Chapter I

General introduction to fabrication, characterization and application of solid state gas sensors

I.1. Introduction

A device which detects a change in the physical and/or chemical stimulus and converts it into an electrical signal that can be measured or recorded is known as ‘sensor’. A wide field of sensors have been developed with the growth of science and technology leading to the development of various sensing devices. This is an interdisciplinary branch involving physics, electronics, chemistry, sometimes biology involving biosensors. ‘Sensor’ and ‘transducer’ are two important words which are widely used now a days for the description of various measurement systems. Transducer is a device which transfers power in same or in different form from one system to another. Due to large number of sensors that may exist one may categorize sensors depending upon the principle of operation. Sensors are normally prepared in the amorphous, single crystalline, polycrystalline, as well as nanostructural forms. Finally, the newly emerged sensing technology is utilizing nanomaterials for very efficient low temperature gas sensing. In the present chapter, we will discuss about theoretical background of solid state semiconductor gas sensors, more particularly about metal oxide sensor (MOS).

I.2. List of solid state Gas Sensors and their Detection Principles

i) Chemiresistive : Change in the conductivity while exposure to different analyte gases.

ii) Potentiometric : Here the signal is measured as potential difference/voltage obtained between the working electrode and that of the reference electrode. The potential of working electrode must depend on the analyte gas concentration.

iii) Chemical field effect transistors : Current–Voltage (I-V) curves of this type are sensitive to a particular gas when it interacts with a gas.

iv) Calorimetric : Oxidation on a catalytic element results the rise in temperature which measures the concentration of a particular combustible gas.

I.3. Operating principle of the transition metal oxide semiconductor gas sensors

Surface of the sensing element and the microstructure of the same acts as receptor and transducer respectively for transition metal oxide semiconductor gas sensor . A change in output resistance occurs due to the receptor and transducer function of these active metal oxide layer of the gas sensor.

Under exposure of a reducing or oxidizing species sensor undergoes an exponential change in conductance across the sensing layer of the sensor under constant flow rate and operating temperature which is assumed to be the stationary condition. The response of semiconductor gas sensor materials towards the reducing gases are denoted by the change in the concentration of the adsorbed oxygen. Oxidizing species can interact with sensor surface by any of the two ways viz. interacting with the sensor surface directly which results an negatively charged ionosorbed species and also competes with the ionosorbed oxygen ions already present at the relative adsorption sites.[1,2] Conductance of sensing layer are modulated by the change in the height of potential barriers. Thus sensitivity depends upon the structural characteristic of the sensor materials, the working temperature. The surface with dopants or without dopant which are catalytically active plays an important role in determining the sensitivity. Brief review of various established models are depicted hereunder.

I.3.1. Potential Barrier Model

Potential barrier is the most authentic model for the semiconductor gas sensors operation, representing the simplified metal oxide grains chain model. According to the physical model (Figure I.a) the grains contain adsorbed oxygen in its surface, where the adsorbed oxygen contains trapped electrons coming from the subsurface grains region leading to an insulating surface layer. Moreover, it is assumed that electrons are more in bulk. Conduction occurs when electrons go from one grain to another through the insulating layer. Band model has been illustrated in the Figure I.b which well depicts the insulating layer with potential barrier. The adsorbed oxygen present at the surface removes electrons leaving a positively charged surface. Consequently, an electric field develops between the positively charged ions and the negatively charged oxygen ions present upon the surface.[3] To move to the neighbouring grain the barrier associated with the electric field must be overcome by the electrons present in conduction band. The potential barrier is indicated as qV_s. V_s increases proportionately with the concentration of O^-.[4] n_s represents the density of electrons having sufficient energy to cross the potential barrier. This is given by the Boltzmann equation:

$$n_s = N_d \exp\left(\frac{-qV_S}{kT}\right)$$

N_d is density of donors. With increasing concentration of oxygen on the surface the barrier increases. As a consequence transition of fewer electrons are possible increasing the resistance thereby. The adsorbed oxygen shows a capacity of 1 eV band bending at high coverage.

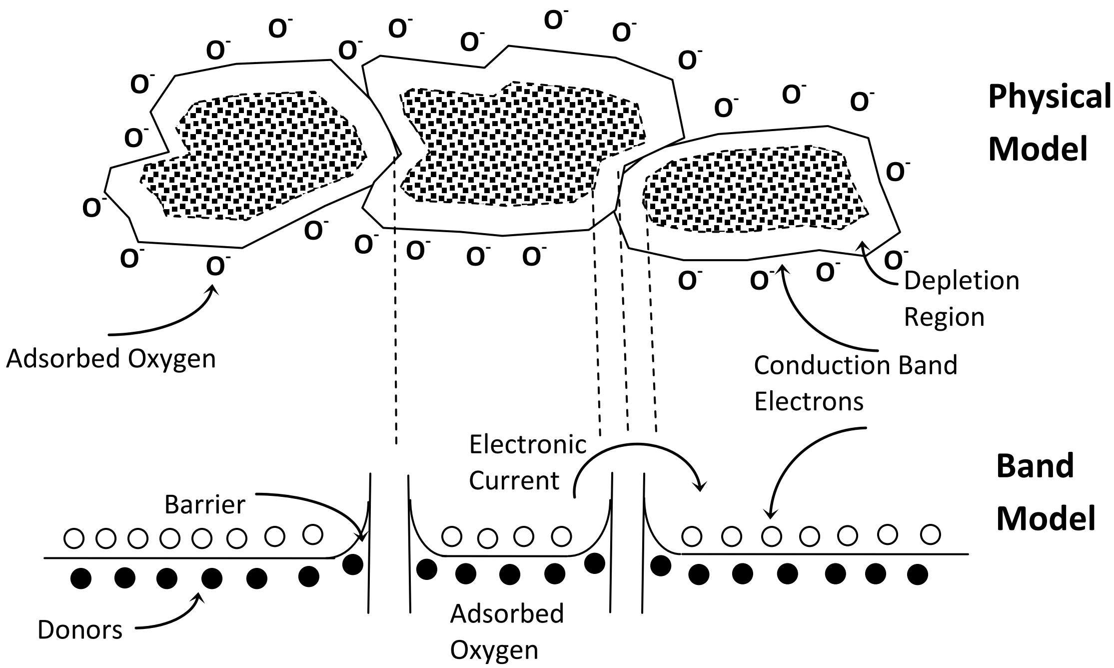

Figure I.1.a) Physical model and b) Band model showing the development of potential barrier on oxygen adsorption.

Relaxation of surface charge takes place when the surface comes in contact with reducing gas present in air due to reduction of the surface oxygen level to a steady state. That is oxygen is removed by the reducing gas from surface is proportional to the concentration of the gas. Hence decrease in the depletion region and also in resistance occur due to the reinjection of electrons into the bulk of the semiconductor material. These are represented by the reactions given below.[5]

$$O_2 + 2e^- \rightarrow 2O^-$$

$$RH_2 + 2O^- \rightarrow RO + H_2O + 2e^-$$

H_2O and gases are given up to the atmosphere. Surface layers enriched with charge carrier form a complex interlacing of conducting channels which determine the conductance of semiconductor.

I.3.2. Band Bending

Oxygen is ionosorbed on surface of the metal oxide in absence of humidity. The ionosorbed species can act as an electron acceptor due to their varrying relative energetic position about Fermi level, E_F as depicted by the Figure I.2. Absorption of oxygen on the surface depends on the temperature predominantly. In case of oxide(O^{2-}) ions the operating temperature is below 420 K and in case of superoxide (O^-) ions it is between 420-670 K. Above 670 K, formation of oxide (O^{2-}) occurs again and above 870 K it is directly impregnated to the lattice.[6] The electrons required for this process originates inherently from oxygen vacancies, they are extracted from unconduction band, E_C and trapped to the surface which leads to an electron-depleted region on the surface, widely known as the space-charge layer, Λ_{air}.[7-10] E_V, E_F and E_C represents the valence band energy, fermi level energy and conduction band energy respectively. Λ_{air} and $eV_{surface}$ indicates thickness of the space-charge layer and the potential barrier respectively. The e^- and (+) represents the conducting electrons and the donor sites respectively.

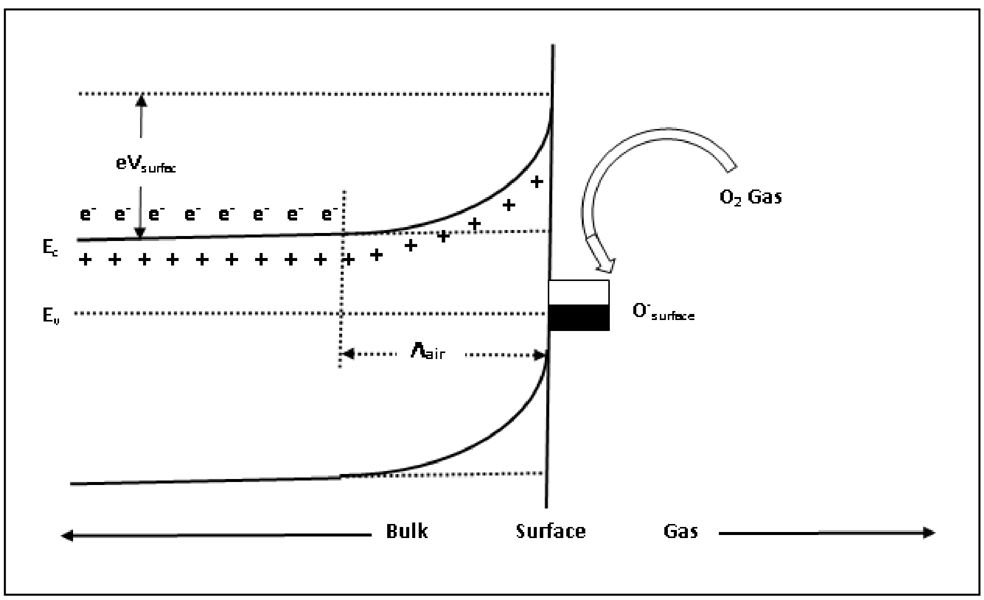

Figure I.2. Band bending model showing semiconductor with a wide band gap

Figure I.2 reveals that presence of negative charge on the surface leads band bending. It creates a surface potential barrier (expressed as $eV_{surface}$) with value 0.5 to 1.0 eV. $eV_{surface}$, Λ_{air} both are determined by the amount as well as type of the adsorbed oxygen and depend upon the surface charge.[11] Λ_{air} also depends upon L_D, the Debye length which is an important characteristic of semiconductor sensor material for any particular donor concentration. It is determined by the following equation,

$$L_D = \sqrt{\frac{\varepsilon\varepsilon_0 k_B T}{e^2 n_d}}$$

Here ,

k_B = Boltzmann's constant,

ε_0 = Permittivity of free space,

ε = Dielectric constant,

T = Operating temperature,

e = Charge of electron,

n_d = Concentration of carrier corresponding to the concentration of donor assuming complete ionization.

The ideal case does not involve any humidity in the surface. But under atmospheric conditions sensor performance may be altered by water molecules which form hydroxyl groups.

In case of polycrystalline sensing materials, the electronic conductivity occurs through the grain to grain contacts known as percolation path. Thus it depends upon the value of Schottky barrier, $eV_{surface}$ of neighbouring grains. Here the conductance G of sensing material is represented as[12] :

$$G \approx \exp\left(\frac{-eV_{surface}}{k_B T}\right)$$

CO, a reducing gas, react with the ionosorbed oxygen species to form bound carbonate groups either unidentately or bidentately and desorb as CO_2.[13,14] Hence the amount of adsorbed oxygen decrease considerably in the presence of traces of reducing gas. As a consequence the electrons trapped at the surface are pushed back to the bulk, which reduces the height of Schottky barrier. As a result, the conductance of entire sensing layer increases.

I.3.3. Electrical Conduction Mechanisms

How the surface reactions allow to detect a gas are determined by the microstructure of sensing layers for selected operational mode and transduced into output signal. The deposition technique mainly decides the microstructure, but addition of promoters, dopants etc also plays important role. Figure I.3 illustrates the energy profile diagram of a semiconductor between a pair of electrodes which possess energy barriers at the grain boundaries and at semiconductor interface. During adsorption of species like O_2, H_2O, CO, charge transfer takes place from the gas to sensor material or to the electrodes which leads to surface chemical reaction between chemisorbed oxygen species and CO. A simple difference between two different types of layers can be illustrated.[6,15] The interaction with chemical species in gas phase occurs at compact oxide layers, the geometrical one. Here electron flow is parallel to the depletion layer. The volume of the porous polycrystalline layer is accessible to gases and the active surface of this layer is greater than the previous one. These two varying behaviour can be easily differentiated for a particular compact layer, which depends upon the ratio between t (thickness of the layers) and x_o (width of the depletion layer (which is equivalent to Debye length $2L_D$).

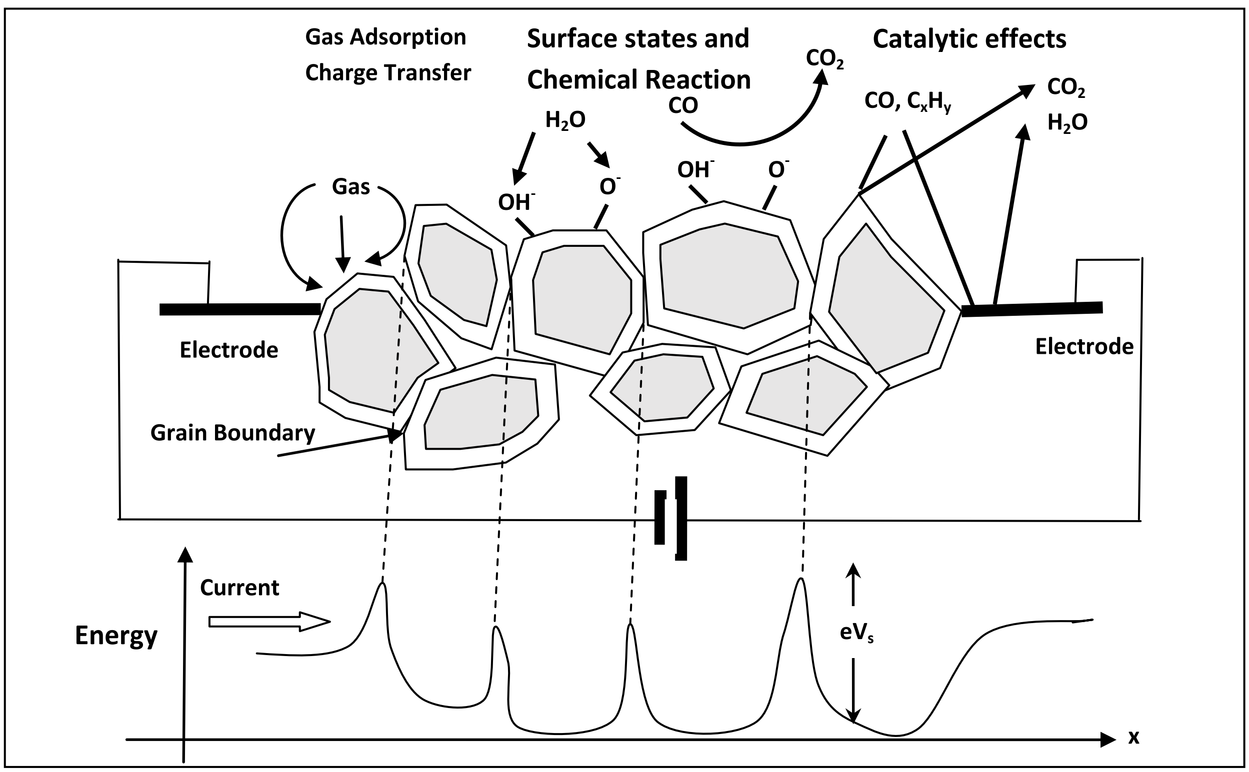

Figure I.3. Schematic representation of a conductometric gas sensor with electrodes placed in the sensor face

Surface traps restrict the conductance when the layer is fully depleted that is $t \sim L_D$. Here the electrons which are excited from the surface determine the conductance and the activation energy is equal to the surface-state energy (E_{SS}).

The surface reactions do not affect the conduction when the layer is partially depleted that is $t > L_D$. Here the conduction takes place by the electrons provided by the donor states in the bulk layer with variable width, ($t-x_o$) and the conductance is far more than the depleted layer. The energy E_D of the bulk donor acts as activation energy. The surface gas reactions and surface states change ($t-x_o$) i.e. conduction channel width which is also known as bulk trap-limited conduction (Figure I.4).

Here, x_0 = thickness of the surface layer,

t = thickness of the layer,

$e\Delta V_S$ = Height of the energy barrier.

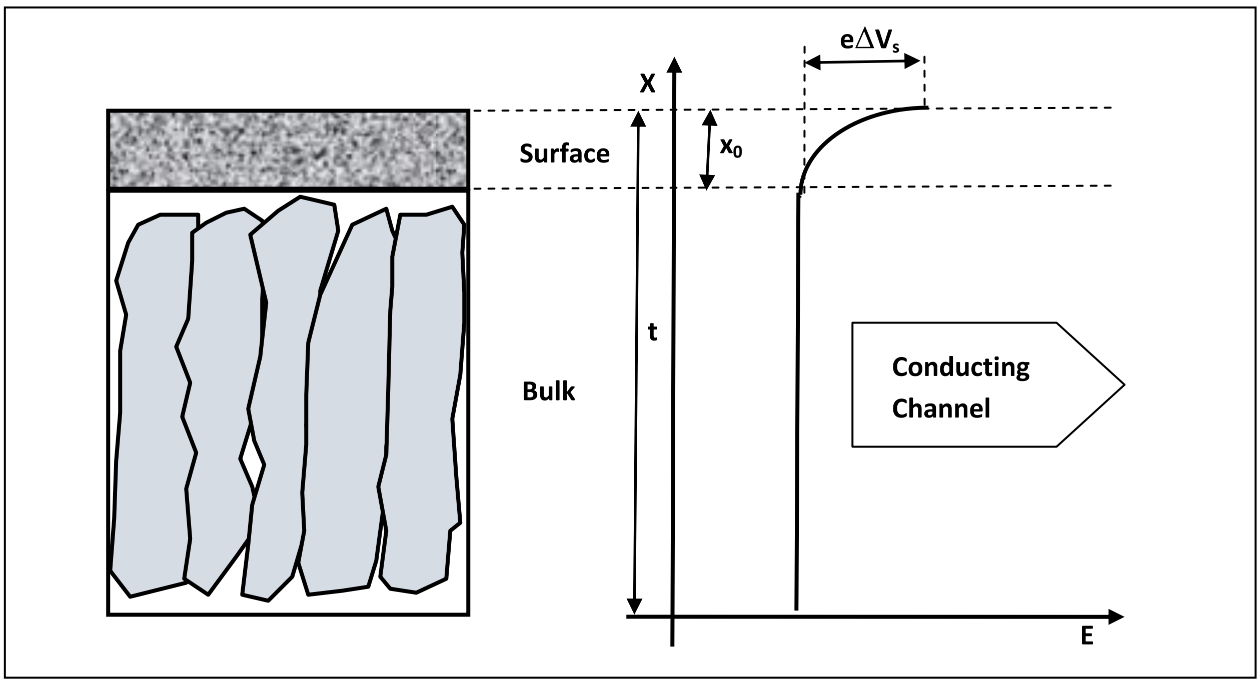

Figure I.4. Schematic diagram depicting compact sensing with geometry and band.

From, geometric considerations, conductance (G) of a thin single crystal layer is given by,

$$G = G_0\left(\frac{W_t}{L}\right)\left(1 - \frac{x_0}{t}\right) \text{ where,}$$

$$x_0 = \sqrt{\frac{2e\Delta V_s \varepsilon\varepsilon_0}{e^2 N_D}}$$

Here, t = thickness , W = width, and L = length of the layer.

In case of partly depleted layer on exposure to reducing gases, the gases operate as switch to inject free electrons. Further, partly depleted layer turns to absolutely depleted layer, when it is exposed to oxidizing gases that operate as switch. But it is noteworthy that the sensitivity to gases is very poor in this state. Moreover, substantial sensitivity values can be obtained by the use of very thin sample. The conduction mechanism for porous nanocrystalline layers vary depending upon the existence of schottky barriers, necks between grains and on grain size. The nanocrystalline structure possess smaller resistance paths. There are three common cases regarding the degree of sintering for the sensor material which are well illustrated in the figure I.5.

Figure I.5a illustrates the case of a well-sintered material possessing an open neck between the adjacent grains. Depletion layers are extended by the surface states below the grains to the depth. This is marked by the dashed lines which is present in the both sides of neck. The conduction mechanism occurs in the bulk layer of variable width of ($Z_n - 2Z_o$). Furthermore the bulk layer is much more conductive compared to the depleted layer. The electrons are provided by the bulk donor states in the process. The activation energy is expressed as E_D. ($Z_n - 2Z_o$), conduction channel width is changed by the surface states and surface gas reactions.

Figure I.5b depicts a closed neck case where the depletion zones from surfaces of neighboring grains udergo overlap causing a path through the center with higher resistance. The geometry corresponds to less complete sintering which cause a narrower neck. Here the conductance is influenced directly by the gases that occupy the surface states. The conductance is measured by activation of electrons from surface states to conduction band.

Figure I.5c illustrates the case where a schottky barrier is formed. This barrier exists at the boundaries of the two adjacent grains and the conduction mechanism involved between the grains is through thermionic emission. The conductance G depends on the barrier height $e\Delta V_S$. This is given by,

$$G = G_b \exp\left[-\frac{e\Delta V_s}{kT} \right]$$

This conduction mechanism is different from the former two cases. $e\Delta V$ is the activation energy for the conductance and it is directly related to the surface charge. Changes in Schottky barrier leads to high gas sensitivity as it is a function of the sensing gaseous composition.

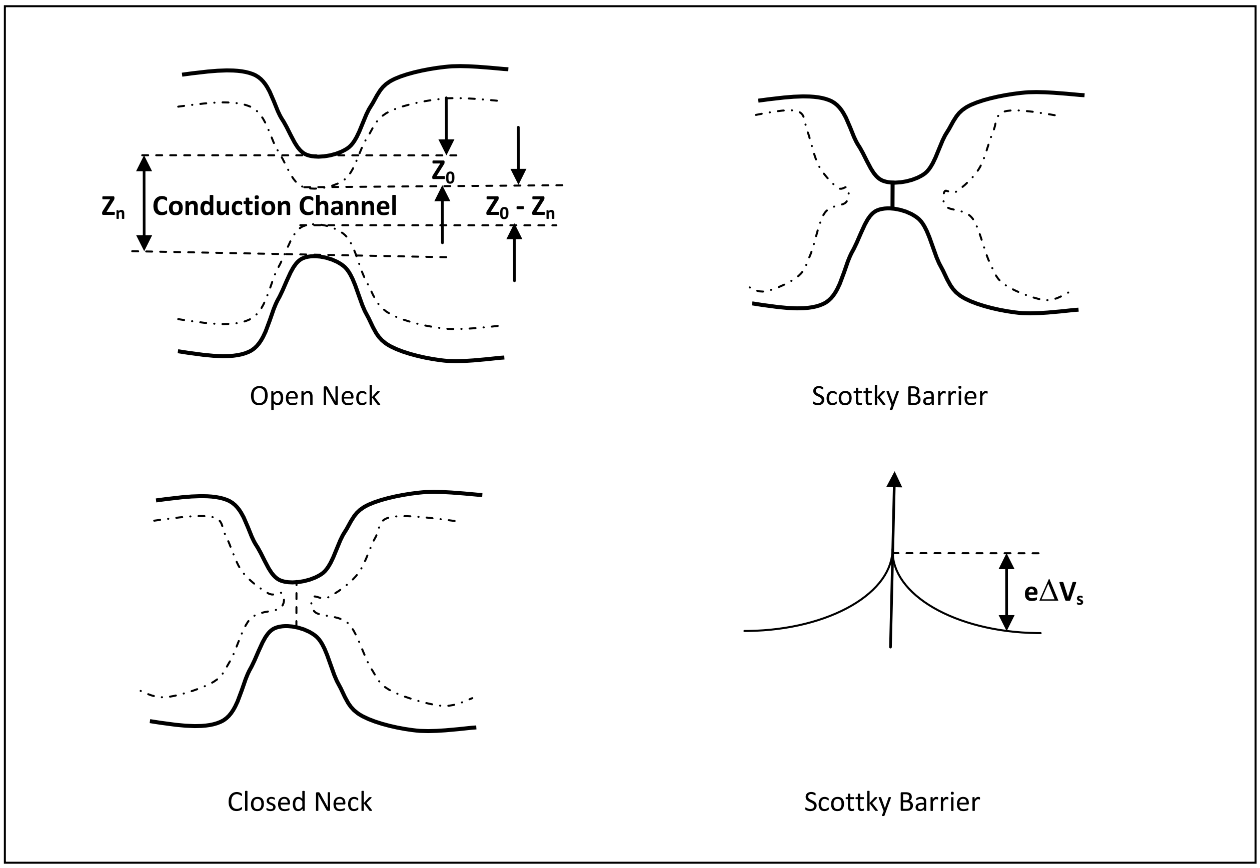

Figure I.5. a) Open neck, b) Close neck, c) Schottky barrier models for conductance limited by intergrain connections

I.4. Gas Sensing Mechanism

Though the working principle of the chemiresistive gas sensor is simple but the gas-sensing mechanism is a bit complex. The interaction between gas phase and gas sensing material are mainly two types.

I.4.1. Physisorption

This occurs due to the van der Waals' forces and solid-gas interaction is weak in this case. The adsorbent surface and adsorbed gas molecules become feebly polarized. Thus interaction due to this induced dipoles causes physisorption. The energy of interaction is very weak (~10–100 meV) in the physisorption process. Sensors based on physisorption are sensitive to wide range of gaseous species due to unselective character of adsorbate-adsorbent interaction.

I.4.2. Chemisorption

In this process activation energy is supplied thermally or by illumination. Chemisorption involves interaction which is often the formation of chemical bonds between adsorbates and the surface atoms of sensor materials. Thus the electronic structure of adsorbate as well as that of surface are modified which is mainly promoted by the surface defects. The energy of interaction is high. Interaction mechanism depends on the nature of material and on the operating conditions. The surface reactions of the gas sensors are well known example of heterogeneous catalysis. Usually the surface just provides a better place for a reaction between gaseous species to occur. However, during normal sensor operation all the products of reaction should desorb and thus the adsorption sites are freed and the sensor can be reused.

I.4.3. Mechanism of Gas Interaction

Metal oxide layers acting as gas sensor may undergo conductance changes in surface and/or bulk when come in contact of ambient gases. Electron transport processes cause change in surface conductance while ion transport is responsible for bulk conductance changes. Chemiresistive gas sensors find its application for the detection of concentrations of toxic as well as combustible gases present in air even in minute amount. Some groups has illustrated the gas sensing mechanisms so well that it can be well understood.[16,17] Becker et al. observed that sensor response reaches a maximum with increasing layer temperare and at higher temperatures it aproaches towards zero.[18] Selectivity of the sensor can be controlled by the operating temperature of the analyte gas. Response variation to different concentration of sensed gases are also different. These sensors usually show low resolution towards high concentration and high resolution at low concentration. These sensors can be used to detect very low concentration of the toxic gases present in atmosphere as response times are fast. More important applications of these type of sensors include humidity sensors, oxygen sensors etc.[19, 20] The gas detection mechanism of these type of sensors usually requires oxygen in atmosphere and is also influenced by the presence of humidity in air. Oxygen is adsorbed from air and it creates surface states. For n-type metal oxide electrons are captured from the conduction band by the surface states and for p-type metal oxide it is from valance band in. The oxygen adsorption follows the steps below,

$$O_{2gas} \rightarrow O_{2ads}$$

$$O_{2gas} + e^- \rightarrow O^-_{2ads}$$

$$O^-_{2ads} + e^- \rightarrow 2O^-_{ads}$$

$$O^-_{ads} + e^- \rightarrow O^{2-}_{ads}$$

Brailford et al. described that the ionic forms of oxygen are function of operating temperature.[21] Oxygen shows 2O$^-$, O$^-$ and O^{2-} character at temperature less than 100 ºC, at temperature 100 ºC to 300 ºC and at temperature higher than 300 °C respectively. G. Bläser et al. showed oxygen adsorption with potential barrier formed due to the motion of charge carriers in terms of (a) physical and (b) band model (Figure I.1). [22] (, Physics A, 266, 218-223, 1999). Following reactions occurs when the gas sensor is exposed to a reducing gas represented as R.

$$R + O^-_{2ads} \rightarrow RO_{2gas} + e^-$$

$$R + O^-{}_{ads} \rightarrow RO_{gas} + e^-$$

$$R + O^{2-}_{ads} \rightarrow RO_{gas} + 2e^-$$

Removal of adsorbed oxygen takes place when it reacts with a reducing gas. It results lowering of potential barrier hence return of the captured electrons. As a result the conductivity increases for n-type metal oxides but the conductivity for p-type metal oxides tumbles. When oxidizing gases are used the changes are opposite. The sensing materials can be classified as n-type or p-type on the basis of these type of conductance change.[23]

I.4.4. Role of Defects

In semiconductors, surface defects play important role as active sites for the catalysis process and reaction occurs predominantly at these defects.[24] The basic theory of semiconductor materials possessing deviations from the ideal stoichiometric compositions, was developed by Wagner and Schottky.[25] A solid must be non-ideal and possess some defects for conduction process to occur as charge transfer is only possible in case of this type of solids. Entropy of solid is directly related to the defects. According to 2nd law of thermodynamics, zero entropy is only possible at temperature 0 K. But normally even at 0 K a finite concentration of defects exist hence entropy never becomes zero and does so for a perfectly arranged system. The solids that we operate possess certain defects that has made them special. Defects can be classified as line defects, impurities or vacancies and defects at grain boundaries. Line and point defects assume importance as gas sensing is surface phenomena. Point defects are important for the bulk. Insertion of the foreign particle in lattice causes extrinsic defects. Hence, adsorbed atoms are considered to be point defects. The interstitial positions may occupy excess metal ions and equal number of free electrons which are present in conduction band that leads to n-type semiconductivity. Whereas Cation vacancies lead to an equal number of positive holes present in valence band that are responsible for p-type conductivity

I.4.5. Role of Particle Size

Gas-sensor response mainly depends upon the reaction between metal oxide surface material and gas molecules present in the atmosphere. Generally nanocrystalline metal oxides possess large surface-to-bulk ratio. Hence they show an improved sensitivity compared to microcrystalline materials with a better response and recovery time. Sensitivity largely depends on the particle size and smaller particles sizes show improved sensitivity which results numerous structural and electronic defects. The conductance is proportional to the energy difference of E_F (that of Fermi level) and E_C, the conduction band.[10,26]

I.4.6. Influence of Microstructure

The microstructure specially film thickness and porosity play important role to control the response time and sensitivity. Oxygen and other analyte molecules penetrates the sensor surface layer. Thus it is essential that the diffusion rate of the analyte/oxygen would be fast.

which also depends on the working temperature and its mean pore size. Lower film thickness and higher porosity gives rise to faster response time and higher sensitivity.[27,28]

I.4.7. Effect of Surface Doping

Sensor performance is largely influenced by the doping with metals and/or oxides. Moreover, this doping process is different from that of the bulk doping of the semiconductors. Here the doping process accompanies addition of the base material to the catalytically active sites of the surface. The doping process increasing the sensitivity by improving sensor performance. Surface doping also enhances the thermal and long-term stability. Parameters which control the process include particle size, composition, redox state of the surface modifiers and their dispersion onto the metal oxide surface. The particle size effectively controls the temperature range and also the efficiency of a particular catalytic reaction.[29,30]

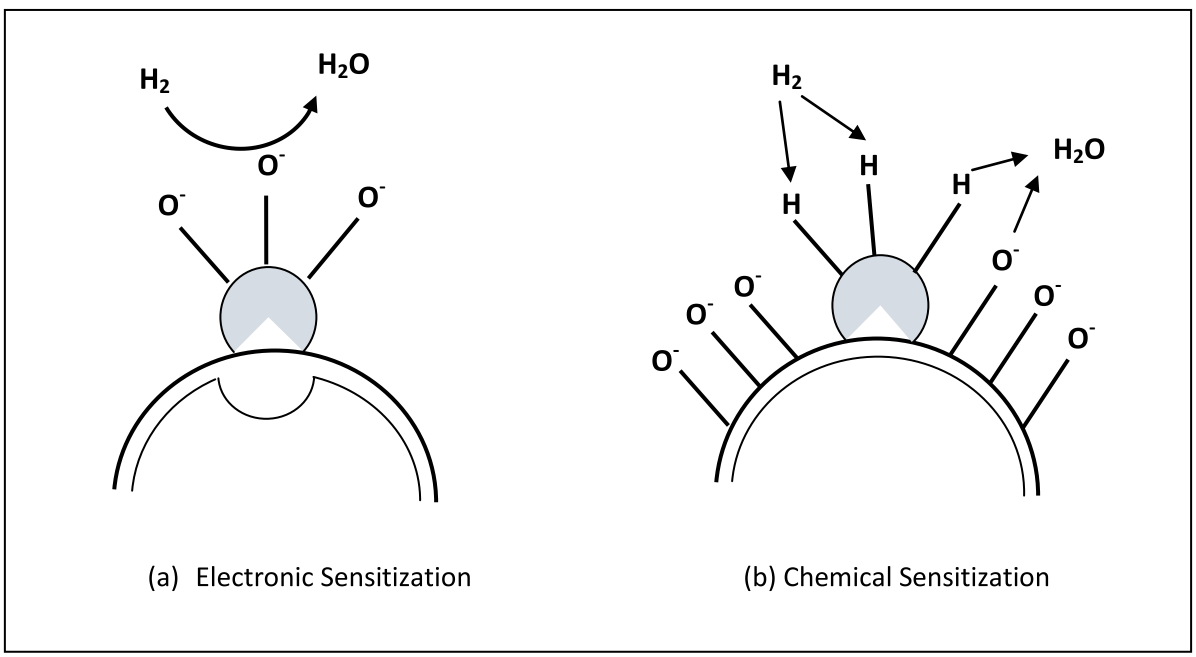

Figure I.6. Mechanism of Electronic and Chemical sensitization process by metal/metal oxide additives

Two different mechanisms, i.e, electronic and chemical sensitization are applied to illustrate the surface additive effect.[10, 11, 31–33] In case of electronic sensitization process, the electrons are accepted by the semiconductor metal ion in its particular oxidized state. As a result an electron depleted space-charge layer is induced near the interface. Figure I.6a illustrates the electronic sensitization, where the additive H_2 is an electron acceptor and the redox state or the chemical potential is modified by the reaction of analyte with the semiconductor.

The chemical sensitization results from the catalytic surface reaction. Figure I.6b shows chemical sensitization by the activation of the target analyte (H_2) which changes the surface oxygen concentration.[11] As a result, $eV_{surface}$, is reduced by the surface coverage of oxygen, which causes conductance change.

I.5. Criteria for the Choice of Sensor

An ideal sensor should have high sensitivity so that it can detect least quantity of gas with the variation of resistance. It should exhibit high selectivity for a particular gas and the response and recovery should be fast. Good sensor should have tolerance various adverse effect like humidity, temperature, acid, baser, dust etc. Moreover the sensing material should be safe and non-toxic. It should have high sturdiness and simple to operate. Low temperature operating miniaturized materials are preferred to couple the materials with electronic circuitry possessing low power consumption.

I.5.1. Types of Metal Oxide Sensors

The operating principle of the metal oxide sensors is that the conductance of the sensor material will change with the interaction of the gas. This change is proportional to the gas concentration. Two types of metal oxide sensors are there. The n-type such as ZnO, SnO_2, TiO_2, Fe_2O_3 etc which responds to the reducing gases and p-type like NiO, CoO etc that respond to oxidizing gases.[34] Oxygen in the air reacts with the surface of the n-type sensor which traps the free electrons on the material surface or it may be trapped at the grain boundaries of this metal oxide grains. Due to lack of the carriers large resistance is produced in these areas. The potential barriers produced in this process between the grains inhibit the mobility of the carrier. If the sensor come in contact with the reducing gas such as hydrogen, methane, carbon monoxide etc. resistance drops due to the reaction of the gas with oxygen which releases electron and lowers the potential barrier thereby. It also allows the electrons to flow which increases the conductivity. Whereas p-type sensors respond to the oxidizing gases such as oxygen, nitrogen di oxide and chlorinre because these gases produce holes by releasing electrons. The reactions taking place at the surface can be represented as

$$\frac{1}{2}O_2 + e^- \rightarrow O^-(s)$$

$$R(g) + O^-(s) \rightarrow RO(g) + e^-$$

Where, R (g) = The reducing gas,
e = An electron from the oxide,
g = gas, s = surface.[34, 35]

I.5.2. Transition Metal Oxide Chemiresistive Sensor Materials

A consize discussion of such transition metal oxide based gas sensing material has been illustrated below:

i) Chromium Oxide (Cr_2O_3): Thermodynamic stability, hardness and resistance power towards chemical attack has made p-type Cr_2O_3 an importat material for sensors now a days.[36] It is sensitive towards H_2 and CH_4 gases.[37] TiO_2-doped Cr_2O_3 has been found to be sensitive towards the gases NO_2, O_2 and also towards humidity.[38, 39]

ii) Cobalt Oxide (Co_3O_4): It is very promising towards the gas sensing applications due to its catalytic activity towards oxidation reactions.[40] Co_3O_4 is very sensitive to a variety of gases like NH_3, CO, CH_4, C_3H_8, NO_2 and Cl_2.[41]

iii) Copper Oxide (CuO): Among the oxides of copper, only the cupric form of oxide (CuO) is sensitive towards gas. CuO is a p-type semiconductor and possess a band gap of 1.2 eV. It's electrical resistance is also low and is sensitive towards NO_2 and CO.[42, 43] CuO-doped SnO_2 has been found to be highly selective towards the sensing of H_2S.[44]

iv) Iron Oxide (FeO, Fe_3O_4, Fe_2O_3): There are three different polymorphic forms like FeO, Fe_3O_4 and Fe_2O_3 are possible for iron-oxide system. Among them only Fe_2O_3 is gas sensitive due to its good thermo-dynamic and structural stability. Three types of defect, viz, oxygen vacancies, Fe^{2+} interstitials, Fe^{3+} interstitials are present in the complex defect structure of Fe_2O_3. These defects gives rise to the semiconductor properties of the material. Fe_2O_3 has been found to be high sensitive towards various organic gases. ZnO doped Fe_2O_3 works as a selective NH_3 gas sensor which works at room temperature.[45] Au or Zn doped Fe_2O_3 is sensitive towards CO and NO_2.[46] When doped with Pt, Pd or RuO_2, Fe_2O_3 sensor can also detect acetone.

v) Molybdenum Trioxide (MoO_3): It is an n-type semiconductor having band gap 3.2 eV. Its selectivity and no cross-sensitivity are the main causes of its excellent use as a gas sensitive material. acts as a well-known catalyst towards the oxidation process of hydrocarbons and also towards the conversion of harmful NO_x gas to nitrogen. Currently the gas sensing properties of this material has been investigated.[47] It has been found that the sensitivity of MoO_3 sensing material for NH_3 can be enhanced considerably by using a coating of Ti over MoO_3 films

vi) Niobium Oxide (Nb_2O_5): Nb_2O_5 has been found to be a popular n-type semiconductor for the detection of H_2 gas.[48]

vii) Nickel oxide (NiO): NiO acts as a p-type semiconductor possessing band gap 4.2 eV. Good chemical stability and excellent optical as well as electrical properties are the causes of wide applicability of NiO. NiO has been found to be a good gas-sensing material for both thermoelectric and chemiresistive type gas sensors.[49, 50]

viii) Tantalum Oxide (Ta_2O_5): Ta_2O_5 is a good humidity sensor. It acts as a good promoter in gas sensors. An over layer of Ta_2O_5 improves the sensitivity, response time of $In_xO_yN_z$ films significantly towards the sensing of gases like CO, H_2, CH_4 etc.

ix) Titanium Dioxide (TiO_2): High thermal stability and tolerance to harsh environments has made TiO_2 an important gas sensing material with comparable thermal expansion coefficient with Al_2O_3, which has also made it a suitable material for fabrication of thin film based sensors. TiO_2 is a high resistive n-type semiconductor. The addition of Chromium with TiO_2 alters the electronic conductivity from n-type to p-type that helps the development of the novel gas sensors.[51] These p-type materials which were obtained at appropriate conditions responded excellently with a sharp decrease in resistance when exposed towards diluted NO_2.

x) Tungsten Oxide (WO_3): Operability at high temperatures for long time has made WO_3 a potential and selective sensor towards various gases. It is an n-type semiconductor with wide band gap.[52] Mo, Mg, Au, Zn, Re etc. doped WO_3 films have been found to detect toxic gases selectively.[53] Surface of WO_3 films modified with Au and Pt were found to be more sensitive towards NH_3.[54]

xi) Vanadium Oxide (V_2O_5): V_2O_5 has been used extensively as catalyst in the oxidation reactions. This feature has made V_2O_5 a good promoter towards the enhancement of the sensitivity of sensors like TiO_2, MoO_3 and ZnO.[55]

I.6. Sensor Fabrication Methods

High performance gas sensors can be achieved by controling the structure of the sensing material. Particular sensing material, a heater which increases the temperature of the sensing material and the electrodes for measuring the resistance of the sensing element are required for the fabrication procedure. Different response characteristics are produced for different gas sensors by different techniques.It happens because different material structures can be achieved by applying different preparation techniques. For the fabrication procedure various methods are used which can be discussed hereunder.

I.6.1. Bulk Form

In this process the sensing element i.e. compressed pellets of metal oxide powder is by sintered at 900-1000 °C temperatures. Electrodes on sintered pellets in this type of sensors are prepared by depositing Au by thermal evaporation process. These sensors are very cheap to produce. But these sensors also possess several disadvantages like poor selectivity and sensitivity, slow response and recovery times, high power consumption at temperature greater than 200°C.

I.6.2. Thick Film Form

Thick film possess thickness of the order of microns. The powder form of semiconductor oxide material is mixed with binders like propandyol/terpineol to form a paste. Calcination of the binder is important to create porosity. This can also be done by adding some chemical substances to the paste which decomposes on thermal treatment. Fractures appearing in the sintering of powders increase sensor resistance. This can be reduced by addition of some Al_2O_3 powder with mean size 100 to 150 μm to the paste. The powders have a natural tendency to agglomerate. Hence the paste must be well mixed before the deposition process.

I.6.3. Thin Film Form

Thin films form possess different properties comparede to bulk form. The thickness are of the order of few nanometers to few microns for this kind of sensors. Sensors with high selectivity, small size and possessing low power consumption can be developed by silicon microelectronic technology. Thus thin film forms are found to be the most suitable. Thin films can be divided into two types namely single crystalline and polycrystalline, based on the structural properties. Single crystalline thin films do not possess grain boundaries and they show small variations of electrical resistance when they are brought to the contact of oxidizing or reducing gases. So they are not used as gas sensors.[56] Whereas in polycrystalline thin films charge transport across grain boundaries plays important role in developing the sensor response to gases.[57] That is why these are more suitable as gas sensors. In fact sensor response improves significantly as the grain size approaches nano form.

I.6.4. Nanostructure Form

Gas sensing is a surface phenomena and high surface area to volume ratio in the nanostructure form enhances the response. Hence different nanostructured forms like single nanowire, mat type, film, thick film technology[58-68] etc. have been used for dropcasting, di-electrophoresis, pick and place etc. approaches.

I.6.5. Substrates used in thick film technology

The substrates used in the thick film technology should possess the following criteria.

i) It should be able to support the circuit.

ii) It should be able to protect the circuit from any mechanical damage.

iii) It should be able to dissipate heat.

iv) It should be chemically inert and it can provide electrical isolation.

The properties like relative dielectric constant, resistivity, surface characteristics, chemical reactivity, strength, thermal expansions coefficient, thermal conductivity, dimensional stability etc. are important factors for the selection of the substrates for the above phenomena.

The polycrystalline ceramics are ideal for that prpose. Aluminum oxide, beryllium oxide, barium titanate etc. are popularly used materials. Beryllium oxide ceramics possess high relative dielectric constant because of high thermal conductivity. This substrates can be used to make high capacity devices. Al_2O_3 ceramics are popularly used with combination which gives the best performance. The unglazed Al_2O_3 substrates with 96% purity are widely used in thick film industry.[69]

I.7. Applications of Chemiresistive Gas Sensors

Several applications of the gas sensors are noteworthy. Some applications of chemiresistive gas sensors are illustrated below:

I.7.1. Environmental Monitoring

Volatile organic compounds (VOC's) and various toxic gases can be actively detected by these chemiresistive gas sensors. The present methods are very much costly and time consuming. High level of various gases, VOC's and ozone in atmosphere causes harm to human respiratory system by causing inflammation, congestion of respiratory tract. The O_3 level rises because of the interaction of sunlight with various chemicals excruited by the industries. Several materials based on WO_3,[70] SnO_2 [71] are useful to detect the ozone level in atmosphere, when fabricated. Thus chemiresistive gas sensors serve as efficient environment monitors owing to their simplicity in operation and low cost. Thus importance of research on this ground are increasing now a days.

I.7.2. Chemical Warfare

Gas sensors can be used for detecting toxic chemical warfare agents (CWAs) used in war as weapons for mass destruction. Spectroscopic techniques like FTIR[72], Raman[73] spectra have been employed to monitor CWAs. However, this procedure is costly and complex. Thus it is important to develop low cost, selective devices that will provide effective CWA detection quickly. Semiconductor metal oxides like SnO_2, ZnO, WO_3 etc. and their modified form effectively possess sensing property towards various CWAs. For example, SnO_2 is highly sensitive towards acetonitrile and dimethyl methyl phosphonate (DMMP)[74] which is the simulant molecule for sarin ($[(CH_3)_2CHO]CH_3P(O)F$), a liquid extensively used as chemical weapon.

I.7.3. Automobiles

Chemiresistive gas sensors are also applied in the car ventilation and filter control, alcohol breath test and gasoline vapor detection. Although cars are designed in such a fashion that outside air can constantly ventilate through the air inlets. Yet in the closed car, as the concentration of CO_2, smoke gets increased, the air quality becomes lowered. Chemiresistive gas sensors capable of detecting organic pollutants can be used as air quality sensor. In auto-damper system (ADS) these sensors can be also used which can monitor various inflammable gases like hydrocarbons, NO_x etc.

I.7.4. Safety

The functioning of fire alarms are basically smoke sensor or heat sensor based. Various inflammable gases result on the occasion of fire, however H_2 gas diffuses more rapidly compared to smoke and it is easy to detect than the conventional methods where sounding fire alarm is used widely. For this reason, conventional fire alarms now use chemiresistor gas sensor as an active component.[75]

I.7.5. Food and Beverage Industry

Analytical analysis of foodstuff and beverages can be done by using electronic nose of the chemiresistive sensors in the industry. Work on this ground that is on the tea quality detection has been discussed in the last chapter of this thesis.

I.7.6. Medicine

Chemiresistive sensors with electronic nose system can diagnose certain disease which can be an effective criteria in the medicinal ground. As for example, patients with certain kidney disorders produce some characteristic VOC, which can be detected using particular gas sensor and it can be a useful tool for the diagnosis and control of some renal disorder.[76] Also, studies non-selective gas sensors have been shown to be active in lung cancer detection by simple breath analysis.[77] In future electronic nose devices can be an effective tool for doctors, which can be used by them for rapid detection of specific diseases.

I.8. Reference

References are given in BIBLIOGRAPHY under Chapter I page no. 86-89.