Mimic of a Gas sensor, Metal Oxide Gas Sensing Mechanism, Factors Influencing the Sensor Performance and Role of nanomaterials based gas sensors

R. John Bosco Balaguru
Professor
School of Electrical & Electronics Engineering
SASTRA University

B. G. Jeyaprakash
Assistant Professor
School of Electrical & Electronics Engineering
SASTRA University
# Table of Content

1 MIMIC OF A GAS SENSOR .................................................................4  
  1.1 IN A SIMILAR WAY .................................................................4  

2 EVOLUTION OF GAS SENSORS.........................................................5  
  2.1 CANARY IN A CAGE.................................................................5  
  2.2 FLAME SAFETY LAMP (DAVEY’S LAMP).................................5  

3 MILESTONE IN GAS DETECTION.......................................................5  

4 CHOICE OF METAL OXIDE SEMICONDUCTORS..............................7  

5 OTHER TYPES OF GAS SENSORS....................................................8  
  5.1 CAPACITANCE BASED GAS SENSOR........................................8  
  5.2 ACOUSTIC WAVE BASED GAS SENSORS.................................8  
  5.3 CALORIMETRIC GAS SENSORS...............................................9  
  5.4 OPTICAL GAS SENSORS..........................................................9  
  5.5 ELECTROCHEMICAL GAS SENSORS.........................................9  

6 METAL OXIDE GAS SENSING MECHANISM....................................9  
  6.1 WORKING PRINCIPLE OF METAL OXIDE SEMICONDUCTOR BASED SENSORS......10  
  6.2 EXAMPLES FOR GAS SENSING MECHANISM................................13  

7 FACTORS INFLUENCING THE SENSOR PERFORMANCE.....................14  
  7.1 FACTORS INFLUENCING SENSING PERFORMANCE........................16  
  7.2 GAS SENSING CHARACTERISTICS OF METAL OXIDES.........................18  
    7.2.1 Sensitivity.............................................................................18  
    7.2.2 Selectivity.............................................................................18  
    7.2.3 Accuracy..............................................................................19  
    7.2.4 Speed of response...............................................................19  
    7.2.5 Recovery time.................................................................19  
    7.2.6 Detection limit.................................................................20  
    7.2.7 Precision..........................................................................20  
    7.2.8 Error..................................................................................20  
    7.2.9 Dynamic range.................................................................21  
    7.2.10 Linearity............................................................................21  
    7.2.11 Resolution.........................................................................21  
    7.2.12 Stability............................................................................21  
    7.2.13 Life cycle..........................................................................21
8 ROLE OF NANOMATERIALS BASED GAS SENSORS.................................22

8.1 SURFACE & QUANTUM EFFECTS OF NANOMATERIALS AND NANOSTRUCTURES……..24
  8.1.1 Surface effects.................................................................24
  8.1.2 Quantum effects.............................................................24

8.2 MERITS AND DEMERITS OF DIFFERENT TYPES OF NANOSTRUCTURES AS SENSING MATERIALS .........................................................25
  8.2.1 Metal Oxides.......................................................................25
  8.2.2 Metal nanoparticles............................................................25
  8.2.3 Metal complexes ...............................................................26
  8.2.4 Polymers............................................................................26
  8.2.5 Carbon nanotubes..............................................................26
  8.2.6 Over all Merits.................................................................27
  8.2.7 Over all Demerits...............................................................27

9 REFERENCES....................................................................................27
1 MIMIC OF A GAS SENSOR

One might consider the ears, eyes, nose and fingers to be physical sensors as they detect physical sensations of sound, light, smell and heat respectively.

What we detect with the nose - smells - are in fact small quantities of chemicals. The nose is an extremely sensitive and selective instrument, which is very difficult to emulate artificially. It can distinguish between many different chemical substances qualitatively and can give a general idea of ‘quantity’ down to very low detection limits.

The chemicals to be detected pass through the olfactory membrane to the olfactory bulbs, which contain biological receptors that sense the substrate. The response is an electrical signal which is transmitted to the brain via the olfactory nerves. The brain then transduces this response into the sensation we know as smell.

1.1 In a similar way

Gas sensor can be defined as a device that informs about the composition of its ambient atmosphere. Particularly, upon interaction with chemical species (adsorption, chemical reaction, and charge transfer), the physicochemical properties of the metal oxide sensitive layer (such as its mass, temperature, and electrical resistance) reversibly change. These changes are translated into an electrical signal such as frequency, current, voltage, or impedance/conductance, which is then read out and subjected to further data treatment and processing.
2 EVOLUTION OF GAS SENSORS

2.1 Canary in a cage

The canary, normally a very songful bird, is more susceptible than humans to low oxygen, methane gas, or CO gas. Because of its highly sensitive nature towards gases, people used them to detect poisonous gases in mines. They would stop singing and eventually die in the presence of these gases, signaling the miners to exit the mine quickly. This was the first kind of gas sensors used in 1920s.

2.2 Flame Safety Lamp (Davey’s Lamp)

Later, people started using Davey’s lamp as a gas sensor. The flame height was calibrated with reference to the concentration of the gas present in the ambient.
- Oil flame adjusted to specific height in fresh air
- High flame means methane gas
- Low flame means low oxygen

3 Milestone in Gas Detection

The idea of using semiconductors as gas sensitive devices leads back to 1953 when Brattain and Bardeen first reported gas sensitive effects on Ge. Later, Heiland, Bielanski et al. and Seiyama et al. found gas sensing effects on metal oxides. In 1968, Taguchi (Figaro) revolutionized this field by identifying the metal oxide materials as gas sensing elements. Taguchi finally brought semiconductor sensors based on metal oxides to an industrial product (Taguchi-type sensors). Today, there are many companies offering semiconducting gas sensors, such as Figaro, FIS, MICS, CityTech, Applied Sensor, UST, Microsens and Paragon.

A Typical Metal Oxide Gas Sensor =

*An interactive material which interacts with environment and generates a response*
**Device which reads the response and converts it into an interpretable and quantifiable term.**

Metal oxides represent an assorted and appealing class of materials whose properties cover entire range from metals to semiconductors and insulators and almost all aspects of material science and physics in areas including superconductivity and magnetism. Metal oxides possess a broad range of electronic, chemical, and physical properties that are often highly sensitive to changes in their chemical environment. Many scientists and engineers have studied metal oxide thin films as electronic materials due to their semiconducting behaviour, structural simplicity and low cost.

In the field of gas/chemical sensing, it has been known that the electrical conductivity of semiconductors varies with the composition of the gas/chemical atmosphere surrounding them. Gas sensors have a great influence in many areas such as environmental monitoring, domestic safety, public security, automotive applications, air conditioning in airplanes, space crafts and houses, sensors networks.

Semiconductor oxide-based gas sensors are classified according to the direction of the conductance change due to the exposure to reducing gases as “n”-type (conductance increases, e.g., In$_2$O$_3$, ZnO, and SnO$_2$) or “p”-type (conductance decreases, e.g., Cr$_2$O$_3$ and CuO). This classification is related to the (surface) conductivity type of the oxides, which is determined by the nature of the dominant charge carriers at the surface, that is, electrons or holes.

A gas/chemical sensor consists of two functions:

One is the receptor function, which recognizes a chemical substance at the surfaces of the semiconducting particles, and the second one is transducer function, which transduces the chemical signal on the semiconductor surface through the micro/nano structure of the sensing semiconductor material into the measurable output signals like resistance, voltage, etc. The change in resistance of the sensing element or voltage across the sensing element is recorded as the signal.

The gas-sensing properties strongly depend on the surface and operating temperature of the materials. The surface of these oxides can be modified using various synthesis techniques. Metal oxide gas sensors use an appropriate material, either in bulk form or in thick or thin film form as gas sensing element. The working principle for gas detection of these sensors based on changes in

i) work function
ii) resistance
iii) dielectric constant
iv) mass of the sensing element due to adsorption of gas

The resultant change in any one of these properties is measured to determine the presence and percentage of the gas in the ambient. Most of conventional sensors employ bulk or thick films as a gas sensing material. However, in recent time, nanostructured thin films are used, since it gives better control on gas sensing properties of a material and large surface to volume ratio.

The gas sensors based on thin films are of three kinds according to the material used. They are,
1. Metal oxides thin film sensors (SnO₂, ZnO, Ga²O₃ etc.)
2. Catalytic metal thin film sensors (Pd and Pt)
3. Special class of organic material thin film sensor (Phthalozyanine, Poly-pyrol)

Due to selectivity problem in catalytic sensor and lack of compatibility of organic materials films and short life time in organic material thin film sensors, metal oxide thin film sensors are being used for commercial purpose.

4 Choice of Metal Oxide Semiconductors

Based on the electronic structure, metal oxide semiconductor elements like, Cr₂O₃, ZnO, SnO₂, Mn₂O₃, Co₃O₄, NiO, CuO, SrO, In₂O₃, WO₃, TiO₂, V₂O₃, Fe₂O₃, GeO₂, Nb₂O₅, MoO₃, Ta₂O₅, La₂O₃, CeO₂, Nd₂O₃ are suitable for detecting reducing or oxidizing gases through conductive measurements. As the range of these metal oxides, electronic structures are so wide; they were divided into following categories:

1) Transition-metal oxides (Fe₂O₃, NiO, Cr₂O₃, etc.)
2) Non-transition-metal oxides, which include
   a. Pre-transition metal oxides (Al₂O₃, MgO, etc.)
   b. Post-transition metal oxides (ZnO, SnO₂, etc.).

The pre-transition metal oxides are found to be quite inert, due to their large band gap, which in turn lowers the chances of electrons/holes formation. Due to the difficulties in electrical conductivity measurements, they are rarely selected as gas sensor materials.

On the other hand, the post transition-metal oxides are found to be more sensitive than pre-transition-metal oxides to environment. However, structural instability and non-optimality of other parameters important for conductometric gas sensors limit their field of application.
Therefore, only transition-metal oxides with $d^0$ and $d^{10}$ electronic configurations find their real gas sensing application. The $d^0$ configuration is found in binary transition-metal oxides such as TiO$_2$, V$_2$O$_5$, etc., while $d^{10}$ configuration is found in post-transition-metal oxides, such as ZnO and SnO$_2$.

Among different materials studied for gas-sensing applications, SnO$_2$ is the most extensively studied compared to other metal oxides. The gas-sensing properties of this material have been widely reported in the literature. Well known advantages of this material include its low cost and higher response for different gas species. A large number of dopants in SnO$_2$ have also been investigated to improve response times, operating temperature, selectivity, and so on.

In the post-transition-metal oxide, next to SnO$_2$, ZnO stands as one of the most popular materials for gas-sensing applications. Their use as a gas sensor, in which the surface conductivity changes in response to adsorbed gases, made them an ideal candidate in the field of surface science. Point defects on ZnO surfaces are extremely important in gas sensing as they produce very large changes in the surface conductivity. The changes occur at the surface of the grains as a result of charge transfer and band bending caused by the adsorbates. The dominant defects identified in these films are oxygen vacancies. Heating the films to high temperatures generally creates these vacancies. These surface defects do not produce any new filled electronic states in the band gap, due to the stable oxidation states of zinc.

5 OTHER TYPES OF GAS SENSORS

Over the years researchers have developed and studied different types of gas sensors based on different working principles. These could be classified as:

5.1 Capacitance Based Gas Sensor

They measure the change in dielectric constant of films between the electrodes as a function of the gas concentration. The capacitive sensor relies on inter-digitated electrode structures, which correspond to the two plates of a standard capacitor, to monitor changes of the dielectric coefficient of the film.

5.2 Acoustic Wave Based Gas Sensors

Sound based gas sensors are known as acoustic wave based gas sensors. To launch the acoustic waves, this type of sensor use piezoelectric material either in the thin film form or in bulk form which has one or more transducers on its surface.
5.3 Calorimetric Gas Sensors

The principle of calorimetric gas sensors based on change in temperature at catalytic surfaces. It consists of a surface of a film of a catalytically active metal (e.g. Platinum, Palladium or Rhodium). It burns combustible gases. Heat is generated due to the combustion. This heat is balanced by a reduction in the electrical heating power. Thus the power consumption indicates the concentration of gas.

5.4 Optical Gas Sensors

Some materials undergo a change in absorbance on exposure to the analyte. This principle is used to monitor the change in absorption of the sensing film on exposure to the analyte.

5.5 Electrochemical Gas Sensors

Electrochemical gas sensors are gas detectors that measure the concentration of a target gas by oxidizing or reducing the target gas at an electrode and measuring the resulting current. The target gas being measured diffuses into the cell through the diffusion barrier (capillary) and filters. When it comes into contact with the sensing electrode, the target gas present in the sample undergoes an electrochemical reaction (oxidation and reduction). The generated electrons from the electrochemical reaction charge the sensing electrode resulting in current generation.

6 METAL OXIDE GAS SENSING MECHANISM

The gas-detection principle of metal oxide is based on the variations of the depletion layer at the grain boundaries in the presence of reducing or oxidizing gases, which lead to modulations in the height of the energy barriers for free charge carriers to flow, thus leading to a change in the conductivity of the sensing material.

The active sensing layer of sintered and thick-film type gas sensors consists of numerous interconnected metal oxide grains. As shown in Fig.1 the adsorption of \( \text{O}_2 \) removes the charge carriers (electron) from the surface region of the grains, is to forms oxygen ion species as \( \text{O}_2^-, \text{O}^- \) and \( \text{O}^{2-} \) depending on the temperature, and forms a depletion layer around the grain boundaries. The depth of the depletion layer is determined by the oxygen partial pressure and the surface characteristics of metal oxide materials.
The depletion layer on the grain boundaries results in a higher potential barrier; thus, the grain boundaries become the bottlenecks for electric grain-grain transfer. When the sensor is exposed to combustible gases, the surface oxygen species react to form combustion products. This reaction lowers the oxygen species coverage, returns the free electron charge carriers to the bulk of the oxide material and increases electrical conductivity. This surface reaction modulated conductance serves as a gas response signal of the sensor.

### 6.1 Working principle of metal oxide semiconductor based sensors

The sensing element of chemiresistive type sensors normally comprises of a semiconducting material with high surface-to-volume ratio on a ceramic (glass) substrate with ohmic contacts to measure the change in resistance/conductance. When, gas/volatile organic compounds (VOC) samples interact on the surface of metal oxide semiconductor, due to the combustion reaction that occurs with the oxygen species on the surface of metal oxide particles leads to change in resistance and forms the basic principle of detection.

At elevated temperatures, reactive oxygen species such as $O_2^-$, $O^2-$ and $O^-$ are adsorbed on the surface of metal oxide semiconductor. The sequence of processes involved in the adsorption of oxygen on the metal oxide surface can be described by the following formulae:
\[ O_2 \text{(gas)} \leftrightarrow O_2 \text{(adsorbed)} \]  
(1)

\[ O_2 \text{(adsorbed)} + e^- \leftrightarrow O_2^- \text{(adsorbed)} \]  
(2)

\[ O_2^- \text{(adsorbed)} + e^- \leftrightarrow 2O^- \text{(lattice)} \]  
(3)

During the adsorption of oxygen species on the surface of sensing element, capturing of electrons from conduction band and the associated decrease in the charge carrier concentration \((e^-)\) leads to an increase in the resistance of the n-typesensing element until it attains equilibrium. Thus, the surface resistance increases and attains equilibrium during the chemisorption process. Any process that disturbs the equilibrium leads to a change in the resistance of metal oxide semiconductor. This change in resistance has a strong correlation with the concentration of VOCs/gases in dry air atmospheric conditions as shown in Fig. 2.

According to the conductivity behavior of semiconductor metal oxide, the response varies. In n-type semiconductor, the majority charge carriers are electrons. When it interacts with a reducing gas an increase in conductivity occurs. On the other hand, an oxidizing gas depletes the charge carriers, leading to a decrease in conductivity.

Similarly, in the case of p-type semiconductors, where positive holes are the majority charge carriers, an increase in the conductivity is observed in the presence of an oxidizing gas (the target gas increases the number of positive charge carriers or holes). On the other hand an increase in resistance is observed in the presence of reducing gas, where negative charge introduced into the material reduces the positive (hole) charge carrier concentration. Table 1 clearly summarizes the response of the sensing element
towards oxidizing and reducing gases and some n and p-type metal oxide semiconductor elements are listed in Table 2.

<table>
<thead>
<tr>
<th>Classification</th>
<th>Oxidising Gases</th>
<th>Reducing Gases</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-type</td>
<td>Resistance increase</td>
<td>Resistance decrease</td>
</tr>
<tr>
<td>p-type</td>
<td>Resistance decrease</td>
<td>Resistance increase</td>
</tr>
</tbody>
</table>

Table 2: Classification of metal oxides based on the conductivity type

<table>
<thead>
<tr>
<th>Type of Conductivity</th>
<th>Metal oxides</th>
</tr>
</thead>
<tbody>
<tr>
<td>n – type</td>
<td>ZnO, MgO, CaO, TiO₂, WO₃, SnO₂, In₂O₃, Al₂O₃, Ga₂O₃, V₂O₅, Nb₂O₅, ZrO₂</td>
</tr>
<tr>
<td>p – type</td>
<td>Y₂O₃, La₂O₃, CeO₂, Mn₂O₃, NiO, PdO, Ag₂O₃, Bi₂O₃, Sb₂O₃, TeO₂</td>
</tr>
</tbody>
</table>

Trapping of electrons by the adsorbed molecules leads to band bending, this affects the conductivity of the metal oxides. The upward bending of the energy bands due to the negative charges trapped in these oxygen species leads to a decrease in the conductivity.

As shown in Fig. 3, when O₂ molecules are adsorbed on the surface of metal oxides, they would extract electrons from the conduction band E_c and form ions. This will lead to band bending and an electron depleted region (space charge region). The thickness of this space charge region is equivalent to the length of band bending region.
Reverse in band bending occurs when there is a decrease in the reaction of oxygen species with reducing gases or when competitive adsorption and replacement of adsorbed oxygen occur. The reverse in band bending, leads to an increase in the conductivity as shown in. On the other hand a decrease in conductivity occurs in the case of oxidizing gases.

6.2 Examples for Gas sensing Mechanism

The overall interaction process of oxygen on the surface of metal oxide is given in the Eqn. 1. This reaction completely depends upon the temperature, i.e., below 100°C single molecular oxygen absorbs only one electron and formed a molecular ionic oxygen species \(O_2^-\), but above the temperature (100°C) it has capable to absorbs two electrons and forms to be atomic \((O^- \text{ or } O^{2-})\) (Eqn. 2&3)

\[
\frac{\beta}{2}O_2^{gas} + \alpha e^{-}_{surface} \rightleftharpoons O_\beta^{-\alpha}_{surface} (\alpha, \beta = 1,2)
\]

\[
O_2(gas) + e^{-}(Surface) \rightleftharpoons O_2^- (ads)
\]

\[
O_2(gas) + 2e^{-}(Surface) \rightleftharpoons 2O^- (ads)
\]

\[
O_2^{-} (ads) + e^{-}(Surface) \rightleftharpoons 2O^- (ads)
\]

When the reducing gas like ethanol interacts with n-type semiconductor, then the surface conductivity increases based on the following reaction:
$\text{ZnO} + \text{O}_2 \rightarrow (\text{ZnO})\text{O}_2^-$

$(ZnO)O_2^- + C_2H_5OH \rightarrow ZnO + 2CO_2 \uparrow + 2H_2O \uparrow + 3e^- \downarrow$

Note: Can be viewed only by Acrobat 9.0 and above
When the oxidizing gas like NO₂ interacts with n-type semiconductor, then the surface conductivity decrease based on the following reaction:

\[
\text{ZnO} + O_2 \rightarrow (\text{ZnO})O_2^-
\]

\[
(ZnO)O_2^- + NO_2 \rightarrow (ZnO)O_2^{2-} + NO \uparrow
\]

or

\[
(ZnO)O_2^- + NO_2 \rightarrow (ZnO)O^- + NO \uparrow
\]

When the oxidizing gas like NO₂ interacts with p-type semiconductor, then the surface conductivity increases based on the following reaction:

\[
\text{CuO} + O_2 \rightarrow (\text{CuO})O_2^-
\]

\[
(CuO)O_2^- + NO_2 \rightarrow (CuO)O_2^{2-} + NO \uparrow
\]

\[
(CuO)O_2^- + NO_2 \rightarrow (CuO)O^- + NO \uparrow
\]
When the reducing gas like ethanol interacts with p-type semiconductor, then the surface conductivity decreases based on the following reaction:

\[ CuO + O_2 \rightarrow (CuO)O_2^- \]

\[ (CuO)O_2^- + C_2H_5OH \rightarrow CuO + 2CO_2 \uparrow + 2H_2O \uparrow + 3e^- \]

7 FACTORS INFLUENCING THE SENSOR PERFORMANCE

Numerous researchers have shown that the reversible interaction of gas with the surface of material is the characteristic of conductometric semiconducting metal oxide gas sensors. This reaction can be influenced by many factors, including internal and external causes, such as the natural properties of base materials, surface area, microstructure of sensing layers, surface additives, temperature, humidity, etc.

There are many metal oxide semiconductor based chemical and gas sensors available commercially in the market with thick and thin film form of SnO₂ as sensor elements. Though they have been widely used to make arrays for odour measurement, they have long response and recovery time and show appreciable sensitivity only at elevated temperatures. On the other hand, selectivity of these sensors remains as a great challenge. Also, influence of humidity is found to have greater impact on sensor response.

Hence, in the recent years, researchers are working towards the development of metal oxide semiconductor based sensor elements with improved sensitivity and significant selectivity. The optimization of structural parameters, such as grain size, porosity, texture, grain network, etc. is an important factor for improving gas-sensing characteristics of resistive (conductometric) type sensors.

Sensor’s performance from the point of reducing gas detection depends on both the sensor material and the nature of detecting gas (Fig. 4).
The change in any one of the parameters may be accompanied by an adverse change in other characteristics. For example, thin film sensors possess a maximum rate of response, but along with that they might have very high sheet resistance, which can complicate their compatibility with peripheral measuring devices.

Similarly, sensitivity and stability are interconnected parameters as well. As a rule, smaller the crystallite size, higher the sensor response is. But at the same time, stability of gas sensors with finely dispersed grains is often decreased. The ambiguity of the effect of grain size decrease on parameters of solid-state gas sensors is shown in Fig. 5. Hence, in the process of fine tuning sensor performance by altering the parameters of sensor element or gas sensors, one should be aware of the effect of one parameter over other parameters and in turn the response and selectivity.
7.1 Factors Influencing Sensing Performance

- Gas sensing process is strongly related to the surface reactions.

- Different metal oxide based materials have different reaction activation to the target gases.

- Composite metal oxides usually show better gas response than the single component if the catalytic actions of the components complement each other.

- Noble metal additives with high-effective oxidation catalytic activity can be used to enhance the sensitivity of pure metal oxides due to the “spillover effect”.

- Good catalyst supporting materials are also a key point to determine how much potential of catalysts can be developed.

- High surface areas are necessary to obtain highly-dispersed catalyst particles.

- Furthermore, high surface areas can provide large reaction contact area between gas sensing materials and target gases.

- Porous structure with high surface areas seems to be the standard structure of metal oxide gas sensor layers. It is assembled by lots of small grains with voids and pores among them.

- Grain size is useful to enhance the sensitivity.

- At high temperatures, small grains tend to agglomerate into large entities, decreasing both surface areas and catalytic properties of the material.

- It is important to keep balance between decreasing grain sizes and stability.

- Another important structure factor is crystallographic facets.

- One-dimension materials are prospective material platform for the next generation of durable conductometric gas sensors due to open surface, high gas sensitivity and long-term stability, etc.
• External causes, such as temperature and humidity, also play an important role in the testing of sensitivity.

• Humidity will decrease the sensitivity and be harmful to repeatability.

• Fortunately, it can be eliminated by heating to high temperatures (usually >400 °C).

• Operating Temperature

  o Adsorption and desorption are temperature activated processes, thus dynamic properties of the sensors (response and recovery times) depend exponentially on the operating temperature.

  o The surface coverage, co-adsorption, chemical decomposition, or other reactions are also temperature dependent, resulting in different static characteristics at different temperature.

  o Temperature has an effect on the physical properties of the semiconductor sensor material (charge-carrier concentration, Debye length, and work function).

  o At higher temperature the charge-carrier concentration (and the conductivity) increases and the Debye length decreases. This is one possible reason for the decreasing sensitivity of sensors at higher temperatures.

### 7.2 Gas Sensing Characteristics of Metal Oxides

#### 7.2.1 Sensitivity

It is the response of a gas sensor per unit change in the gas concentration. Since, metal oxide gas sensors are based on the principle of chemiresistivity; it is generally defined in terms of conductance or resistance. For n-type material in the presence of reducing gas and p-type material in the presence of oxidizing gas, sensitivity can be defined as,
S = \frac{(R_a - R_g)}{R_g}, \text{ where, } R_a, R_g \text{ are the stable values of the resistance of the material before and after exposure to gas.}

7.2.2 Selectivity

A sensor should respond to only a particular molecule in a mixture of environment. The selectivity of a gas sensor towards a particular molecule is the ratio of its response towards it and that of another dominant interfering molecule in the atmosphere.

Selectivity of a gas sensor = \frac{\text{sensitivity of a particular molecule}}{\text{sensitivity towards an interferent}}

Selectivity of a gas sensor should be always greater than one.
7.2.3 **Accuracy**

Accuracy represents the degree of exactness of a measurement compared to the true value.

7.2.4 **Speed of response**

The time required for a sensor to reach 90% of total response of the signal such as resistance upon exposure to the target gas

7.2.5 **Recovery time**

The time required for a sensor to return to 90% of original baseline signal upon removal of target gas
7.2.6 Detection limit

It is the lowest concentration of the gas that can be detected under given conditions, particularly at a given temperature.

7.2.7 Precision

It is a measure of repeatability of a gas sensor

7.2.8 Error

It is the difference between the measurand value and true value.

$$\text{Accuracy} = \frac{1}{\text{Error}}$$

Where K is the constant of proportionality and it depends on the type of sensing element as well as measurement system.

7.2.9 Dynamic range

The concentration range between the detection limit and the upper limiting concentration.

7.2.10 Linearity

The relative deviation of an experimentally determined calibration graph from an ideal straight line. Usually values for linearity are specified for a definite concentration range.

7.2.11 Resolution

The lowest concentration difference which can be distinguished when the composition is varied continuously. This parameter is important chiefly for detectors in flowing streams.

7.2.12 Stability
The ability of the sensor to maintain its performance for a certain period of time. As a measure of stability, drift values are used, e.g. the signal variation for zero concentration.

7.2.13 Life cycle

The length of time over which the sensor will operate. The maximum storage time (shelf life) must be distinguished from the maximum operating life. The latter can be specified either for continuous operation or for repeated on-off cycles.

8 Role of nanomaterials based gas sensors

In the recent past, the focus of scientists to gas-sensitive materials has gained significant momentum due to the birth of nanotechnology. This trend is mainly due to the promising electronic, optical, thermal properties of nanomaterials, their size and shape dependence and ability to control the material structure by new experimental techniques.

In 1991, Yamazoe et al. proved that the reduction of crystalline size leads to significant increase in sensor performance. Further, sensitivity can also be improved by controlling the dimension of nanomaterials. Thus, the increase in surface volume ratio...
has a great impact on increasing sensitivity. Numerous reports in the literature have
documented that the response and recovery time of nanomaterials based gas sensors is in
milliseconds. Nano sized grains of metal oxide semiconductors – all the carriers are
trapped in surface state transition from activated to strongly non activated carrier density,
produced by target gases (huge effect on sensor conductance).

Metal oxide nanostructures particularly one dimensional have several advantages
over the traditional thin film and thick film sensing elements namely

- Very large surface-to-volume ratio
  
  This favours the adsorption of gases on the sensor and can increase the sensitivity
  of the device because the interaction between the analytes and the sensing part is
  higher.

- Dimensions comparable to the extension of surface charge region
- Superior stability owing to the high crystallinity
- Relatively simple preparation methods that allow large-scale production
- Possible functionalization of their surface with a target-specific receptor species
- Modulation of their operating temperature to select the proper gas semiconductor
  reactions
- Catalyst deposition over the surface for promotion or inhibition of specific
  reactions
- FET configuration that allows the use of gate potential controlling the sensitivity
  and selectivity
- Density of States of charge carriers is concentrated in specific energy levels
  (charge confinement ability)
- Crystalline structure with well-defined chemical composition
- More Porous nature which can enhance the sensitivity
- Leads to enhancement of catalytic activity & surface adsorption
- Superior stability

Various forms of metal oxide nanostructures used in the fabrication of gas sensors are:

- Nanorods
- Nanowires
- Nanofibers
- Nanotubes
- Nanobelts
- Nanoribbons
- Nanowhiskers
- Nanoneedles
Nanopushpins
Fibre-Mats
Urchin
Lamellar
Hierarchical Dendrites

Various processing routes for nanostructured metal-oxides are:

Hydrothermal
Ultrasonic irradiation
Electro-spinning
Anodization
Sol-gel
Molten-salt
Carbothermal reduction
Solid-state chemical reaction
Thermal evaporation
Vapor-phase transport
Aerosol
RF sputtering
Molecular beam epitaxy
Chemical vapor deposition
Gas-phase assisted nanocarving
UV lithography
Dry plasma etching

8.1 Surface & Quantum Effects of Nanomaterials and Nanostructures

8.1.1 Surface effects

- Fraction of atoms on the surface is proportional to surface to volume ratio (S/V) scales as r^{-1}
- Atoms at the surface have few direct neighbors than atoms in bulk (low coordination number)
- Atoms in the interior are more coordinated; form more bonds and more stable than those at the surface (which are less stable)
- Less stability of surface atoms leads to lower melting points of surface layers
- Melting point scales as r^{-1}
- Au (2.5 nm) – 930 K; bulk gold - 1336 K
8.1.2 Quantum effects

- Discontinuous behavior due to completion of shells in systems with delocalized electrons
- Free electrons are assumed to be constrained within a potential well which essentially stops them from leaving the metal (particle in a box model). This is called quantum confinement
- Energy of the electronic level (En) is inversely proportional to size (ranges from microns to millimeters to even centimeters) for bulk material
- Alterations in electronic structure leads to change in total energy
- Arrangement of outermost electronic levels are different at nano scale (hence different elect/mag/opt)
- When the gap between HOMO & LUMO is lower than thermal energy insulators become conductors
- Nanoparticles or Nano-dimensional layers adopt a crystal structure different from that of the bulk
- For Nano-crystalline materials, large proportions of atoms will be either at or near grain boundaries
- Linear strain is inversely proportional to particle size.
- Interatomic spacing will decrease for small nanoparticles. Nano-crystals are expected to be vacancy free.
- All thermo mechanical properties and processes that are dependent on presence and migration of vacancies are expected to be different for Nano-crystals.

8.2 Merits and Demerits of Different types of nanostructures as sensing materials

8.2.1 Metal Oxides

- **Merits**
  - High area/volume ratio
  - Low response times and high sensitivity
  - Doping processes with metal nanoparticles increase the sensitivity and the stability of the sensors
  - Lower working temperatures (than bulk materials)
  - The results can be improved using annealing processes

- **Demerits**
  - The nanostructures require post-treatments, such as calcination and annealing, and the use of high temperatures and advanced techniques for film deposition
– Additional characterization processes are required to obtain information about the size and form of the materials

8.2.2 Metal nanoparticles

➢ Merits

– The sensing layer does not require so much material. Some nanoparticles act as catalysts and increase the speed of the detection process
– Specific interactions with biomolecules can be used to immobilize the sensing layer (e.g. Au–cysteine)

➢ Demerits

– Nanoparticles require annealing and advanced techniques for deposition
– The characterization techniques are expensive

8.2.3 Metal complexes

➢ Merits

– The detection is based on specific reactions. These devices are therefore selective and, in many cases, reversible

➢ Demerits

➢ Synthesizing the complexes is expensive

8.2.4 Polymers

➢ Merits

– With a thin polymer layer, response times are short and reproducibility is high

➢ Demerits
– Stability and selectivity are low

8.2.5 Carbon nanotubes

➢ Merits

– Shorter response and recovery times, high sensitivity, reversibility and stability for raw CNTs
– Several techniques can be used to obtain CNTs (synthesis or deposition)
– Responses at room temperature
– Aging and thermal processes increase the sensitivity of the sensors
– When metal oxides are deposited as nanoparticles on the surface of the CNTs, working temperatures are lower
– Gas ionization sensors are small and have lower ionization voltages. Therefore, power consumption, cost and operational risk are lower

➢ Demerits

– Additional purification processes are required
– Lack of selectivity for raw CNTs
– CNTs are relatively expensive in comparison with other materials
– Networks of CNTs decrease the repeatability of the sensors

8.2.6 Over all Merits

High sensitivity, small size, smaller amounts of sensing material, short response and recovery times, low working temperature and power consumption

8.2.7 Over all Demerits

Post-treatments, expensive characterization techniques, advanced and expensive techniques for depositing the materials, low repeatability and reproducibility of the signals, and functionalization processes are required to increase the selectivity
9 REFERENCES


2. George W. Hanson, Fundamentals of Nanoelectronics, 2007, Prentice-Hall.


