because the change of resistance of metal oxides can be measured by using miniaturized and inexpensive read out electronics circuits [Meixner et al., 1995].

1.2.2 Various parts of Metal Oxide gas sensors

From the beginning of the metal oxide based technology, alumina, glass, silicon or other flexible material have been used to fabricate metal oxide based gas sensor and it consists of the various sub-parts:

a) Gas sensing layer
b) Electrode
c) Heating platform

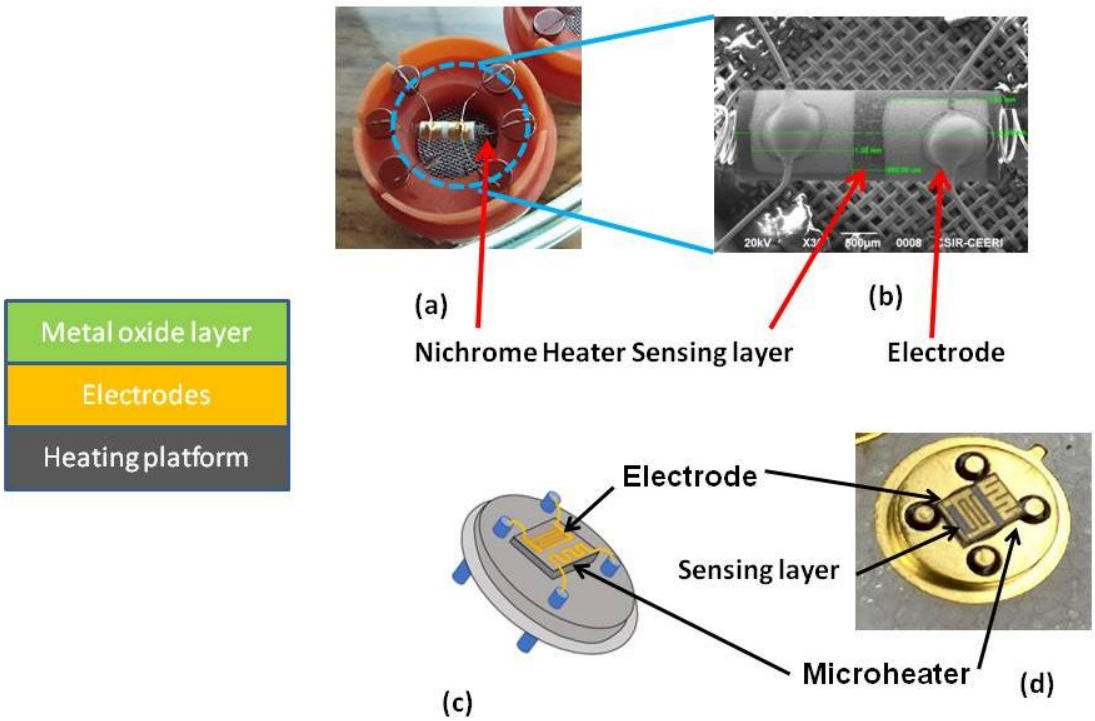


Figure 1.8: Type of metal oxide gas sensors: (a) and (b) thick film gas sensor with plastic package. (c) and (d) thin film metal oxide sensors with metal packages (TO-39 headers).

a) **Gas sensing layer**: Various types of metal oxide (Tin oxide, Zinc oxide, Tungsten oxide, Nickel oxide etc.) have been used for the fabrication of gas sensors. The bulk metal oxide materials generally are crystalline in nature but the thick and thin film layer of metal oxide have a lots of grain and grain boundaries. The grain boundaries are connected to their neighbouring grains by their necks [Yi et al., 2011]. In the presence of analyte gas, the resistance of the gas sensing materials changes and the change in resistance depends on the concentration of the analyte gas and the flow of current through the grains represents the change in concentration of the analyte gases. Recently, researchers have been using nanostructured materials instead of thick or thin film materials due to the enhancement of gas sensing performance. The thick and thin film based metal oxide gas sensors are shown in figure 1.8 (a) and (c), respectively.

b) **Electrode**: To connect the gas sensing materials with circuit, there is a requirement of the metal line which is called electrode. Normally, highly conductive materials such as Pt and Au are used as electrode material and the sensing layer is deposited on the top of the electrode material to flow the current to the required terminals as shown in figure 1.8 (a),(b),(c) and (d). Conventionally, the electrodes are fabricated using screen printing or CMOS based microfabrication technologies. The array of electrodes is called Interdigitated Electrode (IDE) (Figure 1.8 (d)).

c) **Microheater:** Metal oxide gas sensor works at elevated temperature and for this requirement, the sensing layer is heated by microheater (Figure 1.8 (b) and (d)). The microheater works on the principle of the Joule heating effect [Zhang et al., 2007][Baroncini et al., 2004]. For the development of gas sensors, researchers commonly used commercially available hollow alumina tube having length of about 4 mm. The external and internal diameter of the hollow tube are 1.2 mm and 0.8 mm, respectively. On the alumina tube a pair of Au electrodes are pre-printed and the electrodes are connected with platinum (Pt) conducting wires at both ends

(Figure 1.8 (a)) which were bonded onto the pins of the plastic package. A nichrome (Ni-Cr) heater coil is inserted through the hollow alumina tube. The heater coil is connected with a source measure unit (SMU) to act as a temperature source and it maintains the operating temperature (range of 200 to 400°C) of the gas sensing layer. In our lab, we have developed a co-planner gas sensor platform where meander shape Au microheater was used as a heater to heat the surrounding sensing layer as shown in figure 1.8 (c). Generally, the metal oxide based gas sensor should integrate with a microheater which has some salient features such as low power consumption, short response time, uniformity in heat distribution, good mechanical stability and so on [Scorzoni et al., 2015].

1.2.3 Gas sensing mechanism of Metal Oxide gas sensor

The gas sensing mechanism of any metal oxide based gas sensors is based on two functions: one is receptor and another is transducer functions [Jian et al., 2020]. First, in receptor function, on the surface of the gas sensing layer, the electron exchange occurs with target gases at the gas-solid interface at an elevated temperature range of 100 to 400°C. Due to the effect of temperature on the metal oxide layer, free electrons are generated from the conduction band and it flow through grain boundaries of the metal oxide surface via an interdigitated electrode (IDE) in the presence of applied DC bias as shown in figure 1.9 (a). In air, on the top surface of metal oxide oxygen molecules have been physisorbed at room temperature and chemisorbtion of oxygen molecules has occurred at higher temperature (100 to 400°C) due to their highly reactive properties. Physisorbed and chemisorbed oxygen molecules on the surface of metal oxide form ions on the surface of the grains. The formation of oxygen ions (O_2^- , O^- and O^{2-} ions) occurs at different temperatures [Das et al., 2014]. At low temperatures (T < 100°C), chemisorbed oxygen molecules (O_2) captured the free electrons from the metal oxide surface to form O_2^- ions. Moreover, at higher temperatures (T > 100°C), O_2^- ions again combine with electrons to form O^- ions. The formation of oxygen ions at different temperatures on the surface of metal oxide is summarised here [Miller et al., 2006]:

$$O_{2(gas)} + e^- \leftrightarrow O_{2\,(ads)}^- \qquad (T < 100°C) \qquad (1.1)$$

$$O_{2\,(ads)}^- + e^- \leftrightarrow 2O_{(ads)}^- \qquad (100°C < T < 300°C) \qquad (1.2)$$

$$O_{(ads)}^- + e^- \leftrightarrow O_{(ads)}^{2-} \qquad (T > 300°C) \qquad (1.3)$$

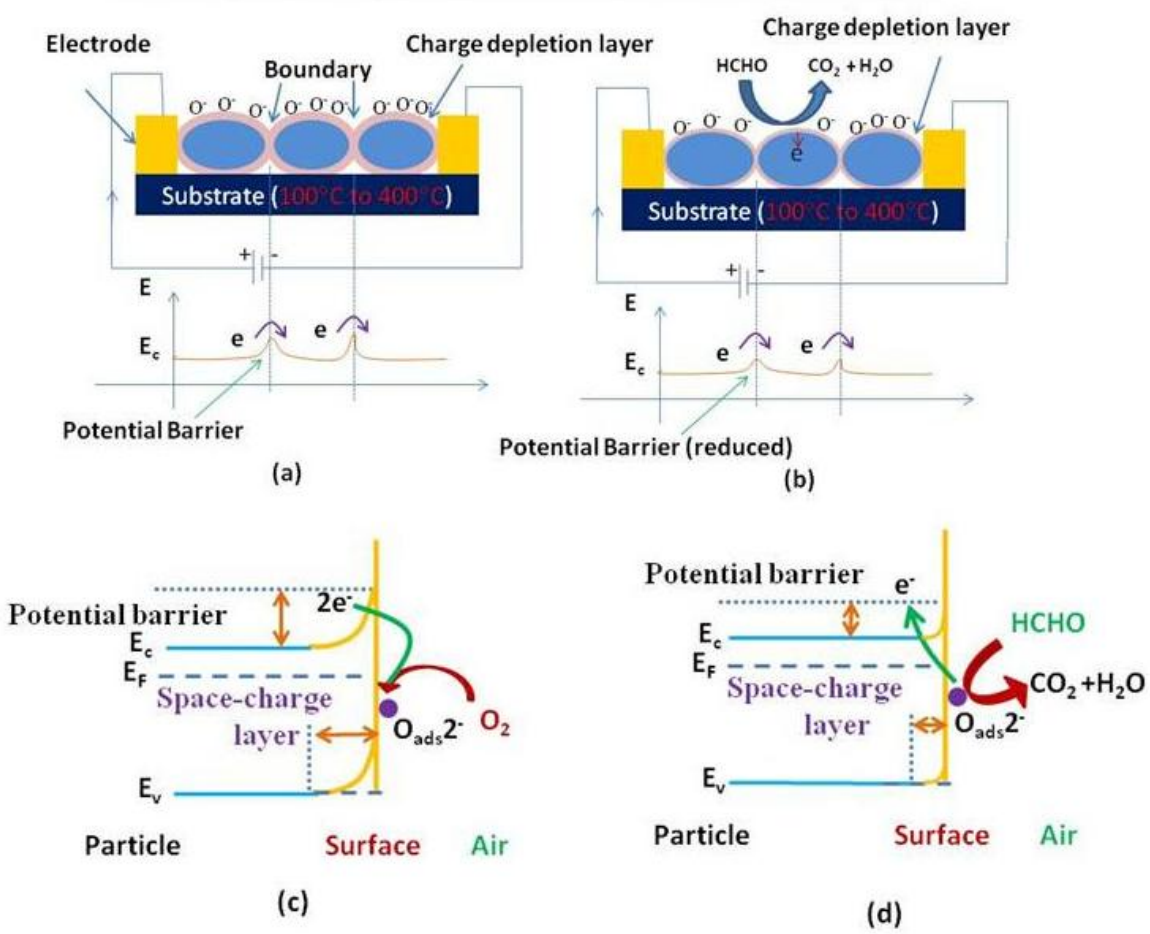


Figure 1.9: (a) and (c) Band diagram of metal oxide gas sensor in oxygen ambient. (b) and (d) Band diagram of metal oxide gas sensor in the presence of formaldehyde gases.

On the other hand, the adsorbed oxygen ions (O_2^- , O^- or O^{2-}) on the metal oxide surface repel other electrons from interacting with the bulk of films. As a result, a depletion layer (also called space charge layer) has been formed at the grain boundary of the surface of metal oxide [Barsan et al., 2001a] and band bending occurs as shown in figure 1.9 (a), (b), (c) and (d). This phenomenon restricts the flow of electrons via the grain boundaries and increases (n-type) or decreases (p-type) the resistance of the sensing layer (as shown in Table 1.1) [Tonezzer et al., 2018] in the presence of reducing gases. The accumulation of oxygen species on the surface of metal oxide and the concentration of charge accumulation changes into an electrical resistance change in the sensors is called the transducer function [Korotcenkov, 2008]. When the metal oxide sensor was exposed to formaldehyde gas (HCHO), the reaction between HCHO and the adsorbed oxygen ions (O_2^- , O^- or O^{2-}) have occurred, consequently, CO_2 (g), H_2O (g), and electrons (e^-) were released. After the reaction, the electrons return into the conduction band of the metal oxide surface, leading to the reduction of resistance of metal oxide materials. The possible reactions to happen with formaldehyde via adsorbed oxygen ions, are shown as follows [David, 1999]:

$$HCHO_{(gas)} \rightarrow HCHO_{(ads)} + 2O^-_{(ads)} \rightarrow CO_{2(gas)} + H_2O_{(gas)} + 2e^- \qquad (1.4)$$

In this manner, the metal oxide gas sensors act as variable resistors whose resistance value depends on the analyte gas concentration.

1.2.4 Types of metal oxide materials for gas sensing

Metal oxide gas sensor works at elevated temperature and at elevated temperature (100-400°C), the oxygen molecules adsorb on the surface of the metal oxide materials and electron transfer occurs from metal oxide to oxygen. In the case of n-type metal oxide

semiconductor material, the resistance of the gas sensors increases due to the reduction of electrons from the surface when they are exposed with reducing gases (H_2S, CO, etc.) or volatile organic compounds (VOCs) (HCHO, Methanol, Ethanol, Acetone etc.). The reverse phenomenon occurs during the exposure to oxidizing gases (NO_2). On the other hand, in p-type metal oxide semiconductors, the free electron has been adsorbed by oxygen molecules and the resistance of the sensing materials has been reduced due to the increase of hole in the surface when the sensors have been exposed with reducing gases. Table 1.1 shows the examples of n- and p-type metal oxide semiconductors :

Table 1.1: Types of metal oxide and changes in conductivity

Type of metal oxide	Conductivity		Example
	Reducing gases and VOCs	Oxidizing gas (NO_2)	
n-type	Increases ↑	Decreases ↓	SnO_2, ZnO, TiO_2 etc.
p-type	Decreases ↓	Increases ↑	NiO, CuO etc.

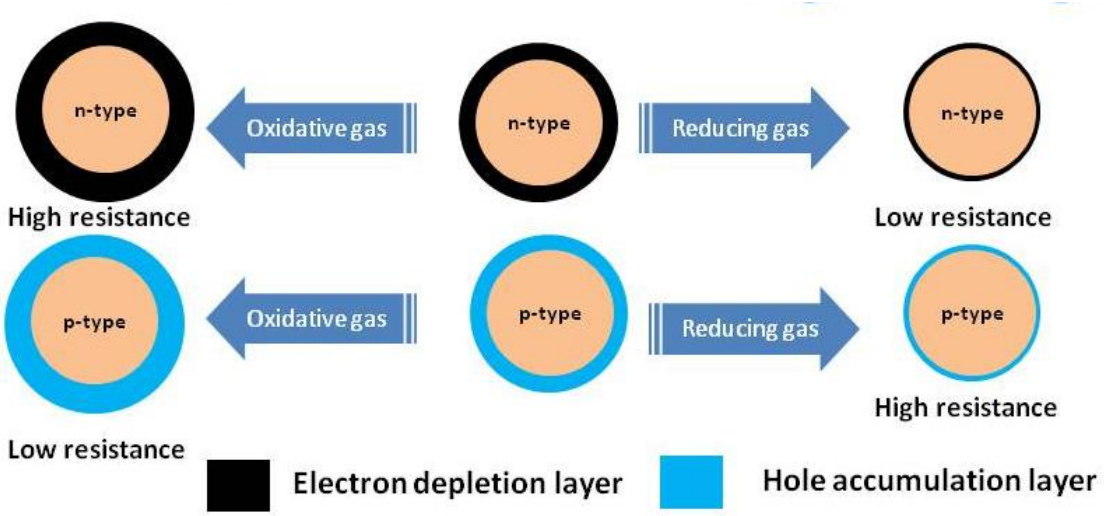


Figure 1.10: Type of metal oxide gas sensor and the change in conductivity in the presence of reducing and oxidizing gases.

1.2.5 Characteristics of metal oxide Gas Sensors

The various parameters of gas sensors which are used to characterize the sensor's performance are described below. Here, all the parameters are described based on the metal oxide based sensor which are used in this thesis work.

(a) **Sensor Response (β)**: The sensor response (β) is a ratio of sensor resistance in ambient air (R_a) and sensor resistance in the presence of target gas (R_g). So, sensor response (β) is defined as R_a/R_g. Response can be defined as R_a/R_g for reducing gas and R_g/R_a for the oxidizing gas. In general, the response of any metal oxide gas sensor should be high.

(b) **Response (τ_{res}) and Recovery (τ_{rec}) time:** The sensor response time (τ_{res}) is the amount of time required by the sensor to achieve a response from 10 % to 90% value of the highest response in the presence of analyte gas. On the other hand, recovery time (τ_{rec}) is the time which

will be required by the sensor at which sensor's response falls from 90 % to 10 % of highest response during the gas desorption process. Response time (τ_{res}) and recovery time (τ_{rec}) of the sensor should be low.

(c) **Selectivity**: The selectivity of the gas sensor is defined as the ability of the gas sensor to detect a specific target gas from a mixture of gases. Thus, the sensor should be selective to that particular gas to avoid any interference of other gases.

(d) **Limit of Detection (LoD) :** Limit of detection of the gas sensor is defined as the lowest concentration of an analyte gas that can be detected by the sensor.

(e) **Stability :** Stability is the ability of a gas sensor to reproduce results for a certain period of time.

An ideal sensor should possess high sensitivity, selectivity, stability, low response time and fast recovery time.

1.2.6 Fabrication technology of metal oxide sensors

According to fabrication methodology, the metal oxide based gas sensors can be classified into thick film, thin film and nanostructured (Figure 1.11). The first two (thick and thin films) types sensors are fabricated by conventional fabrication techniques such as screen printing, physical vapour deposition, and chemical vapour deposition method. The development of nanotechnology is enhancing the fabrication of nanostructured-based sensors.

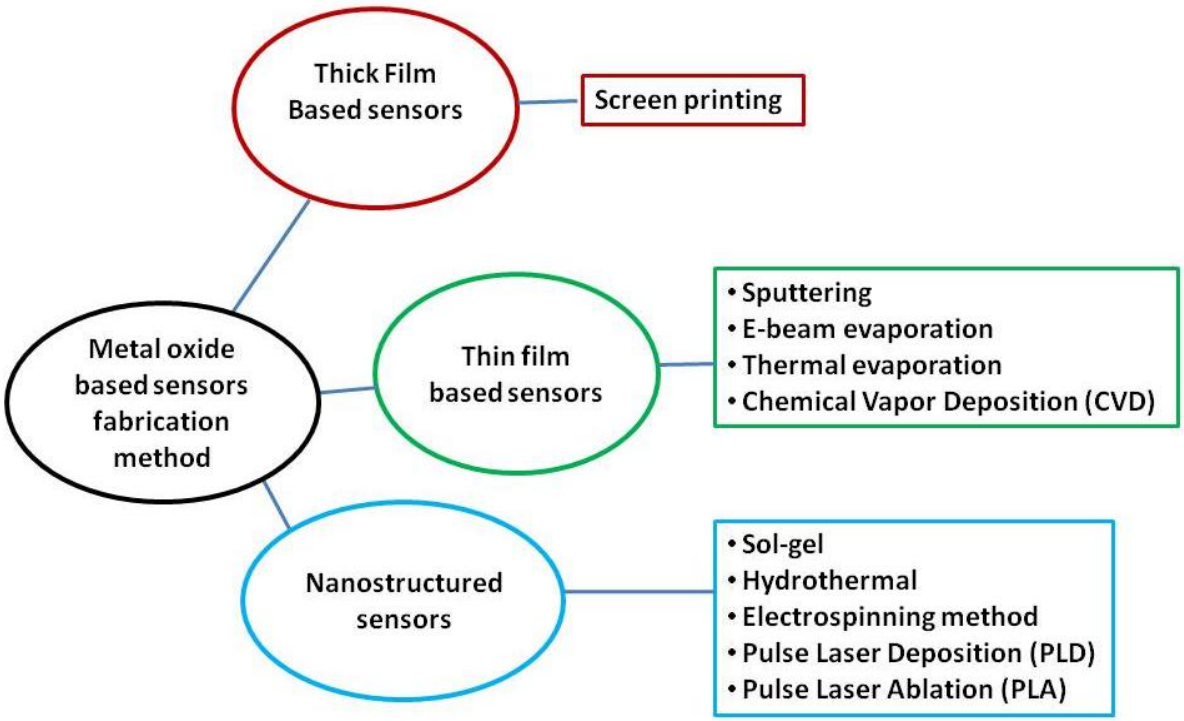


Figure 1.11 : Classification of metal oxide sensors according to the fabrication technology.

(a) Thick film-based sensors

Generally, screen printing methods are used to fabricate thick film based gas sensors and the process is cost effective but thick film sensors suffer from low sensitivity and poor selectivity. In thick film fabrication technology, a paste or ink was used which is synthesized by a mixture of material powders and solvents. Further, this paste is applied onto the interdigitated electrode (IDE) of substrate, followed by drying and firing operations. The typical thickness of sensing film has a range of 1–10 µm. Till today, most of the commercial sensors are made by thick film based technology. For the synthesis of thick film sensing material, hydrothermal and screen-printing method are the most commonly used techniques.

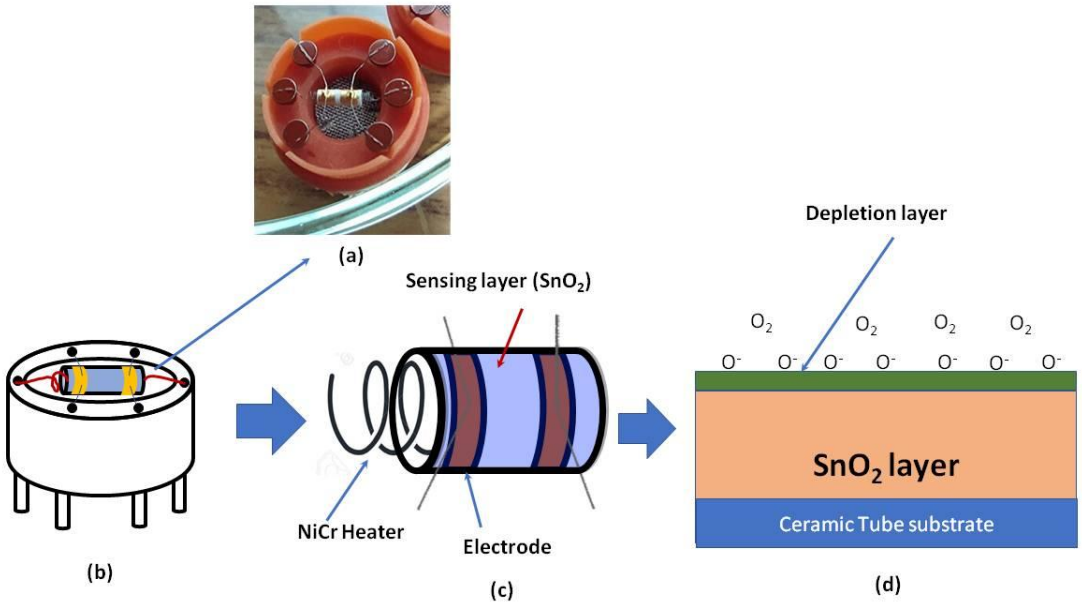


Figure 1.12: Thick-film based sensor (a) Optical image of sensor, (b) Schematic view of sensor with package, (c) Schematic image of gas sensor platform and (d) Schematic diagram of sensing layer in oxygen ambient.

(b) Thin film-based sensors

There are two main fabrication process to deposit thin films: physical vapor deposition (PVD) (sputtering, thermal and e-beam evaporation techniques) and chemical vapor deposition (CVD). In physical vapor deposition (PVD) methods the metal oxide thin film coating has been produced via the condensed phase to a vapor phase and back to a thin film condensed phase. The most common PVD process are sputtering and evaporation. In this process sophisticated equipments have been used and process is also lengthy and time consuming. In thin film-based technology, individual atoms, molecules or ions are generated via physical or chemical methods in a controlled deposition chamber and they are deposited onto substrate (silicon, glass or alumina) via condensation. It consists of three steps: generation of atomic or molecular species in the controlled environment, transport of these species to the substrate and deposition of the species via condensation on the substrate directly or by a chemical reaction. The typical thickness of thin film layer is within the range from 100 nm to 5 µm. Figure 1.13 shows the SnO_2 based thin film-based sensors.

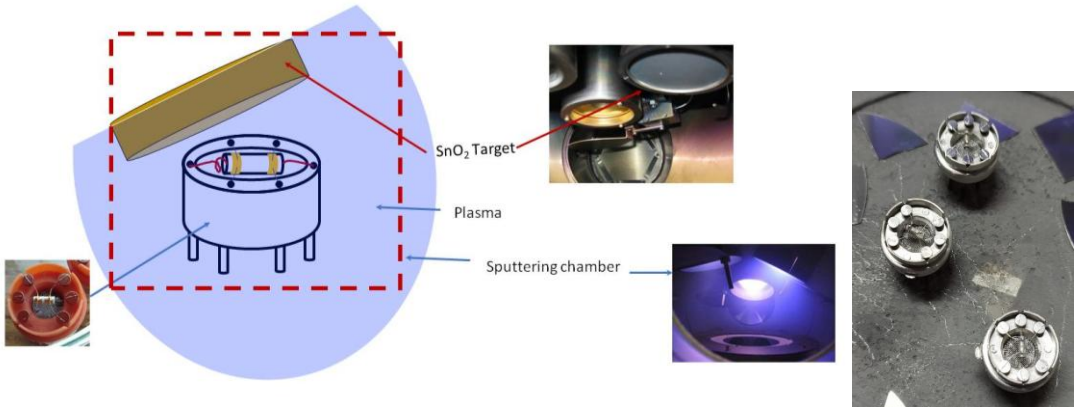


Figure 1.13 : Optical images of sputtered deposited SnO_2 based thin film sensors.

(c) Nanostructured material-based sensors

Nowadays, researchers are using nanostructured materials for the improvement of sensitivity towards target gases using various synthesis methods as shown in figure 1.11. At present, after development of nanoscience and nanomaterials, researchers are using these techniques to develop various nanostructured-based metal oxide gas sensors due to their high surface-to-volume ratio per unit mass, high density of porosity, more numbers of active sites and so on. In addition, new physical and chemical properties have been generated when particle sizes are in nano-meter scale. The specific surface area of the nanoparticles as well as surface-to-volume ratio increases enormously when the size of the nanoparticles decreases. Furthermore, the flow of the electron and holes in the metal oxide semiconductor are affected by size and geometry of the nanomaterials. Various shapes and sizes are formed in the nanostructured metal oxide such as nanorods, nanotubes, nanofibers, nanopillar, nanoparticles and nanosheets etc. FESEM images of the nanostructured material with various shapes are shown in figure 1.14.

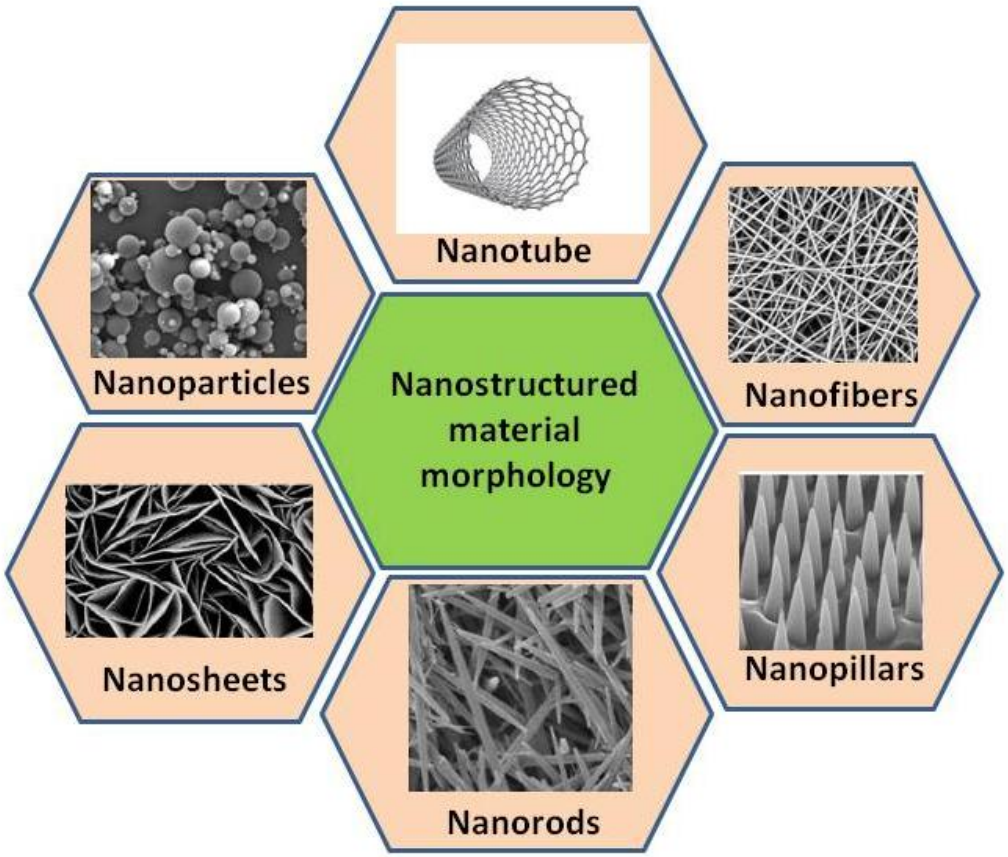


Figure 1.14 : Various types of nanostructured morphology used in gas sensing applications.

There are many methods to synthesise the nanostructured metal oxide material such as Sol-gel, Electrospinning, Hydrothermal, Pulse Laser Deposition (PLD) etc.

1.3 Methods for improving gas response towards target gases

Metal oxide based gas sensors have a lot of advantages such as low cost, simple fabrication methods and small size, and they require a simple read-out electronics circuit for the development of gas detector system. But till now, researchers have to face various challenges such as low sensitivity and poor selectivity towards target gas molecules. The sensitivity and selectivity towards the target gas can be improved by various methods as shown in figure 1.15. We have discussed each point step by step in the following section:

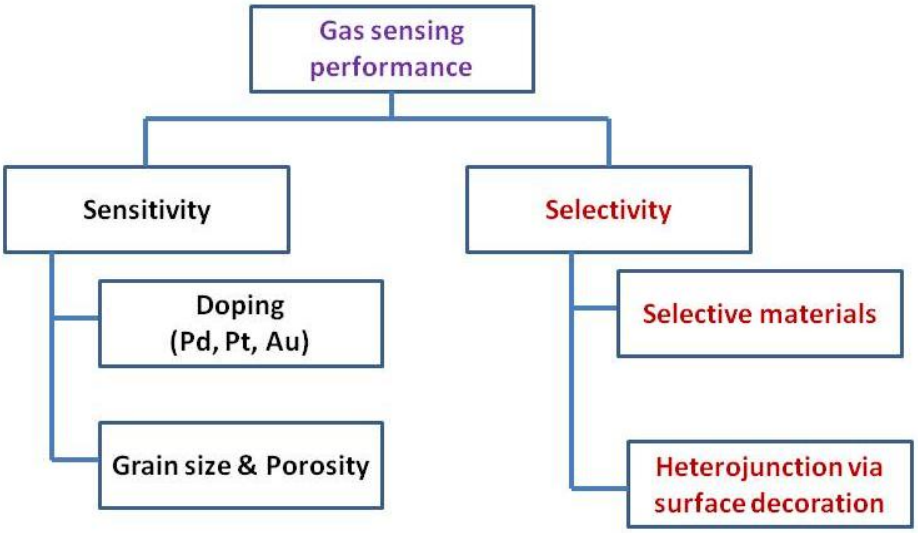


Figure 1.15 : Various methods of fabrication technology for improving gas response used in metal oxide.

1.3.1 Improvement of sensitivity

The sensitivity of the metal oxide sensor can be improved by two methods: one is doping, and another is reducing the grain size.

(a) Doping with noble metals

The sensitivity of the metal oxide based gas sensors can be enhanced by the addition of dopants with noble metals such as Au, Pd, Pt, Al etc. [Guo et al., 2014; Yu et al., 2019a]. Many authors report an enhanced response when the metal oxides have been doped with noble metal nanoparticles. The enhancement of response due to dopant material depends on mainly on two mechanisms: firstly chemical sensitization and secondly, electronic sensitization, as shown in figure 1.16 (a) and (b), respectively.

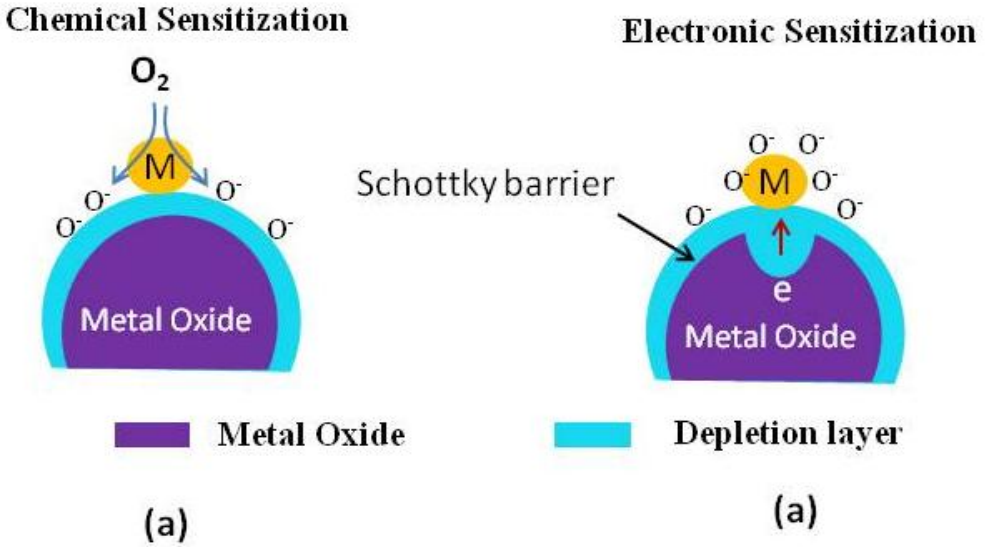


Figure 1.16: Enhancement of gas response via doping of noble metals (a) Chemical sensitization and (b) Electronic Sensitization.

In the case of chemical sensitization, more numbers of oxygen molecules are adsorbed and ionized on the surface of metal nanoparticles due to catalytic oxidation reaction over the surface. During the detection of target gases, the adsorbed oxygen is utilized for the oxidation reaction, and the consumption of surface oxygen reduces the surface space charge, which causes a change in electrical conductivity. If the metal oxide material is not active enough, the presence of metal nanoparticles (Au, Pd, Pt, Al) enhances the adsorption or desorption properties of

oxygen molecules on the metal oxide surface, and therefore it enhances the catalytic oxidation of gases.

(b) Reducing the Grain size

The sensitivity of the metal oxide based gas sensor can be increased significantly by changing some microstructure of the sensing materials like grain size, shape and porosity (Figure 1.17). Porous metal oxides with reduced grain size exhibit increased gas sensitivity because more active sites are available for interaction with the analyte gas molecules. The sensitivity of gas sensors depends on the its surface interaction.

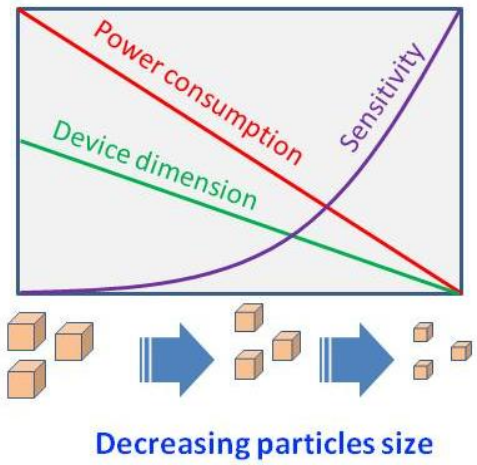


Figure 1.17 : Effect of particle sizes on gas sensing performance for metal oxide based gas sensor.

The gas molecules interact with the grain boundaries of the polycrystalline metal oxide sensing film. Various types of current conduction phenomenons occur in the polycrystalline metal oxides sensing film due to the relation between grain size (D) and the space charge layer thickness (L) (Figure 1.18). It was observed by various researchers that the sensitivity of the film increases when the nanoparticle size (D) of the polycrystalline sensing film is equal to or less than two times of the thickness of the depletion or space-charge thickness (L) (Figure 1.18 (a)). The flow of current of the sensing film is controlled by it grain boundary if the grain size (D) $\gg$ thickness of the space charge layer (2L), and the Schottky barrier at grain boundaries play a major role in this case (Figure 1.18 (b)). The current flow is controlled by the necks between two grains if the grain size (D) = twice of the space charge layer thickness (2L). The current flow in the sensing film is fully controlled by every grain when the grain size (D) < twice the thickness of the space charge layer (2L), and it is called grain control, as shown in figure 1.18 (c).

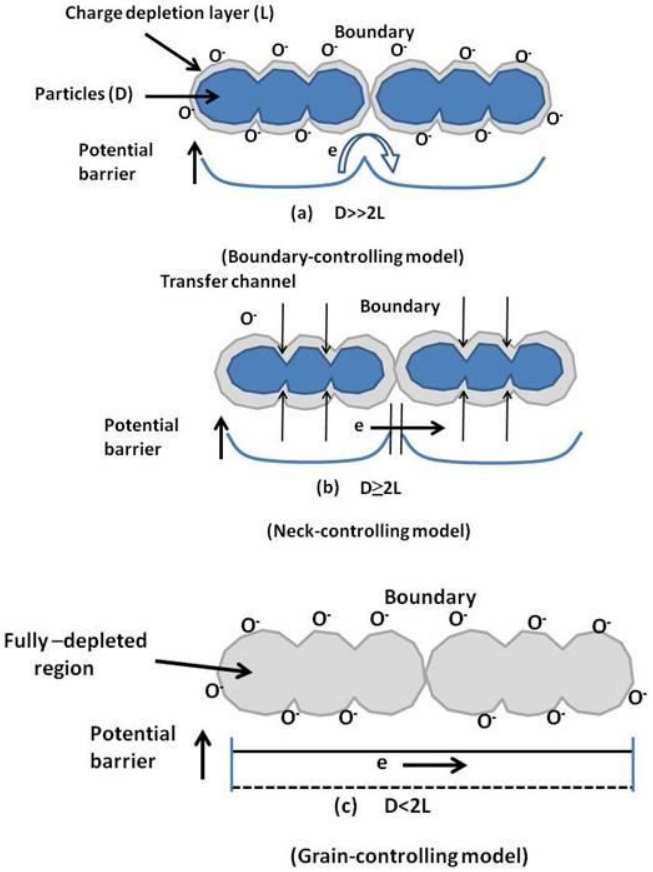


Figure 1.18: Effect of grain sizes on gas response.

1.3.2 Improvement of selectivity

Till now, researchers are continuously working to improve the selectivity of the metal oxide based sensors for the detection of target gases by removing other gas interferences. So, to overcome this challenge, they have applied some strategies to improve the selectivity of the metal oxide based sensor, and they obtained good results. These methods have been discussed in the following sections:

(a) Synthesis of functional pristine metal oxide

It is a very challenging task to detect a single gas using a metal oxide based sensing layer, and among the various techniques adopted to enhance the selectivity, using functional materials which is selective to one analyte and have very low or zero cross-sensitivity for other analytes, is the most used method. Our target is to develop a metal oxide based formaldehyde sensor. From the literature review, we have seen that, in the last few years, researchers have been used p-type NiO material for the detection of formaldehyde gases due to its catalytic effect, which accelerates target gas decomposition, enlarged surface depletion layer and researchers are getting good results by using these techniques.

(b) Formation of Heterojunction (n-n or p-n)

The second approach is to use heterostructures (a combination of a metal oxide with another metal oxide, noble metal or CNTs). The last few decades, researchers have been using heterojunction (n-n or p-n) based metal oxide sensors instead of using pristine metal oxide for the detection of formaldehyde. Recently, instead of using pristine SnO_2, researchers are developing heterojunction based sensors by modifying the top surface of SnO_2 with n-type (ZnO) or p-type (NiO) semiconductors to incorporate the various physical and chemical

properties of individual materials into one for the improvement of formaldehyde sensing performance of SnO_2 at reduced operating temperature. For example, Lou C et al. [Lou et al., 2021] developed heterojunction-based (n-n) formaldehyde sensor via surface modification of n-type SnO_2 heterospheres with n-type ZnO nanomaterials using atomic layer deposition (ALD) technique. The fabricated sensor showed the response of 38.2 to 20 ppm formaldehyde vapor with fast response and recovery time (17/25 s) at the lower operating temperature of 100°C.

Some researchers have used p-n heterojunction for the selective detection of formaldehyde. For example, G. Zhang et al. [Zhang et al., 2016] reported the obtained NiO/SnO_2 p-n heterojunction nanospheres using an electrospinning process which exhibited a high response 26.03 towards 100 ppm formaldehyde at the operating temperature of 100°C with excellent selectivity. On the other hand, Dan Meng et al. [Meng et al., 2018a] synthesized NiO/SnO_2 formaldehyde sensor using the hydrothermal method and obtained good response of 39.2 at 100 ppm of HCHO at 100°C operating temperature. For example, Zhu Li Yuan et al. [Zhu et al., 2019a] fabricated p-CuO/n-SnO_2 heterojunction based sensors to detect formaldehyde gas and observed a low response of about 2.42 to 5 at the temperature of 250°C. K. Khamfoo et al. [Khamfoo et al., 2020] fabricated a formaldehyde sensor via doping with n-type SnO_2 nanoparticles on p-type AgO thin film using a flame spray pyrolysis process and obtained a high response of 495 towards 2000 ppm HCHO at high temperature of 350°C. G. Zhang et al. [Zhang et al., 2016] developed formaldehyde sensor via the formation of NiO/SnO_2 p-n heterojunction nanospheres by an electrospinning process, which showed a good response of 20 towards 100 ppm HCHO at 200°C with superior selectivity to HCHO against other gases.

1.4 Motivation

In the last few decades, metal oxides semiconductor (SnO_2, ZnO, NiO, WO_3 etc.) have shown strong potential as promising gas sensing materials for measuring a low level formaldehyde gases with good stability over time [Allouch et al., 2013; Das et al., 2014; Lei et al., 2021; Li et al., 2019b, 2021]. But, the sensitivity and selectivity towards formaldehyde gases are still a problematic for the metal oxide sensors [Simon et al., 2001]. Recently, researchers have made a huge effort to synthesize metal oxide nanostructured materials with various morphologies (size and shape) such as nanorods, nanowires, nanocubes, nanosheets, nanobelts, nanospheres, nanoparticles (NPs). These nanostructured materials have been synthesized via physical and chemical solution routes such as pulse laser deposition (PLD) [Brilis et al., 2005][Ristoscu et al., 2007][Ju et al., 2015], drop casting [Fang et al., 2017], hydrothermal [Gu et al., 2017][Din et al., 2020][Pascariu et al., 2016], electrospinning [Zheng et al., 2011][Hu et al., 2018][Tang et al., 2016] etc. It is well known that the selectivity and sensitivity have been improved by using nanomaterial for the fabrication of pristine or heterostructure based metal oxide sensors. The obtained nanomaterials are also used to fabricate heterojunction via surface decoration or doping. Till now, researchers have used chemical synthesis routes for surface modification or doping of metal oxide, in which various toxic chemicals are used as precursors to prepare the heterojunctions and a post-process treatment like making paste or spin coating over the sensing electrode to prepare the gas sensors. But, these conventional chemical synthesis processes are time-consuming and also some chemical residues are left in the synthesized nanostructured. In addition, in this synthesis process, the use of sophisticated instruments and costly vacuum deposition systems are still major constraints. So, to avoid these situations, researchers are finding a new alternative method for surface-decoration or doping of metal oxide nanostructures to build a low-cost gas sensors.

To date, few investigations have been focused on finding a chemical free alternative synthesis route to generate metal oxide nanoparticles for the gas sensing applications. At present, the synthesis of nanoparticles and micromachining using pulsed-laser ablation method is drawing more attention from researchers. For that purpose, nano- or femto-second solid-state laser has been used. In recent years, various metal oxide nanoparticles (CuO, AgO, ZnO, SnO_2, NiO etc.) are synthesized via laser ablation method from a pure solid metals target in air or liquid is shown its great potential [Nedialkov et al., 2004][Hongseok Choi, 2007][Haupt et al., 2007][Boutinguiza et al., 2018][Fernández-Arias et al., 2020]. Nowadays, there is a huge scope of research for the synthesis of metal oxide nanoparticles (NPs) using Pulse Laser Deposition

(PLD) and Pulse Laser Ablation (PLA) techniques, which have great potential as an alternative route to produce nanoparticles without using toxic chemicals [Hongseok Choi, 2007]. In recent years, various researchers are synthesizing metal oxide nanoparticles (NPs) in air or liquid by ablation of solid metal or metal oxide targets using solid state laser and they are exploring the gas sensing potential of obtained nanoparticles [Boutinguiza et al., 2015; Fernández-Arias et al., 2020; Boutinguiza et al., 2018]. The synthesized nanoparticles exhibited accurate stoichiometry with good structural symmetry to their source material. As it was observed in various research articles, the synthesis of nanoparticles via ablation of a solid target using pulsed laser ablation showed an effective route without the requirement of toxic chemicals, vacuum chambers, and additional sophisticated vacuum controlling equipment. It is already been reported by various researchers about the laser-ablated nanoparticles-based gas sensors. For example, Gondal *et al.* [Gondal et al., 2012] fabricated NiO NPs having a diameter size of about 8 nm using Nd:YAG solid state laser with 355 nm wavelength from a solid nickel target immersed in a 3% H_2O_2 aqueous liquid solution. He *et al.*[He et al., 2008] synthesized ZnO NPs by ablating Zn metal which was immersed in aqueous media using a Nd:YAG laser (355 nm wavelength) and they got NPs with spherical shapes of variable sizes ranging from 10 to 25 nm. Gondal *et al.* [Gondal et al., 2010] synthesized SnO_2 NPs with a size of 3 nm via irradiation of laser beam from a pure tin metal immersed in deionized (DI) water using Nd:YAG laser. Fernandez et al. [Fernández-Arias et al., 2020] developed CuO NPs with spherical shapes and an average size of 5 nm by laser ablation of pure copper target (Cu) in open air using nanosecond Nd:YVO4 laser having 532 nm wavelength.

1.5 Objective

Due to the harmful effect of formaldehyde on human health, there is an urgent requirement for formaldehyde sensors for indoor air quality monitoring and also to find the residue of formaldehyde in food items, especially in fish [Kołodziejska et al., 1994; Wang et al., 2007; Zhang et al., 2008]. So, we need a formaldehyde sensor to develop a portable system for rapid screening. As we have seen in the literature, a variety of sensing mechanisms are involved to detect formaldehyde, and each sensor technology has its advantages and disadvantages. At present, metal oxide nanoparticles heterojunction based sensors (ZnO/SnO_2, NiO/SnO_2 etc.) are commonly used on commercial application platforms due to their some salient features, such as easy to fabricate the sensor at a miniaturized level, cheap as compared to other sensor technology such as optical and electrochemical sensor technology etc. [Sun et al., 2012; N. Barsan et al., 2007; C. Wang et al., 2010; Miller et al., 2014; Eranna et al., 2004; Eranna et al., 2016; Mazloom et al., 2014; and Jun Zhang et al., 2019].

Till now, several unresolved issues are present in the present metal oxide based formaldehyde sensor technology and researchers are working on it continuously to solve the practical limitations. The most significant issue are requirement of a high operating temperature (>200 °C) to operate the gas sensors. This limits practical application for the detection of explosive gases (for example methane, etc.) in a risky environment because of an explosion of combustible gases at elevated temperatures. Integration of microheater with metal oxide fulfils the requirement of temperature, but it increases the complexity, size and power consumption of the sensor. Moreover, due to the heating of metal oxide sensing layer at high temperature, various sensing layer performance parameters such as sensitivity and stability degrades with time. During the analysis of the reliability test of metal oxide sensors, other gas sensing parameters such as baseline resistance drift and poor selectivity were observed by researchers. Several research articles addressed these issues and described the various routes for further developments through optimizing the material structure, surface modification of sensing material and using different metal oxide synthesis techniques. Thus, to develop new synthesis methods for the fabrication of new types of sensors and implementing these fabrication techniques with existing industry technologies, are basic goals for further improvement of 4S aspects of a gas sensor, i.e., sensitivity, selectivity, stability and speed (response/recovery time). In addition, this, due to advancement of Internet of Things (IoT), some other important sensor parameters such as flexible, wearable, wireless, and small size have also demanded in current

years. Furthermore, recent progress in nanotechnology has opened scientific and technological interest in gas sensing for miniaturizing the device with enhanced sensing performance using new low dimensional materials.

In this thesis work, the author aims to:

- Develop and optimize a rapid prototype for the detection of formaldehyde gas using laser micro-pattering technique using Au microheater platform.
- Develop cost effective, chemical free, rapid methods for the synthesis of metal oxides nanoparticles (ZnO, NiO etc.) using laser ablation techniques in air for gas sensing applications.
- Study the morphological and structural behaviour of laser ablated nanoparticles (ZnO, NiO etc.).
- Fabricate a highly selective and ultra-sensitive n-ZnO/n-SnO_2 (n-n) and p-NiO/n-SnO_2 (p-n) heterojunction based formaldehyde (HCHO) gas sensor.
- Study the gas sensing performance of fabricated heterojunction sensor using the laser ablated nanoparticles.
- Extract various gas sensing parameters via the Langmuir adsorption-desorption model using experimental results.

1.6 Thesis Outline

This thesis work includes the synthesis and fabrication of laser ablated nanoparticles based formaldehyde sensors. Figure 1.19 illustrating the schematic diagram of various strategies which were adopted for developing highly sensitive and selective formaldehyde sensor. In this work, we focused on the synthesis of metal oxide nanoparticles (ZnO, NiO etc.) using a pure (Ni) or oxide pellet (ZnO). To achieve the best results, the laser ablated nanoparticles (ZnO, NiO etc.) were used to decorate the surface of pristine metal oxide (SnO_2) to prepare heterojunction based formaldehyde sensors. The outline of this thesis is described below:

Chapter 1: This chapter describes the various mechanisms for sensing formaldehyde gas in air, in particular, metal oxide (SnO_2, ZnO, NiO etc.) for gas sensing applications. The challenges associated with metal oxide gas sensors are discussed in detail. Further, brief literature review on metal oxide gas sensor followed by motivation, objective and outline of the thesis were mentioned.

Chapter 2: This chapter describes the different experimental and analytical tools used for material synthesis, device fabrication and characterization. In addition, gas sensing characterization systems which was used in this thesis work are discussed briefly.

Chapter 3: This chapter describes a new rapid method for the fabrication of co-planner metal oxide gas sensing platform using Au microheater. First, co-plannar meander shaped microheaters and interdigitated electrodes (IDE) were realized via laser ablation technique using laser-patterning techniques on sputtered deposited Au thin film. Heat distribution profile, Temperature Coefficient of Resistance (TCR), and long-term reliability of the fabricated microheater were systematically investigated. The surface morphology and geometrical changes of metal lines were observed by SEM. We have also studied the heat distribution profile and power versus operating temperature of a commercially available hollow alumina tube based gas sensor platform through which a nichrome (Ni-Cr) heater coil is inserted.

Chapter 4: Then, in this chapter, the formaldehyde sensing behaviour was studied by depositing a SnO_2 thin film on the Au electrode of a commercially available hollow alumina tube based gas sensor platform. The surface morphology and crystalline phase of the SnO_2 thin film layer were measured by FESEM and XRD, respectively. The formaldehyde gas sensing performance test was carried out for the SnO_2 thin film sensor. Along with this, we also

explained in detail the new rapid method for the synthesis of ZnO NPs using a locally designed PLA set-up by vaporizing a solid source of polycrystalline ZnO pellet in an open air atmosphere. Later, we discussed the rapid prototype method for the development of formaldehyde sensor using laser-ablated ZnO NPs. At the end of this chapter, the gas-sensing performance of the ZnO NPs has been carefully investigated in the presence of formaldehyde gas molecules.

Chapter 5: This chapter describes the gas sensing behaviour of ZnO/SnO_2 n-n heterojunction based formaldehyde sensor by decoration of SnO_2 thin film with laser ablated ZnO NPs over sputtered deposited SnO_2 thin film. In addition, the gas sensing behaviour of ZnO/SnO_2 heterojunction sensor towards formaldehyde was studied. Later, we discussed the synthesis mechanism of NiO NPs by a scanning high power UV laser (355 nm wavelength) beam on the surface of pure (99.99%) Ni pellet in ambient air and surface decoration technique to fabricate NiO/SnO_2 p-n heterojunction based formaldehyde sensor by modifying the surface of sputtered deposited SnO_2 thin film with laser ablated NiO NPs.

Chapter 6: In the beginning of this chapter, the enhanced formaldehyde gas sensing mechanism of n-ZnO/n-SnO_2 and p-NiO/n-SnO_2 heterojunction based sensors compared to pristine SnO_2 and ZnO sensors was discussed systematically. Furthermore, response time (τ_{res}), recovery time (τ_{rec}), surface coverage (θ), adsorption (K_a) and desorption rate constant (K_d) of NiO/SnO_2 sensor were extracted from the experimental data using Langmuir gas adsorption-desorption model via curve fitting method.

Chapter 7: In the last chapter of this thesis, we summarized this thesis work and also described the future scope of this work. In addition, the developed microsensor has also been used for on-site rapid screening for the detection and quantifying of formaldehyde gas in formalin-treated fish sample. Moreover, challenges and future perspectives in the emerging laser ablated nanoparticles metal oxide for sensing applications were also explained.

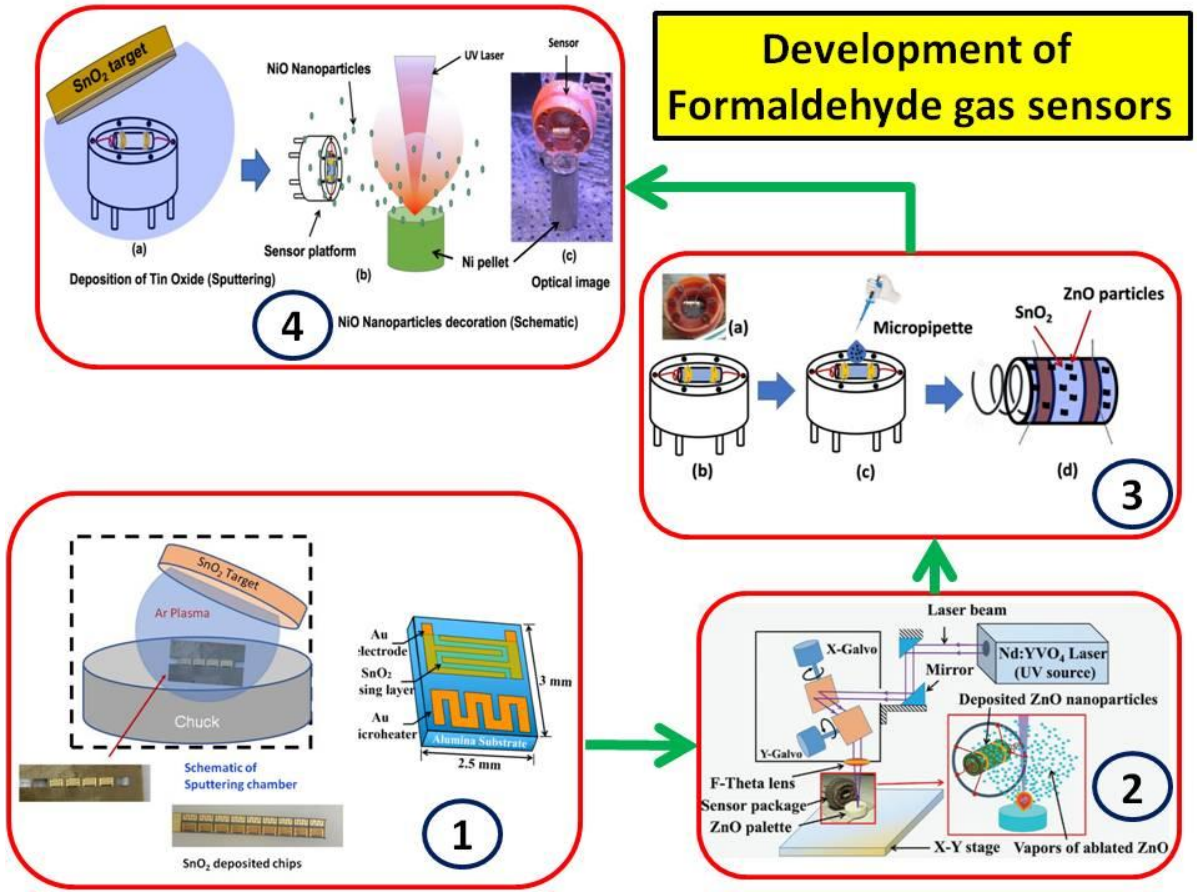


Figure 1.19: Schematic illustrating the several strategies adopted for developing the formaldehyde sensor using laser ablation methods in this thesis work. First, co-planner gas sensor platform was fabricated using an Au microheater and sputtered deposited SnO2 thin film. Second, gas response towards HCHO was tested using laser ablated ZnO nanoparticles. Third, HCHO response has been improved via the decoration of ZnO nanoparticles on SnO_2 thin film to form n-n heterojunction. Fourth, highly sensitive and selective p-n heterojunction based formaldehyde sensor fabricated by surface decoration of n-type SnO_2 thin film using laser ablated p-type NiO nanoparticles.