Chapter 2

Micro-Gas Sensors and Gas Sensing Materials

2.1 Introduction

A wide spectrum of gas sensors is commercially available to detect toxic, pollutant, hazardous and explosive gases. However, research is still ongoing to enhance the performance and to miniaturize these gas sensors. The performance of the sensors is measured by sensitivity, selectivity, stability, response time and recovery time. The miniaturized or small sized gas sensors are referred to as Micro-Gas sensors which are a small sized transducer that converts any change in gas composition of ambience into the change in electrical quantity. The electrical quantity is measured in terms of current, voltage, resistance, inductance or capacitance. These Micro-gas sensors are further divided into two major categories: (i) Thick-film gas sensors (ii) Thin film gas sensors. The thick film micro gas sensor can be easily fabricated using screen printing technology. The thin film micro-gas sensor can be produced through atom by atom deposition in vacuum.

A gas sensing material plays a very crucial role for gas sensing mechanism e.g. physisorption and chemisorption. These materials have their unique properties such as molecular size, affinity and polarisability etc. (Nisha, 2013). In order to improve the sensor performance, a large number of different materials have been employed by various researchers. These materials are broadly categorized into four subcategories (i) semiconducting metal oxide (SMO) (ii) polymers and (iii) transition metal dichalcogenide and (iv) carbon allotropes etc.

SMO materials are prominent and have been used since last few decades because of their prevalent properties such as high thermal stability, easy to synthesise, easy to dope, cost-effective, robust and long-lasting. An n-type and p-type SMO materials are widely used for detection of the reducing as well as oxidizing gases. When n-type semiconductor (having electrons as majority charge carriers) is exposed to reducing gas molecules, the electron concentration increases at the material surface which results in an increase in conductivity. In contrast the exposure of oxidizing gas, the gas molecules capture electrons from the material surface that leads to the formation of depletion layer near the surface of SMO material, which results in a decrease in conductivity of the material. Similarly, a p-type semiconductor (having holes as a majority charge carriers) shows the reverse phenomenon with the gas molecules. In case of a p-type semiconductor, the conductivity increases upon exposure to oxidizing gas molecules and decrease in conductivity with reducing gas molecules (Fine *et al.*, 2010).

It is very important to detect the very low concentration of toxic, hazardous and inflammable gases even at room temperature in order to prevent unintentional and unfortunate incidents of massive explosion, immediate death, blistering and other health complications. As per the available literature, it has been observed that these SMO materials fail to extend the advantage of detection of gases at low temperature. That's why polymer has been introduced in the field of gas sensors. An important advantage of polymer-based gas sensors is their efficiency.The polymers are also of two types; conducting and non-conducting polymers.

Now-a-days transition metal dichalcogenide (TMD) is a predominant as gas sensing material because of its atomic-thin layered structure, large surface-to-volume ratio, and large adsorbing capacity of gas molecules with strong surface activities (Kim *et al.*, 2017). Another gas sensing material which attracts the attention of the researchers is

carbon allotropes i.e. carbon nano-tube (CNT), graphene because of its unique properties to provide high-sensitive gas sensors even at room temperature. CNT is also classified into two types; single-walled CNTs and multi-walled CNTs.

Among all these gas sensing materials, semiconducting metal oxide (SMO) material (such as ZnO, SnO_2, WO_3, TiO_2 etc.) are prominently used for detection of oxidizing as well as reducing gas because of its highly thermal stability and good sensing response. ZnO is one of the SMO materials which have been used in the present work for improving H_2 and NO_2 response at relatively low operating temperature. ZnO has a wide band gap (3.37 eV) at 300 K and a large exciton binding energy (60 meV) (Liu *et al.*, 2014) which exhibits either cubic zincblende (ZB) or hexagonal wurtzite (WZ) structure. The utilization of ZnO as a gas sensor has been studied by many researchers because of its high chemical sensitivity toward various toxic and in-toxic gases.

The nanostructure of ZnO material has sparked the attention of researchers. The nano-material has drawn a great deal of attention from its prefix nano because of its meaning ‘dwarf’ or extremely small which lead to potential application in the area such as optoelectronics, single electron transistor, a light emitter, gas sensor etc. The one or more dimensions less than or approximately 100 nm is considered to be ZnO-nanomaterial. The ZnO-nanomaterial is a new structure of bulk ZnO. In the gas sensor, the ZnO nano-material provides the large surface to volume ratio of material which finally leads to prominence sensitive response towards various gases.

2.2 Micro Gas-Sensors

` A micro gas sensor is a small sized sensor that converts any change in gaseous composition into the electrical signal. This electrical signal is measured in terms of voltage, current, resistance, capacitance, and inductance etc. According to their fabrication techniques these sensors are classified as:

1. Thick film gas sensors
2. Thin film gas sensors

2.2.1 Thick Film Gas Sensors

Thick film gas sensors use thick film technology for the fabrication of sensor and the associated elements. This technology uses conductive, resistive or insulating paste for depositing or printing film on a ceramic substrate by using screen printer. The thick film technology is used for the fabrication of only passive elements (i.e. resistive, capacitive type sensors) because of its tandem deposition technique and large thickness of the layer. Figure 2.1 depicts the thick film sensor in the form of resistive pattern. A thick film sensor comprises of a gas sensitive layer printed over electrode which is printed and fired first onto the ceramic substrate. These electrodes help in connecting the gas sensitive layer to the outside world and are used for monitoring the characteristics of the sensor in presence of gases. Generally, the heater pattern is also printed over the rear side of the substrate for generating appropriate temperature necessary for the sensors. Nowadays, a number of companies are using this technology such as Envin scientific, Zellweger Analytics, Trafag and Oliver IGD, Industrial Scientific Corporation, Draerger Industrie and KANE (gas detectors) (Nisha, 2013).

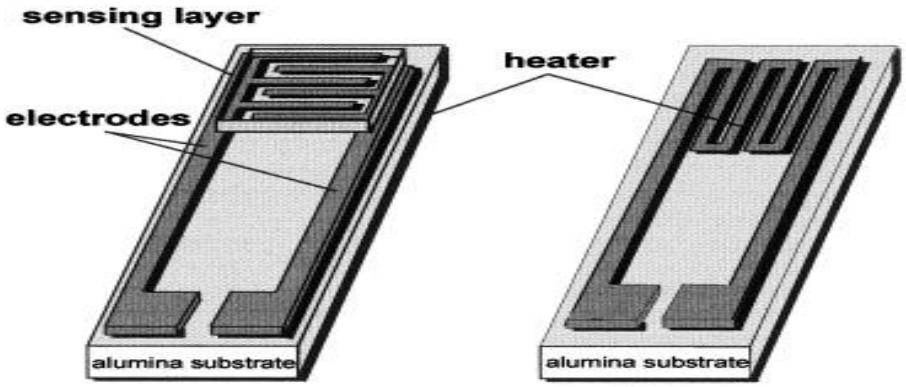

Figure 2.1: The test pattern of thick film gas sensor (Teterycz *et al.*, 1998).

2.2.2 Thin Film Gas Sensors

Thin film sensors involve, deposition of a thin layer using standard thin-film technology on a substrate. The thin film technology is a traditional well-established atom by atom material deposition technique in vacuum. It is commonly used for growing a thin layer of a material ranging from fractions of a nano-meter to several micrometers in thickness (Chopra, 1983). The thin film deposition techniques follow three vital steps: (i) evolution of the molecular atoms (ii) transportation of these atoms to the substrate through an appropriate medium (vacuum) and (iii) allows condensation on the substrate, either directly or via chemical and /or electrochemical reaction. Figure 2.2 depicts the thin film resistor as a gas sensor. Thin film sensors have been found more suitable as it allows the control of material composition at a monolayer level which eventually causes the tremendous improvement in the sensitivity and the long-term stability of the sensor (Sberveglieri, 1995).

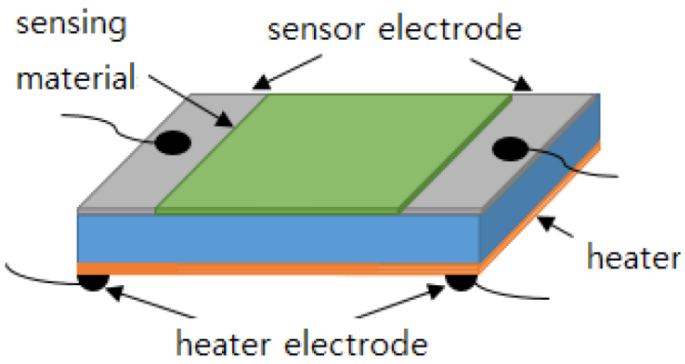

Figure 2.2: A thin film resistor as a gas sensor (Lee, 2017).

2.3 Performance Parameters of Micro-Gas Sensors

The change in solid-state gas sensor characteristic upon exposure of gases depends on the nature of sensors material (n-type or p-type) and gas (oxidizing and reducing). The response curve with respect to time is shown in Figure 2.3 that depicts the performance of the sensor. Various parameters that affect the sensors are listed below:

1. Sensitivity
2. Selectivity
3. Stability
4. Response time
5. Recovery time

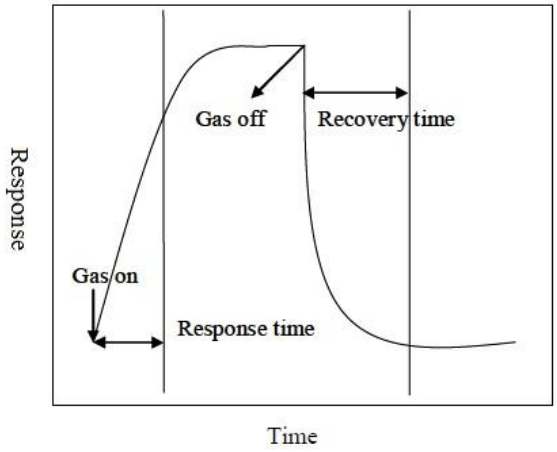

Figure 2.3: A Schematic response curve of the gas sensor.

2.3.1 Sensitivity

It is the sensor characteristic that shows a variation in physical and chemical properties of the sensing material under the gas exposure. The sensitivity is generally defined as the ratio of the change in sensor parameter (i.e. resistance, current, voltage etc.) in the presence of target gas to that in the air (Chougule, Sen and Patil, 2012). The sensitivity is highly dependent on film thickness, operating temperature, film porosity, the presence of additives and crystallite size. The percentage sensitivity of the sensor is calculated through given Equation (2.1)

$$S\ \% = \frac{\text{change in senser's parameter}}{\text{sensor's parameter in air}} \qquad (2.1)$$

2.3.2 Selectivity

It is the characteristic of the sensor which discriminates the sensor towards a perticular species of the gas in the mixture of the gases. Selectivity plays a major role in the gas identification

2.3.3 Stability

It is a characteristic of the sensor that shows the repeatability of the device response after a long use. The scope of the fabricated sensor will be limited if the sensor's response is not repeatable over long-term.

2.3.4 Response time

It is measured as the time interval in which response curve attains a 90% percent of its final value when the sensor is exposed to the full-scale concentration of the gas.

2.3.5 Recovery time

It is the time required in which the sensor's response reaches to 10% of the saturated value when the sensor is exposed to a full-scale concentration of the gas and then placed in clean air.

2.4 Gas Sensing Materials

Since material plays a very crucial and vital role in the detection of gases. The pioneers have searched out various materials that are prone to be sensitive towards toxic and explosive gases. From a material selection point of view, the materials should be compact in size, low cost along with simple processing steps. The favourite characteristic of gas sensing materials is its high surface to volume ratio which increases the interaction between gases and sensor surface which results in the enhancement of the sensing performance of the sensor. To meet all requirements for gas sensing, materials are characterized in four broad categories:

1. Semiconducting metal oxide
2. Transition metal dichalcogenide
3. Polymers
4. Carbon allotropes

2.4.1 Semiconducting Metal Oxides (SMO)

The most promising gas sensing material is a SMO which provides many advantages such as low cost and easy production. SMO Material based gas sensors have been widely used as domestic and industrial gas detectors for gas-leak alarm, process control and pollution control (Nisha, 2013). The SMO Materials are made from the chemical composition of transition/ nontransition metals with oxygen. This SMOs such as ZnO, SnO_2, CuO, TiO_2, In_2O_3, Fe_2O_3 WO_3 and MgO etc (Bassey, 2014) are used to detect various reducing, or oxidizing gases which are mainly based on the change in conductivity upon exposure of the reducing as well as oxidizing gases. The SMOs are classified into two types of semiconductor as n-type and p-type. An n-type semiconductor (such as ZnO, SnO_2, In_2O_3) consist of electrons as a majority charge carriers and conductivity of semiconductor increase as a result of interaction with reducing gas molecules upon the semiconductor surface. In contrast the oxidizing gas molecule depletes the charge carrying electrons of semiconductor, results as decreasing in conductivity. Similarly, p-type semiconductor (such as CeO_2, TeO_2, Ag_2O etc.) conducts holes as a majority charge carriers. The reverse effects are observed with the p-type semiconductor and it shows an increase in conductivity upon oxidizing gas molecules and decreases in conductivity with a reducing gas (Fine *et al.*, 2010). The n-type and p-type SMO upon exposure of oxidizing and reducing gases are summarized in Table 2.1.

Table 2.1: Classification of n-type and p-type SMOs.

Classification	Semi-conducting metal oxides	Oxidizing gas	Reducing gas
n-type	ZrO_2, ZnO, CaO, TiO_2, WO_3, SnO_2, In_3O_3, MgO, Al_2O_3, Ga_2O_3, V_2O_3, Nb_2O_3	Resistance increases	Resistance decreases
p-type	Y_2O_3, La_2O_3, CeO_2, Mn_2O_3, NiO, PdO, Ag_2O, Bi_2O_3, Sb_2O_3, TeO_2	Resistance decreases	Resistance increases

One of the main challenges in the development of SMO based gas sensors is encountered by researchers is the selectivity of the sensor toward a particular gas. Currently, researchers have been using two general approaches for enhancing the selectivity, of the gas sensors. The first one is focused at preparing a SMO material through surface modification or metal doping that is specifically sensitive to one gas/compound and has low or zero cross-sensitivity to other gas/compound. The other approach is based on the preparation of SMO materials to discriminate between several mixture by offering a directional sensitivity e.g. showing positive or upward directional sensitivity toward on gas and negative sensitivity or downward directional toward others gases (Nisha, 2013).

2.4.2 Transition Metal Dichalcogenide (TMD)

Recently these transition metal dichalcogenide (2-dimensional) materials have been used for gas sensing application because of its inherent advantages in terms of atomic-thin layered structure, the large adsorbing capacity of gas molecules, large surface-to-volume ratio, and strong surface activities necessary for sensing the gas species. The transition metal dichalcogenides is represented as MX_2. In these materials, the layered structures are X-M-X, where M represents layer of transition metal atoms (W, Mo, Re and Cr), which is hexagonally packed and sandwiched between two X, which represent chalcogen atoms (S, Se, Te etc) as shown in Figure 2.4. In general, the thickness of each layer is about 6–7 Å (Ugeda *et al.*, 2014).

These materials include MoS_2, $MoSe_2$, WS_2, ReS_2, WSe_2, and $ReSe_2$ etc. TMDs monolayers have the potential to exist in more than one possible crystal structure that implies: Semiconducting (2H) phase, Semi-metal (1T') phase, Tunable Bandgap, high sensitivity for varieties of chemicals (Kim *et al.*, 2017). Thickness is dependent on Physical and Chemical properties. The Gas sensing mechanism using TMD is based on

the transfer of charges, in which the sensing material acts as absorber or donors of charges. The charge transfer between the gas molecules and the sensing material will causes a change in the sensing material properties (Guo, Rani and Zaghloul, 2017). The difficulties in the synthesis of these TMD restrict its uses in the gas sensing application.

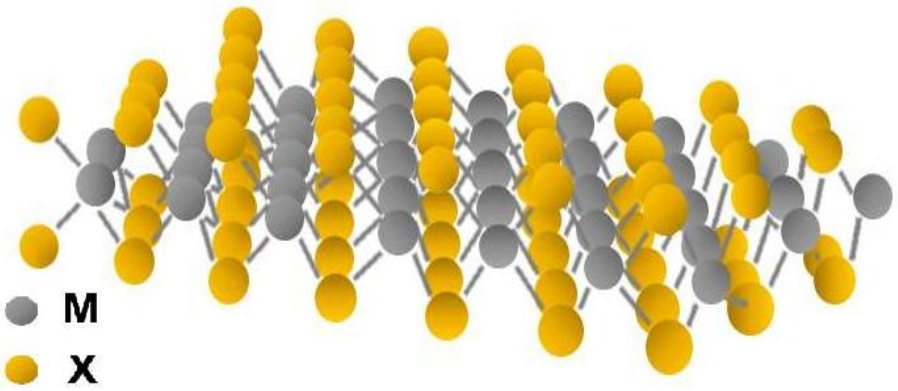

Figure 2.4: Atomically thin transition metal dichalcogenide [IR2]

2.4.3 Polymers

Polymers are materials made of long, periodical chains of molecules as shown in Figure 2.5. The materials show unique electrical, mechanical and chemical properties, depending on the type of molecules being bonded and how they are bonded. Depending upon arrangement of their molecules, some polymers bend and stretch, like rubber and polyester while others are hard and tough, like epoxies and glass.

Most of the sensors based on SMO materials exhibit a very large sensitivity towards organic and inorganic gases like ammonia, alcohol (C_2H_5OH) and formaldehyde. However, there are some organic gases that make adverse health effects, when their concentration goes down to a certain threshold level. This minimum concentration could not be detected by the metal oxide material. Since, these gases are usually used as ingredients of household products or in industrial processes where they normally get

vaporized at room temperature. Therefore, it is important to detect the low concentration of these vapors at room temperature much before they cause adverse effect on health and other complications at the household/work place. This will also help in maintaining the environmental emission well below the permissible limit. These needs could be fulfilled conveniently by polymer material.

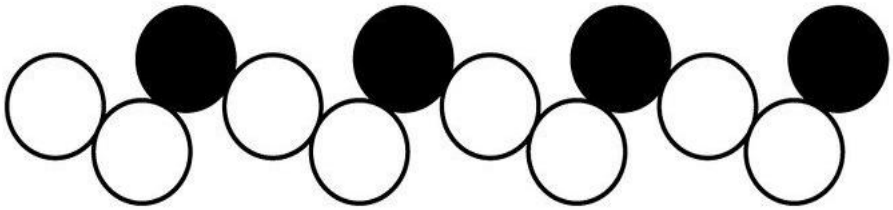

Figure 2.5: A long chain molecules made of polymer.

Polymers can be further classified into two basic types; conducting polymers, and non-conducting polymers. In conducting polymer, the electrical conductivity is affected under the exposure of diverse organic and inorganic gases. The non-conducting polymer has been widely used as a coated film on a different transducer device. This polymer's layers cause a change in resonance frequency, dielectric constant and enthalpy upon absorption of exposed gases. In addition to that, the non-conducting polymer is also used along with semiconducting metal oxide gas sensors to improve the overall performance.

2.4.4 Carbon Allotropes (CA)

Recently, carbon allotropes have drawn a great attention due to its extraordinary electronic, chemical, mechanical, thermal and gas sensing properties. These materials are used as gas sensing materials due to its high specific surface area and unique electrical properties such as low electrical noise and high mobility. These materials are further classified into two categories: (i) Carbon nano tubes (CNT) (ii) Graphene. As shown in Figure 2.6.

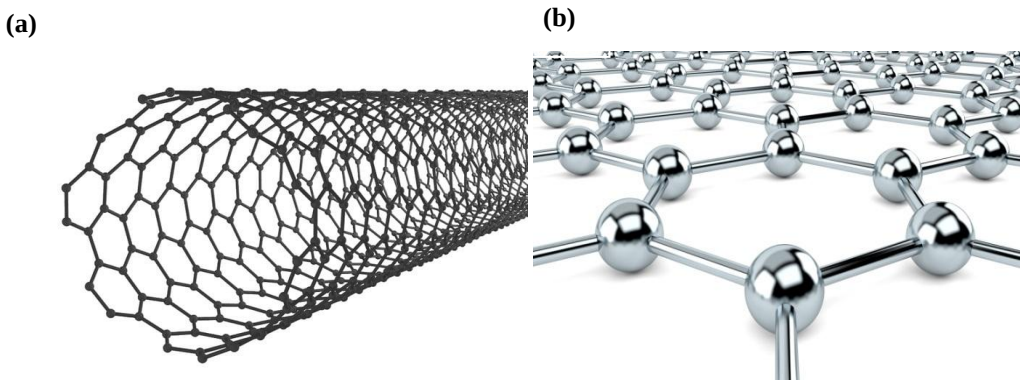

Figure 2.6: A view of (a) Carbon nano tube (CNT) [IR3] (b) grapheme [IR4].

2.4.4.1 Carbon-nano Tubes (CNT)

It is cylindrically nano-structured Carbon allotropes that was discovered and described by S. Injima, Japan, in 1991. One of the amazing phenomena associated with the nanotubes is the dependence of their properties on their shape. Nanotubes are elongated cylindrical structures with diameters of 1 to several dozens of nanometers and lengths up to several microns consisting of one or several hexagonal graphite planes rolled in form of tubes. Their surface consists of regular hexagonal carbon cycles. As a nano tube is a surface structure, its whole weight is concentrated in the surface of its layers which enhances the adsorption capacity of CNT to a great extent. As compared to SMO material, CNT has exhibited micro-fabrication process, needs low power supply, and possesses good corrosion resistance. It is found in two types: (i) single walled (ii) multi walled. The single-walled carbon nanotube (SW-CNT) consists of a single layered cylinder whereas a multi-walled carbon nanotube (MW-CNT) comprises of several concentric layered cylinders. The use of these CNTs is restricted due to the complex synthesis process and its unstable behavior.

2.4.4.2 Graphene

Graphene is a unique and attractive sensing material for gas sensors. It has been widely explored for the fabrication of gas sensors because of their atomic- thick two-

dimensional structures, high conductivity and large specific surface areas. The two dimensional structure of graphene makes the electron transport a highly sensitive parameter due to the adsorption of gas molecules (Shi, 2013).

The detection of gases by graphene and CNT materials is mainly based on their conductance changes upon the adsorption of sensing species. The adsorption of gas molecules on carbon allotropes surface leads to changes in its electrical conductivity that can be attributed to the change in the local carrier concentration induced by the surface adsorbates. The carbon allotropes are restricted to use as gas sensor material because of its very complex synthesis process and thermally unstable in nature. Most of the carbon allotropes based gas sensors have been reported poor reversibility. Insufficient recovery of the sensor generally restricts their use in particularity in the sensor application.

2.5 Choice of Gas Sensing Materials

All the materials discussed above have shown their super properties toward gas sensing application. However, each material has their own limitation for meeting essential requirements such as high sensitivity, high selectivity, stability and reproducibility, as well as logical requirement of small size, low power consumption and low production cost. For the selection point of view among all, the above discussed materials, only SMO has shown superior properties to meet the essential requirements like highly thermal stable and logical requirements like very low production cost. SMO has worked long term and produce reversible response which is very difficult to achieve by other gas sensing materials i.e. TMD, Polymer and carbon allotropes.

However, among many SMOs materials i.e. V_2O_3, Nb_2O_3, ZnO, TiO_2, SnO_2, WO_3, Y_2O_3, La_2O_3, CeO_2, Mn_2O_3, NiO etc. only few metal oxides (such as ZnO, SnO_2, TiO_2, WO_3) has shown preferable characteristics toward gas sensing application. Among

these few SMO materials, ZnO has shown unique characteristics towards reducing as well as oxidizing gases. Some of ZnO properties are listed below:

- High electron mobility
- Non toxic in nature
- High thermal stability
- Easily doping possible
- Act as a catalytic
- Able to absorb visible spectrum
- Highly photo stable
- High oxidation resistibility

2.6 General Properties of Zinc Oxide (ZnO)

ZnO has long been a promising material in the field of gas sensing. Its non-toxicity and availability in abundance on the earth surface has made it prominent material for various applications like optoelectronics, gas sensors, spintronics and solar cell etc. ZnO is a wide bandgap (3.37 eV) and a large exciton binding energy (60 meV) (Morkoc and Ozgur, 2009) piezoelectric material. The present work focuses on some important properties of ZnO material.

2.6.1 Structural Properties

ZnO is II-VI binary compound semiconductors crystalline, which exhibit cubic zinc blende (ZB), hexagonal wurtzite (WZ) and rock salt structure (Nisha, 2013),(Morkoc and Ozgur, 2009) in which each anion is encompassed by four other cations at the corners of a tetrahedron and vice versa. The stable zinc blend structure can be grown only on cubic substrates and rock-salt structure only formed at high pressure (~10 GPa). The wurtzite structure is widely used because of its highest stability at normal ambient

condition (Nisha, 2013),(Morkoc and Ozgur, 2009). The structural data is elaborated in the below Table 2.2.

Table 2.2: Structural details of Zinc oxide of the wurtzite structure.

1. Lattice constants	a = 0.32498 nm, c = 0.52066, c/a = 1.6021 where a and c is lattice dimensions
2. Density	5.67 gm/cm^3, 4.2 x 10^{22} ZnO molecules /cm^3
3. Hardness	5 GPa
4. Bulk modulus	142.4 GPa

The wurtzite structure has a hexagonal close packing (HCP) structure. The structure of ZnO consists of alternating planes having Zn^{2+} and O^{2-} ions as shown in Figure 1.7. These ions are tetrahedrally coordinated and stacked along the c-axis on an alternate basis.

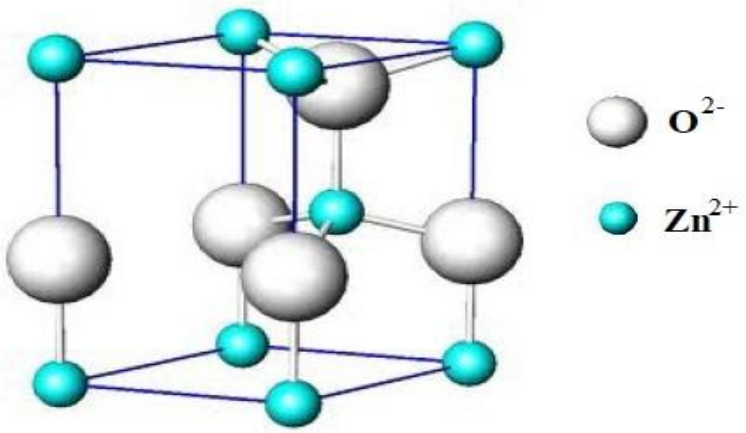

Figure 2.7: Hexagonal wurtzite structure of Zin Oxide (ZnO) (Nisha, 2013).

Figure 2.7 clearly indicates that each sub-lattice of ZnO crystal are bonded with another four atoms per unit cell and every atom of one kind (group - II) is surrounded by four atoms of the other kind (group - IV) or vice versa, which are coordinated at the edges of a tetrahedron.

2.6.2 Electronic Properties of ZnO

The electronic band structure of any materials represents the electron energy that determines the potential utility of the materials. In the E-$\vec{K}$ band diagram of ZnO as shown in Figure 2.8, the separation between the top of valance band and bottom of conduction band can be easily characterized as energy band gap. The difference between maxima of valance band and minima of conduction band at the Γ point $\vec{K}$ = 0 indicating that ZnO is a direct band material with a bandgap of 3.3 eV (Bassey, 2014).

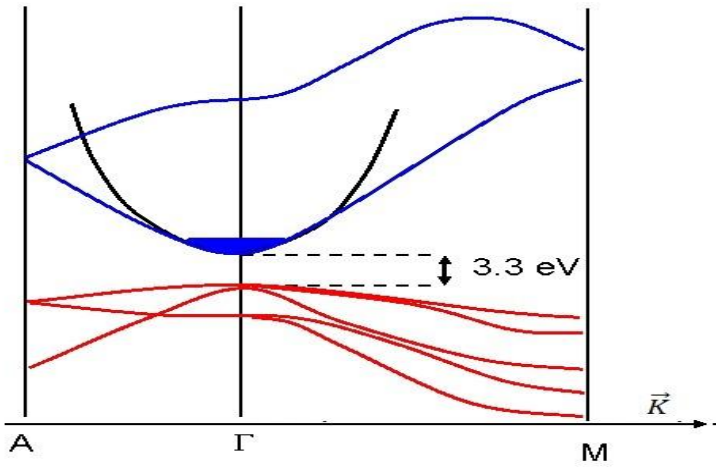

Figure 2.8: E-K representation of valance and conduction band of ZnO (Hyde, 1967).

2.6.3 Gas Sensing Properties of ZnO

Gas sensing by the ZnO is basically a surface phenomenon. The sensing properties of the ZnO based gas sensor can be explained by the sorption of target gases on the ZnO surface. To understand the surface reaction, the adsorption has to be considered carefully. When the gas molecules interact with the ZnO surface, it experiences imbalanced forces of intermolecular interaction which contributes to the surface energy. This causes accumulation of gas molecules at the surface. This accumulation of gas molecules at the surface is called adsorption which is purely a surface phenomenon. The ZnO surface consists of a large number of active or traps sites onto which the gas

molecules get adsorbed. These adsorbed gaseous molecules are independent and could interact with its nearest neighboring atom. These adsorptions are classified into two types: physisorption and chemisorption. The strength by which adsorbate (target gas molecules) molecules are attached with the adsorbents (surface adsorption sites) determines the nature of adsorption as shown in Figure 2.9.

2.6.3.1 Physisorption

Physical adsorption is termed as physisorption in which the adsorbate adheres to the ZnO surface only through reversible Vander walls (weak intermolecular) forces. Physisorption generally takes place at a relatively large distance away from the surface. This is the first interaction between a gas molecule and the ZnO surface (sensing element). In the physisorption at monolayer, the physisorption coverage X is defined as follows

$$X = \frac{N}{N_t}$$

Where N = Number of molecules adsorbed per surface unit.

N_t = Total number of surface adsorption sites.

2.6.3.2 Chemisorption

Chemical adsorption is termed as chemisorption in which the gas molecule adheres to a sensing surface (ZnO) through the formation of a chemical bond instead of Vander wall force as it cause of physisorption. This sorption is characterized by strong interaction between sensing surface and target gaseous molecules which results in higher bonding energy. There are two different kinds of chemisorption mechanism.

(i) Associative chemisorption: In this mechanism, all atomic bonding are kept in the adsorbed molecule.

(ii) Dissociative chemisorption: In the mechanism, the bonding of the adsorbed molecule is decomposed and individual molecule fragments are bonded on the metal oxide surface.

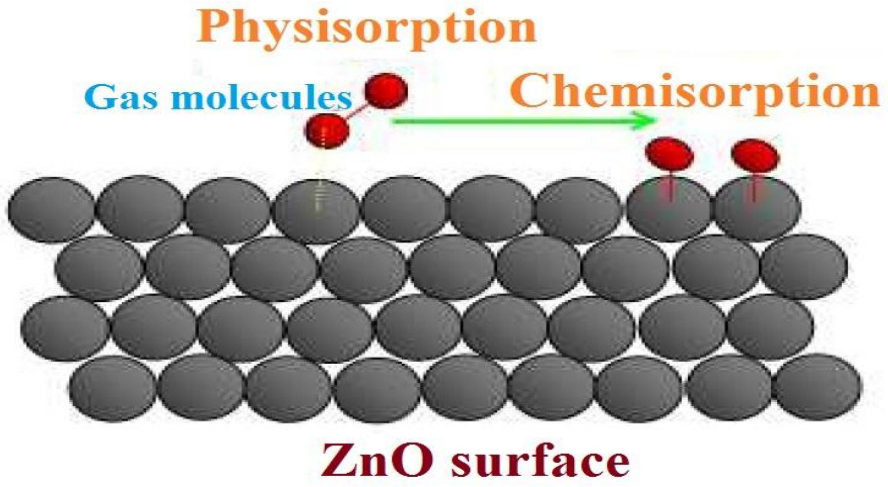

Figure 2.9: Physisorption and Chemisorption process on the ZnO Surface (Griffiths, 2012).

2.7 Summary

This chapter deliberates about the micro gas sensors and various gas sensing materials. The thick film micro gas sensor can be easily fabricated using screen printing technology. The thin film micro-gas sensor can be fabricated through atom by atom deposition in vacuum. The performance parameter of Micro-gas sensor is elaborated by sensitivity, selectivity, stability, response time and recovery time of the sensors. This chapter has also thrown light on transition metal dichalcogenide (TMD), semiconducting metal oxide (SMO), polymers and carbon allotropes as a prominent gas sensing materials. Among various gas sensing materials, SMO (such as ZnO, SnO_2, WO_3 etc.) is a promising candidate because of it's long-lasting, reproducible and stable gas sensing response. Among SMO materials, ZnO has emerged as a very promissing material due to its thermal stability and non toxic behavior. The structural and gas sensing properties of ZnO has also been discussed in this chapter.

References

Bassey, E. E. *'Development and Characterisation of Metal Oxide Gas Sensors'*. PhD Thesis, Auckland University of Technolgy, 2014,

Chopra, K. L. C. I. K. "'Thin Film Device Applications'", in. Springer, 1983,

Chougule, M. A., Sen, S. and Patil, V. B. "Development of nanostructured polypyrrole (PPy) thin film sensor for NO2 detection", *Sensors and Transducers*, 2012, vol. 9, no. 5, pp. 482–490.

Fine, G. F. *et al.* "Metal oxide semi-conductor gas sensors in environmental monitoring", *Sensors*, 2010, vol. 10, no. 6, pp. 5469–5502.

Griffiths, H. E. *Layered Double Hydroxides : Structure, Synthesis and Catalytic Applications*. PhD Thesis, University of Huddersfield, 2012,

Guo, S., Rani, A. and Zaghloul, M. E. *'2D Materials for Gas Sensing'*. Washington DC, 2017,

Hyde, F. J. "The Physics of Semiconductors", *Electronics and Power*, 1967, vol. 13, no. 5, p. 176.

Kim, T. *et al.* "Two-Dimensional Transition Metal Disulfides for Chemoresistive Gas Sensing: Perspective and Challenges", *Chemosensors*, 2017, vol. 5, no. 2, p. 15.

Lee, S. P. "Electrodes for Semiconductor Gas Sensors", *Sensors*, 2017, vol. 17, no. 4, p. 683.

Liu, S. *et al.* "Enhancing NO2 gas sensing performances at room temperature based on reduced graphene oide-ZnO nanoparticles hybrids", *Sensors and Actuators B: Chemical*, 2014, vol. 202, pp. 272–278.

Morkoc, H. and Ozgur, U. "'General Properties of ZnO'", in. Verlag, Weinheim, 2009, , pp. 1–76.

Nisha, R. *'Development of semiconductor metal oxide gas sensors for the detection of*

NO2 and H2S gases ’. PhD Thesis, Cochin University, 2013,

Sberveglieri, G. "Recent developments in semiconducting thin-film gas sensors", *Sensors and Actuators: B. Chemical*, 1995, vol. 23, pp. 103–109.

Shi, W. Y. and G. "Graphene-Based Gas Sensors", *Journal of Material Chemistry A*, 2013, vol. 23, no. 10, pp. 133–152.

Teterycz, H. *et al.* "Anomalous behaviour of new thick film gas sensitive composition", *Sensors and Actuators B*, 1998, vol. 47, pp. 153–157.

Ugeda, M. M. *et al.* "Giant bandgap renormalization and excitonic effects in a monolayer transition metal dichalcogenide semiconductor", *Nature Materials*, 2014, vol. 13, no. 12, pp. 1091–1095.

[IR2] http://www.iae.kyoto-u.ac.jp/conv/en/research_matsuda_TMD.html.

[IR3] https://phys.org/news/2017-11-subset-carbon-nanotubes-poses-cancer.html.

[IR4] https://www.azom.com/article.aspx?ArticleID=15050.