1
Introduction

Nowadays, global warming is becoming a serious issue due to the emission of large amount of combustible gases from on-board vehicles, wastage from chemical industries, and other environmental pollutants. The detection of these pollutant gases which are toxic and combustible has become necessary to protect the lives as well as properties of human beings. Thus, a highly sensitive and selective gas sensor is considerable demand which will reduce risky hazards associated to human beings. An excellent design and superior sensing capability of a gas sensor is the major prerequisite to overcome general problems related to conventional gas sensors. Herein, this chapter focuses on the introduction of gas sensors, with a brief history about the sensors, and their classification. Then we will proceed with a description of the basic gas sensing mechanisms of metal oxide based gas sensors, their characteristics and few techniques which may improve the gas sensing response. Finally, the chapter is concluded motivation, objective, and layout of the Thesis.

1.1 DEFINITION

In the nomenclature of chemical elements and compounds, the International Union of Pure and Applied Chemistry (IUPAC) is known as the most prestigious organization committee. According to them, a gas sensor is a chemical sensor based device which converts the chemical information into controlled readable signal. The transformation of chemical information can be a concentration of specific sample component to total composition investigation. Also, the chemical information may arise from the chemical reaction of analyte or from the physical characteristics of the system explored [Hulanicki *et al.*, 1991]. Basically, a chemical sensor is made up of two segments, which are called as receptor and transducer. The receptor converts chemical information into a form of energy and that energy is detected by the transducer. Furthermore, the transducer transforms this energy into electrical form. The chemical sensors can be categorized in a several ways. Among all, one of the categories of chemical sensor utilizes the working principle of a receptor. Thus, differentiations involved in the working principle of a receptor function. Such sensors include chemical sensors, biochemical sensors, and physical sensors. In chemical sensors, the reaction happens between the target molecules and the receptor, while the biochemical sensor is also a type of chemical sensors where the target molecules are biomolecules like protein, vitamin, and DNA. Biochemical reaction occurs in the biochemical sensors. Lastly, there is no chemical reaction that takes place at the receptor part in physical sensors, and the signal mainly involves temperature, mass, refractive index, and absorbance [Hulanicki *et al.*, 1991].

1.2 SHORT HISTORY OF GAS SENSORS

The presence of toxic and harmful gases has badly affected human beings. Therefore, early detection of these gases has become mandatory to avoid accidents. Till now, the early detection techniques in the available sensors were less precise. The journey of gas sensor initiated from a cute bird named “canary” in the early 1930s. Usually, the coal miners brought canary inside the mines as their early warning system to remain protected from hazardous gases. This bird was known to have a singing nature. Whenever the miners brought canary

inside the mines, the bird stops singing or die after expose to these gases, and the miners used to save their lives from this signal. However, the first gas detector was the flame safety lamp in industrial age, invented by Humphry Davy in 1815. It was also used to protect the miners as the early detection system in coal mines. Basically, an oil flame with adjusted height in fresh air used to burn in the flame safety lamp. The miners marked the line or height of the flame in the flame safety lamp before they entered into the mines. If there was an oxygen deficient region, the flame went below the line, and if flame went above the lines it meant that there was a place inside the mine which was oxygen enriched. Also, flickering with different colors predicted the presence of other gases. Till then, there were some gas detectors but they were not able to detect precisely at low concentration. After that, the catalytic combustion type gas detector was invented in the early 1920s. This detector mainly used to detect combustible gases and its working principle was based on the variation of temperature when gas interacts with it. The detector comprised of a platinum wire (active) and coupled with a catalyst. The whole device is formed of the Wheatstone bridge circuit in which one part is active and second part is reference. When combustible gas is exposed to the catalyst embedded Pt wire, it increases the temperature of the wire due to increase in resistance of the active region. Contrastingly, the resistance remains unchanged in reference part. Thus, the overall change in resistance will lead to increase in the temperature of the device, and therefore the concentration of the target gas can be detected by output voltage of Wheatstone bridge. After some time, the gas detector became popular when researchers found the use of semiconductor oxide material as the sensing layer for the detection of combustible gases in 1962 [Seiyama *et al.*, 1962]. The popularity of these sensing layers was mainly due to their increased conductivity at high temperature. Taguchi and his co-workers were involved in commercialized tin oxide based gas sensors at Figaro Engineering Inc. [Taguchi *et al.*, 1971]. Furthermore, they enhanced the sensitivity of the sensors by using noble metals. Later on, many researches had started gas sensing studies with other semiconductor oxide materials and proposed the mechanism for better understanding about this area. Then other investigations came up to develop gas sensors for other target molecules like oxygen and humidity. In 1970s, the ion selective field effect transistor (ISFET) was also discovered and the device structure was like MOSFET having no gate region and presence of an insulating membrane [Bergveld *et al.*, 1970]. This insulating membrane was used to sense the target ions and their signal was then converted in the form of current. Recently, advancement of gas sensor technology led to the development of "electronic nose" [Gardner *et al.*, 1994]. Nowadays, several nanomaterials like 1D (carbon nanotubes, nanorods, nanowires) and 2D (graphene, MoS_2, WS_2) have been combined with metal oxide semiconductor to further enhanced the sensitivity of gas sensors [Bhati *et al.*, 2019].

1.3 NEED OF GAS SENSORS

A large number of inventions have been done by the scientific community worldwide, and the technology thus discovered makes our life styles luxurious and simple. But there are some drawbacks along with these luxurious items like environmental pollution, and emission of toxic, bad odour combustible gases produced by heavy machines, vehicles, and many industries. From the point of view of industries, there are various gases that have been used for processing of raw materials, and some of them are byproducts such as NO_2, SO_2, H_2S, NH_3, CO_2, CO, and NO. These gases are highly responsible for air pollution and are affecting human beings. While LPG is commonly known as a domestic purpose gas or cooking gas, its leaking in the open environment may severely impact human health. On the other hand, hydrogen (H_2) gas is widely used in space, automobile, chemical factories and crude oil refining process. However, it has some adverse effect, when it is exposed to the atmosphere, as it explodes if there is any sparking present in the environment. Thus, monitoring of these gases is mandatory to avoid the risk even at low concentration. Consequently, the necessity of gas sensors arises in day to day life. The gas sensors are used in several fields ranging from industrial to domestic purpose depending upon the type of gases. Nowadays, three types of gas sensors are required depending on the chemical properties of the desired gas. For example, O_2 gas sensor is needed

for combustion engine. Second, toxic gases like NO_2 and H_2S should be detected even at low concentration (1 ppm), and the design of such type of gas sensors is required. Thirdly, there is need for flammable gases such as H_2 and CH_4 based gas sensors to avoid unwanted explosion in environment. Therefore, detection of these gases is highly required, and one needs to develop highly sensitive and selective gas sensors. However, still efforts are being done to increase the sensitivity and selectivity of gas sensors, like doping of transition metals, noble nanoparticle decoration, and the use of 2D nanomaterials with pristine gas sensors.

1.4 CLASSIFICATION OF GAS SENSORS

The classification of gas sensors are generally based on their sensing mechanism and listed as below:

1.4.1 Electrochemical

The working principle of electrochemical gas sensors is based on target gas reactions with the sensors, which subsequently produce the electrical signal. The output of an electrical signal is proportional to the concentration of target gas. An electrochemical sensor comprises of a working electrode (sensing electrode) and counter electrode which is separated by the electrolyte as shown in Figure 1.1.

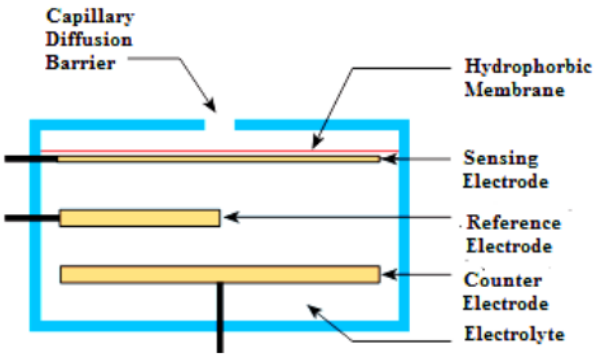

Figure 1.1: Basic design of an electrochemical gas sensor (Source: Electrochemical Sensors, (www.intlsensor.com))

The electrolyte material is responsible for moving the ionic charges in between the electrodes. Initially, when the target gas interacts with the sensor, it has to come across a small capillary shaped membrane, and then diffuse through the hydrophobic barrier. Finally, the gas reaches the sensing electrode surface. During the entire process of gas sensing, it should be noted that a proper amount of gas concentration may react with the sensing electrode while the electrolyte material should not come out from the sensor [Yunusa *et al.,* 2014]. An oxidation or reduction mechanism occurs when the target gas is reacting with the surface of the sensing electrode after passing through the hydrophobic membrane. These electrode materials provide catalytic reaction during gas reaction with it. It means a resistor is connected between both the electrodes, and current is proportional to the gas concentration which flows between the anode and the cathode. Also, current is produced in this process, and thus electrochemical gas sensor is known as the amperometric gas sensor. In this gas sensor, a reference electrode is also attached whose aim is to maintain stable and constant potential at the working electrode during the entire electrochemical process, which mainly occurs due to continuous reactions at the electrode. There are few drawbacks of the electrochemical sensors such as lack of long term stability (1-3 years), and poor capability to sense the gases which are not electrochemically active.

1.4.2 Acoustic Wave

As the name implies, acoustic wave sensors work on the basis of acoustic wave as their detection method. This acoustic wave propagates on the surface of sensor material, and then any kind of changes in the propagation path characteristics will lead to change in the wave velocity or the amplitude of the wave [Mujahid *et al.*, 2017]. The corresponding change in velocity can be detecting by using the frequency of a sensor and this is also related to the gas analyte. The acoustic wave sensor generally comprises of a receptor (sensitive element to the target gas) and a transducer (converts signal from gas concentration into electrical form). The receptor film is deposited on the vibrating surface and any change on the receptor film occurs in the form of mass and thickness when an analytic gas is exposed on it. The change in mass and thickness directly affects the wave amplitude, vibration frequency, and phase shift, and this change is directly proportional to the incoming gas concentration. The working principle of the acoustic wave sensor is based on the transduction method [Liu *et al.*, 2018]. Initially, the mechanical wave is converted from the input electrical signal by the sensor and henceforth, the mechanical wave is reconverted into an electrical form. The transduction process in this sensor is used by interdigitated transducer (IDT) which is based on the piezoelectric effect. The IDTs can be made by using the Pt, Au and Al metal. In a typical surface acoustic wave (SAW) sensor are comprised of two IDT (one is as an input and second one works as output) with spacing between two IDT which is known as delay line as shown in Figure 1.2.

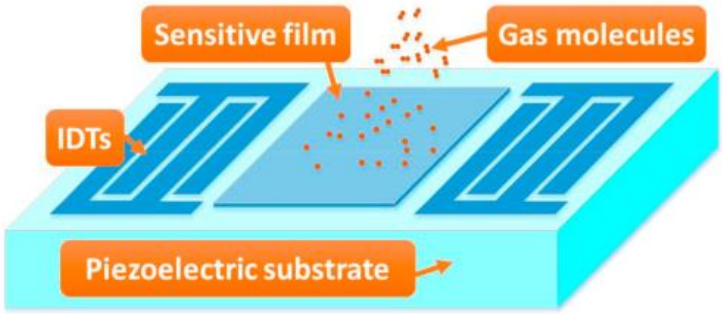

Figure 1.2: Schematic diagram of SAW gas sensor (Source: Liu *et al.*, 2018)

Usually, a gas sensitive layer is deposited across the delay line and change in the acoustic wave is observed when gaseous species are interacting on the gas sensitive layer. This change is detected by the output of IDT in the form of an electrical signal.

1.4.3 Optical

The optical gas sensors are basically working on the fact that the interaction between the sensing material and target gas leads to change in optical properties [Bogue, 2015]. Also, one of the most prominent types of optical gas sensor is the non-dispersive infrared (NDIR) gas sensor. The sensor is designed in such a way that the change in IR radiation intensity is measured in the presence of gas molecules because the gas molecules have absorption capability of infrared light. Figure 1.3 shows the schematic diagram of NDIR gas sensor.

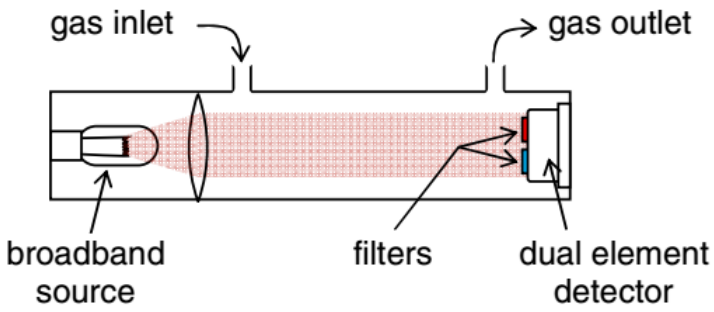

Figure 1.3: Schematic diagram of NDIR gas sensor (Source: Hodgkinson *et al.*, 2013)

The sensor structures comprises of a light source (IR emitter), detector, optical filter, inlet/outlet port for gas molecules and a gas chamber. Initially, a light source emits IR light inside the gas chamber, and the intensity of light is measured by the IR detector followed by optical filter. As the gas molecules absorb IR light, it results in change in the intensity of incoming IR light. While unchanged IR light is blocked by optical filter (bandpass filter) and consequently, a change in IR intensity is measured by the detector [Hodgkinson *et al.,* 2013]. NDIR gas sensors are typically expensive due to the availability of laser source and IR detector inside the gas chamber. Another type of optical gas sensor is based on surface plasmon resonance (SPR) which is closely related to the refractive index near the surface of the sensor.

1.4.4 Capacitance

The capacitive based gas sensor relies on the alteration in permittivity of the dielectric material during exposure of target gas. The device structure is mainly composed of dielectric layer (sensing material) and electrode.

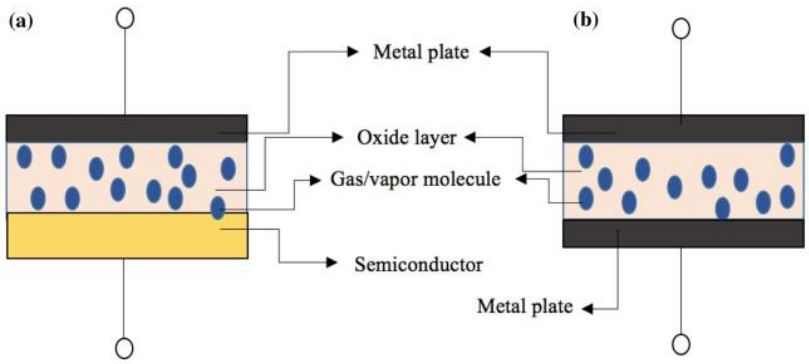

Figure 1.4: Basic device structure of capacitive gas sensors (a) MOS (b) MOM (Source: Bindra *et al.*, 2018)

Moreover, there are two types of structures available for capacitance gas sensors which include metal/oxide/semiconductor (MOS) and metal/oxide/metal (MOM) as shown in Figure 1.4 (a-b). When target gas comes in contact with the sensor, there is change in permittivity, sensor area, or thickness. This will lead to increase or decrease in the capacitance of the sensor depending upon different dielectric constant values of a sensing material and target gas. Apart from this, the nanostructured material as a sensing layer is also an efficient way to increase the sensing response of the capacitive gas sensor due to high surface area and more gas absorption capability [Li *et al.,* 2007].

1.4.5 Calorimetric

Calorimetric gas sensors are generally solid state detectors in which the sensor detects combustible gases as well as gases whose thermal conductivity is different as compared to the conductivity in air. Pellistor is one the most important gas sensors in the calorimetric. The word pellistor is made of two words "pellet" and "resistor". The detector element in pellistor is a ceramic pellet which is combined with a catalytic material. The resistance of the pellet changes when a combustible gas is interacting with it. The pellistor is categorized into two types. First one is catalytic, and second one is thermal conductivity [Yunusa *et al.,* 2014]. Similarity between both types of sensors is their detecting property, like change in temperature can be measured. The heat produced in heating wire will change the resistance of Pt wire during exposure of the combustible gas. This sensor is thus categorized as catalytic type gas sensor as shown in Figure 1.5.

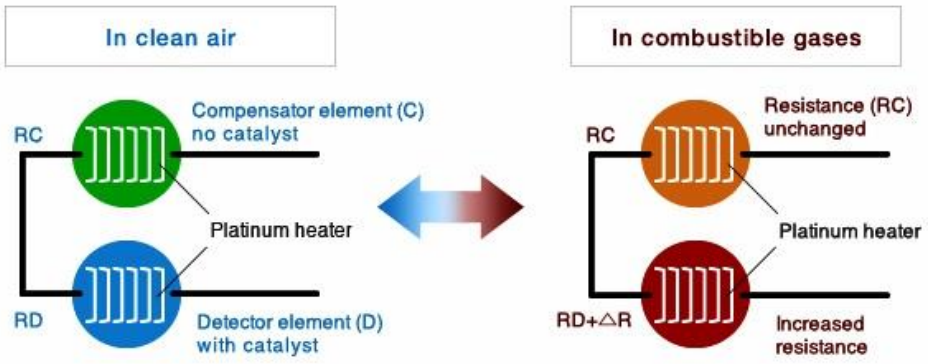

Figure 1.5: Schematic representations of catalytic gas sensors in clean air and combustible gas (Source: https://instrumentationtools.com/catalytic-type-gas-sensor-principle)

The increase in temperature occurs mainly due to the catalytic oxidation when a combustible gas reacts with Pt wire. The whole device is arranged in Wheatstone bridge in which one resistor (active or catalytic Pt wire) is active and another resistor is inactive (compensator). When a target gas is exposed to this sensor, the temperature of the detector or active element increases, while the temperature of an inactive part remains unchanged, which leads to imbalance in the Wheatstone bridge circuit. Therefore, the corresponding output voltage is proportional to the gas concentration. In case of thermal conductivity based gas sensors, the heat dissipation is measured in presence of target gas and correspondingly, the gas concentration of the desired gas is detected based on their thermal conductivity value [Tardy *et al.,* 2004]. These types of sensors are cost effective and simple but they are less sensitive and selective towards other combustible gases.

1.4.6 Metal Oxide (MO_x)

Metal oxide (MO_x) semiconductor based gas sensors are commonly known as solid state gas sensors in which the sensing material is metal oxide. These kind of gas sensors are simple, cost effective, and highly capable of detecting low concentration of target gas. The resistance of the MO_x changes when a target gas interacts with it at a particular temperature. There are several MO_x such as ZnO, SnO_2, TiO_2, CuO, MgO, Fe_2O_3, NiO, V_2O_5, WO_3 etc. The electronic structures of different MO_x are usually different and can be categorized into two types, which include non- transition MO_x and transition MO_x. Also, the most commonly MO_x material for gas sensing application is n- type such as ZnO, SnO_2, TiO_2 and V_2O_5 [Neri *et al.,* 2015]. These gas sensors are highly sensitive and selective for reducing gases like H_2, CH_4, H_2S and oxidative gases such as NO_2 and SO_2 [Sun *et al.,* 2012]. Apart from this, MO_x nanostructured materials are far better than bulk MO_x as a gas sensor due to their superior qualities like large surface area and more absorption sites for target gas. Such types of nanostructured materials enhance the gas sensing response of gas molecules at low concentration; along with reduction in power consumption. However, selectivity and high operating temperature for these MO_x based gas sensors are the key issues, and researchers has been extensively studying different ways to overcome these drawbacks as well.

1.5 BRIEF COMPARISON OF GAS SENSORS

Till now, several types of gas sensors have been investigated according to their different sensing mechanisms. A brief comparison of all gas sensors with their merits and demerits are shown in Table 1.1.

Table 1.1: Relative comparison of advantages and disadvantages of different types of gas sensors

Classification of Gas sensors	Advantages	Disadvantages
Electrochemical	• Lower detection limit • Low power consumption	• Lack of long term stability • Cross sensitivity
Acoustic Wave (SAW)	• Long life time	• Sensitive to environmental changes • Less sensitive
Optical (NDIR)	• Long life time • Not affected by environmental changes	• High power consumption • Miniaturization issues • High cost
Capacitance	• Low power consumption • High accuracy • Temperature independence	• Less effective in humid condition • Parasitic capacitance
Calorimetric (Pellistor)	• Low cost • High stability • Low limit detection	• Low selectivity • Hazardous due to catalyst poisoning and ignition
Metal Oxide	• Good sensitive • Long life time • Short response time • Low cost • Wide range of incoming gases	• Poor selectivity • High power consumption • Affected by environmental factors

Among all, MO_x based gas sensor exhibits superior qualities like low cost, short response time, and good sensitive to a wide range of target gases. Thus, keeping all technological aspects of a gas sensor in mind, the aim of this Thesis is to fabricate gas sensors with suitable and facile approaches so as to further enhance the sensitivity of MO_x based gas sensors. The enhancement in sensitivity of MO_x gas sensors can be done by modification of nanostructures via doping, addition of noble nanoparticles, and formation of p-n heterojunction. These techniques are widely used in improving the sensing performance of MO_x gas sensors and making them cost effective for low power consumption based devices.

1.6 GAS SENSOR CHARACTERISTICS

The gas sensing is basically a surface phenomenon and mainly depends on the type of gas sensing material and nature of the target gas. There are some of the key factors such as sensitivity, selectivity, response time, recovery time, long-term stability, reproducibility and detection limit, for which the gas sensors can be studied. For an excellent gas sensor, the sensitivity and selectivity should be high while the response time, power consumption, and operating temperature should be low [Bochenkov *et al.,* 2010]. A brief discussion about gas sensor characteristics is shown below.

1.6.1 Sensitivity

The relative change in resistance/current/voltage in air to the change in presence of target gas is known as sensitivity or relative response of a sensor. There are various forms that represent the sensitivity of a sensor. On the other hand, the relative change in resistance/current/voltage to the base resistance/current/voltage of a sensor is called the relative response or sensitivity. It can be represented as [Kumar *et al.,* 2015]

$$S=\left(\frac{Ra-Rg}{Ra}=\frac{\Delta R}{Ra}\right)\ or\ \left(\frac{\Delta V}{Va}\right)\ or\ \left(\frac{\Delta I}{Ia}\right) \quad (1.1)$$

where R_a, V_a, and I_a are the resistance, voltage, and current in air, respectively. While the relative change in resistance, voltage, and current can be denoted as ΔR, ΔV and ΔI, respectively.

1.6.2 Selectivity

The ability of the sensor to exhibit high sensitivity towards a particular gas among the presence of many interfering gases is known as the cross sensitivity or selectivity. For an ideal gas sensor, the selectivity should be high at the same operating conditions. Apart from this, the sensor should be able to sense even at low concentration of the target gas.

1.6.3 Response and Recovery Time

The response time is defined as the time required by the sensor to reach 90% of the saturated signal when introduced to a target gas. Whereas, the time required by the sensor to reach 90% of its original value or baseline signal after removal of target gas, is known as the recovery time [Hung *et al.,* 2009]. In order to have an excellent gas sensor, both response and recovery time should be low.

1.6.4 Detection Limit

The ability of a gas sensor to detect the least possible target gas concentration is known as detection limit. The detection limit for any gas sensor should be high. On the other hand, the gas sensor performance is also noticed by its lower limit of detection (LOD). Lowest LOD means that detection of gas sensor is possible with the lowest concentration of gas.

1.6.5 Reproducibility

The gas sensor should be reproducible or the output characteristics (sensitivity and selectivity) should be similar to the results which were taken previously for the same sensor at same operating condition.

1.6.6 Long-Term Stability

It is the ability of a gas sensor by which the sensitivity, selectivity, response, and recovery remains almost same over a period of time at same operating conditions. Thus, long term stability of any gas sensor should be high.

1.7 STRUCTURE OF GAS SENSORS

MO_x based gas sensors comprise of four types which include metal electrode, sensing layer, heater, and substrate. The sensing layer or MO_x is sensitive towards the gas molecules, and the resistance of the gas sensor changes during exposure of target gas. The optimum temperature of the gas sensor is given by the heater which is connected externally or may be internally in the form of microheater. Nowadays, the MO_x based gas sensor is being fabricated in different configuration such as coductometric and field effect transistor (FET) which is displayed in Figure 1.6. The fabrication of FET type gas sensor is complex because single or an array of 1D MO_x nanomaterials are usually fabricated in between the source and the drain for formation of conducting channel.

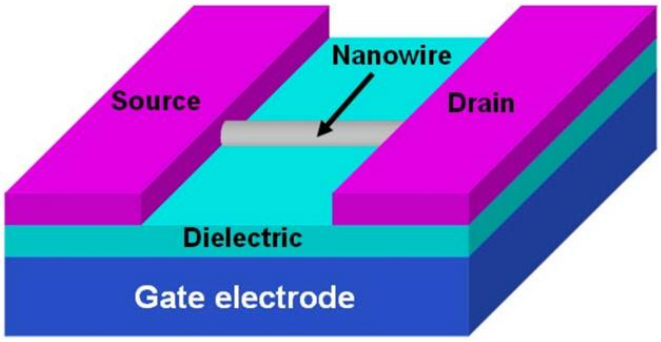

Figure 1.6: Schematic diagram of FET based gas sensor where nanowire (1D nanostructure) is placed in between the source and drain (Source: Huang *et al.*, 2009)

While, the conductometric gas sensors are easy to fabricate and widely used in several applications. Here, two types of gas sensors in conductometric type are used, for example cylindrical and planner type as shown in Figure 1.7 (a-b) [Sung *et al.*, 2012]. In cylindrical type, alumina ceramic tube or small cylinders are employed as the substrate to deposit the MO_x sensing layer in the form of paste.

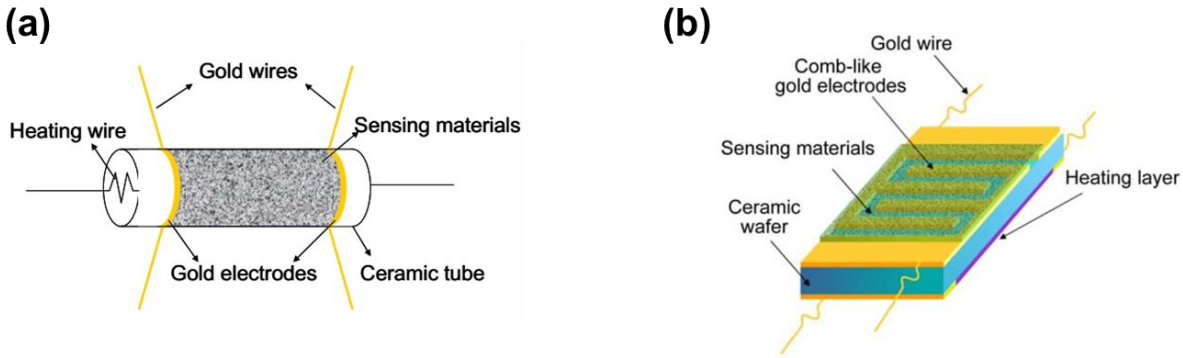

Figure 1.7: Schematic device structures of metal oxide gas sensors (a) ceramic tube (Taguchi type) (b) Planner type gas sensors (Source: Sung *et al.*, 2012)

The thick film of MO_x as a sensing layer is mostly deposited by screen printing. A heating wire is placed inside the alumina tube to provide heating to the sensing layer. Such types of sensors are also known as Taguchi sensors. These sensors have some disadvantages like more power consumption due to thick MO_x layer and inability to keep MO_x sensing layer in planner form on the ceramic tube. In planner type gas sensor, a thin/thick film can be fabricated onto a planner substrate (mostly Si/SiO_2/flexible substrate). The predominant feature of the sensor is that it gets uniformly heated with low power consumption and good thermal isolation as compared to Taguchi type sensors. The planner type gas sensors are also subcategorized depending upon the different electrode structures (circular pattern, rectangular pattern, and interdigitated type).

Some of planner type gas sensors can also be realized into the involvement of heater in such a case where microheater is placed to provide uniform heating to the sensing layer.

1.8 TYPES OF MO_x GAS SENSORS

There are several types of MO_x which can be distinguished according to their electronic structures. In general, MO_x are divided into two types: (a) transition MO_x (NiO, Cr_2O_3, TiO_2, and V_2O_5) (b) non-transition MO_x, which can further be classified into two types: (b-1) pre-transition MO_x (MgO and Al_2O_3) and (b-2) post-transition MO_x (SnO_2 and ZnO) [Korotcenkov, 2007]. Transition MO_x that have multiple oxidation states and d^0 configuration of MO_x gathers utmost attention in gas sensing applications. On the contrary, pre-transition MO_x are quite inert and have large band gaps. Therefore, formation of electrons and holes in such types of MO_x is not easy, and results in rare uses of gas sensors. In case of post transition MO_x, d^{10} configuration based MO_x are one of the most popular in the gas sensor field. It is well known that MO_x are of two types (n-type and p-type) based on their conduction type. The majority charge carrier in n-type is electrons whereas holes are the majority charge carrier in p-type MO_x. Hence, the gas sensing behaviour of both type materials is different. Oxidative gas species such as O_2, NO_2, and SO_2 act as acceptor for n-type MO_x and increases the resistance of MOx when interact with it. However, opposite phenomenon can be seen for p-type MO_x in terms of resistance [Liu *et al.,* 2007], while the reductive gases (H_2, NH_3, CH_4, CO) act as donors to n-type MO_x and decrease the resistance. According to the survey, n-type MO_x based gas sensors have been largely compared to p-type MO_x [Neri *et al.,* 2015]. It has been observed that the sensing response of p-type MO_x based sensors is equal to the square root of n-type MO_x where the target gas and surface morphology of both materials were identical [Zhang *et al.,* 2017].

1.9 GAS SENSING MECHANISM

Gas sensing mechanism of MO_x based gas sensors depends on the modification of the depletion layer on the MO_x surface. Oxygen molecules are adsorbed on the MO_x surface in presence of atmospheric air. Therefore, accumulation of oxygen ions take place on the surface of MO_x caused due to the removal of electrons from the conduction band of MO_x which leads to rise in the resistance of MO_x (for n-type). The gas sensing mechanism can also be interpreted using band bending theory. Oxygen ions adsorbed on the surface of MO_x increase the band bending in upward direction in atmospheric oxygen due to high electronegativity of oxygen molecules, thus increasing the barrier height [Dey, 2018]. The adsorbed oxygen ions such as O_2^-, O^-, and O^{2-} on MO_x highly rely on operating temperature [Ranwa *et al.,* 2014]. In addition, UV light illumination on MO_x can also increase reaction kinetics at lower temperature as compared to thermally activated MO_x. When reductive gases such as NH_3, H_2, HCHO, and CH_4 are interacting with chemisorbed oxygen ions on MO_x surface, it reduces the resistance. This is due to donation of free electrons from oxygen ions to the conduction band of MO_x which causes decrease in the barrier height. On the other hand, the behavior of MO_x (p-type) for oxidative gases such as NO_2 and CO_2 is a complete reverse to the behavior of the above-discussed reductive gases [Dey, 2018].

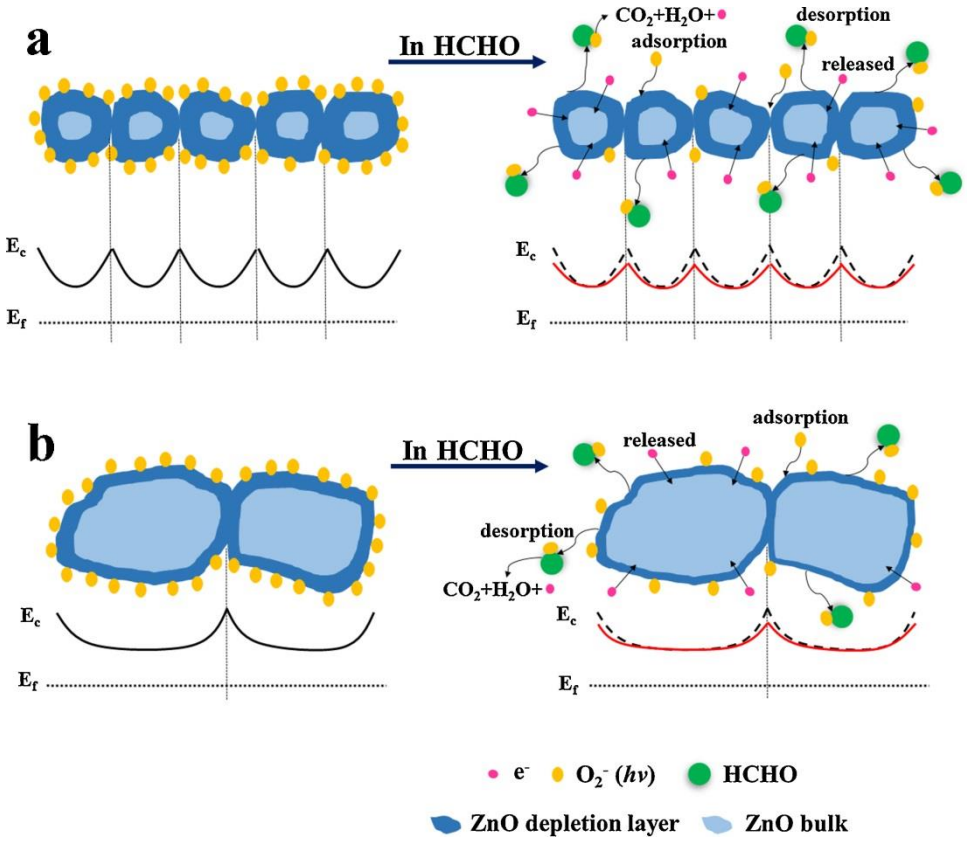

Figure 1.8: Gas sensing mechanism of ZnO nanofibers under UV illumination: (a) ZnO nanoplates and (b) ZnO nanoflowers in the presence of HCHO (Source: Cui *et al.*, 2016)

Grains boundaries in thin films like structures are mainly responsible for modification in electrical behaviour, while the electrical behaviour of 1-D nanostructures is mainly followed through the entire surface. Therefore, large depletion layer and high surface area of 1-D nanostructures of MO_x will result in sufficiently higher resistance as compared to thin films under the exposure of target gases. Figure 1.8 (a-b) displays gas sensing mechanism for nanofibers, nanoplates, and nanoflowers to HCHO gas by UV activation at room temperature [Cui *et al.*, 2016]. Among all, the sensing response was the highest for nanofibers, which was attributed to small grain size. Thus, the formation of large depletion layer occurred as shown in Figure 1.8 (a). On the contrary, the large particle size of nanoplates and nanoflowers resulted in a small change in the depletion layer, and corresponding to lower sensing response than nanofibers (Figure1.8 (b)). However, the change in barrier height was greater for nanofibers as compared to nanoplates and nanoflowers [Bhati *et al.*, 2019].

1.10 KEY FACTORS OF MO_x GAS SENSORS

There are some key factors on which MO_x based gas sensors are highly dependent, like grain size, operating temperature, and humidity, and whose detailed explanation is given as follows:

1.10.1 Grain Size Effect

It is most obvious that the sensors having small crystalline particles show high sensing response. Gas sensors based on nanostructured materials also confirm that sensitivity can be improved using fine particles (act as active material) [Wang *et al.*, 2010]. Thus, the effect of particle size (D) on sensitivity can be explained by comparing with the thickness of the depletion layer (L). Rothschild *et al.* reported sintered SnO_2 and found that the D>20 nm based sensor's sensitivity was nearly independent of grain size; while sensitivity increased with

decreased D<20 nm; and increased drastically with D<10 nm [Rothschild *et al.*, 2004]. The sensor response influenced by grain size can be understood using the schematic Figure 1.9.

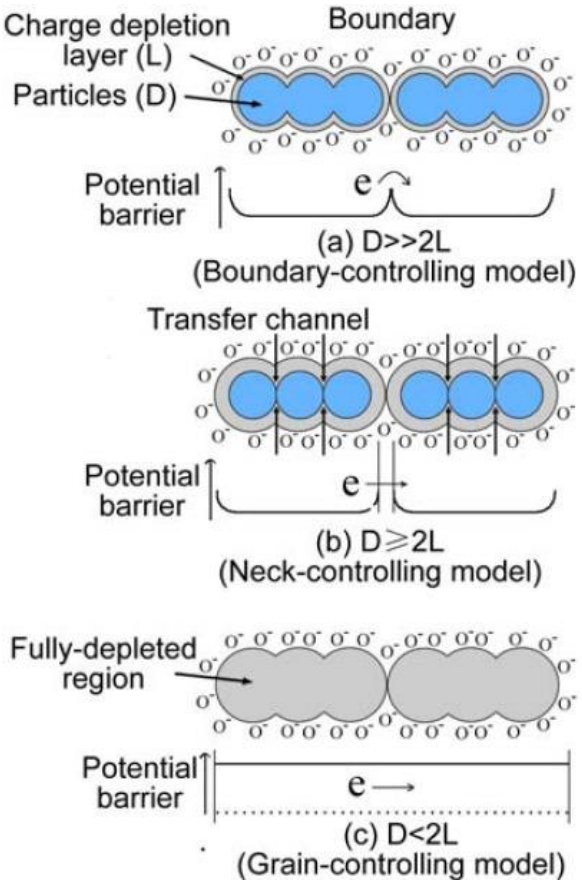

Figure 1.9: Schematic diagram of the effect of grain size of MO_x for gas sensing response (Sun *et al.*, 2012)

In this model, the sensor comprises of small grains which also connect with their adjacent grain by necks. Then, interconnected grains are agglomerated to each other and also connected with their neighbours by grain boundaries. For an n-type MO_x based sensor, three types of possibilities arise according to their grain size (D) and width of depletion layer (L), which is formed on the grain surface caused by chemisorbed oxygen ions.

(a) D>>2L: The sensors having large grain size usually show low sensing response as most of the volume of crystallites is less affected due to limited surface of sensor available for gas interaction as shown in Figure 1.9 (a). When exposing to gas, the conductivity of sensor for D>>2L is dominated through the grain boundaries barrier for inter-grain charge transportation from one grain to another grain. Hence, the electrical conductivity of sensors relies exponentially on barrier height.

(b) D≥2L: In this case, the depletion region spreads more on the grains, as the grain size decreases, which leads to decrease in the core region, which is actually a conductive region of the grain. For this situation, the depletion regions are formulated on the neck of each grain aggregate, followed by conduction through the neck which can be seen in Figure 1.9 (b). Here, the conductivity of the sensor relies not only on the grain boundaries barrier but also on the cross section area of the conductive channels in the grains. Such type of sensing mechanism is known as neck controlled.

(c) D<2L: If the grains size is smaller than the depletion region, the depletion region covers the entire grain, leading to crystallite having fully depleted charge carriers as depicted in Figure 1.9 (c). Consequently, the conductivity decreases with the removal of conduction channel between the grains. Furthermore, the energy bands are almost flat throughout

the structure of the interconnected grains. Since there is no barrier for charge transport, the conductivity as well as sensing mechanism is grain controlled. However, few charges are required from the surface reaction to obtain large alterations in conductivity [Sun *et al.*, 2012].

1.10.2 Operating Temperature

MO_x based gas sensors are highly affected by operating temperature. The adsorption/desorption of oxygen gas as well as target gas depends on operating temperature. Hence, it directly impacts the dynamic properties of sensor such as response and recovery time. Apart from this, chemical decomposition and surface coverage are also affected by temperature. i.e. sensing properties are modulated as the chemisorbed oxygen ions (O^-, O_2^- and O^{2-}) on the surface of MO_x changes at different operating temperature. At low operating temperature, O^{2-} ions are predominantly adsorbed on MO_x. However, O^- ions are adsorbed on MO_x at high operating temperature [Ranwa *et al.*, 2014]. Moreover, operating temperature also change the physical properties of MO_x based sensors such as work function and charge concentration. If the operating temperature of MO_x sensor is high, then charge concentration also becomes high, which leads to increased conductivity of MO_x based sensor. However, it was also found that the sensitivity of the MO_x sensors decreased at higher temperature which was mainly due to decrease in the depletion layer [Kolmakov *et al.*, 2005]. Apart from this, the surface morphology of MO_x based gas sensor also changes at high operating temperature. That is why there should be optimum operating temperature for a MO_x based gas sensor where it responds with high sensitivity.

1.10.3 Humidity Effect

The adsorption of water molecules on the surface of MO_x gas sensor can reduce its sensitivity. There are some reasons for the decreased sensitivity in presence of humidity which are listed as below:

(a) The adsorbed water molecules on sensor's surface decrease the surface area that is available for chemisorbed oxygen ions, and resulting in decreased sensitivity.

(b) The existence of water molecules on the surface of MO_x gas sensor stops the movement of target gas molecules. Thus, decrease in sensitivity and increased response and recovery time can be observed.

(c) Moreover, the reactions between the water molecules and chemisorbed oxygen on MO_x reduces the baseline resistance of the sensor, which leads to reduction in sensitivity [Gong *et al.*, 2006].

(d) Apart from this, long-term occurrence of humidity on MO_x surface will lead to the creation of chemisorbed OH^- ions which continuously degrade the sensing performance of the sensor [Traversa, 1995].

1.11 FACTOR INVOLVED IN IMPROVEMENT IN SENSITIVITY

There are few techniques which can be used to increase the sensing properties of MO_x based gas sensors like metal doping into MO_x, functionalization of noble metal nanoparticles on MO_x surface, inclusion of carbon based nanostructures, making composition of different MO_x nanostructures, UV activation, and e-beam irradiation. This Thesis will comprise of investigation of the techniques which are mentioned above to improve the sensing properties with their possible gas sensing mechanism. For this purpose, ZnO based gas sensor are considered as an example because most of the experimental work in this Thesis has been performed using ZnO.

1.11.1 Metal Doping

Doping of metal element into MO_x is one of the prominent factors which enhance the sensing response of MO_x sensor. Transition metals such as Ni, Co, Fe and Cu, have been largely

used as dopants into MO_x [Zhang *et al.*, 2017; Maswanganye *et al.*, 2017; Bai *et al.*, 2014;Gong *et al.*, 2006]. Dopants not only change the resistance but also enhance the sensing response of the MO_x sensor. These metal dopants also decrease the operating temperature of the gas sensor, improves selectivity, stability, and fast response for target gas molecules [Bhati *et al.*, 2018]. It has been observed that the surface morphology of ZnO has been changed after introduction of metal dopants. The particle size of doped ZnO nanostructures becomes smaller than pure ZnO nanostructures because of further restriction of the movement of crystallites when the boundaries between the dopant and the host material interacts [Maciel *et al.*, 2003]. Hence, the crystal growth stops due to the introduction of dopant element. Gas sensing can be improved due to small-sized particles having high surface area, which results in enhancement of the number of chemisorbed oxygen ions and barrier height. In [Sett *et al.*, 2017], they prepared Co-doped ZnO (0, 2, 4, 6, 8 % Co) nanorods on glass substrate by hydrothermal method.

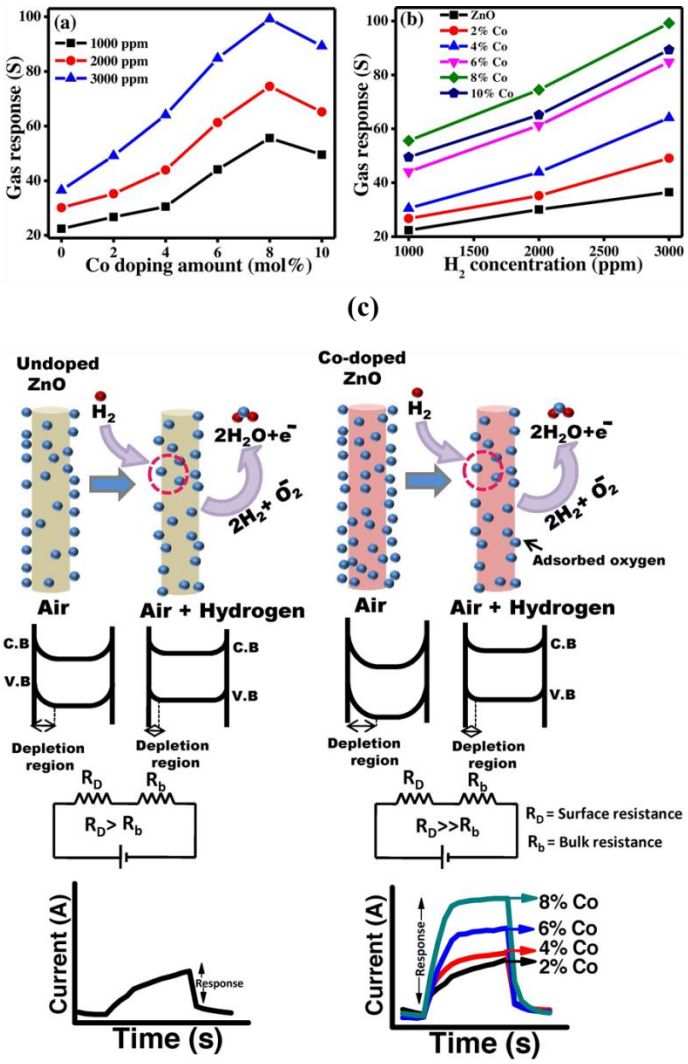

Figure 1.10 (a) Gas response with different Co doping concentration at 300°C, (b) gas response of all sensors for different H_2 concentration at 300°C, and (c) gas sensing mechanism of undoped and Co-doped ZnO NRs (Source: Sett *et al.*, 2017)

Gas sensing response was measured for different concentrations of H_2 at 300°C. It was noticed that the highest sensing response was obtained for 8% Co-doped ZnO nanorods, as shown in Figure 1.10 (a-b). The enhancement in sensing response was due to high surface to volume ratio of nanorods, and large number of surface defects (oxygen vacancies) as depicted in Figure 1.10 (c). Other studies have shown that the sensing response can also be enhanced by the creation of *p-n* junction between *p*-type dopants (Ni, and Cr) and *n*-type ZnO nanostructures [Cheng *et al.*,

2012; Wang *et al.,* 2010]. Table 1.2 represents different metals-doped ZnO nanostructures-based gas sensors at different working temperatures.

Table 1.2: Gas sensing response based on doped ZnO nanostructures at different temperatures

Dopant	Morphology	Synthesis (ZnO) method	gas	Temp. (°C)	Sensing response	Res. time	Ref.
In	3-D ordered macroporous	Template method	Ethanol, 100 ppm	250	~88 (R_a/R_g)	25 s	Wang *et al.*, 2016
Co	Thin film	Spray pyrolysis	NH_3, 100 ppm	RT	3.48 (R_a/R_g)	100 s	Mani *et al.*, 2015
Ni	Nanorods	Hydrothermal	H_2S, 100 ppm	200	45.3 (R_a/R_g)	48 s	Modaberi *et al.*, 2018
Cr	Nano-whiskers array	Spray pyrolysis	H_2, 400 ppm	RT	133 (R_a/R_g)	-	Renitta *et al.*, 2016
Al	nanoparticles	Flame spray pyrolysis (FSP)	Acetone, 10 ppm	450	245 (R_a-R_g)/R_g	3 s	Yoo *et al.*, 2019

1.11.2 Functionalization of Noble Metal Nanoparticles

The gas sensing response can be increased by functionalization of noble metal nanoparticles (e.g., Pd, Pt, and Au) on the surface of ZnO nanostructures [Zhang *et al.,* 2016; Kondalkar *et al.,* 2019; Kim *et al.,* 2019]. Two types of mechanisms are generally used to describe the enhanced sensing response via functionalized noble metal nanoparticles on ZnO nanostructures. The first one is known as "*chemical mechanism*" and the second is "*electronic mechanism*". The "chemical mechanism" is based on the spill-over effect [Dey, 2018]. Functionalized noble metal nanoparticles on ZnO nanostructures stimulate the adsorption /desorption process for oxygen molecules. When oxygen molecules are exposed on these noble metal nanoparticles, they are split into oxygen atoms and distribute on the entire surface. Then, these oxygen atoms take electrons from the conduction band of ZnO and transform themselves into the oxygen ions. Furthermore, the depletion layer enhances on the ZnO surface, which increases the overall resistance of the sensor. When reductive gases are interacted with sensor surface, they react on these catalytic nanoparticles and split on the ZnO surface. Therefore, a large number of oxygen ions are formed to react with the atoms of the reductive gas, and subsequently, there is a large reduction in depletion layer as well as resistance of the sensor, and free electrons are given back to the conduction band of ZnO. Hence, this effect not only decreases the working temperature of ZnO-based sensor, but also enhances its sensing response and selectivity. In the case of "electronic mechanism", a nano-Schottky junction is created between the noble metal nanoparticles and ZnO. This may be due to the movement of electrons towards the nanoparticles which is attributed to difference in work functions. Thus, band bending is formed at the interface of noble metal nanoparticles and ZnO, leading to increase in the resistance of the sensor and its depletion layer.

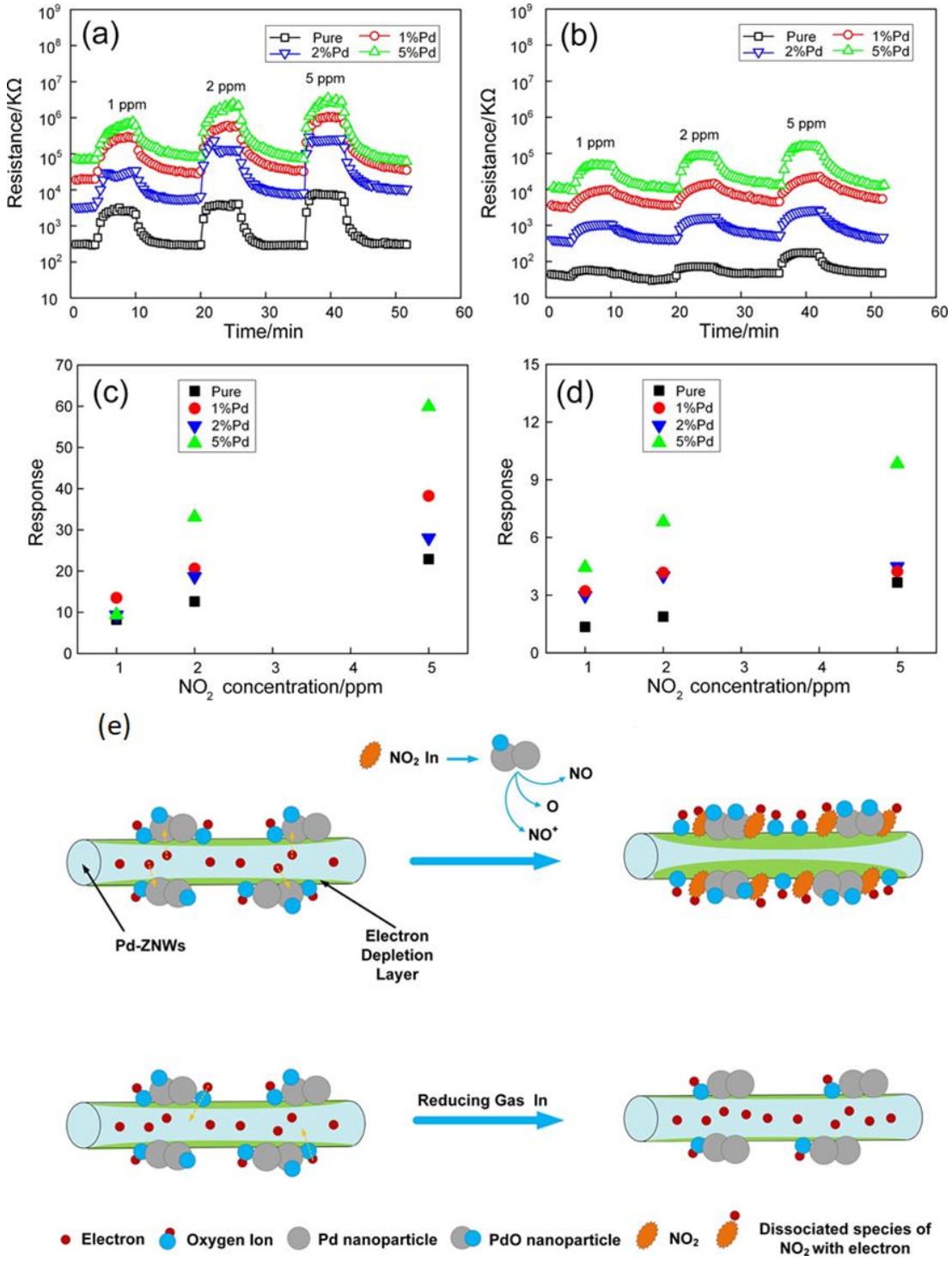

Figure 1.11: Dynamic response of gas sensor under different concentrations of NO_2 for pure ZNWs (150°C) and Pd-ZNWs (100°C) at (a) 30% RH and (b) 60% RH and (c-d) corresponding gas sensor response at (c) 30% RH and (d) 60% RH (e) gas sensing mechanism for Pd-ZNWs under NO_2 and reducing gases (Source: Chen *et al.*, 2019)

Furthermore, Kim *et al.* [Kim *et al.*, 2019] fabricated Pt- and Pd-functionalized ZnO nanowires. The sensors were operated in self-heating mode for reduction in working temperature. It was observed that Pt-functionalized nanowires exhibited a maximum sensing response of around 2.86 for 50 ppm toluene, while Pd-functionalized nanowires revealed a maximum sensing response of 2.20 for 50 ppm benzene at room temperature. The sensing mechanism was attributed to the excellent catalytic behavior of Pt and Pd, resulting in the formation of Schottky barrier that provides more adsorption sites on the sensor surface. The authors [Chen *et al.*, 2019] have grown ZnO nanowires by hydrothermal technique and functionalized them with Pd nanoparticles (0, 1, 2 and 5% Pd) so as to utilize them for NO_2 gas sensing, as can be seen in

Figure 1.11 (a-d). The sensor displayed a high sensing response ~13.5 (R_a/R_g), and a fast response time for 1 ppm at 100°C. The enhanced sensing mechanism was described by the synergistic effect of chemical and electronic mechanisms as shown in Figure 1.11 (e). Table 2.3 shows a comparison of gas sensing response based on functionalized noble metal nanoparticles/ZnO nanostructures at different temperatures.

Table 1.3: Gas sensing response based on functionalized noble metal nanoparticles/ZnO nanostructures at different temperatures

Nano-particles	Morphology (ZnO)	Synthesis method (ZnO)	Gas	Temp. (°C)	Sensing res.	Res. time	Ref.
Pd	Nanorod arrays	Photochemical	H_2, 500 ppm	260	1106 (R_a/R_g)	-	Chang *et al.*, 2013
Bimetallic Au/Pd	Nanowires	Hydrothermal and dipping	NO_2, 1 ppm	100	94.2 (R_g/R_a)	35 s	Chen *et al.*, 2019
Au	Nanowires	Hydrothermal	Ethanol, 100 ppm	380	33.6 (R_aR_g)	3 s	Guo *et al.*, 2014
Ag	Hollow nanocages	Precipitation	Ethane, 100 ppm	250	84.6 (R_a/R_g)	5 s	Zhang *et al.*, 2019
Pt-Au bimetallic	Nanorods	Hydrothermal	H_2, 250 ppm	RT	25 (R_a/R_g)	115 s	Fan *et al.*, 2017

1.11.3 Inclusion of Carbon-Based Nanomaterials

The combination of carbonaceous nanomaterials with ZnO nanostructures is the most effective approach to enhance the sensing response, with high selectivity, and fast response time [Xiao *et al.,* 2018]. Several types of carbon materials are available such as carbon nanofibers (1-D), carbon nanotubes (1-D), graphene (2-D) and its derivatives. Pure graphene-based gas sensors are not employed due to the absence of functional groups and band gap. Thus, the attachment of functional groups on the graphene surface is highly essential to modify the band gap, which provides extra active sites to the target gas molecules [Gupta *et al.,* 2015]. Among all carbon nanomaterials, reduced graphene oxide (rGO)/ZnO-based sensors have been extensively investigated due to their superior qualities such as fast response, excellent sensing response and good selectivity.

The basic idea of enhancement in sensing response depends upon the formation of a heterojunction between carbon materials and ZnO because of different work functions and semiconducting properties. Another reason of enhancement in sensing response is the nanoporous structure of carbon materials that diffuses the target gas molecules. Moreover, the presence of functionalized oxygen groups also gives some active sites to increase the sensing response. In [Abidden *et al.,* 2015], RGO nanosheets (0, 0.04, 0.11, 0.17, 0.44, 0.77, 1.04 wt% RGO)-loaded ZnO nanofibers were proposed via electrospinning method for NO_2 gas. All

sensors were utilized to detect 5 ppm NO_2 at 400°C. It was found that 0.44 wt% RGO-loaded ZnO-based sensors showed the highest sensing response (Figure 1.12 (a-b)).

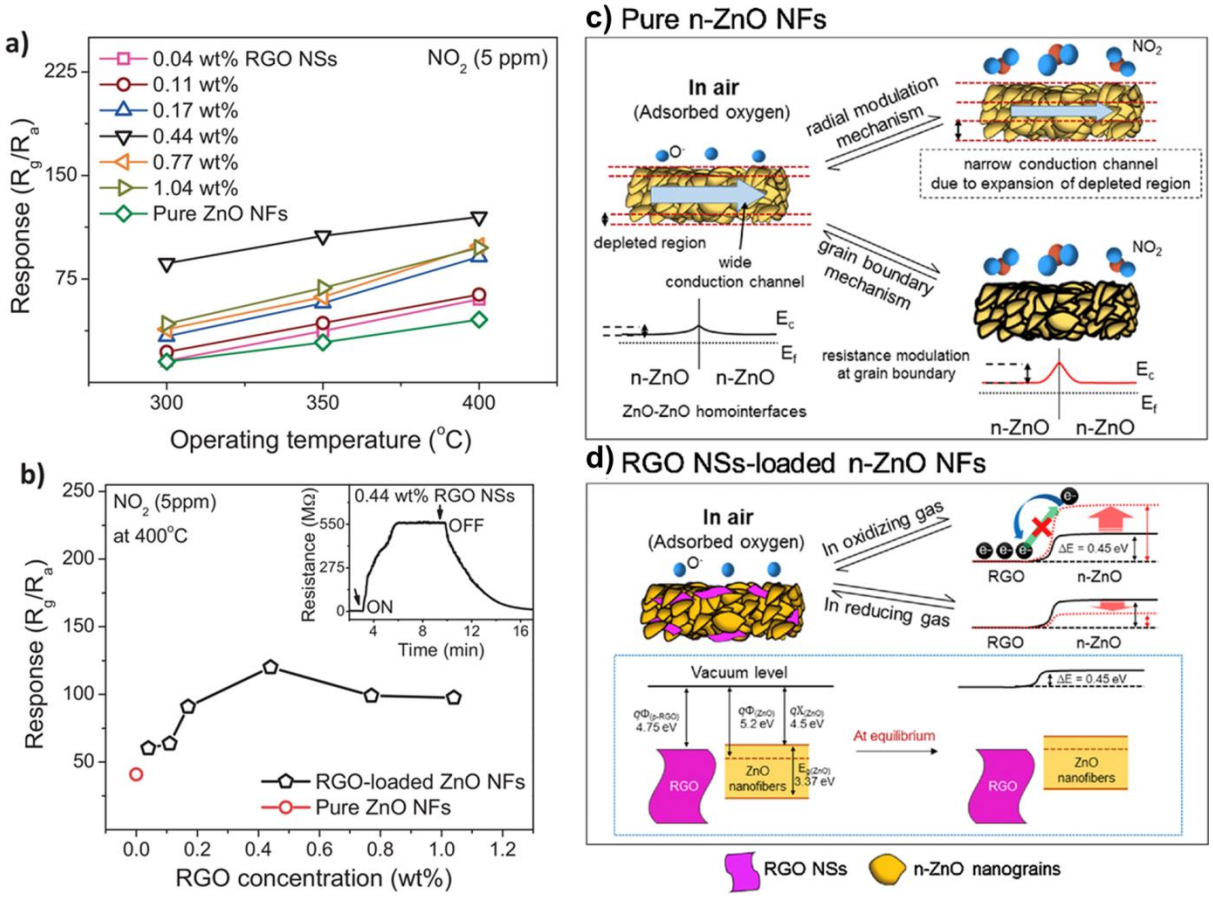

Figure 1.12: (a) Sensors response of 5 ppm NO_2 with different temperatures, (b) sensors response of 5 ppm NO_2 with different RGO concentrations at 400°C, (c-d) sensing mechanism of pure *n*-ZnO NFs and RGO-ZnO heterojunctions (Source: Abideen *et al.*, 2015)

Excellent sensing response as described in Figure 1.12 (c-d) was attributed to the following reasons: (i) surface adsorption/desorption in the presence of air and NO_2; (ii) enhanced depletion layer due to the formation of ZnO/ZnO homointerfaces; (iii) creation of heterointerfaces between RGO (*p*-type) and ZnO (*n*-type) provides more adsorption sites for NO_2 gas; (iv) attachment of functional groups on RGO. Authors in [Schutt *et al.*, 2017] deposited ZnO-CNT hybrid tetrapods for NH_3 sensing. Firstly, ZnO tetrapodal networks were synthesized by flame transport synthesis process and then CNT was attached to ZnO tetrapodal networks using dipping method. They found that the highest sensing response ~6.4 was achieved as compared to other sensors towards 100 ppm NH_3 at room temperature. Table 1.4 shows gas sensing response based on different carbon nanomaterials/ZnO nanostructures at different temperatures.

Table 1.4: Gas sensing response based on carbon nanomaterials/ZnO nanostructures at different temperatures

Carbon nanomat.	Morphology (ZnO)	Synthesis method (ZnO)	Gas	Temp. (°C)	Sensing response	Res. time	Ref.
rGO	nanoparticles	In situ	NO_2,	RT	25.6%	165	Liu *et al.*,

		method	5 ppm		(Ra – Rg)/Ra × 100%		2014
Carbon	nanofibers	Electrospinning	H_2S, 50 ppm	250	102 (R_a/R_g)	-	Zhang *et al.*, 2018
graphene	nanoparticles	In situ method	H_2, 200 ppm	150	3.5 (R_a/R_g)	22 s	Anand *et al.*, 2014
CNT	Nanowires network	Flame transport	NH_3, 50 ppm	RT	430 (R_a/R_g)	-	Lupan *et al.*, 2017
nanoparticle	nanoparticles	grafting	Acetone, 300 ppm	400	~52.5 (R_a/R_g)	-	Tian *et al.*, 2014

1.11.4 Nanocomposites with Different MO_x

A homojunction is created between the particles of ZnO nanostructures, exhibiting sensing response due to ZnO-ZnO barrier height under the exposure of target gases. On the other hand, when two dissimilar MO_x are composited together with different work functions value, electrons will flow from low work function of MO_x to high work function of MO_x until their Fermi levels become equal. Therefore, band bending occurs at the interface of two dissimilar MO_x, creating a heterojunction. This leads to an increase in the overall resistance and barrier height. It has been noted that the nanocomposite of *p*-type and *n*-type nanostructures gives rise to barrier height because of large difference in their work functions. When reductive/oxidative gases are exposed on these heterojunctions, dramatic change in the resistance and depletion layer occurs [Han *et al.*, 2019]. Therefore, the sensing response of ZnO nanostructures can be increased using this technique.

Zhang *et al.* [Zhang *et al.*, 2014] fabricated flower-like *p*-CuO (0, 0.125, 0.25, and 0.5)/*n*-ZnO heterojunction nanorods by hydrothermal technique, and their morphologies can be seen in FESEM images are shown in Figure 1.13 (a-h). They showed that the highest sensing response was observed for 0.25:1 CuO/ZnO nanorod based sensor for 100 ppm ethanol at 300°C. This sensing response was 2.5 times higher as compared to ZnO-based sensor (Figure 2.13 (i)). The enhancement in sensing response was due to the formation of a heterojunction between *p*-type of CuO and *n*-type of ZnO, as shown in Figure 1.13 (j-k). Moreover, a large reduction in barrier height was observed under ethanol vapor. Authors [Katoch *et al.*, 2015] have reported the SnO_2-ZnO composite nanofibers and detected 10 ppm H_2 at 300°C. The increased sensing response to H_2 was due to the formation of the SnO_2-SnO_2 homointerfaces and metallization effect at SnO_2-ZnO heterointerfaces. A complete list of other reported studies on heterostructures-based on ZnO nanostructures is depicted in Table 1.5.

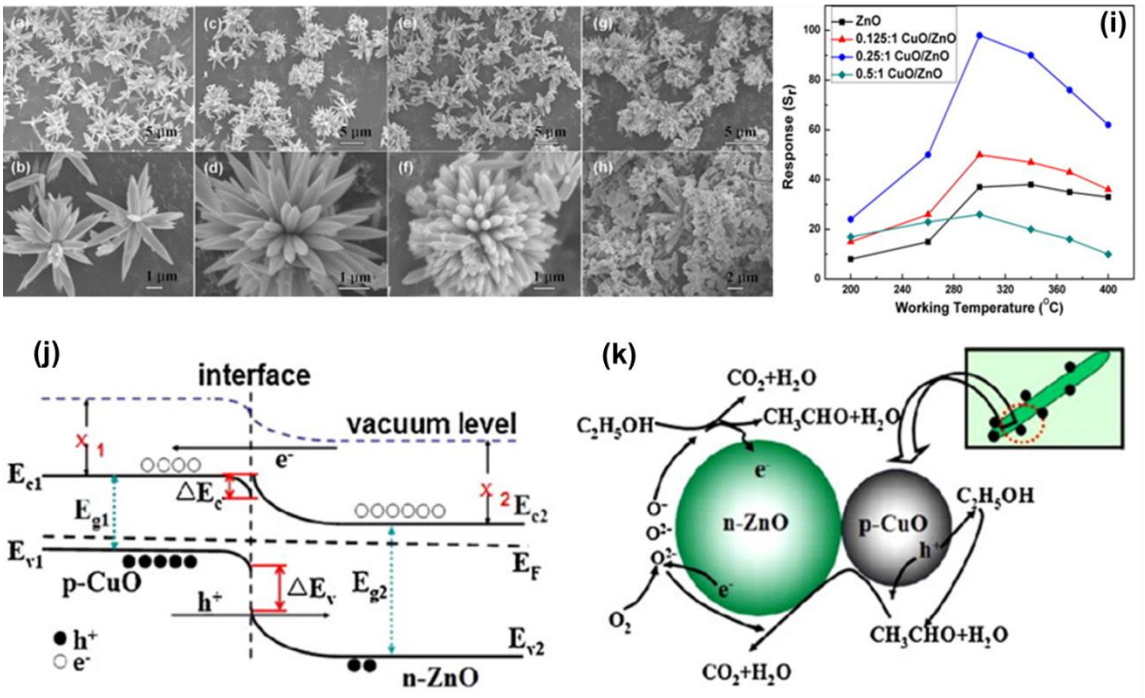

Figure 1.13: FESEM images of all samples: (a,b) pure ZnO, (c,d) 0.125:1 CuO/ZnO, (e,f) 0.25:1 CuO/ZnO and (g,h) 0.5:1 CuO/ZnO, (i) sensing response of all samples for 100 ppm ethanol at different temperatures, and (j,k) sensing mechanism using band bending diagram (Source: Zhang *et al.*, 2014)

Table 1.5: Gas sensing response based on MO_x/ZnO nanocomposite at different temperatures

Metal oxide	Morphology (ZnO)	Synthesis method (ZnO)	Gas	Temp. (°C)	Sensing response	Res. time	Ref.
SnO_2	Nanorods	hydrothermal	Triethylamine, 50 ppm	40	6.8 (R_a/R_g)	~2.0	Ju *et al.*, 2015
SnO_2	Nanofibers	Electrospinning	H_2, 0.1 ppm	350	78 (R_a/R_g)	74 s	Katoch *et al.*, 2015
CuO	Nanofibers	ALD	H_2S, 100 ppm	250	60 (R_a/R_g)	26 s	Han *et al.*, 2019
SnO_2	Nanorods	Hydrothermal	Ethanol, 100 ppm	275	18.1 (R_a/R_g)	3 s	Yang *et al.*, 2019
Fe_3O_4	3-D ordered inverse opal	Template	Acetone, 50 ppm	485	47 (R_a/R_g)	~5 s	Zhang *et al.*, 2017

1.11.5 UV Activation

Gas sensing response of ZnO nanostructures-based gas sensors relies on the adsorbed oxygen ions. The formation of these adsorbed oxygen ions on the ZnO surface strongly depend

upon the working temperature. However, it is not advisable to use the gas sensors at high operating temperature due to the reasons, like modification in sensor's morphology, high power consumption, and reduction of depletion layer on ZnO surface. Hence, high sensing response, good selectivity, and fast response time must be achieved either at low operating temperature or room temperature. As high temperature creates a thick depletion layer on the sensor's surface, UV activation does the same job at room temperature, thus making it one of the most efficient ways to introduce a large depletion layer on the sensor's surface [Chen *et al.*, 2016]. The analogy is based on the generation of electron-hole pairs on the semiconductor materials, where the band gap is less than or equal to the photon energy. On similar grounds, when UV light is incident on the ZnO nanostructures, electron–hole pairs are produced. Under atmospheric air at room temperature, this leads to the adsorption of oxygen molecules on the ZnO surface, and a large number of electrons are extracted from the conduction band of ZnO under the influence of UV light as compared to the number of extracted electrons without UV light. Thus, the formation of depletion layer results in an increase in the resistance and barrier height of ZnO. When reductive gas molecules are interacted with UV-activated adsorbed oxygen ions, captured electrons return to the conduction band of ZnO and decrease the overall resistance [Park *et al.*, 2016].

However, Au nanoparticles on the ZnO surface would also enhance the photogenerated electron-hole pairs via resonant plasmonic effect due to more light absorption capacity of Au nanoparticles [Xu *et al.*, 2018]. As the creation of nano-Schottky barrier takes place between Au nanoparticles and ZnO surface because of their different work functions, hot electrons have enough energy to cross the nano-Schottky barrier from Au nanoparticles to the conduction band of ZnO under the photoactivation process. This leads to the formation of a higher depletion layer on the ZnO surface because of the extraction of more electrons from the conduction band by oxygen molecules under UV light. Consequently, the sensing response increases using decoration of Au nanoparticles on ZnO rather than simply using ZnO nanostructures under UV light. In [Drmosh *et al.*, 2019], the authors deposited Au nanoparticles on an rGO/ZnO heterostructured nanocomposite for room temperature H_2 detection under UV light. They measured H_2 sensing of pure ZnO, rGO/ZnO, and Au/rGO/ZnO with and without UV light at different working temperatures, as can be seen in Figure 1.14 (a-d). Among all sensors, the sensor fabrication based on Au/rGO/ZnO revealed highest H_2 sensing response even at room temperature, while other sensors depicted a low response at high working temperature. The enhanced H_2 sensing response was due to the high surface area of ZnO, creation of rGO/ZnO heterostructures, different work functions between Au and ZnO, and generation of free electrons/holes via UV light (Figure 1.14 (e-g)).

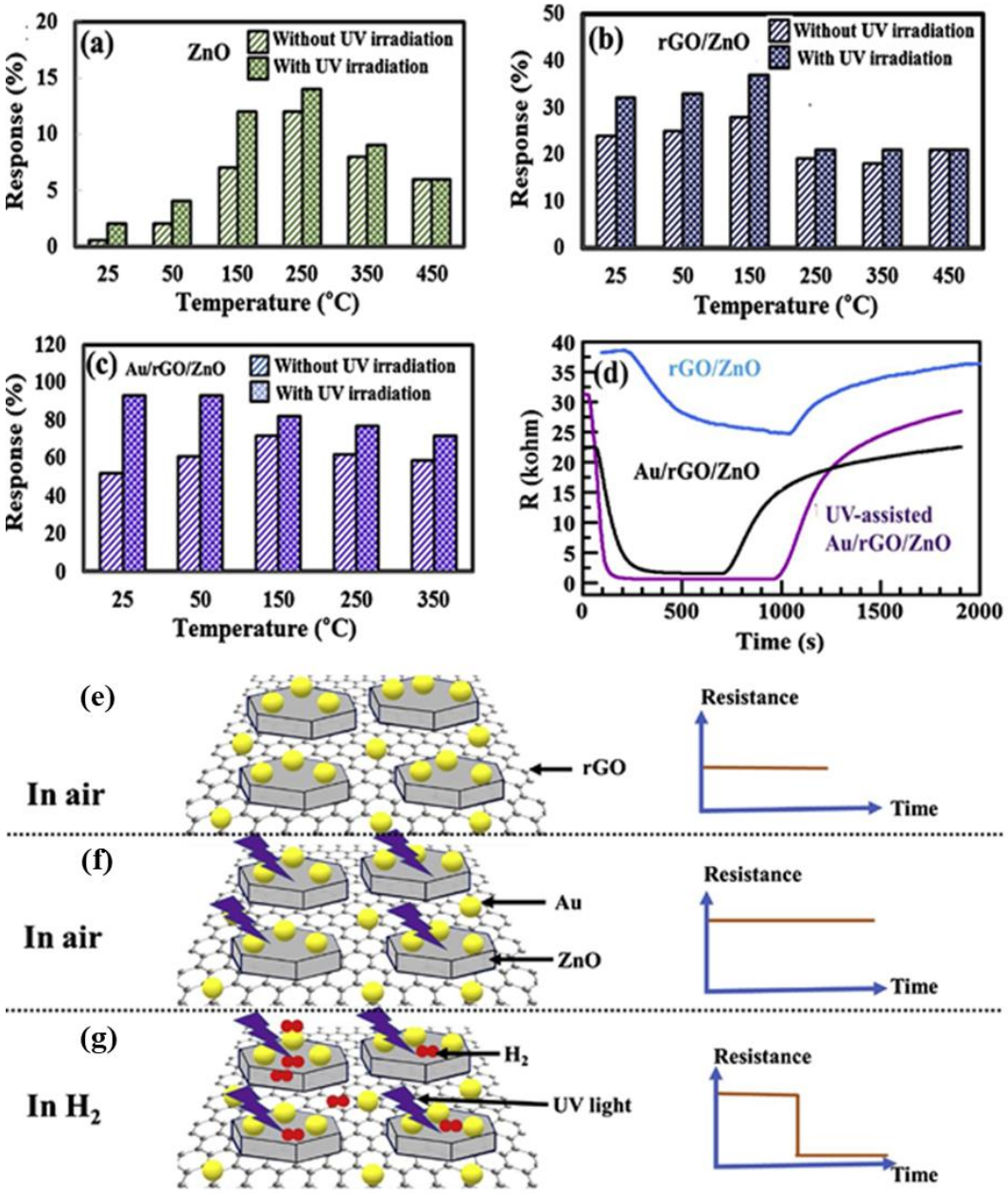

Figure 1.14: (a-c) Comparison of sensing responses for sensors with and without UV irradiation at different temperatures, (d) dynamic responses of sensors under UV irradiation, (e-g) sensing mechanism of Au/rGO/ZnO sensor in (e) air (f) air with UV, and (g) in H_2 gas with UV irradiation (Source: Drmosh *et al.*, 2019)

Authors [Xu *et al.,* 2018] showed a light-activated ethanol vapor sensing of Au nanoparticles-decorated ZnO nanotetrapods. In this case, an improved sensing response was explained by photogenerated electron-hole pairs and localized surface plasmon resonance (LSPR) by using decorated Au nanoparticles under UV light. Other reports show the gas sensing response of ZnO nanostructures at room temperature under UV activation as shown in Table 1.6.

Table 1.6: Gas sensing response based on UV activation for ZnO nanostructures at room temperature

Second material	Morphology (ZnO)	Synthesis method (ZnO)	Gas	Sensing response	Res. time	Ref.

In_2O_3	Film	Co-precipitation	NO_2, 5 ppm	2.21, $(R_g–R_a)/R_a$	-	Espid *et al.*, 2017
Na dopant	Nanoflowers	Solution route	Acetone, 100 ppm	3.35, (R_g/R_a)	18 s	Jaisutti *et al.*, 2017
Granular activated carbon	Nanorods	Hydrothermal	H_2, 200 ppm	23.2%, (R_g/R_a)%	18 s	Saravanan *et al.*, 2017
SnO_2	Polyporous	Water bath	Formaldehyde, 10 ppm	30% $(I_a-I_g/I_g)\times100\%$	-	Jiang *et al.*, 2018
SnO_2	Nanorods	Wet chemical	NO_2, 500 ppm	1266, $(R_g–R_a)/R_a$	-	Lu *et al.*, 2012

1.11.6 High Energy Irradiation

The sensing response can also be enhanced by a post-treatment method, such as high energy irradiation on ZnO nanostructures. These irradiation sources include gamma ray irradiation, ion beam irradiation, electron-beam irradiation, and laser irradiation [Kim *et al.,* 2019]. Moreover, the physical and chemical properties of the sensor can be modulated using these sources. While irradiating the ZnO nanostructures, energy is released in the form of core-level ionization and generation of electron-hole pairs [Ranwa *et al.,* 2016]. However, irradiation-induced modification of the structural properties of the sensor occurs due to the introduction of several defects, such as oxygen vacancies and Zn interstitials. The sensing response of irradiation-induced ZnO sensor is strongly dependent on irradiation dose and radiation energy.

Kim *et al.* [Kim *et al.,* 2019] deposited ZnO nanofibers via electrospinning technique, and irradiated them using e-beam energy of 1 MeV at different doses (50, 100, and 150 kGy) before H_2 sensing. They showed that the sensing response was enhanced with 150 kGy for 10 ppm H_2, and it was found to be highly selective against C_7H_8, CO, C_6H_6, and C_2H_5OH. Figure 1.15 (a) represents the dynamic curves of sensors with different doses of e-beam radiation, and Figure 1.15 (b) displays their calibration curve. The possible sensing mechanism of e^- beam-irradiated ZnO nanofibers was described by the combined effect of radiation modulation, grain boundary modulation, metallization effect, and e^- beam effect as shown in Figure 1.15(c-f). Authors [Ranwa *et al.,* 2016] have investigated the impact of gamma irradiation (0, 1, 2, 5, and 10 kGy) on H_2 sensing behavior for Schottky-contacted vertically-aligned ZnO nanorods-based sensors. It was noticed that the sensing response of 1kGy gamma-irradiated ZnO nanorods was for a maximum of 1% H_2 at 150°C as compared to other sensors. However, the sensing response was decreased for higher doses (5 and 10 kGy). The excellent sensing response of 1kGy-irradiated ZnO was attributed to the generation of a few charge centers and defects by ionization process. Therefore, adsorbed oxygen ions increased on the surface of ZnO nanorods due to creation of electrons in the ionization process. In order to explain further, Table 1.7 shows the sensing response based on different energy sources irradiated on ZnO nanostructures.

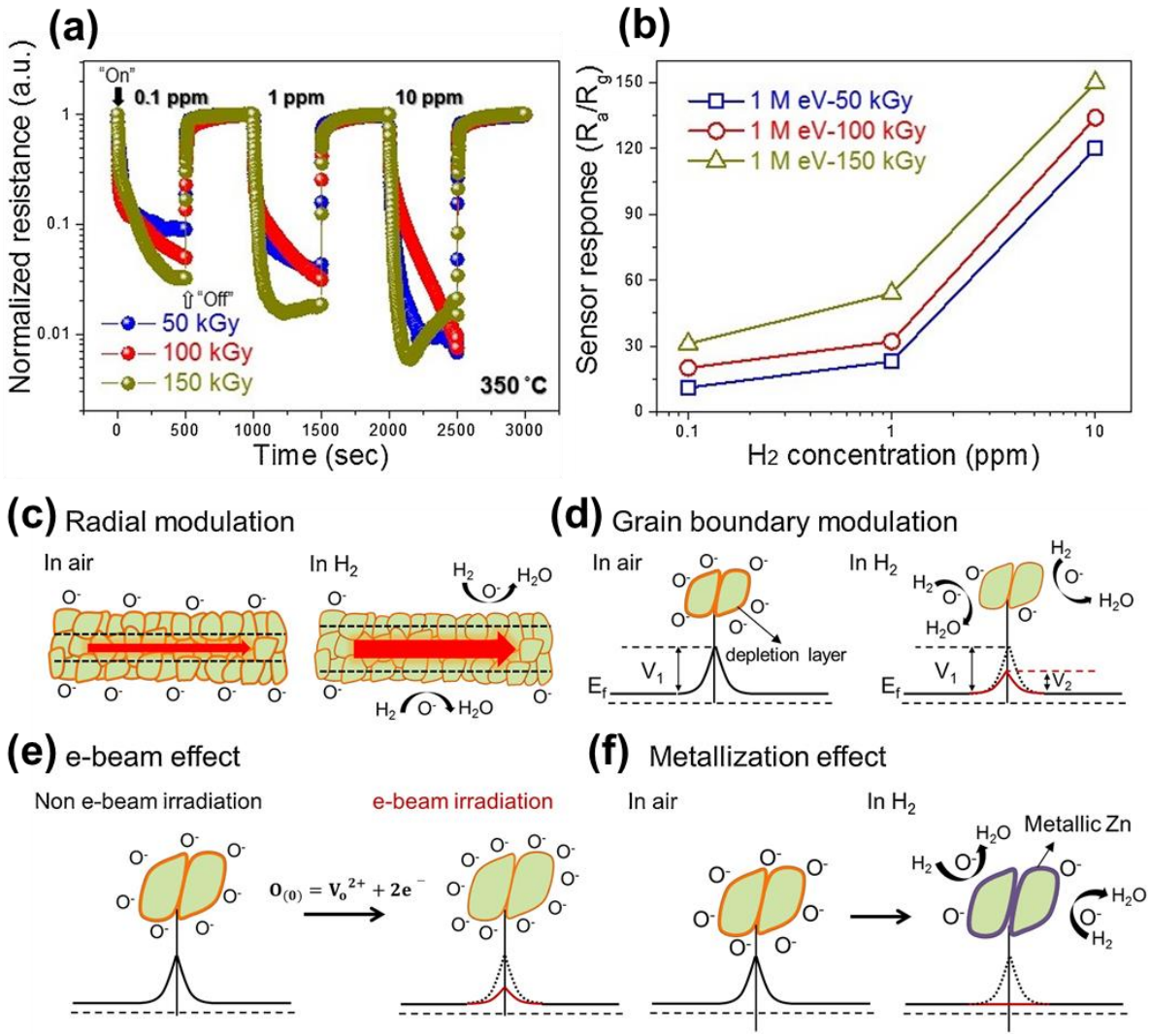

Figure 1.15: (a) Normalized dynamic resistances of ZnO NF with different doses of e-beam for 0.1, 1, and 10 ppm H_2 at 350°C, (b) calibration curves, (c-f) sensing mechanism of e-beam irradiated H_2 sensor (Source: Kim *et al.*, 2019)

Table 1.7: Gas sensing response based on irradiated ZnO nanostructures

Second material	Irrad. source	Morp. (ZnO)	Syn. method (ZnO)	Gas	Temp (°C)	Sen. Res.	Res. time	Ref.
Pd	electron beam	Nano-fibers	Electrospinning	H_2, 0.1 ppm	350	74.7 (R_a/R_g)	-	Kim *et al.*, 2019
-	Au ions	Thin film	RF sputtering	H_2, 50000 ppm	175	89.94% ($\Delta R/R_a$) %	35 s	Ranwa *et al.*, 2016
SiO_2	electron beam	Thin film	Sol-gel	Acetone	300	~38 (R_a-R_g)/	-	Nalimova *et al.*, 2016

						R_a		
-	He ions	nanowire	Reactive vapor deposition	H_2S, 300 ppm	RT	~9 (R_a/R_g)	-	Liao *et al.*, 2007

1.12 MOTIVATION

Rapid enlargement of growing population and industrialization in cities has resulted in air pollution. Air pollution is mainly attributed to automobile's exhaust and by-products of factories which has created a major survival problem for living beings. Therefore, there is a need for clean air supply to preserve our ecosystem. On the other hand, leakages of flammable and explosive gases are extremely dangerous for human beings and their belongings. Hence, accurate real-time gas monitoring sensors/devices are highly required, which also save the environment and human beings within time. Nowadays, gas sensors have become more popular because of their several applications in fuel cells (for the detection of hydrogen gas), in mining industries (methane detection), in automobile industries (NO_2 from vehicle exhaust), in oil refineries (for the detection of hydrocarbons), and in fertilizer industries (ammonia detection) [Sansone, 1992; Bhattacharyya *et al.,* 2007; Wales *et al.,* 2015; Wetchakun *et al.,* 2011; Ghosh *et al.,* 2013]. Therefore, a cost-effective, reliable, low power consuming, highly sensitive, and small size gas sensor is the most effective candidate to avoid unexpected situations caused by toxic and flammable gases [Özgür *et al.,* 2005; Dey, 2018]. Last few decades have witnessed an immense exploration of metal oxide (MO_x) semiconductor-based gas sensors which have superior properties that an ideal gas sensor must possess.

Recently, the evolution of nanostructured materials has resulted in enhanced gas sensing performance as compared to bulk material due to their excellent qualities such as large surface area, and small size. The sensing response of a gas sensor usually depends upon the size of nanostructures. For example, ZnO is a resistive sensor; the change in its resistance is highly dependent on the presence of chemisorbed oxygen ions. The oxygen molecules are adsorbed on the surface of ZnO in atmospheric air. The formation of oxygen ions on ZnO surface occur due to the removal of electrons from the conduction band of ZnO which increases the resistance of ZnO. When the reducing gases are exposed to the chemisorbed oxygen ions on the surface of ZnO, reduction in resistance takes place because oxygen ions donate free electrons to the conduction band of ZnO. The dependency of MO_x gas sensors on working temperature usually requires sufficient thermal or light energy on sensor's surface. Therefore, activation energy barrier is surpassed for the enhancement of the redox reaction which leads to enhancement in the sensing response. The working temperature of a gas sensor is kept as low as possible so that less power is consumed. Overall, the need for an enhancement in sensing response, fast response time, long-term stability, selectivity, and reproducibility at low working temperature has paved advanced method for the alteration of MO_x nanostructures. There are few techniques available for improvement in gas sensing properties of MO_x which include doping of metals into MO_x, functionalization of noble metal nanoparticles on the surface of MO_x, composition of two dissimilar MO_x, and inclusion of carbonaceous nanomaterials with MO_x [Zhang *et al.,* 2018; Lupan *et al.,* 2018; Yang *et al.,* 2019; Barthwal *et al.,* 2017; Bhati *et al.,* 2018].

1.13 OBJECTIVES

The main objective of this Thesis is to fabricate the MO_x nanostructures and analyze their structural, morphological, electrical, and gas sensing properties. Major emphasis is led on the excellent gas sensing response for a particular gas at lowest possible gas concentration as well as at low operating temperature of the sensor. The precise aim is to investigate hydrogen gas

sensing properties using MO_x sensor, especially from ZnO as it is a suitable option in the gas sensing realm. Apart from the pure ZnO, the inclusion of additional nanomaterials on ZnO nanostructures has been performed in order to enhance the sensing response. Further, possible gas sensing mechanisms are studied in detail. There are some objectives of the Thesis are briefly listed as below.

- Fabrication and characterization of different MO_x nanostructures such as TiO_2, ZnO, and V_2O_5 on Si-substrate, and subsequently their gas sensing study.
- Effect of Schottky barrier height of different metal contact on TiO_2 nanostructures and their sensing response towards hydrogen gas.
- Improvement in the gas sensing response of ZnO nanostructures for extremely low concentration (~1 ppm), and reduction in the sensor's operating temperature.
- Transition of metal doping (Ni, and Co) into ZnO nanostructures for the study of structural, morphological, and electrical properties, and enhancement of hydrogen sensing response.
- Decoration of carbonaceous nanomaterials on ZnO nanostructures for improving the hydrogen sensing properties.

1.14 LAYOUT OF THE THESIS

Chapter 1 introduces this Thesis, presents a brief history on gas sensors, classification of gas sensors, importance of metal oxide based gas sensors, sensor's characteristics, design of gas sensors, types of MO_x gas sensors, sensing mechanism, and factors responsible for enhancement of gas sensing response. Finally this chapter ends up with the motivation, objectives, and the layout of the Thesis

Chapter 2 presents a brief discussion on materials and experimental techniques used in this Thesis. This includes different fabrication techniques for gas sensors using different additives, characterization techniques, and gas sensing measurement. The chapter includes description of different MO_x such as ZnO, TiO_2 and V_2O_5; however ZnO is mainly focused for sensor measurement and sensing improvement via additional additives.

Chapter 3 presents the effect of Schottky barrier height in MO_x using different metal contacts, where TiO_2 was used in this chapter. This includes the deposition steps, structural, morphological, and electrical characterization. The hydrogen gas sensing response was evaluated for all samples and explained their different Schottky barrier height using their different workfunction.

Chapter 4 shows that how doping of transition metals into MO_x affects to surface morphology, structures, optical, current-voltage behavior and hydrogen gas sensing properties. Ni (0, 2, 4, 6%) doping into ZnO nanostructures was also studied in this chapter, and enhanced hydrogen gas sensing properties were correlated by the availability of extra active site and activation energy.

Chapter 5 describes about the decoration of 2-D nanomaterial onto ZnO nanostructures and improvement in sensing response towards hydrogen gas. Reduced graphene oxide was chosen as 2-D nanomaterial and their different concentration were considered to find the optimum concentration that shows maximum sensing response for hydrogen. Moreover, this chapter includes all the fabrication steps used for final device structures. Thereafter, the structural, morphological, and gas sensing properties were analyzed. Furthermore, NO_2 gas sensing behavior is also explained using decoration of reduced graphene oxide on V_2O_5 thin films.

Chapter 6 represents the effect of 1-D nanomaterial on ZnO nanostructures for the enhancement of sensing response towards hydrogen gas. Different amount of PAN/(PAN-b-PMMA) derived

carbon nanofiber was used to check the sensing response. This chapter includes synthesis of carbon nanofiber, device structural and morphological characterization, electrical behavior, and hydrogen sensing properties. Lastly, the gas sensing mechanism has been explained systematically.

Chapter 7 summarizes the results obtained from the research in detail, and lists few future aspects in the area of gas sensors.