**Book Chapter**

**Recent Trends Chemical Sensor Technology**

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**Abstract:**

Recently, the interest in development of rapid, sensitive and selective smart gas sensors devices has increased for environment protection and healthcare uses. Substantial exploration has been carried out in the field of sensor technology. Nevertheless, there exist certain challenges. This chapter discusses the fundamentals of chemical gas sensors, sensor characteristics, gas sensing performance-enhancing methods, Factors influencing the performance of gas sensor, Ways to improve the sensor performance, Sensing mechanism, Types of adsorption depletion models.

**Introduction:**

A sensor is a device that can receive and respond to a signal or stimulus. The stimulus/measurand can be the quantity, property, or condition that is sensed and converted into electrical signal. The purpose of a sensor is to respond to some kind of an input (physical or chemical property) and convert it into electrical signal that is compatible with the electronic circuits. Sensor is ‘a device that responds to a physical (or chemical) stimulus (such as heat, light, sound, pressure etc.) and transmits a resulting impulse (for measurement or operating a control) [1, 2]. Thus sensor can detect an input signal and convert it into an appropriate output signal. Generally, sensors provide an interface between the electronic equipments and the physical world typically by converting nonelectrical, physical or chemical quantities into electrical signals.

Nowadays, due to the increase in the environmental pollution, and industrialization sensors have attracted a great deal of interest in environmental monitoring and various industries to improve environmental and safety control of toxic and inflammable gases. There is an urgent need to develop the gas sensors which have several applications in automotive and industrial manufacturing, medical diagnostics and health care, defence and security, detection of harmful gases in mines, grading of agro-products like coffee and spices, in packaging quality control, in weather stations, etc. [3-7]. Requirements for detection and quantification of various gases are classified into following three broad categories [8]:

**1) Oxygen:** For the atmospheric oxygen monitoring as well as for the control of combustion processes such as boilers and internal combustion engines. For these processes the oxygen concentration of 20 % and 0 - 5 %, is required respectively.

**2) Toxic gases:** For the safety of health at different workplaces the detection and monitoring of toxic gases is must. The exposure limits for toxic gases is in the range 1 to several hundred ppm.

**3) Flammable gases:** To avoid the accidental fire or explosion. The concentrations of the flammable gases are up to the lower explosive level (LEL) which, for most gases, is up to a few percent.

The gas sensors can also be broadly classified based on the technology and as: Spectroscopic, Optic and Solid State gas sensors. Spectroscopic gas sensors are based on the molecular mass or vibrational spectrum analysis of the various test gases. These sensors can be used for precise quantification of the test gas concentration. Optical sensors are based on the absorption spectra of the target gas. These sensors require a complex system comprising a monochromatic excitation source and detector for the analysis of the absorption spectra of the test gases.

However, the optic and spectroscopic gas sensors are not only costly but also difficult to implement in reduced space. Whereas, Solid State gas sensors have several benefits such as cost effective, fast response, simple execution and portable [9-11]. The Solid State gas sensors are based on the simple principle of change in physical and/or chemical properties of their sensing materials in the presence of the different gases. Among the several solid state gas sensors, the semiconducting metal oxide sensors based on SnO2 [12, 13], Fe2O3 [14], In2O3 [15], WO3 [16], ZnO [17], LaFeO3 [18] and TiO2 [19] etc. are being extensively studied. The transition metal oxides like SnO2, TiO2, ZnO, etc. seem to be the most suitable materials to be used as gas sensors. These are based on the principle of the change in the resistance upon the exposure of various test gases. However, these materials exhibits some problems such as cross selectivity and higher operating temperatures. In order to improve the gas sensing performance normally two methods are employed; one of the extensively used method is addition of several metals/metal oxides such as Zn [20], Ni [21], Co [22], Ce [23], Cu [24], Sm2O3 [25] etc. whereas in the the second method the sensing material is loaded with the noble metals, such as Pd, Pt, Ru, and Au to promote electronic sensitization.

Metal oxides at higher temperature exhibit change in resistance depending on the target gas composition. Metal oxide semiconductors are known to be of either p-type or n-type semiconductors. For n-type metal oxide semiconductors, the resistance decreases with the concentration of reducing gases, on the other hand it increases with oxidizing gas. The converse is true for p-type semiconductors. The structural and morphological properties such as particle size, surface-to-volume ratio, pore volume and pore size etc. strongly affects the gas sensor performance. In addition to this it is reported that the sensor response properties are also influenced by the synthesis method [26].

**1.2 Fundamentals of semiconducting metal oxide gas sensor:**

Metal oxides semiconducting sensors like ZnO, SnO2, Fe2O3 and WO3 etc. when heated to a suitable temperature in air respond to a wide range of oxidizing and reducing analyte gases via resistivity changes. The gas sensing mechanism is described as below:

**1.** **Diffusion of gases to the active region**

**2. Adsorption of gases on to active region**

**3. Surface reaction**

**4. Desorption of reaction products from active region**

**5. Diffusion of reaction products away from active region.**

The first process i.e. diffusion of gases to active region depends on the ambient temperature of the atmosphere. Once the molecules of gas diffuse into the active layer, they tend to adhere to the sensing surface by process of adsorption. There are two types of adsorption types namely Physisorption and Chemisorption. In the case of physisorption, the species are bonded only by weak physical forces such as van der Waals-type forces to the sensor surface. In the case of chemisorption process, the species are bonded by the re-arrangement of the electron density between adsorbed gas and sensor surface. At the solid surface where the solid is terminated, the surface atoms are incompletely coordinated due to the missing of one or two neighbouring atoms, and there are unsatisfied dangling bonds that are unshared with neighbouring atoms [27]. Specifically, in an ionic crystal like SnO2 both cations and anions have poor coordination. The positively charged Sn ions on the surface have an incomplete shell of negative oxide ions around them. A model rationalizing the behaviour of the sensor in the measurand environment can be explained as below [28].

**------ (1.1)**

**------ (1.2)**

Oxygen gets adsorbed on the surface and dissociates to form various oxygen species such as O-, O2- and O2-. During this process an electron is extracted from the conduction band of semiconductor by adsorbed oxygen species. This process of electron extraction leads to the creation of depletion region near the sensor surface leading to an increase in (assuming n-type semiconductor) the resistance of the gas sensor. Figure 1.1 shows 2D view of the crystallite of gas sensitive material after adsorption of oxygen. Also detailed in the Figure 1.2 is the band bending near the surface. This can be ascribed to the charged double layer formation near the surface.

C:\Users\faiyyaj\Desktop\Ch 1 Fig 1.1.tif

**Figure 1.1 2-D view of the depletion of crystallite in presence of atmospheric oxygen at certain temperature.**

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**Figure 1.2 Corresponding energy band diagram.**

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**Figure 1.3 Distribution of charges for n-type metal-oxide surface on oxygen chemisorption.**

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**Figure 1.4 Energy band diagram for n-type metal-oxide surface on oxygen chemisorption.**

When the reducing gas such as hydrogen is exposed to sensor, the gas reacts with the adsorbed O- to form water (H2O) as a by-product and the electron is released to the conduction band, decreasing the resistance of the semiconductor. There is a competition between oxygen removing the electrons and the reducing gases releasing the electrons back [27]. Since the atmospheric oxygen concentration is constant, the balanced value of the resistance depends on the reducing gas concentration. The competing reactions are shown by equation (1.3) and (1.4) as below:

**--------- (1.3)**

**(1.4)**

When the reducing gas concentration in this case H2 concentration increases, the number of O- species decrease increasing the electron concentration in the conduction band. Therefore, the sensor resistance is lowered. One more model that exists or coexists is that the reducing gas, if it is chemically active, extracts lattice oxygen from the metal oxide. This results in the generation of vacancies that act as donors. The atmospheric oxygen re-oxidize the donor vacancies. Thus there exists a competition between the oxygen removing donor vacancies and the reducing gas creating donor vacancies. The number of donor vacancies (and hence the resistance) depends only on the reducing gas concentration as oxygen pressure is constant. This is depicted by equation (1.5) as below [27]:

**---------- (1.5)**

Where OL is the lattice oxygen and M is the metal cation. Thus two different classes of mechanisms of operation of semiconductor gas sensors can be distinguished for reducing and oxidizing analyte gases. The first class involves changes in conductance due to extraction and re-injection of electrons from the film by surface reaction of reducing gas with adsorbed oxygen. The second involves removal of lattice oxygen by combustible gas leading to creation of donor vacancies .The donor vacancies in turn inject carriers into the conduction band of the semi conducting film leading to change in conductance. After the sensing of the gas by the gas sensor, adsorbed gas can either remain adsorbed on the sensor indefinitely (at low temperatures), react with the sensing material (sensor poisoning) or desorb and diffuse back into the surrounding atmosphere. Desorption refers to disengagement of a molecule or an atom from a surface. Like adsorption, desorption is also a thermally activated process. When the gas desorbs and diffuses away from the sensor surface, the sensor is ready for the next measurement. The period for which the sensor is unusable is termed as dead time.

**1.3 Classification of sensor:**

Sensors are generally categorized depending upon their principle of conversion (the physical or chemical effects on the basis of which they operate) as physical sensors and chemical sensors (Figure 1.5) [29]. Physical sensors employ physical properties like magnetostriction, piezoelectric, ionization, photoelectric, thermoelectric, magnetoelectric etc.

**Figure 1.5 classification of sensor.**

**1.4 Chemical sensor:**

Chemical sensor is a device which transforms chemical information, ranging from the concentration of a specific sample component to total composition analysis, into an analytical useful signal [30]. These devices are miniature as a portable devices designed for the selective and continuous on-line monitoring of the concentration of a specific gas in the complex samples. These devices convert chemical and/or physical property like concentration of a specific gas or total compositional analysis of a system into an analytical useful signal. The basic components of the chemical gas sensors are as follows:

1. **Sensing element**
2. **Chemical/analyte/gas recognition system**
3. **The physicochemical transducer.**

**1.5 Types of chemical sensor:**

In case of the chemical sensors gas molecules react with the sensing material by actuating the change in some physical properties such as mass, volume, resistance etc. The corresponding changes in the physical entity are detected by the chemical sensors, and this change is directly converted in to some electrical signal by transducer. Depending on the types of chemical reactions and the signal transformation there are several types of sensors. These are amperometric [31], volumetric [32], conductometric [33], potentiometric [34], impedencemetric [35], calorimetric [33], chemoresisters [36], field effect transistor [37], chromatographic [38] conducting polymer [39], carbon nanotubes [40] and biochemical sensors [41].

**1.5.1 Solid state gas sensor:**

The solid state sensor works on the principle of change in the physical property of the material with respect to the chemical reaction such as adsorption/desorption on the sensor surface. The key property is the resistance change of the sensing material; this change in the resistance can be converted into measurable electrical signal. A reversible interaction of the gas with the sensor surface of the solid state sensor is an important characteristic. This characteristic has great interest in the solid state gas sensor due to its economic cost, small size, better sensor performance, possibility of real time on-line monitoring and bench production.

**1.5.2 Catalytic sensor:**

Catalytic sensors are employed for the detection of the combustible gases in the ambient air environments, using a certain catalyst such as platinum to sustain the reactions at moderate temperatures. A typical catalytic sensor consists of a detector and compensator. The catalytic palletised resistor surface is constructed around the platinum coil i.e. micro heater to heat the catalyst to adequately high temperature, at which the combustible gas molecules burns and release heat [42]. The compensator consists of a coil made up of fine platinum wire fixed in an alumina bead as a reference resistance. It is used to compensate the effects of several environment factors and obstruct oxidation of other gases other than the volatile combustible gas in the sensor. The operating principle of the catalytic sensor is same as the chemical reaction ie. reaction of combustible gas with the surface of the catalyst. These oxidation reactions release the heat, and change the resistance of wire due to the increase in the temperature [43].

**1.5.3 Metal oxide nanostructured sensors (MOX):**

The unique physical, chemical, electrical, electronic, magnetic and optical properties of metal oxides (MOX) and their capability to behave as semiconductor [44] is the trademark of their applications in the field of sensors. MOX semiconductor sensors are made up of nanoparticles. The sensing material presents a high surface to volume ratio, is mounted on a heater substrate with ohmic contacts. The change in the concentration of free charge carrier is observed due to reaction of gas molecules with the sensor surface. The sensor signal is recorded in the form of the change in the resistance of the sensor with the concentration of the gas composition.

**1.6 Sensor characteristics:**

The vital key in the operation of a chemical sensor is the interactions between an analyte molecule and the surface of receptor. The major determinants in the characterization of nanostructures are morphology, crystal structure, chemistry and electronic structure of the sensing materials. From these determinants, the performance of the chemical sensor is characterized by the parameters such as sensitivity, selectivity, detection limit, dynamic range, resolution, response time and recovery time.

**1.6.1 Sensitivity/Response:**

Response/Sensitivity is the sensor characteristic of perceiving a variation in physical and/or chemical properties of the sensing material under gas exposure. This term is also used to refer either to the lowest level of chemical concentration that can be detected or to the smallest increment of concentration that can be detected in the sensing environment. It is represented in various forms. In other words sensor response/sensitivity is the ratio of change in the resistance in the test gas ΔR=Ra-Rg, to the value of resistance in air Ra where Rg is the resistance in the presence of the test gas.

The percent sensitivity (%S) is given by equation:

**---------------- (1.6)**

Or it is defined as the ratio of the resistance of the sample measured in air to the target gas-containing atmosphere.

Sensitivity for Reducing gases, S =RA/ RG (Rg<Ra)

Sensitivity for Oxidizing gases, S = Rg/Ra (Rg>Ra)

**1.6.2 Selectivity/Specificity:**

Selectivity is the ability of the sensor to respond to a particular gas in the presence of other gases. Selectivity or cross selectivity of the sensor, Sij of the sensor compares sensor signal or sensitivity to be monitored (*Si*) to the sensor signal or sensitivity of the interfering stimulus (*Sj*) [45]. It is its ability to concurrently discriminate and uniquely detect a specific target gas in the presence of the interfering gas(es) [46]. It is represented as a ratio of sensitivity of the target gas, Si to the sensitivity of the competing gas, Sj [45]:

**---------- (1.7)**

However it can be represented in the form of percentage as

**----------- (1.8)**

**1.6.3 Detection time:**

The detection time Tdet is the time taken for the sensor output signal to rise 10% above its initial value after applying the target gas in a step function (Figure 1.6)

**1.6.4 Response time:**

The response time Tres (Figure 1.6) describes the time taken for the sensor output signal to reach 90% of its saturation value after applying the target gas in a step function [46]. **1.6.5 Recovery time:**

The recovery or decay time Tres (Figure 1.6) is the time taken for the sensor output signal to drop to 90% of its saturation value after switching off the target gas in a step function.

**1.6.6 Stability and long term effect:**

Stability is the ability of the sensor to maintain its sensitivity and response behaviour over a period of time. Depending on the application, the period could be between hours to years. Stability could be expressed in terms of drift in the sensor response.

**1.6.7 Reproducibility:**

Reproducibility is the measure of sensor similarity behaviour. In order to compare the reproducibility of two batches one can either calculate the mean value and the standard deviation of the sensor property for both batches and compare them or calculate reproducibility Q for each batch. It can be calculated as [45]:

**---------- (1.9)**

Where n is the number of characterised sensors, Rk the sensor response of the sensor k. The reproducibility values range from 0 to 100.

**C:\Users\faiyyaj\Desktop\Repons eand recovery time ch 1.tif**

**Figure 1.6 response, recovery and detection time.**

**1.7 Factors influencing the performance:**

**1.7.1 Long term effects / Baseline Drift:**

Baseline is the sensor resistance in clean air. For sensors with over long operating times of baseline as well as sensitivity are vital in sensor employment. These factors define the rate at which the calibration checks have to be performed and the rate at which the sensors have to be replaced. These parameters can only be defined over long interval of time and no method is valid to accelerate the sensing performance [47].

**1.7.2 Sensor surface poisoning:**

The surface of metal oxides may become unstable because due to the poisoning phenomenon. Sulfur (as H2S) is a potential poison. The sulphur poisoning can stop the catalytic activity on the sensor surface. The instability of the sensor performance due to H2S in commercial SnO2 based sensors was reported by Wagner et al. Chlorine gas is another major poison which can cause the catalytic activity of the Pd on the sensor surface to block. Therefore it is must to know about other reactive gases in the measurand environment [47].

**1.8 Ways to improve the sensor:**

**1.8.1 Use of catalyst:**

There are several ways to improve the sensor performance of Metal oxide gas sensors. One of the ways is addition of catalyst on the sensor surface. This is explained as below. MOX gas sensors need a catalyst to be deposited on its surface to accelerate the rate of reaction and to enhance the response. A catalyst is is defined as a material that accelerates the rate of chemical reaction without itself getting altered. Catalyst does not increase/decrease the free energy of the chemical reaction but decreases its activation energy. Catalysts are thought to accelerate the speed of response and improve the selectivity of gas sensors [48]. Figure 1.7 illustrates the catalyst effect. Nano-particles, with higher surface area, act as catalysts. Here, R stands for reducing gas [12].

C:\Users\faiyyaj\Desktop\Fig. 1. catalysis effect.tif

**Figure 1.7 illustration of catalyst effect.**

The type of catalyst selected affects the selectivity/specificity of MOX sensor. If one needs to sense a specific gas in a mixture of several gases, one has to select a catalyst combination that can catalyse the oxidation reaction of the gas under study and cannot catalyse the oxidation of any other gas in the mixture. However, ideal combinations are not easily found [49]. The extensive applicability of MOX such as SnO2 or ZnO, as gas sensors is related both to the range of resistance change as well as to the fact that it responds to both oxidizing and reducing gases. Minute quantities of noble metal additives (Pd or Pt) are usually dispersed on the surface of MOX as activators/sensitizers to enhance the gas response, specificity and to decrease operating temperature [50, 51]. The catalyst can influence gas response properties such as the inter-granular contact region and therefore affects the sensor material resistance by two different ways. One of the ways is the spill over mechanism and other is Fermi energy control.

**1.8.2 Spill-over mechanism:**

Spill-over mechanism is a very famous effect in heterogeneous catalysis and is perhaps

most active with metal catalysts. It is a chemical reaction by which additives support the redox process of MOX. The term spill-over refers is a process in which the metal catalysts dissociates the gas molecule, and then atom can spill-over onto the surface of the sensor surface. At suitable temperatures, reactants are pre-adsorbed on to additive particles and then migrate to the sensor surface to react with pre-adsorbed oxygen species, affecting the surface resistivity.

Figure 1.8 illustrates the schematic of Spill Over mechanism. Oxygen approaches on the surface of the catalyst, which in turn causes the dissociation of oxygen / gas [52]. For the above processes to control the sensor resistance, the spilled-over species must migrate to the inter-granular contact as depicted in Figure 1.9. Hence, for a catalyst to be operational there must be good catalyst dispersion, as depicted in the Figure 1.9. The good dispersion of catalyst enables the said effect near all inter-granular contacts and hence catalysts can influence the significant inter-granular contact resistance.

C:\Users\faiyyaj\Desktop\Fig. 2. Spill over.tif

**Figure 1.8 schematic of spill over phenomena.**

C:\Users\faiyyaj\Desktop\Fig. 3. Illustration of spill over.tif

**Figure 1.9 Illustration of Spill Over mechanism caused by catalyst particles on the surface of the grain of the polycrystalline particle.**

The converse effect may also take place [53] when a nascent oxygen/gas atom is newly produced from a reaction on a metal oxide surface. This atom may migrate to a metal site and desorbs into gas molecule. This is known as reverse spill-over/porthole effect.

**1.8.3 Fermi energy control:**

In the second type of interaction additives interact electronically with the MOX as an electron donor/ acceptor species. For example, changes in the work function of the additive in the presence of a gas will result in the Schottky barrier change between the metal additive and metal oxide leading to the change in resistivity. It means that the oxygen gets adsorbed on the surface of sensor in the form of O- by extracting the electrons from the catalyst and as a result the catalyst, in turn, extracts the electrons from the supporting metal oxide semiconductor [54]. Figure 1.10 displays the situation with Fermi energy control.

C:\Users\faiyyaj\Desktop\Fig. 4. Fermi energy control.tif

**Figure 1.10 schematic for Fermi energy control phenomenon.**

Figure 1.10 illustrates that the catalyst, by Fermi energy control, governs the depletion of electrons form the metal oxide surface, however the poor catalyst distribution inhibits the effect on inter-granular contact resistance. In other words, oxygen gas adsorbing on the surface of catalyst extracts electrons from the catalyst and consequently the catalyst, extracts the electrons from the adjacent metal oxide surface of semiconductor. However, if very a few number of catalyst particles are available, only a very small surface region of the metal oxide semiconductor surface has a surface barrier which can be controlled by the catalyst. Then the probabilities of a catalyst particle being close to the inter-granular contact to dominate surface barrier is small.

C:\Users\faiyyaj\Desktop\Catalyst dispersion.tif

**Figure 1.11 an adequate dispersion of the catalysts is required in order to effectively affect the grains of the semi-conducting material to serve the implied purpose of increase in sensitivity.**

Figure 1.11 shows the more desired situation where one has a good dispersion of the catalyst particles such that the depleted region at the surface of a metal-oxide overlap and the influence of the catalyst extends to the inter-granular contact.

**1.8.4 Grain size effects:**

One of the essential factors which influence the gas response performance of metal oxide semiconducting gas sensors is the microstructure of polycrystalline element. Each crystallite of metal oxide in the element possesses an electron depleted region up to a depth say ‘L’ in air, where L is the Debye length. If the diameter D of the crystallite is comparable to 2L, the whole crystallite gets depleted of electrons and this causes the gas response of the element towards the reducing gas to change with D. The crystallites in the gas sensing elements are connected each other either by grain boundary contacts or by necks. In the case of grain boundary contacts the electrons move across potential barrier, the height of which changes with surrounding atmosphere .The gas sensitivity in this case is independent of the grain size. In the case of conduction through necks, electrons move through the channel penetrating through each neck. The aperture of the channel is attenuated by the surface space charge layer. This model is related to the grain size through the neck size. It has been found out experimentally by [Yamazoe et al, 1991] that the neck size X is proportional to D with a proportionality constant of 0.8 ± 0.1. For D>>2L, electron conduction in the element is dominated by conduction through grain boundary contacts (grain boundary control). For D≥2L, neck control forms the primary mechanism of conductivity modulation (neck control). For D<2L, the

electrical resistance of the grains dominates whole resistance of the sensor and thus sensitivity is controlled by grains themselves (grain control). The grain size effects are pictorially depicted in Figure 1.12 and 1.13 respectively.

**C:\Users\faiyyaj\Desktop\Fig. 1. crystallite size dep w.tifFigure 1.12 Crystallite size of sensing film is more than the depletion width, resulting in incomplete depletion of grain with energy barrier for electron in both presence and absence of gas.**

C:\Users\faiyyaj\Desktop\Fig. 1. grain size effect2.tif

**Figure 1.13 Crystallite size of the sensing film is equal to the depletion width, resulting in complete depletion of grain with energy barrier for electron in both presence and absence of gas.**

**1.8.5 Thickness dependence:**

Thin and thick film sensing layers differ in thickness as well as in microstructures and can thus exhibits different transducer functions [55]. The gas response property of the different layers depends intensely on the thickness of layers. In the case, when the electron depletion layer width of the surface is about the thickness of a film, high gas sensitivity may be expected. Thus, gas response properties of the semiconducting metal oxide sensor is directly affected by the size of the depletion layer induced by the oxygen adsorbed at the film surface with respect to the thickness of the bulk semiconductor. This effect has been as illustrated in the Figure 1.14. In general, when the depletion layer width is same as the thickness of the film, enhanced sensitivity can be expected.

**C:\Users\faiyyaj\Desktop\20.05.17 FZ SK THS\24.05.2017 THESIS CHAPTERS\Ch 1 Files\Ch 1 depth in the metal-oxide.tif**

**Figure 1.14 Sensitivity dependence on the depletion layer depth (a) Adsorption of the oxygen on the sensing film surface. (b) Reduction in depletion area upon exposing to reducing gas.**

Figure 1.14(a) illustrates the depletion region in the ambient atmosphere whereas; Figure 1.14(b) illustrates the decrease in the depletion layer depth upon exposure to the reducing gas. When the depletion depth is approximately equal to the film thickness, the resistance will be very high and hence one can expect higher selectivity of the sensor. However, it has been pointed out that the columnar growth of gas sensitive film leads to the thickness-independent gas sensitivity of sensor as reported by H.J. Michel et al [56]. It has also been shown that the thickness of the sensitive layer does play a role in determining the sensitivity of the sensor for different gases [57]. The thin SnO2 layer, (thickness 50-300 nm) mainly responds to the oxidizing gases such as Ozone and NO2 whereas thick films (thickness 15-80 μm) respond to reducing gases like CO and CH4. However, upon reducing the temperature of the sensor, the thick film showed a significant response to oxidizing gases. This behaviour can be explained with the diffusion reaction model. A model for the sensing mechanism in thick-film has been presented in [57].

**1.8.6 Temperature modulation:**

The operating temperature of the sensor is one of the most vital parameters. Firstly, adsorption/desorption are temperature dependent processes, hence dynamic properties of the sensors such as response and recovery time etc. are influenced by on the temperature. There are several temperature dependent reactions such as surface coverage, co-adsorption, chemical decomposition etc. This results in different static properties at different temperatures. Secondly, the temperature also influences the physical properties of the sensing material such as carrier concentration, Debye length and work function etc. The optimal temperature range for an efficient sensor response is where the sensor material is able to catalytically reduce or oxidize the target gas, instantaneously changing the electrical properties of the sensing material. The rate of reaction is determined by the exact reducing agent under investigation. It can be observed that, with a given reducing agent, there is peak in the response curve: At the lower temperatures the reaction rate is too slow to provide a high response, on the other hand at the higher temperature, the overall oxidation reaction takes place so quickly that the diffusion of reducing agent at the sensor surface becomes limited and concentration realized by sensor approaches to zero [58]. At such temperatures, the entire concentration of the test gas reaching the surface of the sensor material could get either reduced or oxidized without producing a noticeable change in the resistance of the metal-oxide. Consequently the response is low again. However, on the one hand, temperature should be sufficiently high enough for permitting the gas reaction on the sensor surface. The operating temperature is determined empirically so as to provide the highest response to the target gases. So, a clear understanding of the relation between the material, catalytic properties and the sensor response is crucial to realize the whole gas sensing mechanism. Therefore, an optimum temperature must be selected. When higher degrees of selectivity are needed, sensor arrays are used for particular sensor-gas combination. Sometimes an array of different sensors is used for identifying the gaseous species by pattern matching. Such sensor array can eliminates the lack of selectivity of the single metal-oxide gas sensor. The array of sensors may consist of same kind of sensor devices operating at different operating temperatures or the different sensors materials at the same operating temperature [59-61].

**1.8.7 Filters for selectivity:**

Filters are devices which can be used to improve the selectivity property of gas sensors. The filters either consume gases that one does not wish to pass to the gas sensor or to permit the passage of selected gases to the sensor. The use of filters is to a great extent empirical. Carbon cloth and low porosity materials are used to prevent highly reactive or large molecules from reaching the sensor. Silica can be used to increase hydrogen sensitivity, as hydrogen passes more freely through a silica surface layer. Similarly Teflon is helpful in stopping H2O reaching the sensor and Zirconia can be used at high temperature to pass oxygen [62]*.*

**1.9 Sensing Mechanism:**

The sensing mechanism of metal oxide is based on the surface reactions, the charge transfer process and the transport phenomenon within the sensing layer. The sensing mechanism takes place in the five steps which are reversible. These are as follows:

1. diffusion of gas to the surface
2. Absorption of gas molecules at the active sites
3. Surface reaction on the surface of the sensor.
4. Desorption of the products from the active site.
5. Diffusion of the products away from the surface.

Thus the sensing mechanism is affected by adsorption-desorption process, surface diffusion reactions and redox reaction between the gas molecules and the sensor surface.

**1.10 Adsorption Mechanism:**

Adsorption is a spontaneous process between the gas molecules and metal oxide surface. In this process the change in the free energy is negative. The adsorption of different gases depends on the surface structure composition and gas molecules. The adsorption occurs in several ways as follows:

* **Physisorption**
* **Hydrogen Bonding**
* **Chemisorption**
* **Ionosoption**

**1.10.1 Physisorption**

Physisorption is the adsorption of gas molecules onto the surface of metal oxide sensor, without a chemical change, geometrical structure or charge change in the electronic structure of the gas molecule as well as the surface of the sensor. It is usually associated with dipole-dipole interaction between the gas molecule and the sensor surface. This process of adsorption occurs at the initial state of interaction of adsorbate with the surface. The weak electrostatic interaction between adsorbate and surface is explained by Van-der-Waals forces or dipole-dipole interaction. As the process is reversible and no activation energy in associated with it the equilibrium state is quickly attained.

At low temperatures usually below 100oC the process is characterised by large surface coverage θ with gas molecules and small surface coverage at relatively high temperatures. Up to the monolayer formation the fractional surface coverage is the ratio of number of gas molecules adsorbed per unit surface area to the total number of surface adsorption sites. [63].

Therefore,

**; ---------- (1.10)**

Where, N is the number of gas molecules adsorbed per unit surface area and Ni is the total number of surface adsorption sites.

The rate of adsorption is defined by the change in the fractional coverage with time (dθ/dt).

The Lennard-Jones potential can be used to describe potential of interacting particles (Figure1.15) [64]. This potential is approximated by the two particle potential, which consist of attractive and a repulsive term:

**---------- (1.11)**

Where, Epot is the potential energy; Eattr is the attraction energy; d: distance between the interacting particles and ε: depth of potential, r is the distance between the atoms in a molecule.

**1.10.2 Hydrogen Bonding**

Hydrogen bonding is another electrostatic interaction. The magnitude of interaction of hydrogen bond lies between that of Physisorption and chemisorption (~0.1 eV) [64]. When a covalently bonded hydrogen atom forms a second bond with another atom, this bond is known as a hydrogen bond. The hydrogen bond usually takes the form as X-Y where Y is any σ or π electron donor site (Lewis base) and X is an atom having electronegativity greater than hydrogen such as C, N, P, O, S, F, Cl, Br etc. The hydrogen bond can be symmetrical or asymmetrical, in symmetrical bond; the proton can tunnel between two equilibrium positions. On the other hand in case of asymmetrical bond the proton is more strongly bound to one atom than to another. The intermolecular force of hydrogen bonds comprises of a Van-der-Waals as well as covalent term. The potential energy of hydrogen bond can be explained with a function similar to the Lennard-Jones potential (Fig. 1.15).

**---------- (1.12)**

**1.10.3 Chemisorption**

Chemisorption is a typical chemical reaction in which the gas molecule (adsorbate) interacts with the surface (adsorbate) through the process of the charge transfer. A interaction between adsorbate and surface is much stronger than physisorption (>5 eV). Chemisorption can take place in the form of atom or molecule of gas. The molecular adsorption proceeds by the process of dissociation of molecules. The chemisorption modifies the electronic structure of the adsorbate and the surface. The chemical bond can be formed due to the capture of electron from the adsorption complex or by transferring it into the conduction band of the semiconductors. The corresponding changes in density of the free charge carriers can be measured in terms of conductivity.

Using the Lennard-Jones model for the adsorption, the net change in the chemisorption is the difference between in adsorption desorption rates [65].

Where, ΔEA is the activation barrier and ΔHchem is the heat of chemisorption.

The heat of chemisorption is same as the binding energy.

Therefore,

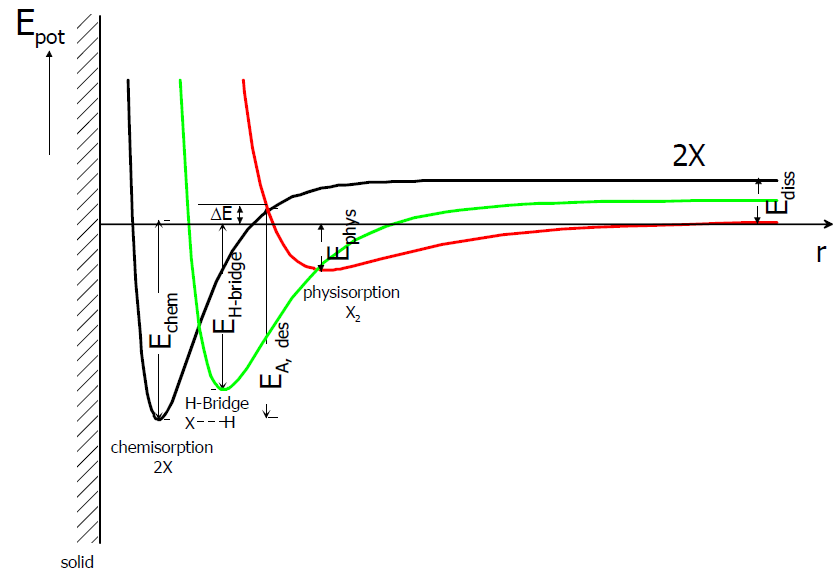
Activation energy is the least energy required for the chemisorption of gas molecule.

At equilibrium, the rate of adsorption is same as the rate of desorption i.e dθ/dt=0 or dH/dt=0. The coverage is given by:

**---------- (1.13)**

**1.10.4 Ionosorption**

Ionosoption is a type of chemisorption in which the atoms/molecules are ionized by capturing an electron when the adsorbate acts as a surface state capturing the electrons from the bulk of the metal oxide material. Therefore ionosorption can be also called as delocalised chemisorption. As a result of the transfer of charge between from molecules to surface (vice versa), the chemical activity of the molecules, as well as their electronic and geometrical structures, are strongly influenced [64].



**Figure 1.15 Potential diagrams for chemisorption, hydrogen bonding and physisorption on the surface.**

Figure 1.15 describes the potential plots of physisorption, hydrogen bonding and chemisorption. In principle, ionosorption is the case where, there is no local adsorbate-to-surface atom bonding, but the adsorbate acts as a surface state, capturing an electron or hole, and is held to the surface by electrostatic attraction. Ionosorption is of particular importance in gas sensors, mainly the “ionosorption” of oxygen. The oxygen can be ionosorbed in several forms: O2−, O− and O2−. Analysis of the adsorption of oxygen on n-type semiconductors suggests that O2−isthe usualform of adsorbed oxygen at low temperature and high pressure of oxygen gas. At higher temperatures, the superoxide ion O2− dissociates to the peroxide form O−, the more reactive form of oxygen. This is the form that usually makes n-type semiconductors moderately active. The last form is doubly charged adsorbed oxygen which is not in general to be expected for adsorbed species because such high charge on the ion may lead to instability.

It is well-known that the sensing mechanism of semiconductor gas sensor materials is a surface controlled process. The adsorption of test gases, which depends on both the type of test gas and the sensor material, might affect both the response characteristics and response time. Better response would be expected for larger concentration of the test gas adsorbed, because the reaction between the adsorbed reducing gas and oxygen species becomes more favorable. When the sensor element is maintained at equilibrium at the operating temperature, oxygen in the form of oxide species like O−, O2−, O2−, etc., localize mobile electrons from the n-type semiconducting oxide in air, creating a depletion layer at the surface of the individual particles and inter-granular regions. Thereafter, the reaction of reducing test gas with the charged oxygen species destroys the electron localization process and is observed as a change in conductivity [66].

The surface and interface states related to the material itself are called intrinsic states [67, 68]. In addition to intrinsic states, extrinsic states can be generated by adsorption of gases [67-70]. The existence of the local electronic states gives rise to electronic trapping processes. In the case of trapping in an adsorbed atom or molecule (extrinsic state) the process is also known as ionization. Two connected semiconductor grains and the electronic energy band in the grain boundary region are illustrated in Figure 1.16. The semiconductor is n-type and the electronic interface states at the grain boundary are acceptor-type. The energy bands along the *x*-axis in the grain-boundary region are plotted, and trapping of a conduction electron in an acceptor-type electronic interface state is illustrated. *NB* is the density of occupied interface states, *Ec* the bottom of the conduction band, *Ev* the top of the valence band, *EF* the Fermi level, *q* the unit charge, and *VB* the grain-boundary potential barrier, respectively. Trapping of electron in the interface state shown in Fig. 1.16 gives rise to local charge at the grain boundary (density *NB* per area). The local charge, in turn, causes the bending of electronic energy bands, which is discussed below. The band bending is characterized by a grain-boundary potential barrier *VB* (Fig. 1.16), which determines the transport of electrons across the grain boundary.

**C:\Documents and Settings\admin\Desktop\grain boundaries 2 new.TIF**

**Figure 1.16 Schematic diagrams of two interconnected grains of n-type semiconducting material.**

In an n-type semiconductor with large band gap, the effect of holes can usually be neglected. In this case the electronic trapping at grain-boundaries takes place. Fig. 1.17 shows the electronic energy bands in the grain-boundary region in the flat-band case and in the thermodynamic equilibrium are illustrated. Fig. 1.17 (a)in the flat-band case (i.e. without band bending, *VB* = 0); and Fig. 1.17 (b)in the thermodynamical equilibrium. *Ec* is the bottom of the conduction band, *Ev* the top of the valence band, *EF* the Fermi level, *ET* the acceptor-type interface trap state level, *q* the electron charge, and *VB* the grain-boundary potential barrier, respectively.

**C:\Documents and Settings\admin\Desktop\Band 2 new.TIF**

**Figure 1.17: Schematic picture of electronic energy bands in the grain-boundary region in n-type semiconductor.**

In a semiconductor material electric fields cause depletion or accumulation of major charge carriers of the material. If the depletion of major charge carriers is strong enough, the minority charge carriers begin to accumulate in the region [71, 72], which is termed as inversion. The band bending, in turn, causes the depletion or accumulation of majority or minority charge carriers depending upon direction of the bending. Acceptor interface states in an n-type semiconductor give rise to depletion or inversion regions. Donor interface states result in accumulation region.

**1.11 Types of adsorption depletion models**

The process of Adsorption is generally studied with the help of the graph known as adsorption isotherm. The graph of the amounts of adsorbate (x) adsorbed on the surface of adsorbent (m) versus pressure at constant temperature is called as Adsorption Isotherm. There are several types of adsorption isotherms modified in different types of models, which are developed to explain the adsorption phenomenon such as Langmuir, Braunauer-Emmett-Teller (BET), Freundlich, Wolkenstein and Kolmogorov Model. These models are designed on the basis of adsorption/desorption kinetics.

**1.11.1 Langmuir Model**

The classical thermodynamic adsorption model is based on Langmuir theory. Irving Langmuir proposed that the rate of sorption process depends on the actual concentration in the bulk and to the number of unoccupied adsorption sites. On the other hand rate of desorption depends merely upon the number of sites occupied by the solute molecules. Hence the adsorption and desorption processes depends on the nature of adsorbate as well as on the availability of adsorbate (partial pressure) and on the temperature. Langmuir model is based on the assumptions as follows:

1. Fixed amount of vacant or adsorption sites are present on the solid surface.
2. Each vacant surface site is of same size and shape on the adsorbent surface.
3. Only single gaseous molecule can occupy each vacant site and a fixed amount of heat is liberated in this process.
4. There is a dynamic equilibrium between adsorbed molecules and the free of gaseous species.

Dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules

Where A (g) is gaseous molecule which is not adsorbed, B(s) is unoccupied surface site and AB is gaseous molecule is desorbed.

1. Adsorption is monolayer

**Derivation:**

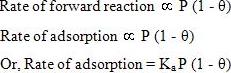
Langmuir Equation shows association between the number of active sites of the surface undergoing adsorption and pressure.

Let θ be the concentration of surface sites which are covered with gas molecules, and P is the pressure.

Hence, the number of surface sites which are not covered by gas molecules is (1 – θ).

Rate of adsorption is governed by two factors namely: (1 – θ) and P.

Hence, rate of adsorption is directly proportional to (1 – θ) and P.



Similarly, Rate of desorption be governed by number of sites occupied by the gaseous species on the adsorbent surface.

Equations

At equilibrium, rate of adsorption is = rate of desorption.

Ka P (1 – θ) = Kd θ

Therefore,

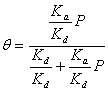
KaP – KaP θ = Kd θ

KaP = KaP θ + Kd θ

KaP = (Kd + KaP) θ

Theta θ

Dividing numerator and denominator on RHS by Kd, we get



Now put

Value of K

Therefore,

**Langmuir Adsorption Equation ---------- (1.14)**

This is the Langmuir Adsorption Equation.

C:\Users\faiyyaj\Desktop\Ch 1 Langmuir Function.tif

**Figure 1.18 Langmuir Isotherms**

### Drawbacks

1. It is valid under low pressure only.
2. It assumes that adsorption occurs only in the form of monolayer. But, monolayer formation is not possible under high pressure condition.
3. The assumption of homogeneous solid does not exist in all practical cases as all real solid surfaces are heterogeneous.
4. It assumed that molecules do not interact with each other. But weak attraction force exists even between same types of molecules.
5. The adsorbed molecules are not always localized i.e. (ΔS is not 0) due to the liquefaction of gases.

From above facts it can be concluded that, **Langmuir equation is valid only under low pressure conditions**.

**1.11.2 Braunauer, Elmer and Teller (BET) model**

As the **Langmuir** fails under certain conditions, Braunauer-Elmer-Teller (BET) proposed another model called as BET model which is simply the extension of Langmuir model which incorporated the multilayer adsorption. The BET model is based on the assumption as follows:

1. All the vacant surface sites are having equivalent adsorption sites;
2. Gas molecules physically adsorb on each solid layers;
3. Surface layers do not interact with each other;
4. Second and all the following layers are weakly adsorbed than first layer;
5. Langmuir theory can be valid for each layer.

The BET equation is given as follows:

**---------- (1.15)**

Where, p is partial pressure of gas at given temperature (Pa);

p0 is saturation pressure at given temperature;

V is the volume of the gas adsorbed at STP;

Vm is the volume of the gas adsorbed at STP to produce an apparent monolayer on the surface of the sample;

a is a constant;

The BET adsorption is used for estimation of surface area and morphology of the sample.

**1.11.3 Freundlich model**

Freundlich Model is an empirical modification of Langmuir model to explain the multilayer adsorption and consequences of the surface heterogeneity of the samples [73]. This model considers the inhomogeneous surface to consist of different areas characterised by various adsorption heats *Qi* or by various inverse adsorption coefficients *bi.* The degree of surface occupation is written as:

Where is the probability of occupying an area with a given value *b(Q);f(Q)* and *f(b)* are the distribution density of adsorption heats and inverse adsorption coefficients.

The adsorption behaviour is describe by the Freundlich isotherm as [1.16]:

**---------- (1.16)**

Where α is the proportionality constant and β is the exponent.

The simplified form of Freundlich isotherm can be written as [1.17]:

**---------- (1.17)**

**For 0<β<1.**

The relative response of the sensor can be associated with the concentration as [1.18]:

**---------- (1.18)**

Where, S is the sensitivity, C is the concentration of the gas.

The time dependent of sensitivity S(t) during response Sres(t) and recovery Srec(t) can be written as [1.19].

**-------- (1.19)**

**-------- (1.20)**

Where A is the amplitude, and tres and trec are time constants for response and recovery respectively. However it is found that this model fails at higher concentrations [1.20].

**1.11.4 Wolkenstein Model**

The Wolkenstein adsorption model incorporates the electronic interactions and their effect on the absorptivity of semiconductor substrate into description of chemisorption on semiconductors. In this process, localised electronic states, created by chemisorbed species, serves as traps for electrons or holes, depending on their nature [77]. The model considers chemical equilibrium at the semiconductor surface.

The basic assumptions of the Wolkenstein adsorption isotherm are as follows:

1. There is only one gas species for adsorption.
2. Chemisorption is only source of charging.

Simply in two successive steps the Wolkenstein adsorption process can occurs by transforming adsorbed particles from neutral state to ionized state, vice versa. During the first step the bond between the adsorbate and the substrate is weak and does not involve electronic transfer from bulk to the surface or vice versa; the electrons of the atoms or the molecules remain located in the vicinity of the adsorbate involving the simple deformation of orbitals [78]. The binding energy of the adsorbate Eads, corresponds to the loss of free energy of the system during the adsorption process.The electrical properties of the material do not changed during this neutral chemisorption, but the perturbation created by the adsorbate induces surface state, ESS in the band gap. Thus, the surface state acts as a trap for the electron.

The second step occurs when an electron or conduction band, with conduction energy EC, is transferred from the semiconductor to the adsorbed species. SThe binding energy of the adsorbate is increased by ES=EC-ESS, that is loss of free energy of the system during the ionization process. This process involves the creation of a negative superficial charge and chemisorption-induced surface potential VS (VS <0), defined by Poisson’s equation.

The surface coverage θis given by the rate equation of non-dissociative chemisorption as follows [1.21]:

***(1.21)***

*Where S0=adsorption probability, p= the ambient gas partial pressure, m is the molecular mass of the target gas, k=Boltzmann constant, T=the thermodynamic temperature, θ=total coverage, θo=partial coverage, θ-=partial coverage of charged adsorbate, ECb=conduction band edge, v0and v-are desorption probabilities.*

On further simplifications the Wolkenstein adsorption isotherm for non-dissociative chemisorption is given as:

*Where,*

*and*

**---------- *(1.22)***

Finally, the Wolkenstein adsorption isotherm resembles the Langmuir isotherm. The major difference is that the coefficient β0 in Langmuir isotherm is independent of the coverage θ, whereas in Wolkenstein isotherm β is a function of θ.

The applications of Wolkenstein model include numerical computation of SnO2, stimulation of dynamic response of sensors to gas and modelling of noise in sensor signal.

**1.11.5 Kolmogorov model**

The Kolmogorov model is based on the interaction between two reservoirs; the target gas molecules and sensor surface [1.23]:

1. Analysed gas with concentration *n*, temperature *T* and partial pressure *p*,
2. Sensor adsorbent surface with total surface density of sites for adsorption of analysed gas *N0* with surface density of sites occupied by analysed gas molecules *Nt*.

For the transition probabilities, the system is supposed to be Markowian, near equilibrium and generation-recombination processes can occur between the two reservoirs. The random process of adsorption on the surface site is supposed to have two states and to be stationary with a constant transition probability density as below:

Where, *pij*is the transition probability at time *s* from *i*-state to *j*-state at time *t*. The process is similar to generation-recombination in semiconductors; the adsorption process corresponds to recombination, while desorption corresponds to generation from sorbent. The transition probability density for a molecule capture i.e response and molecule emission recovery is denoted by *μ1*0 and *μ01* respectively. The characteristic time tres is inversely proportional to the transition probability density *μ1*0:

Similarly,

The probability of transition pij(t) is expressed as [79]:

For *I, j=0,1,* with the condition *pii(0)=1, pjj=0, for i≠j.*

In thermodynamic equilibrium the statistics that the surface site is free or occupied by molecule is described by the absolute probability distribution ∏0 and∏1 as follows:

Where,

The absolute probability distributions are similar to the Fermi-Dirac statistics.

Hence, the surface density of adsorbed molecules is given by:

Where, *μ00 and μ11* are the densities of state 0 or 1, respectively.

With *μ10=CNn for adsorption, μ01=CNn1for desrption and CN as a coefficient of adsorption,*

**-------- (1.23)**

Thus the surface density of adsorbed molecules is proportional to the coefficient of adsorption C­N, concentration of adsorbed molecules n, surface density sites N0 and the effective density of occupied sites n1.

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