Chapter 1

Introduction and Literature Review

1.1 Introduction

The sensors are similar to human sensory organs: optical sensors are similar to human eyes as they detect light, pressure sensors are similar to the skin as it senses the touch, and gas sensors are analogus to the human nose as it sense odor/presence of wide variety of gases. In the present scenario, the rapid development in all sectors has led to a serious health hazard for mankind. In addition, accidental leakage of such gases leads to a fatal condition for all living being. A lot of toxic and hazardous gases present which can't be recognized through the ordinary human nose that causes immediate death. Therefore, it is required to look for a device or instrument which helps to detect and recognize the specific gas. The application of the gas sensors is different in various fields such as medicine, pollution control, industrial production, safety and food processing etc.

Earth is surrounded by numerous atmospheric gases. The troposphere layer mainly consists of Nitrogen (N_2), Oxygen (O), hydrogen (H_2) and argon (Ar) (Sharp, 2013). These gases are very important for the sustenance of normal life at each instant. Besides these gases, there are various hazardous, toxic and greenhouse gases like NO_2, CO,CO_2, CH_4 and N_2O [IR1] etc. being produced through regular industrial activities, incomplete combustion in automobile and excessive use of pesticide and insecticide etc. particularly in the agriculture fields. These gases cause innumerable disease/complications and many of these health complications/disease are irremediable.

The present work focuses more attention towards two critical gases H_2 (being explosive) and NO_2 (being toxic). H_2 is a very simplest structured element, consisting of only one electron and proton. It is colorless, odorless and tasteless gas which is not abundant in the earth's atmosphere. It always associated with other elements like water and hydrocarbons. H_2 is also driving as a renewable clean energy source to alleviate energy crisis created due to limited sources of non-renewable energy. As a fuel, H_2 burns cleanly in presence of oxygen and produces only environment-friendly water and harmless by-products. H_2 has been also used in the fields of electronic manufacture, industrial and medical applications (Chiu *et al.*, 2009). However, hydrogen causes many potential risks such as a wide explosion at concentration range (4–75%), low ignition energy (0.02 mJ) (Wang *et al.*, 2015) and largely flammable.

Nitrogen dioxide (NO_2) is an air polluting, reddish-brown gas that has a sharp and harsh odor. It is formed by byproducts of burning fuel from automobiles and power plants etc. The excess nitrogen dioxide can significantly contribute to the acid rain, photochemical smog and ozone depletion (Deepak B. Kamble, 2017). It is severely toxic, even at low concentration (10 -100 ppm) which aggravates the human nervous system. It causes irritation to the throat, and the respiratory system (Shendage *et al.*, 2017). These harmful attributes compel the researchers for immediate detection of H_2 and NO_2, using very facile and low-cost sensors.

In earlier days, Canary bird were utilized for detection of gas(es). In the presence of gas(es), if the bird stop singing or eventually died then gas(es) was/were generally considered as toxic in nature. With the course of time, people started to use flame safety lamp which used to illuminate high flame in presence of methane gas and illuminate low flame in presence of oxygen. But with the advancement of technology, a simpler approach through the scientific development of gas sensors has been taken place.

Nowadays, many of gas sensors are commercially available in the market. Gas sensors can be classified according to their operational mechanism such as electro-chemical, Infrared, ultrasonic, infrared, thermal and solid-state etc.

Electro-chemical gas sensors detect gases in terms of change in current upon interaction of gases to an electrode. The amount of current change is measured by how much of the gas oxidized or reduced at the electrode. The working principle of these gas sensors can be understood by diffusion of exposed gases through porous membrane to an electrode.

Infrared (IR) gas sensors detect change in radiation energy passing through a known volume of gas. The energy from the IR source beam is absorbed at certain wavelengths, depending on the properties of a specific gas. The difference in energy between these two wavelengths is proportional to the concentration of gas present.

Ultrasonic gas sensor works in the change of background noise of its environment. Since most high-pressure gas leaks generate sound in the ultrasonic range of 25 kHz to 10 MHz. These sensors are capable of discriminating these frequencies from background acoustic noise which occurs in the audible range of 20 Hz to 20 kHz.

Thermal gas sensors consist of a element, comprised of a wire coil. The element is heated to an elevated temperature approximately 300°C. Heat is transferred from the element to the surrounding gases. The amount of heat transferred depends on the thermal conductivity of the gas.

Solid state gas sensors detect gases by a chemical reaction that takes place when the gas comes in direct contact with the sensor surface. Semi-conducing metal oxides are the most common material used in these sensors. The electrical resistance of the sensor element changes in-accordance to the concentration of exposed gases.

1.2 Application of Gas Sensor

Gas sensors are widely used for various applications in domestic and industrial health and safety, environmental monitoring, and process control. The major field and concerned applications are given in Table 1.1

Table 1.1: List of various applications of gas sensors.

S.No.	Fields	Applications
1.	Environment and pollution control	Weather anticipation Air pollution index
2.	Human healthcare	Severe disease detection Breath analysis
3.	Industrial production	Fermentation control Process control Methane detection in mines
4.	Safety	Personal gas monitor Chemical warfare Gas Leakage detection Fire detection
5.	Food processing	Process monitoring Food quality monitoring Packaging monitoring
6.	Automobile Industry	Filter control Car ventilation control Alcohol breath tests Ignition monitoring

1.3 Solid State Gas Sensors

The solid-state gas sensors have drawn a great interest in the field of industry and scientific world. In contrast to the conventional method of gas chromatography, this is very bulky and expensive. These sensors have numerous advantages, like high sensitivity, small size and low cost. In addition, it is also prove the flexibility of integrating the associated circuitry to develop IC compatibility. The gas sensing process through solid state sensors is reversible, i.e. sensor characteristics could be retained back after exposure in air. Generally, solid-state gas sensor not only measures the change in carrier concentration i.e. conductivity upon exposure of gases, but it also exhibits change in other vital electrical parameters such as the capacitance, electric field, barrier height and work function. A various solid-state devices have been using as gas sensors for their viability towards oxidizing as well as reducing gases. Different type of solid state gas sensors are listed below:

(i) Chemi-resistor
(ii) MOS- capacitor
(iii) Metal-semiconductor Schottky diode
(iv) Field effect transistor

1.3.1 Chemi-resistor

It is a resistive sensor that detects exposed gases as a function of resistance. The terminal resistance of sensing element changes in accordance to the concentration of exposed gases. The structure is shown in Figure 1.1 (a) of Chemi-resistor which depicts the quite simple resistor. It includes electrodes over which gas sensing materials. The complexity comes in the sensor due to the additional temperature controlling element. It is required, since many gases respond at elevated temperature (Nisha, 2013). The gas sensing in the chemi-resistor depends on two sorption process (i) physisorption (ii) chemisorption (Nisha, 2013). Generally, physisorption takes place at room temperature, but chemisorption requires a higher temperature (Nisha, 2013), (Bassey, 2014). Physisorption is the first step of interaction between the gas molecule and the sensor surface. The chemisorption is a type of adsorption where a gas molecule adheres to the surface through the formation of a chemical bond with resistor surface. It results change in the carrier concentration near the surface, which manifests itself in the form of change in resistance. The effect of these surface phenomena is reversible. This change in resistance is measured through a change in I-V plot of the resistor as shown in Figure 1.1(b).

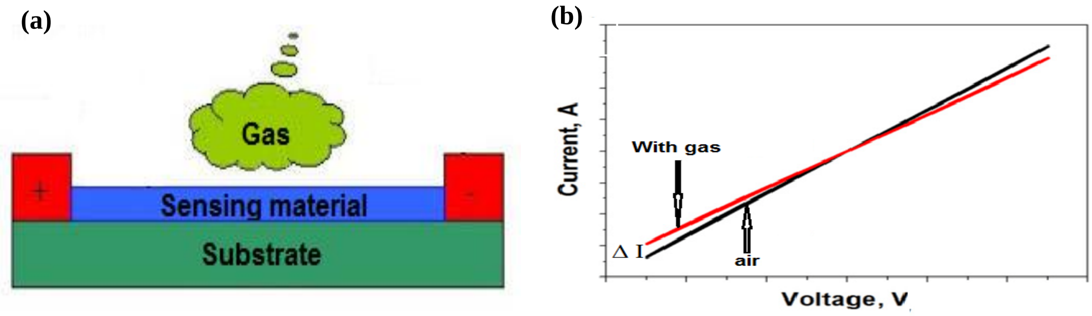

Figure 1.1: Schematic diagram of (a) resistive gas sensor (b) I-V characteristics with and without gas.

1.3.2 Metal Oxide Semiconductor (MOS)-Capacitor

In MOS capacitor based gas sensors, the thin catalytic metal (such as Platinum (Pt), palladium (Pd), Iridium (Ir) etc.) are deposited onto the insulating oxide layer (usually SiO_2), on silicon (Si) substrate as shown in Figure 1.2 (a). It also works on the principle of physisorption and chemisorption of the gas molecules to the material surface. In the MOS-capacitor type gas sensor, the metal acts as a catalyst for the gas molecules. In MOS-capacitor, gas sensing starts with adsorption of the gas molecule on the catalyst surface. Further, these adsorbed molecules diffuse into the metal catalyst and form dipoles moment at the metal-oxide interface. It results shift in the barrier potential of the junctions (Jain, 2011) which leads to changes in the capacitance of the MOS capacitor which is proportionate to dipoles formed. This C-V shift is measured as a gas response as shown in Figure 1.2 (b).

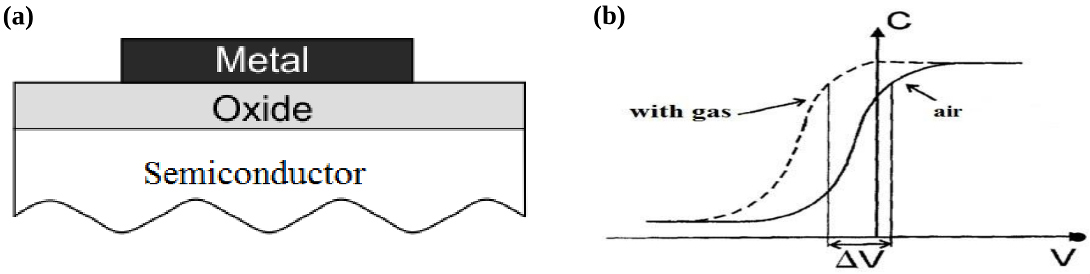

Figure 1.2: Schematic diagram of (a) MOS-Capacitor (b) C-V Characteristic with and without gas (Kandasamy, 2007).

1.3.3 Metal semiconductor based Schottky diode

Metal-semiconductor (M-S) Schottky diode based gas sensors are widely used in industries and warfare. The simple Schottky structured is shown in Figure 1.3 (a) that is more preferable over MOS capacitor type gas sensors. In the M-S Schottky diode, transition metals such as palladium (Pd), platinum (Pt), Gold (Au), Silver (Ag) etc. (Sarkar *et al.*, 2015) deposited on the semiconductor material. A Schottky diode is a two-terminal electronic device in which a voltage is applied across the terminals and current flows unilaterally. When the Schottky sensor is exposed to the gases, then gas molecules first dissociates and diffuses into the metal. These diffused gas molecules form a dipole layer at the metal-semiconductor interface (Chik and Yu, 2011). These dipoles layers enforce to change in Schottky barrier either in an upward or in downward direction. The barrier change leads to change in the current through the device that is measured as gas response. It is shown in Figure 1.3 (b).

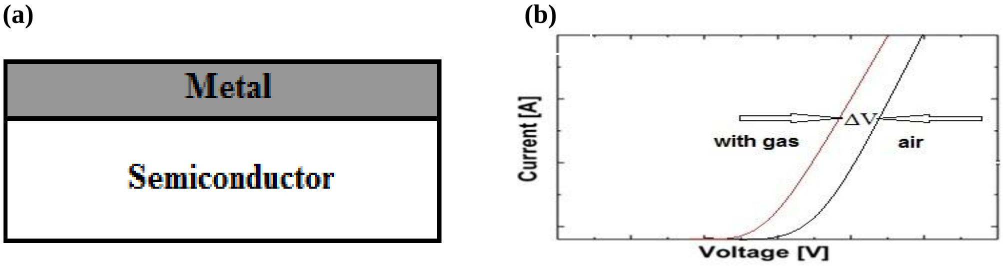

Figure 1.3: Schematic diagram of (a) Metal-semiconductor Schottky diode and (b) I-V Characteristic with and without gas (Kandasamy, 2007).

1.3.4 Field effect transistor

Nowadays, Field effect transistor (FET) is a prevalent device for gas sensing because of its vulnerable electric field. It is operated by modulation of the field in the presence of the target gases. FETs are a layered structure, as shown in Figure 1.4 (a). Here, the gas molecule interacts with the gate metal and further gas molecules diffused into the metal and constitute dipole layer at the interface of the gate-oxide. These formed dipoles deflect the applied electric field in proportionate to the diffused gas molecules into the gate. It results change in voltage (I-V), capacitance-voltage (C-V) or conductance-voltage (G-V) characteristic of FETs (Kandasamy, 2007) as shown in Figure 1.4 (b).

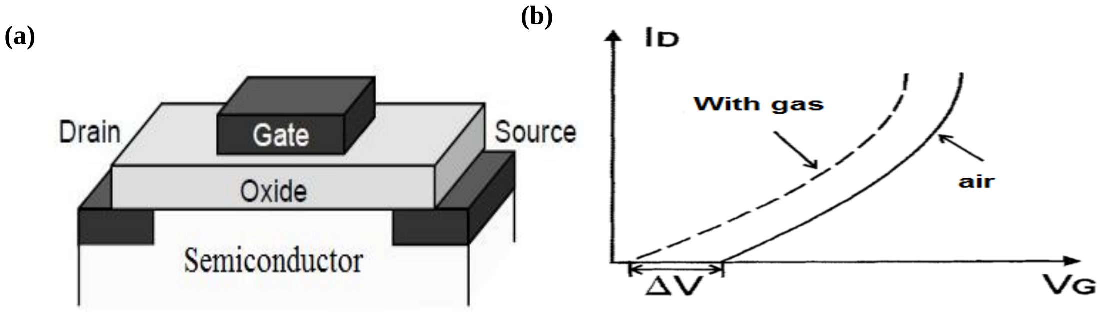

Figure 1.4: Schematic diagram of (a) FET and (b) Drain current (I_D) and Gate Voltage (V_G) with and without gas (Kandasamy, 2007).

1.4 Literature Review

The literature review is mainly focused on the advancement of solid state gas sensors. These sensors have been widely used by different researches for detecting and monitoring toxic, polluting and combustible gases efficiently (Dilonardo *et al.*, 2016). The resistor and Schottky diode based gas sensors have drawn more attention and these are most preferred structures with a lot of scope to further improve performance towards gas sensing application. In addition these sensors offer simplicity in design, fabrication and relatively less costlier then other approaches.

1.4.1 Literature Review on the Resistor-Based Gas Sensors

Over the course of time, extensive research has been pursuing on resistor based gas sensor for improving gas sensing performance at low operating temperature. So far, many scholars have been reported several resistive gas sensors using various modification techniques as surface treatment, metal impregnate and composite preparation etc. Firstly, Brattain and Bardeen (Brattain and Bardeent, 1952) have reported the germanium semiconductor based solid state gas sensor in which the sensitivity of the sensor is affected by the change in conductance due to adsorption of a gas on the surface of the semiconductor.

Seiyama *et al*. (Seiyama, T., Kato, A., Fujiishi, 1962) have discovered the change in electron concentration or electrical conductivity of ZnO film in the presence of gas molecules. They have developed a ZnO based resistive sensor on borosilicate glass by depositing the zinc metal using thermal evaporation technique followed by oxidization of this thin film at 450 °C. They observed the response of sensor under-exposure of various gases such as H_2, CO, CO_2, propane, and toluene etc. It was also found that the sensor possesses the highest sensitivity for H_2 at a temperature around 300 °C.

Nanto *et al.* (Malbon, Walsh and Winslow, 1967) have reported resistor based gas sensor using sputtered ZnO thin film for gas sensing application. The sensor exhibits an increase in the resistance upon exposure to ammonia gas whereas it exhibits a decrease in the resistance of other gases. This results in an, excellent selectivity toward ammonia. They have also found that the sensing of ammonia gas in ZnO-based sensors is related to the adsorption of atmospheric oxygen at an operating temperature of 350 °C.

Oyabu *et al* (Oyabu, 1982) have studied Pd and Pt-doped SnO_2 thick film sensor. They reported that the printing method is helpful in mass production. The Pd-SnO_2 sensor has shown an excellent selective detection of hydrogen at 250 °C. Further Pt-SnO_2 has also a high selectivity toward CO at temperature of 350 °C.

Yamazoe *et al* (Yamazoe, Kurokawa and Seiyama, 1983) have investigated Sintered SnO_2 film. They demonstrated the monitoring of operating temperature (< 450 °C) upon exposure of H_2, CH_4 and CO_2, at which sensor shows maximum sensitivity. The researchers have utilized the operating temperature to enhance the selectivity.

Akiyama *et al* (Akiyama *et al.*, 1991) have investigated Sintered WO_3 film based NO and NO_2 sensor. They found that the film was most responsive to the presence of 200 ppm NO_2 gas at 300 °C. They have also observed the high NO response at 200 °C. These results indicate the present sensor is suitable for detecting low concentration (about 40 to 200 ppm) NO and NO_2 even at a low temperature such as 200 and 300 °C.

Azad *et al* (Azad, 1992) have reported the self-built experimental setup for gas sensing application using ZnO thin film. They have also elaborated the gas sensing mechanism under-exposure of reducing and oxidizing gases such as CO, CO_2, O_2, H_2, NO_2 and CH_2OH etc. at temperature range around 200 to 500°C. Eventually, they concluded that the H_2 sensor can be easily developed using ZnO thin film at high temperature but this sensor is not only sensitive for H_2 gas but also respond to other reducing and oxidizing gases at very high temperature 400 °C.

Tamaki *et al* (Tamaki *et al.*, 1994) have studied varying WO_3 grain size upon exposure of NO_2 gas. They optimized the effects of grain size (between 16 and 57 nm) of WO_3 on the response over NO_2 gas. They found that 25 nm grain sizes were most sensitive to NO_2.

Mitra *et al.* (Mitra, Chatterjee and Maiti, 1998) have reported chemically deposited ZnO films for sensing the reducing gases, e.g. H_2 and LPG, in ambient. They further found that

Pd-sensitization (by a wet chemical method) enhance the film resistance and showed sensitivity more than 99 % for 3 vol % hydrogen while sensor showed the poor recovery when H_2 is mixed with air. They also observed a high sensitivity around 75 % for 0.4–1.6 vol% LPG in the air and the degree of sensitivity could be varied by changing either the LPG concentration or operating temperature.

Shieh *et a*l.(Shieh *et al.*, 2002) have prepared the WTiO and WO_3 films using sol-gel dip coating for NO_2 detection. They concluded that WO_3 has shown a sensitivity of 82% for 10 ppm NO_2, at an operating temperature of 200 °C compared to a sensitivity of 1,786% for the WTiO film. The large difference in sensitivity is attributed to the reduction in grain size of the material.

Tomchenko *et. al.* (Tomchenko *et al.*, 2003) have reported SnO_2, ZnO, WO_3, In_2O_3 and CuO based sensor array for detection of combustion gases (CH_4, CO, NO, NO_2 etc.). They observed different responses at different temperatures. At 200 °C, the In_2O_3 showed the highest response towards NO_2 but CuO showed no response at all, and ZnO showing a very poor response. At 400 °C, the response changes, ZnO shows the highest response and CuO still showed no response to the presence of the gas.

J X Wang *et al.* (Wang *et al.*, 2006) has reported the hydrothermal process for ZnO nano-rod (diameter varying from 20 to 100 nm) which showed the high sensitivity and reproducible response to H_2, NH_3, and CO at a relatively low operating temperature. They grew ZnO nanorod in aqueous solution at low temperature (<100 °C) on a silicon substrate with SiO_2 and observed enhanced gas sensing properties at 250 °C due to large surface to volume ratio of the film.

Karunagaran *et. al* (Karunagaran *et al.*, 2007) have reported a thin film gas sensor fabricated with the TiO_2 film. They deposited film using RF Sputtering and annealed the film at 600 °C. The sensor has shown a high sensitivity toward ammonia gas range in 500–1,000 ppm at an optimum temperature of 250 °C. Sensor has shown a fast response time of 90 s and recovery time of 110 s.

Sadek *et al*. (Sadek *et al.*, 2007) have fabricated a conductometric gas sensor, based on ZnO nanobelts, synthesized by RF sputtering of a zinc oxide target under controlled conditions. The fabricated sensor has been investigated upon H_2, $NO_{2,}$ and hydrocarbons at different operating temperatures in the range between 150 and 450 °C. The sensor showed the optimum, fastest response and recovery with greater repeatability for H_2, NO_2 and propane gases occurred at temperature 385, 350 and 370 °C respectively. At these temperatures, the sensitivity of the sensor was calculated to be 14.3 for 1% H_2, 0.81 for 8.5 ppm NO_2, and 0.17 for 1% propane.

Frank Retting and Ralf Moos (Retting and Moos, 2007) have reported Thick film SnO_2 having modulation heater in the rear side of the substrate. They observed the independence of Seebeck coefficient with the geometry of the SnO_2 film but vary strongly in contrast to conductance. Eventually, they reported the high response of sensor upon exposure of propane.

Tischner et al. (Tischner *et al.*, 2008) have investigated SnO_2 thin film sensor. In which thin film was deposited through spray pyrolysis. They observed CO, CO_2 and CH_4 responses at 250–400 °C, in the concentrations ranging from 0 - 100 ppm. The sensor is able to detect carbon monoxide to a concentration of less than 5ppm, which demonstrates the superior sensing properties of ultrathin SnO_2-films as compared to conventional sensor structures.

Izu *et al* (Izu *et al.*, 2009) have reported Sintered ceramic oxide based thick film sensor with various particle size for combustible gases (such as methane, ethane, propane, ethylene CO_2, hydrogen, and CO). The sensor has shown the best response to the presence of CO of 5,000 ppm and selectivity towards propane at a temperature of 450 °C.

Jing *et al*. (Jing and Zhan, 2008) have successfully synthesized porous ZnO nanoplates through the annealing of a plate-like precursor hydrozincite at 400 °C for 2 h. The ZnO nanoplates based gas sensor exhibits a high response to chlorobenzene at relatively low operating temperatures, from 150 to 250 °C, and also showed a strong response to ethanol at relatively high operating temperatures in the range from 250 to 450 °C. These results showed that the porous ZnO nanoplates possess multifunctional properties, and have potential application in chlorobenzene and ethanol detection at different operating temperatures.

Jun *et al.* (Jun *et al.*, 2009) have reported ZnO nanoparticles (NPs) based resistive type NO_2 sensor which showed a large and fast response. They have also fabricated the sensor using ZnO NPs with low-temperature heat treatment process. As a result of heat treatment, ZnO NPs were slightly necked with the neighboring NPs without any agglomeration. When these sensors were exposed to 5 ppm NO_2 gas, they observed the higher response of heat treated ZnO NPs rather than normal ZnO.

Huang *et al*. (Huang *et al.*, 2010) have reported flowerlike ZnO nanostructures made up of nanosheets which have been successfully synthesized by a very facile chemical route method. The controllable fabrication of novel three dimensional (3D) ZnO structures has thrown a simple synthesis approach of ZnO nanostructure. Furthermore, the fabricated sensor was tested on various gases such as methanol, n-butanol 2-propanol and acetone in the temperature range from 260 to 360 °C. The flowerlike ZnO nanostructures has exhibited high sensitivity, fast response and recovery time with good reversibility towards tested gases. The sensitivity ($\frac{R_g}{R_a}$) to 100 ppm of n-butanol and ethanol were reported at 25.4 and 24.1, respectively, at an operating temperature of 320 °C. The good gas-sensing properties were attributed to the small thickness of ZnO nanosheets and 3D structures of the flowerlike ZnO nanostructures.

Hardan *et al.* (Al-Hardan, Abdullah and Aziz, 2010) have reported RF sputtered ZnO thin film for H_2 sensing. They have investigated sensing characteristic as a function of temperature in the voltage range from -5 to 5 V. The nearly ohmic behavior of I–V characteristics has revealed high carrier concentrations of prepared film. It was also observed that the sensitivity of the sensor had increased with the hydrogen concentrations and sensing was attributed to the superficial surface charge of the ZnO film.

Huiqing Fan *et al.* (Fan and Jia, 2011) have successfully synthesized ZnO nanosheets by using a simple mixed hydrothermal method. They observed the thickness of the ZnO nanosheets is in the range of 10–20 nm and the width-to-thickness ratios of the ZnO sheets almost reach up to one thousand. They have studied response to acetone, ammonia, ethanol, gasoline, and toluene. Interestingly, they have observed the excellent response at magnitude of 30 to gasoline at 180 °C by these ZnO nanosheets and others gases represent only response magnitude of 5.

Rai *et al.* (Rai and Yu, 2012) have reported the citrate-assisted hydrothermal synthesis of single crystalline ZnO nanoparticles (NPs) for gas sensor application. These ZnO NPs based gas sensor showed the high response for CO, ethanol, and acetaldehyde at a temperature around 400 °C and response decreased with decreasing operating temperature. In the case of NO_2 gas, the sensor has shown response even at room temperature and it has increased with increasing operating temperature until 300 °C and sharply decreased at 400 °C.

Wen *et al.* (Wen, Wu and Wang, 2012) have developed a simple top-down route in order to obtain large size porous ZnO flake. They firstly prepared a composite containing homogeneously distributed, poorly crystallized ZnO and carbon/organics by solution combustion synthesis process. Further, porous ZnO flakes were then achieved by a subsequent calcination in the air to remove the carbon/organics and to induce the crystallization of ZnO. The large-size porous ZnO flakes were investigated upon various gases and it exhibited high sensitivity to ethanol while, its responses to other gases of gasoline, ammonia, and methylbenzene are very weak. The excellent gas sensing properties for detecting acetone and ethanol due to the large size porous ZnO flakes porous structure and the small thickness of the 2D architecture, which effectively shortens the gas diffusion distance and provides highly accessible open channels and active surfaces for the target gas

Mun *et al.* (Mun *et al.*, 2013) have synthesized Au-functionalized porous ZnO nanosheets using a three-step process (i) Thermal evaporation of Zn metals (ii) Au sputter- deposition (iii) Thermal annealing. The multiple networked pristine ZnO nanosheets have shown responses ranging from ~111 to ~137 % for NO_2 concentrations ranging from 1 to 5 ppm. Interestingly, the Au-functionalized ZnO nanosheets showed responses ranging from ~205 to ~455% over the same concentration range. The response of the Au-functionalized ZnO nanosheets increased from ~133 to ~455% with increasing UV illumination intensity from 0.35 to 1.2 mW/cm^2. The significant enhancement in the response of the ZnO nanosheets to NO_2 gas by UV irradiation was attributed to the increased change in resistance due to the photo-generation of electrons and holes.

Zhang *et al.* (Zhang *et al.*, 2013) have demonstrated large-scale production of dispersed single-crystalline ZnO nanosheets using two-step fabrication method consisting of the sonochemical process and chemical etching treatment. They observed that the ZnO nanosheets based sensor exhibits high sensitivity to formaldehyde and acetaldehyde with a detection limit lower than 50 ppb at the optimal operating temperature of 220 °C. The high sensitivity and ppb-level detection limit were ascribed to the large specific surface area and less agglomerated configuration of the ZnO nanosheets.

Guo *et al.* (Guo *et al.*, 2014) have successfully fabricated the hexagonal ZnO nanosheets having a thickness of 17 nm *via* a simple yet efficient hydrothermal approach. They investigated the role of the additives (CTAB) on the morphology evolution of the nanosheets and also examined the gas-sensing properties of the fabricated sensors which reveal that the sensor made of hexagonal ZnO nanosheets exhibits a gas response ratio ($\frac{R_{air}}{R_{gas}}$) of 37.8 along with a response and recovery time of 9 and 11 s respectively, to the formaldehyde gas of 50 ppm at an optimal temperature of 350 °C.

Yu *et al.* (Yu *et al.*, 2014) have demonstrated the effectiveness of the aqueous solution on tailoring morphology of ZnO nanowalls using two-step solution methods. They observed the role of Al^{3+} in the synthesis of ZnO nanowalls that results in the vertical standing of ZnO nanowall networks were well crystallized in a wurtzite structure and a highly oriented direction parallel to (0001). They also investigated the sensing properties of fabricated sensor towards NO_2 in the concentration range of 1–50 ppm at high temperature. Under optimize working temperature 220 °C, this fabricated sensor showed a high response ($\frac{R_g}{R_a}$) to 30 for 50 ppm NO_2 due to the porous structure, highly exposed surface area and singe-crystal structure. These results well illustrated that the controlling of the structure of ZnO nanowall films was an effective way to meet the needs of ZnO devices with good performances.

Alenezi *et al.* (Alenezi *et al.*, 2014) have reported novel hierarchical ZnO nanowires (ZNWs) and ZnO nanodisks with controllable density on initial 1D and 2D ZnO nanostructures through a simple and economical hydrothermal route. The experiment has revealed that the formation of these hierarchical structures depends significantly on the concentration of the growth solution as well as the growth time. The grown hierarchically structured ZnO has induced enhancement of gas sensing performance with a much better sensitivity toward acetone and fast response compared to other mono-morphological ZnO, such as ZnO nanoparticles, nanorods, and nano-sheets. The results were primarily attributed to their high surface-to-volume ratio as well as the formation of the secondary nano-wire NW–initial nanostructure junctions.

Chang *et al.* (Chang, Wen and Chang, 2014) have grown ZnO nanowalls through a fast and low-temperature process in a tube furnace. These ZnO nanowalls were used for CO detection and response was evaluated in term of relative sensitivity ratio $\left(\frac{I_{gas}-I_{air}}{I_{air}}\right)$ at different temperatures (100 – 400 °C) and concentrations (100 – 3000 ppm). They obtained interconnected ZnO nanowalls with (0001) exposed crystal planes, vertically grown on a glass substrate, with width and height typically ranging from 70 nm to 200 nm and 3.7 nm to 6.5 nm. I-V characteristics showed that the ZnO nanowalls gas sensor has the highest relative sensitivity ratio around 1 at 300°C upon 3000 ppm carbon monoxide.

Giancaterini *et al.* (Giancaterini *et al.*, 2015) have reported the effects of Au and Pt nanoparticles on gas sensing properties of sol-gel based ZnO thin-film. They have investigated the conductometric response of sol-gel based ZnO thin film sensors embedded with 5% mol. each of Au and Pt nanoparticles and have observed electrical sensing response to H_2, CO and NO_2 gases in the dry air and different operational temperatures. The catalytic action of Au and Pt NPs additions powerfully has improved the H_2 and CO and NO_2 response.

Fan *et al.* (Fan *et al.*, 2015) have prepared 3-D hierarchical porous ZnO which were composed of nanoparticles-based nanosheets with an average particles size of about 9.2 nm. The prepared tubular three-dimensional hierarchical porous ZnO have the outer and inner diameters of 0.4 - 0.7 μm and 71 - 108 nm, respectively. Furthermore, they investigated the gas sensing performances of the prepared ZnO samples, and the results indicated that the prepared three-dimensional hierarchical porous ZnO exhibit low operating temperature, high and fast response, and good selectivity to ethanol. The superior gas sensing performance of the three dimensional hierarchical porous ZnO is essentially attributed to its highly open and porous structure, high specific surface area, and small nanoparticle size.

Ling-min Yu *et al*. (Yu *et al.*, 2015) have synthesized 3-D mesoporous ZnO nanowall *via* two-step solution method and coated over Ag- interdigitated electrodes. Further, as-prepared ZnO film has been tested on ethanol and it has shown good sensitivity with response/recovery speed (20 s and 33 s). The obtained excellent ethanol sensing properties has been mainly originated from the mesoporous walls structure and contact controlled effect.

Arun kumar *et al*. (Arunkumar *et al.*, 2016) have successfully demonstrated a facile hydrothermal process for the synthesis of hierarchical ZnO with impressive unique architectures. The prepared ZnO architectures were used for investigation of gas sensing characteristics towards CO by evaluating the sensitivity, sensor response and recovery time. The authors have optimized the sensing temperature (275 °C) where the sensor exhibits the maximum response of S_R $(\frac{R_{air}}{R_{gas}})$ ~ 681 upon exposure to 1000 ppm of CO. This sensor also showed excellent selectivity (S ~ 8.1 to 50 ppm of CO) than to other gases such as metshanol, ethanol, acetone and H_2.

Xie *et al.* (Xie *et al.*, 2016) have reported growth of porous ZnO single crystal hierarchical architectures in order to achieve ultrahigh sensing performances upon exposure to ethanol and acetone gases. They assembled porous ZnO hierarchical architectures from 2D porous single crystal nanosheets having (0001) crystal phase through annealing of the $Zn_5(CO_3)_2(OH)_6$ precursor. The enhanced gas sensing properties of as-prepared porous ZnO hierarchical architectures at low operating temperature may be attributed to the unique structure, single crystal nature, and the exposed polar crystal face.

Chen *et al*. (Chen *et al.*, 2017) have reported pure ZnO and graphene-modified ZnO using simple hydrothermal processes at temperature 150 °C for sake of formaldehyde detection. Gas sensing device was prepared by coating synthesized gas sensitive pastes onto an alumina tube including Au electrodes. They observed the response towards a low concentration of formaldehyde (10–500 ppm) and found significant enhancement in response ($\frac{R_g}{R_a}$) from 5 to 12 in particular, loading ZnO with 2 wt% graphene (G-ZnO).

1.4.2 Literature review on Schottky diode based gas sensors

Extensive research works have been devoted to the development of gas sensors based on Junction. The junction based gas sensor was first reported in 1975 by Lundström *et al*. in which Pd/MOS based structures were exposed to hydrogen gas. The junction based gas sensors have been reported as a very promising candidate for the gas sensing application. Schottky junction based sensor has been using due to its easy fabrication and top thin catalytic metal layers (generally group VIII transition metals such as Pt or Pd) that acts as both a Schottky contact and a catalyst for gas adsorption.

Yamamoto *et. al.*(Yamamoto *et al.*, 1980) have reported the Pd/TiO_2 diode can monitor hydrogen selectively and quantitatively in the air at the temperature range from 25 to 200 °C. This diode has a strong rectification effect in air, indicating the presence of a Schottky barrier. They described the exponential method for the estimation of the work function changes of various metals or catalysts caused by surface adsorption or surface chemical reactions.

Poteat *et al.* (Poteat *et al.*, 1983) have fabricated the MOS and various Schottky barrier diodes for hydrogen detection. They reported four types of Schottky barrier (a) Pd-InP (n-type) Schottky Barrier (b) Pd-InP (p-type) Schottky Barrier (c) Pd-GaAs (n-type) Schottky Barrier (d) Pd-GaAs (p-type) Schottky Barrier. They infer that the gaseous detection mechanism in the MOS devices can be attributed to a change in metal-semiconductor work function. They observed that hydrogen diffuses in all of the fabricated Schottky sensors, through the metal (Pd) and creates an excess of surface states (dipole moments) at the interface. This additional charge severely affects the device response and measured as a sensitivity.

Petty *et al*. (Petty, 1986) have reported the electrical characteristics of Pd/SiO_2/n-Si Schottky barrier type devices at different temperatures and under different ambient conditions (air, nitrogen, and hydrogen). The forward conductivity of the devices is dominated at different bias voltages by the generation-recombination or tunneling process at the interface. They identified that the interface states have an imperfect oxide layer and thought that the exposure to hydrogen increases the interface state density in the devices and also to lower the work function of the palladium metal.

Lechuga *et al*. (Lechuga, Calle and Golmayo, 1994) have reported a urea biosensor by combining an NH_3 gas sensor based on a Pt/n-GaAs Schottky diode with the urease-immobilizing membrane. The sensitivity of the biosensor is well adapted to the millimolar range usual for clinical tests. They observed all experiments at 333 K and obtained the sensitivity (0.85%) of the sensor for a urea concentration of 10 mM in a period of about 5 min and the recovery process in flowing buffer takes about 25 min.

Hunter *et al.* (Hunter *et al.*, 1998) have demonstrated two types of structures (i) The catalytic alloy, palladium chrome (PdCr) was deposited directly on the SiC forming a metal-semiconductor (MS) structure and (ii) The catalytic metal (Pd) deposited on a chemically reactive insulator tin oxide (SnO_2) adherent on the SiC forming a metal-reactive insulator-semiconductor structure (MRIS) as a gas sensor. They observed the response of both the fabricated sensor to H_2, methane, and propylene at operating temperature of 350 °C and noted that Pd/SiC sensor response degraded over several weak periods while another fabricated sensor remained relatively stable. They also found that SnO_2 changed the basic electronics behavior and possible to detect gases which are not detected without this layer.

Polishchuck *et al.* (Polishchuk *et al.*, 1998) have reported hydrogen detection with palladium modified porous silicon using a contact potential difference method. They observed the sensor's characteristic having considerable sensitivity in the range from 200 – 4000 ppm H_2 concentration at room temperature. The sensor's temporal response was found in the few minutes range and the recovery takes tens of minutes.

Kim *et al.* (Kim *et al.*, 2000) have fabricated Pt/SiC-based Schottky diodes for hydrogen sensing and analyzed the hydrogen adsorption performance at a high temperature (450 °C). They observed that the current conduction mechanism of the Schottky diode is controlled by the thermionic field emission mechanism. It is found that the change in the barrier height upon hydrogen adsorption increases with increasing operating temperature which indicates an increased sensitivity of the Pt/SiC Schottky diode sensor to hydrogen gas.

Talazac *et al.* (Talazac *et al.*, 2004) have reported a comparative study of two different structures (resistive and pseudo-Schottky) using n-type InP as a sensitive material that detects ozone and nitrogen dioxide. They observed the consequences of sensors (resistor and diode type) different structures in terms of sensitivities and selectivity toward NO_2 and O_3. Resistive based sensors were low-sensitive and selective indicators upon the various gases but pseudo-Schottky diodes with palladium containing Schottky metallizations respond to the double objective of having a high sensitivity and a strong selectivity, without any modification of the sensitive material which remains an n-type Indium Phosphide layer.

Chou *et al.* (Chou *et al.*, 2005) have reported an ultra-high-sensitive hydrogen sensor based on Pd-InP Schottky diode which fabricated by electrophoretic deposition (EPD) combining with Pd nanoparticles as the sensing metal. The fabricated diode has demonstrated excellent junction qualities with a very high Schottky barrier hight (SBH) value of 829 meV at 303 K and a high saturation sensitivity ratio ($\frac{I_{H_2} - I_{air}}{I_{air}}$) of 38 in a very low hydrogen concentration of 15 ppm. They concluded the highest promising characteristic of EPD based Pd-InP hydrogen sensor.

Hung *et al*. (Hung *et al.*, 2006) have demonstrated a novel hydrogen sensor based on a Pt/$In_{0.52}Al_{0.48}As$ Schottky diode. They measured temperature dependent I–V characteristics of sensors under the reverse bias upon different-concentration of hydrogen gases and observed high sensitive ratio Sr (%) value (about 2600%) in the wide temperature range from 30 to 200°C. Based on the advantage of integration compatibility with InP-based electronic devices, the studied Pt/$In_{0.52}Al_{0.48}As$ Schottky diode-type hydrogen sensor has provided the compatibility for micro-electromechanical system (MEMS) and high-performance sensor-array applications.

Tsai *et al.* (Tsai *et al.*, 2008) have investigated the interesting hydrogen sensing characteristics for a GaN-based MOS-type Schottky diode with a Pt catalytic. They observed the fabricated sensor upon exposure to hydrogen gas. The Schottky rectification behavior in the air has been gradually shifted to Ohmic-like property. The results have suggested that the hydrogen induces a dipolar layer at the semiconductor interface which leads to the decrease in the effective Schottky barrier height. They concluded that absence of oxygen molecules increases a large number of hydrogen atoms to diffuse into the Pt-oxide interface which attributed to greatly reduce in the Schottky barrier height. These results demonstrated the fast sensitive Pt-oxide-GaN Schottky diode as a hydrogen sensor over a broad range of operating temperatures from 30 to 300°C.

Chiu *et al.* (Chiu *et al.*, 2009) have reported a planar type of Pd–GaN metal-semiconductor-metal (MSM) hydrogen sensor. The proposed sensor was biased at a constant voltage and observed the characteristic in the static and dynamic state both. Effective barrier height variations (EBH) and sensing responses (S) were obtained for the proposed sensor in a static state. Moreover, current transient response and voltage transient response to various hydrogen-containing gases were experimentally studied. The new finding is that the response time in voltage transient curves is shorter than that in current transient ones.

Hossein-Babaei *et al.* (Hossein-babaei, Abbaszadeh and Esfahani, 2009) have reported a noble metal (silver)-rutile/TiO_2 Schottky diode as a gas sensor on Titanium (Ti) substrate. The fabricated samples also has shown the thermal stability of Ag- junctions as it demonstrated the lower leakage current at elevated temperatures (200 - 400 °C). The fabricated sensor was tested to reducing contamination (1-butanol) in the air and a very broad dynamic range for hydrogen detection (200 to 80,000 ppm). The high sensitivity and wide dynamic range make this small, rugged, and cost-effective device as excellent candidacy for use in applications of hydrogen detection and this sensor did not show sensitivity degradation for the tested 500 h. The mass production of the sensor on titanium foil is easy and economical. The stable ohmic connection between the titanium substrate and its native oxide removed the need for a back-contact.

Shafie *et al.* (Shafiei *et al.*, 2010) have reported reversed bias Pt/ZnO nanostructured based Schottky diode with an enhanced electric field for hydrogen sensing. They tested Pt/ZnO nanostructured based Schottky diodes as hydrogen gas sensors in reverse bias. They observed large voltage shift produced by the nanostructures as they interact with the hydrogen molecules. They also observed the voltage shift caused by the increase in free carrier concentration (N_D) and the decrease in permittivity (ε_s). The rectifying electrical characteristics of the devices were studied at different temperatures from 25 °C to 620 °C. These sensors showed stable, reliable and repeatable characteristics.

Chiang *et al.* (Chiang *et al.*, 2010) have investigated the impact of adding a TiO2 interfacial layer (IL) on the Pd/n-LTPS (low-temperature poly-silicon) Schottky diode on hydrogen sensing characteristics. They concluded that, the TiO_2 IL suppress the Fermi level pinning in Pd/n-LTPS interface, which improves the modulation of barrier height at the Pd/TiO_2 interface for various hydrogen concentration ambient. They also observed the hydrogen response (S in %) of the n-LTPS Schottky diode under room temperature and −2 V bias is promoted from 331.5% to 3504% in 8000 ppm H_2/air ambient with the TiO_2 IL.

Shafie *et al.* (Shafiei *et al.*, 2010) have reported Pt/nanostructured ZnO Schottky diodes based H_2 sensor. The authors utilized the reverse bias of diode characteristic for H_2 detection because of the large voltage shift observed. It is caused by nanostructures interact with the hydrogen molecules as the increase in free carrier concentration N_D and the decrease in permittivity ε_s. The rectifying electrical characteristics of the sensor upon H_2 exposure were studied at different temperatures up to 620 °C.

Chi Lu *et al.* (Lu, Chen and Singh, 2010) have reported hydrogen sensors using Pt/SnO_2/SiO_2/Si structure which were fabricated by electron beam deposited SnO_2 nano scale-particle film on oxide grown silicon wafers and platinum as a catalyst used on top of the of nanoparticles. A gas sensing mechanism was explained by the H_2-induced reduction of the Schottky barrier height (SBH) at the Pt/SnO_2. They found Very high and fast responses to H_2 in low concentration on thinner SnO_2 film and also discussed the CO sensitivity as well.

Huang *et al.* (Huang *et al.*, 2011) have investigated an interesting hydrogen sensor based on a Pd/GaN Schottky diode on a sapphire substrate and studied hydrogen sensing over a wide temperature range from 27 to 327 °C. This fabricated sensor was tested under a wide hydrogen concentration range from 14 to 9970 ppm in air. The sensor has shown the remarkable features of very high hydrogen detection sensitivity ratios ($\frac{I_{H_2} - I_{air}}{I_{air}}$) and large Schottky barrier height variations. The high sensitivity value such as 12744 at 27 °C has shown a very promising sensitivity, as compared with other reported hydrogen sensors. Furthermore, they observed that the studied device (hydrogen sensor) has the considerably short response times at hydrogen adsorption and desorption process.

Varenne *et al*. (Varenne *et al.*, 2012) have reported pseudo-Schottky diodes having improved electrical parameters of these rectifying structures rather than Schottky diodes. Further, This Schottky sensor has been tested under NO_2 and O_3 which has confirmed the sensor response dependency on the Schottky barrier height. The higher Schottky barrier has shown proportionality to the sensor’s response. So, they found the realization of pseudo-Schottky diodes is required for optimization of the gas sensor structure than classical Schottky diodes. They have also demonstrated the impact of the metal (Pd layer) upon exposure to NO_2 or O_3 that contaminates the layer and decreases the sensor sensitivity greatly.

Andringa *et al.* (Andringa *et al.*, 2012) have reported NO_2 sensors based on ZnO-FET (field-effect transistors). They also found that ZnO transistors are chemically stable in NO_2 ambient and observed the shift in threshold voltage of a FET upon exposure to NO_2. They observe the he threshold voltage shift caused by the shift in charge carrier trapping which is the functioning temperature. The threshold voltage shifts upward and downward upon charging and recovering. They also verified this methodology by comparing the calculated values with experimentally determining values. Eventually, they optimized the response time and the sensitivity for the desired NO_2 concentration by adjusting the duration of charging and the operating temperature.

Al-Ghamdi *et al.* (Al-Ghamdi, Al-Heniti and Mahmoud, 2013) have prepared ZnO thin film, based on methyl glycol deposited by the sol-gel spin coating technique on the p-Si substrate. They analyzed the Ag/n-ZnO/p-Si heterostructure based Schottky diode upon to H_2S gas and other gases (NH_3, H_2, and CH_3OH). The barrier height was strongly affected by all the tested gases. The lowest barrier height is obtained when the diode is subjected to H_2S gas which resulted in an enhancement of the sensitivity of ZnO film for H_2S gas among other tested gases. The barrier height between ZnO grains decreased and then increased as a function of annealing temperature. The optimum barrier height was achieved at 650 °C. At this annealing temperature, the ZnO film has shown a high sensitivity for H_2S gas.

Du *et al*. (Du *et al.*, 2013) have reported hydrogen (H_2) sensor based on palladium/palladium doped amorphous carbon film/SiO_2/Si (Pd/a-C:Pd/SiO_2/Si) structure by direct current magnetron sputtering method. The low power consumption and operation at RT over the entire range of measured H_2 make the sensor useful for systems with power constraint and harsh environment. The reported simplicity of the structure and easy fabrication technology make the sensors cost-effective. Upon exposure to 1.6 % H_2 in air, the currents of the Pd/a-C:Pd/SiO_2/p-Si and Pd/a-C:Pd/SiO_2/n-Si structures has changed about 840 % and 13,100 %, respectively. They explained phenomenon caused by transferring elections from the Pd film to the a-C:Pd film when exposing the Pd/a-C:Pd/SiO2/Si structure to H_2.

Kanungo *et al.* (Kanungo, Basu and Sarkar, 2015) have reported metal-oxide/p-Si heterostructure using nanocrystalline metal oxides (ZnO and TiO_2) thin films grown using sol-gel method. It has shown a good hydrogen sensing in the temperature range from (150 – 220 °C) at a fixed bias voltage after Pd surface sensitization of the metal-oxide surface. The nanocrystalline of TiO_2 thin film having lower grain size has shown higher hydrogen gas response compared to the nanocrystalline ZnO thin film. Comparatively superior performance of TiO_2/p-Si heterojunction was explained by the qualitative energy band diagram. The stability of both the sensor devices was found to be encouraged after Pd – modification. Both the heterojunction sensors have shown an improved hydrogen response with a short response time in nitrogen ambient with fast recovery time.

Miyoshi *et al*. (Miyoshi, Fujita and Egawa, 2015) have reported planar Pd/ZnO/GaN Hetero Junction Devices (HJDs) and its NOx sensing capability. The fabricated HJDs exhibit good rectifying properties even at a high temperature of 250 °C and have shown obvious current changes as barrier changes even under exposure of low-concentration (10 ppm) of NOx gases. The fabricated sensor also responded to the on/off switching of the gas introduction.

Bishop *et al*. (C. Bishop et.al., 2015) have reported a double Schottky junction gas sensor based on BGaN/GaN superlattice (SL) with Pt contacts. They tested the device under 15 ppm of NH_3, and have observed no current change under the applied gas even at a high temperature around of 250 °C. In contrast to, they have also reported 0–2% sensitivity to 0 –15 ppm NO_2 at the same temperature, indicating that the BGaN/GaN SL device shows a very good selectivity between NH_3 and NO_2 at this concentration range. Additionally, the BGaN/GaN SL sensor exhibited the better thermal stability and a faster response time.

Rajan *et al.* have investigated the electrical and gas sensing characteristics of Pt/ZnO thin film based Schottky contacts. This ZnO based thin film was grown on an n-Si substrate by RF sputtering. They have further obtained the gas sensing characteristics of the device towards different concentrations of hydrogen (200–1000 ppm) at 350 °C and revealed a maximum sensitivity of 57 % at 1000 ppm hydrogen.

Kadhim *et al*. (Kadhim, Abu Hassan and Abdullah, 2016) have reported Nano-crystalline SnO_2 thin films grown on bare Si (100) substrates using a simple cost-effective sol-gel method. The devices with Schottky contact with Pd were fabricated to detect H_2 gas with different concentrations and different temperatures. The devices showed a stable sensitivity of 120 % at RT with a power consumption of 65 μW, which is appropriate in remote regions. The good sensitivity is attributed to the high porosity of nanocrystalline SnO_2 thin film generated by adding glycerin. It makes easy for the adsorption and desorption of gas molecule. Moreover, Pd finger contacts significantly enhance the sensing properties of the gas sensor.

Ling *et al*. (Ling *et al.*, 2016) have reported an easy and effective magnetron sputtering method to fabricate $Pd/SnO_2/SiO_2/Si$ heterojunctions. It has shown excellent H_2 gas sensitivity. The H_2 response characteristics and the optimum operating voltage of this sensor are modulated by interface barrier potential between SnO_2 and Si, which can be understood by the interfacial energy band characteristics of the $Pd/SnO_2/SiO_2/Si$ heterojunction. Moreover, the heterojunctions have shown good sensitivity to O_2, NO_2, N_2, CH_4, CO_2, NH_3 and H_2 along with stability.

Thi Thu *et al*. (Thu *et al.*, 2017) have reported the sensors based on the nano-titanates (NTT) and the metal-electrodes (Au, Pt) on alumina substrate. It exhibited the fast response along with recovery and high selectivity for NO_2 gas in the low concentration range (0–10 ppm) at room temperature. The gas-sensing mechanism of the NTT sensors was explained by a change in the barriers of the Schottky contacts between the metal electrodes (Au, Pt) and the nano-titanates (NTT) when interacted with reducing/oxidizing gases.

1.5 Motivation and Problem Definition of the Thesis

In the recent years, most of the research is being carried out for the development of gas sensors owing to the concern associated with global warming, environmental pollution, public health safety, and security. The primary objective of all researchers is to develop gas sensor, with improved performance and miniaturization of sensing system. There is an essential need to develop gas sensors that are highly sensitive, selective, stable and reproducible. In addition to that, it should also meet logical needs such as small size, low power consumption, and low production costs. Among available many gas sensor, the solid-state gas sensors have shown exciting characteristic upon exposure of gases because of its interesting electrical properties. As literature review has gone deeper, it was felt that the emergence of nano-structures has brought the revolution in the gas sensors domain. It could be exploited further with engineered approach in order to enhance sensors performance. These nanostructures motivate the development of such a gas-sensor that meets all the essential and logical requirement of the sensor needed in the present scenario.

The problem definition is a vital part of any thesis. The present thesis has been revolved around the resistive sensor and Schottky diode based gas sensors because of its simple and promising structure. Based on the literature survey, the problem definition is listed below:

- ✓ To simplify the exhaustive paste preparation method that conventionally used for fabrication of thick film gas sensors i.e. preparation of glass powder and vigorous mixing of organic binder.
- ✓ To simplify the exhaustive fabrication process in thin film gas sensors while using semiconductor (Si, GaN, SiC etc) substrate i.e. RCA cleaning, photolithography, and oxide growth.

- ✓ To fabricate selective and reproducible sensor.
- ✓ To improve the sensitivity of the sensor particularity at low-temperature range.
- ✓ To minimize the fabrication cost of sensors.
- ✓ To minimize the additional treatments that are generally required for sensing film in order to improve sensors performance: surface modification, chemical dipping, doping etc.

1.6 Objectives of the Present Thesis

Based on literature review, it has been decided to fabricate such a gas sensor that meet the essential and logical requirements such as small size, low-temperature operability, mass production but minimum production cost with less complex circuitry. So, the objectives have been framed to develop a nanostructures based resistor and Schottky type gas sensors as shown in Figure 1.5 (a) and (b).

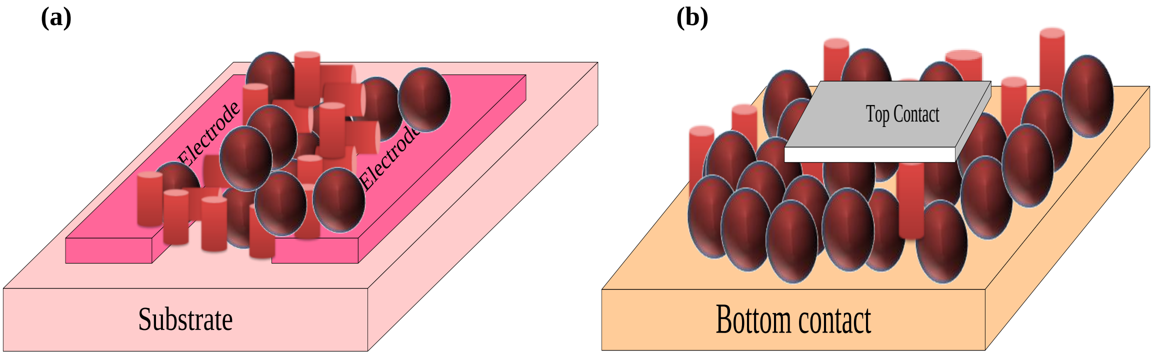

Figure 1.5: Proposed solid-state gas sensors using nanostructures (a) Resistor (b) Schottky diode.

1.8 Organization of the Thesis

The prime target of the present work is to investigate the NO_2 and H_2 sensing characteristic of nanoparticles based ZnO-resistor and Pd/ZnO Schottky diode. The thesis consists of **Six Chapters** including the present Chapter namely “Introduction and

Literature review". The contents of the remaining five chapters of the thesis are outlined as follows.

Chapter 2 discusses the micro-gas sensors and gas sensing materials. The performance parameters of gas sensors have also been listed. This chapter justifies the ZnO as a prominent semiconducing metal oxide among the several gases sensing materials such as polymer, TMD and Carbon allotropes etc.

Chapter 3 deals with the synthesis of nano-sized ZnO powder. It also discusses the fabrication and characterization of ZnO nanoparticles based resistor. Further, this chapter elaborates the fundamental theory of NO_2 gas sensing.

C**hapter 4** describes the fabrication and I-V characteristic of Pd/ZnO nanoparticles based Schottky diode upon exposure to NO_2 gas at room temperature. The barrier height of Pd/ZnO has also been studied as the function of NO_2 concentration in the range from 10 to 50 ppm.

Chapter 5 deals with the hydrogen sensing on fabricated Pd/ZnO nanoparticles based sensor at relatively low temperature (75 – 110 °C). H_2 dependent diode parameters such as barrier height and ideality factor have also been evaluated for 200 to 2000 ppm H_2 concentration.

Chapter 6 includes the summary and conclusions of the present work. Finally, a brief discussion on the future scope of research in the related areas also has been discussed.

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