Chapter 1

General introduction and literature survey
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1.0 Introduction

Many industrial and commercial activities involve the monitoring and control of the environment, with applications ranging from domestic gas alarms, medical domestic apparatus to safety environment, and chemical plant instrumentation. The largest barrier to achieve improved process or environment control often lies at the interface between the system and the environment to be monitored, i.e. the sensor. Without sensors, significant advances in control and instrumentation will not be possible.

The release of various chemical pollutants from industries, automobiles and homes into atmosphere has been causing the global environment issues such as acid rain, the global green house effect and ozone depletion. Hazardous and toxic gases from automobile and industrial exhausts are the polluting the environment. In order to measure and control these gases, one should know the amount and nature of gases present in the environment. Thus the need to monitor and control these gases has led to research and development of wide variety of sensors using different materials and technologies. To increase the efficiency and capability of the instruments in measurement and detection technology, to reduce the cost, shape, size, weight etc, it is necessary to introduce the sensors units at the input parts of domestic, industrial and scientific instruments.

1.1 Health hazards

Different gases cause various health hazards. Exposure to air pollution is associated with numerous effects on human health, including pulmonary, cardiac, vascular, and neurological impairments. The health effects vary greatly from person to person. On the basis of nature and kind of gases few health hazardous gases are discussed below.

(i) Ammonia (NH$_3$)

Ammonia is utilized extensively in many chemical industries, fertilizer plants, refrigeration systems, etc. A leak in the system can result the health hazards. Ammonia is harmful and toxic [1-5] in nature, the exposure of ammonia causes chronic lung disease, irritating and even burning the respiratory track, etc. Therefore all industries working on and for ammonia should have an alarm system detecting and warning for dangerous ammonia concentrations.
(ii) Carbon dioxide (CO$_2$)

The atmospheric concentration of CO$_2$ at present is about 356 ppm. The greenhouse contribution of CO$_2$ is 50%. If the present emission trend of CO$_2$ continues, a global warming of 3.5 to 4.5 °C is likely to occur. It has been estimated that, the sea level may rise 0.5 to 1.5 m in the next 50 to 100 years. An increase in average global temperature is likely to increase the incidence of infectious diseases.

(iii) Chlorine (Cl$_2$)

Chlorine is yellowish-green [6] gas having pungent smell, which is explosively utilized in industrial applications such as to bleach paper pulp, to disinfect sewage and drinking water, etc. As it has wide range of applications, its toxicity [7-9] can affect the health of humans in contact. Chlorine has excellent bleaching ability, but once it is discharged in aquatic systems, it interacts with other industrial effluents to produce a host of chlorinated organic such as dioxin. Dioxin persists in the environment for prolonged periods and has tendency to bioaccumulate in the food chains, which elicits toxic effects to humans, such as skin infection, psychological disorders and even liver damage.

(iv) Hydrogen (H$_2$)

Hydrogen is an energy carrier has widespread application such as fuels. It is colorless and odourless gas. Its leakage cannot be noticed easily. This gas is potentially hazardous because of explosion possibility.

(v) Ethanol (C$_2$H$_5$OH)

Pure ethanol is called as an absolute alcohol. Ethanol is used for beverages, scientific and industrial purposes. Ethanol can be made by fermentation of sugars and it is the alcohol of all alcoholic beverages. The synthesis of ethanol in the form of wine by the fermentation of sugars of fruit juices was probably our first accomplishment in the field of organic synthesis. Sugars from a wide variety of sources can be used in the preparation of alcoholic beverages. Often, these sugars are from grains, so, ethanol is referred as "grain alcohol".
(vi) Liquified petroleum gas (LPG)

Liquified natural gas (LNG) and liquified petroleum gas (LPG) are highly inflammable gases. They are explosively utilized in industrial and domestic fields as fuels. They are referred as town or cooking gases. Cooking gas consists chiefly of butane (55-vol %) [10], a colorless and odourless gas. It is usually mixed with compounds of sulfur (methyl mercaptan and ethyl mercaptan) having foul smell, so that its leakage can be noticed easily. These gases are potentially hazardous because explosion accidents might be caused when they leak out by mistake. It has been reported that, at the concentration up to noticeable leakage, it is very much more than the lower explosive limit (LEL) of the gas in air. So, there is a great demand and emerged challenges for monitoring them for the purpose of control and safety applications in domestic and industrial fields [11].

(vii) Carbon monoxide (CO)

Heamoglobin (Hb) has about 210 times more affinity for CO than for oxygen, hence less oxygen up by heamoglobin, if CO is inhaled during breathing. When CO is inhaled during breathing, it combines with heamoglobin in the blood stream to form more stable complex known as carboxy-heamoglobin (CO-Hb).

\[
\text{HbO}_2 + \text{CO} \rightarrow \text{CO - Hb} + \text{O}_2 \quad \text{------- (1)}
\]

This reduces the ability of Hb to carry the oxygen to the body tissues. Prolonged exposure to low levels of CO causes the reduction of ability of a person to see small objects at a distance, the reduction in night vision, hearing ability, mental performance and time discrimination ability.

(viii) Hydrogen sulfide (H\(_2\)S)

H\(_2\)S is one of the major pollutants, hazardous and toxic in nature, which is also released from industries and laboratories [12]. H\(_2\)S is oxidized to oxides of sulfur either by atomic oxygen (O), molecular oxygen (O\(_2\)) or by ozone (O\(_3\)) as

\[
\text{H}_2\text{S} + \text{O} \rightarrow \text{HS} + \text{OH} \quad \text{------- (2)}
\]

Higher concentrations of gases containing sulfur lead to bronchitis and lung cancer. These gases containing sulfur destroy plant cells and interfere with chlorophyll synthesis.
Leaf blotching and reduction in crop yield occur even at the concentration less than 1 ppm. The exposure of gases containing sulfur can also affect the non living things viz stone leprosy, increase the rate of corrosion of metals and retardation of drying of paints, etc [13-16].

1.2 Sensors

The sensor is a device that receives a signal or stimulus and responds with an electrical, electronic or optical signal. According to the International Electrochemical Committee (IEC), Sensor is the primary part of a measuring chain which converts the input variable into a signal for measurement [17]. According to Gopel et al [18], a sensor is an element with housing and electrical connections included and which incorporates some kind of signal processing (analog or digital). The sensor is the first element to input the information to be measured. The block diagram of the sensor system is shown in Fig. 1.1.

![Block diagram of a typical sensor system.](image)

**Fig. 1.1:** Block diagram of a typical sensor system.

1.3 Need of sensors

Nowadays, there is a general opinion in both scientific and engineering community that there is an urgent need for the development of cheap, reliable sensors for the control and measuring systems, for the automation of services and for the industrial and scientific apparatus. The sensors are required basically for measurement of physical quantities and for use of controlling some systems. Presently the atmospheric pollution has become a global issue. Gases from auto and industrial exhaust are polluting the environment. The reducing gases such as CO, H₂, C₂H₅OH, oxygenic gases such as: CO₂, NOₓ, O₂,
CH$_3$OH, CH$_4$, odourous gases such as: NH$_3$, H$_2$S, explosive gases such as: C$_2$H$_2$, C$_2$H$_4$, C$_3$H$_6$, C$_3$H$_8$, LPG and, toxic gases such: CO, H$_2$S, Cl$_2$, NO$_2$ etc. have to be controlled for the healthy survival of the living beings. Thus, there is an increasing concern about minimization of the emission of autointoxication and also to reduce emission of such unburnt hydrocarbons from automobile and industrial exhausts. In order to detect, measure and control these gases, one should know the amount and types of gases present in the ambient. Thus the need to monitor and control these gases has led to the research and development of a variety of sensors using different materials and technologies.

1.4 Classification of sensors

(I) On the basis of external power requirement

On the basis of external power requirement, the sensors are classified passive sensors and active sensors.

(a) Passive sensors

The sensor which requires external power to generate an output signal in response with input signal is called as a passive sensor. Passive sensor is also referred as parametric sensor, because its own properties change in response to an input signal and change in the properties can be converted into output e.g. thick and thin film sensors.

(b) Active sensors

They directly generate an output signal without any additional energy, in response to the external input, e.g. thermocouple or a pH-meter.

(II) On the basis of applications

On the basis of applications, sensors are classified as physical sensors and chemical sensors as represented in Table 1.1.

(i) Physical sensors

Physical sensors employ physical effect such as piezoelectric, ionization, magnetostrictional, thermoelectric, photoelectric, magnetoelectric, etc.

Physical sensors further classified as:
(a) Optical sensor

The sensor, which gives response to light radiation, is called as optical sensor. The conductivity of the field changes when the radiation of definite frequency or wavelength falls on it. Photoconductivity and photovoltaic effects are the phenomena used for optical sensor. e.g. CdS.

Table 1.1: Sensor classes and their detecting properties.

<table>
<thead>
<tr>
<th>Class</th>
<th>Detecting properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) Physical Sensor</td>
<td></td>
</tr>
<tr>
<td>(a) Optical</td>
<td>light intensity, wavelength, polarization, etc.</td>
</tr>
<tr>
<td>(b) Mechanical</td>
<td>length, acceleration, flow, force, pressure, etc.</td>
</tr>
<tr>
<td>(c) Magnetic</td>
<td>magnetic flux density, magnetic moment, etc.</td>
</tr>
<tr>
<td>(d) Thermal</td>
<td>temperature, specific heat, heat flow, etc.</td>
</tr>
<tr>
<td>(e) Electrical</td>
<td>charge, current, voltage, resistance, inductance, etc.</td>
</tr>
<tr>
<td>(ii) Chemical Sensors</td>
<td></td>
</tr>
<tr>
<td>(a) Gas</td>
<td>organic and inorganic gases.</td>
</tr>
<tr>
<td>(b) Humidity</td>
<td>water molecule</td>
</tr>
</tbody>
</table>

(b) Mechanical sensor

The change in displacement, velocity, pressure, acceleration and sound intensity are the input signals for mechanical sensors. These types of sensors are particularly used for measuring fluid level, velocity, pressure, acceleration etc. These are fluid level sensors, LVDT, pressure sensor, potentiometer etc.

(c) Magnetic sensor

The sensor which gives response to the magnetic field is called as magnetic sensor. The conductivity of the sensor changes when magnetic field strength and direction of magnetic field change. In Hall effect, mobility is used for the magnetic sensor. In magneto-resistive effect, the resistance of the material changes when subjected to the
changing magnetic field. The sensor is used to find the magnetic field strength as well as its direction. Ni based magnetic sensors are well known [19].

(d) **Thermal sensor**

The sensor which gives response to the change in temperature of the environment and the required system is called as temperature sensor e.g. thermocouple, pyrometer, thermisters, IR detectors etc.

(e) **Electrical sensor**

The sensor which gives response to change in charge or current or voltage or resistance or inductance is known as electrical sensor.

(ii) **Chemical sensor**

The sensor which gives response to chemical vapors is called as chemical sensor. Among of all, gas sensor is most important, because various industries and automobiles exhausting toxic and hazardous gases.

(III) **Classification of solid-state gas sensor**

Now a day, solid-state gas sensor is being developed. The solid-state gas sensors are classified in three categories.

i) Solid-electrolyte sensor,

ii) Catalytic combustion gas sensor,

iii) Metal oxide semiconductor (MOS) gas sensor

The solid-state gas sensors are being developed because of their small size, low cost and reliability.

(i) **Solid electrolyte sensor**

These sensors work on the principal of electrochemistry or ionic conductivity of the solid electrolyte materials in the presence of gas. Solid electrolytes are materials that allow the conduction of ions but not the conduction of electrons. The essential function of the solid electrolyte is to separate two regions of distinct activity of the species to be monitored and to allow high mobility of ions of that species between two regions.
(ii) Catalytic combustion gas sensor

These sensors contain sensor material with catalyst. When combustible gas is exposed to the sensor, it reacts with catalyst and burns fuel gas, which increases the resistance. The increase in resistance is then co-related with concentration of the combustible fuel gas.

(iii) Metal oxide semiconductor (MOS) gas sensor

These sensors are based on the semiconducting oxides. These sensors are based on the principle of adsorption-desorption phenomenon. The electrical properties of the surface are changed due to the adsorption of foreign species on the surface of the semi-conducting material. The solid-state gas sensors are fabricated in the form of bulk (pellet), thin films or thick films.

1.5 Sensor technologies

A gas sensor technology has already grown to be indispensable for various aspects in our life. Yet further advancements of the technology are strongly needed in order to improve sustainability of our society and quality of life. Gas sensor technology is interdisciplinary indeed, so that collaborations among people working in different disciplines, ranging from the materials scientists to market developers, would be necessary to open new frontiers. Researchers should be well acquainted with the needs having emerged or newly emerging in the industry and society.

The advancement of science and technology has given an opportunity to use different technologies for fabrication of sensors for getting better performance. Mainly three technologies are being widely used in fabrication of sensors viz., pellet, thin film and thick film technology [20-24].

1.5.1 Thin film sensor

Thin films as the name suggests are thin in nature. Generally thickness of thin films is less than 1 µm. Since the thickness of the film is less than the average mean free path, the resistance of thin film is quite higher than that of thick film. Thin film is defined as the
film having thickness less than the average mean free path of an electron, in the medium [25].

**Thin films**

Fig. 1.2 shows the gas interaction in the compact and porous layers. Thin film semiconducting oxide gas sensors offer various potential advantages via integration with IC-based technology. Thin film sensor mainly consists of sensor layer, electrode, heater and substrate. Usually, the heater is separated from the sensing layer and electrodes by an electrical insulating layer. The gas sensing performance can take place at different sites of the sensing layer depending on its morphology. The morphology of the sensing layer can be simply divided into compact and porous layers. In compact layers, gases cannot penetrate into the layer and the gas sensing reaction is confined to the surface of the sensing layer.

![Schematic view of gas sensing reaction](image)

**Fig. 1.2:** Schematic view of gas sensing reaction (a) compact and (b) porous layer.

This compact layer is usually obtained with one of a number of thin film deposition techniques. In porous layer, gases can access all of the volume of the sensing layer, and the gas sensing reaction can therefore take place at the surface of individual grains, at grain-grain boundaries and interface between grain and electrodes.

For compact layer, the sensing layer can be completely or partly depleted depending on the relation between film thicknesses ($Z_g$) is smaller than the depletion layer thickness ($Z_0$); the compact sensing layer will be completely depleted. When the film thickness is larger than the depleted layer ($Z_g>Z_0$), the sensing layer will be partly depleted and two resistance occur in parallel. One is influenced by surface reaction with the higher resistance value (layer $Z_g-Z_0$) and the other one has the bulk resistance value (layer $Z_0$). Thus, the partly depleted layer can be treated as a conductive layer with a gas reaction
dependent thickness. For the completed depleted layer, the exposure to reducing gases can act as a switch to the partly depleted layer. It is also possible that exposure to oxidizing gases acts a switch from partly to completely depleted layers.

For porous layers, the situation is more complicated because of the presence of the necks between grains. The possible switching role of reducing and oxidizing gases in compact layers is valid for porous layers since the depletion layer of the neck contact is also influenced by the atmosphere.

1.5.2 Thick film sensor

To prepare thick films, the thixotropic paste of functional material is formulated and printed onto an insulating substrate in a definite pattern [26, 27]. The thick film technique involves screen-printing followed by firing process. For thick film technology, paste of the functional material is prepared with the use of some temporary organic binder to achieve adhesion of a film to the substrate. The paste is screen-printed on an insulating substrate (e.g. glass), which can stand at higher temperatures, using screen-printing to get definite pattern. The printed film is dried under an IR lamp to remove the temporary organic binder and then it is fired at a higher temperature with a definite time-temperature profile to obtain stability and better adhesion of the film to the substrate [28].

Thick films

An important and growing application of sensors fabricated using thick film and related techniques is to the detection and monitoring of gases. The materials most widely preferred for sensing oxygen, flammable gas and toxic gases are semiconducting oxides which present an opportunity for reactions that involve molecular chemistry that is confined to the surface layer of atoms but the electrical consequences of which are manifested through a considerable volume of the solid. Surface reactions are followed by a change in resistance only to depth of the order of micron but the semiconducting oxide in the thick film form provides a high surface to bulk form (e.g. in a porous thick film) and so exhibits enormous conductance sensitivity to atmospheric composition. In either case semiconductor gas sensors function as gas sensitive resistors and thus represent a simple, low cost means of atmospheric monitoring.
The effectiveness of gas sensors prepared from thick film of semiconducting depends on several factors including the nature of the reaction taking place at the oxide surface, the temperature, the catalytic properties of the surface, the electronic properties of the bulk oxide and the microstructure.

The effectiveness of gas sensors prepared from thick films of semiconducting oxides depends on several factors including the nature of the reaction taking place at the oxide surface, the temperature, the catalytic properties of the surface, the electronic properties of the bulk oxide and the microstructure.

It is possible to prepare semiconducting oxides in the form of thin films or pellets for gas sensing applications. However, thick film technology offers following advantages.

- a route to small scale at lower cost than that of the thin film equivalently,
- a good control over the thickness and microstructure is possible,
- the expected life time is more, and
- they shows the properties of the bulk material.

1.5.3 Pellet

The pellet technique requires die and hydraulic press. Functional material and binders (e.g. Polyvinyl Alcohol (PVA), Sodium Carboxyl Methyl Cellulose) are thoroughly mixed together in a medium, which depends on solubility of binder. The mixture is dried to obtain the fine powder. The powder in kept in a die and pressed under high pressure. The thickness of the pellets can vary as per the requirement and diameter depends on the die. Thickness of the pellets is in the range of few millimeters. The pellets are fired to evaporate organic binder and to give more strength.

1.6 Gas sensing mechanism of metal oxide semiconductor (MOS) gas sensor

The gas sensing mechanism involves number of steps described as below: The oxygen gas molecule adsorb on the surface of the thick film (Fig. 1.3). The surface of the sensor should be clear and large so that, the gas molecules can easily adsorb on it. The exposed target gas molecules are oxidized by capturing the atomic or molecular oxygen, which holds the electron on the surface, trapping behind the electrons constituting the increase in surface current. The surface is the region where the periodicity of the crystal
is interrupt. Because of this, localized energy levels are form in forbidden gap. Such energy levels can either capture electrons or give up electrons. In case of semiconductor, like SnO$_2$ and Cr$_2$O$_3$, which are ionic, their surface metal ions capture an extra electron (act as an acceptor) and the surface oxygen ions give up electron (act as donar). The donar levels completely ionized if they are near the conduction band; however, if the donar are little below the conduction band, the donar levels are not completely ionized at room temperature. Donar levels get ionized above room temperature.

The test gas present in ambient react with oxygen ions and gives a counter reaction. The trapped electrons are liberated to the conduction band, thereby increasing the conductance of the semiconductor. The simplified reaction is

$$ G + O \rightarrow GO + e^- $$

Fig. 1.3: Model indicating the formation of potential barrier on oxygen adsorption: (a) Physical model and (b) Band model (Courtsey: S. Roy Morrison, Sens. Actuators B 12 (1987) 425).

Fig. 1.3 shows a schematic diagram of a few grains of the sensor material in contact with each other and shows a depletion region and band model. The depletion region, being depleted of electrons will be less conducting than the bulk. From band model, it is seen that carriers must overcome a barrier. Extraction of electrons by oxygen leads to significant increase in barrier height and when reducing gas reacts with oxygen ions,
electrons are injected back to conduction band and barrier height decreases, hence, electrons can overcome the potential barrier and conduction increases.

1.7 Sensing performance measurement

(i) Gas response

Gas response/sensitivity ($S$) is defined as the ratio of the change in conductance of the sensor on exposure to the target gas/simulant to the original conductance in air and is given by following relation:

$$ S = \frac{I_g - I_a}{I_a} \quad \text{-------- (7)} $$

where, $I_a$ is conductance of sensor on air and $I_g$ is conductance of sensor in a target gas/simulant.

(ii) Selectivity

Selectivity is defined as the ability of a sensor to respond to certain gas/simulant in the presence of other gases/simulants.

(iii) Response time

The time taken for the sensor to attain 90% of the maximum increase in conductance on exposure of the target gas/simulant is known as response time.

(iv) Recovery time

The time taken by the sensor to get back 90% of the maximum conductance when the flow of gas/simulant is switched off is known as recovery time.

1.8 Preparation and measurement of gases

(I) Preparation of conventional gases

Table 1.2 shows the treatment required to prepare the gases.
Table 1.2: Preparation of gases.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Treatment</th>
<th>Byproducts</th>
<th>Prepared gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>Heat liquor ammonia</td>
<td>---</td>
<td>Ammonia vapor</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>CaCO₃ + HCl</td>
<td>CaCl₂</td>
<td>CO₂</td>
</tr>
<tr>
<td>Ethanol</td>
<td>Heat ethyl alcohol</td>
<td>---</td>
<td>Ethanol vapor</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>Zn (dust) + 2HCl (dil.)</td>
<td>ZnCl₂</td>
<td>H₂</td>
</tr>
<tr>
<td>Chlorine</td>
<td>KMnO₄ + 2HCl (dil.)</td>
<td>MnO₂, KCl</td>
<td>Cl₂</td>
</tr>
<tr>
<td>LPG</td>
<td>---</td>
<td>---</td>
<td>LPG</td>
</tr>
</tbody>
</table>

1.9 Adsorption studies on semiconducting oxide

Adsorption is a process in which atoms or molecule of one material gets attached on the surface of another. It is fundamental significance in heterogeneous catalysis and gas separation. Adsorption of gases and vapor is physical phenomenon in which adsorb molecules are held to the surface of absorbent by Vander-walls force. There are two types of adsorption: physisorption and chemisorptions, on the basis of bond formation.

(i) Physisorption

The adsorption occurs at the surface of solids is due to Vander-walls forces. When these forces are exerted between the atoms or molecules, there is physical attraction without chemical alteration of the molecules. This type of adsorption is called as physical adsorption or physisorption.

(ii) Chemisorptions

The adsorption occurs due to the molecular interaction with these free valencies, this may regard as a chemical reaction because there is rearrangement, sometimes drastic, if electrons within the molecule. This type of adsorption is called as chemical adsorption or chemisorption. The Fig. 1.4 shows that there is an imbalance of forces at the surface and that surface atom suffer a net force acting inwards.
This gives rise to phenomenon of surface energy, which is related to surface tension in liquid. Semiconducting oxides are employed to detect the minor concentration of potential hazardous gases. The central surface reaction controlling most gas responses of semiconducting oxides operating in air at temperature in the range 100 - 450 °C involves the changes in the concentration of surface oxygen species [29, 30] such as:

\[
O_2^{\text{(gas)}} \rightleftharpoons O_2^{\text{(ad)}} \rightleftharpoons O_2^{-}\text{(ad)} \rightleftharpoons 2O^-\text{(ad)} \rightleftharpoons O_2^2^-\text{(ad)} \quad ------ (8)
\]

The formation of such ions, by oxygen adsorption at the glass-solid interface abstracts electron from the bulk of the solid, the oxygen can thus be thought of as a trap for electrons from the bulk.

(iii) Reducing gases

In case of p-type semiconducting oxide, absorbed oxygen acts a surface acceptor state, abstracting electrons from the valence band and hence giving rise to an increase in the charge-carrier (hole) concentration at the interface. The crystal structure of p-type semiconductor such as Cr₂O₃ contains a small excess of electron and exposure of the sensor to atmospheric air, oxygen is chemisorbed on the surface with each oxygen molecule consuming two electrons as given by equations:

\[
O_2 + 2e^- \rightarrow 2O^-\text{ads} \quad ------ (9)
\]

\[
\text{O}_2 \rightarrow 2\text{O} \quad \text{(Dissociation of oxygen molecules)} \quad ------ (10)
\]

\[
\text{O} + e^- \rightarrow \text{O}^- \quad ------ (11)
\]
This reaction of the surface with oxygen generates a depletion layer and a Schottky potential energy barrier at the semiconductor surface. This leads to a low electrical conductivity, which is measured as a high electrical resistance. On contact with the gas being sensed, the surface reaction in equation below occurs.

\[ G + O^{-}_{\text{ads}} \rightarrow GO_{\text{des}} + e^- \text{ (desorbed)} \]  

For example,  

\[ \text{CH}_4 + 4O^2- \rightarrow CO_2 + 2H_2O + 8e^- \]  

In this gas removes the chemisorbed oxygen and, in doing so, is oxidized. Thus the gas, which is oxidized, i.e. which acts as reducing agent can be sensed with sensor type.

(iv) Oxidizing gases

The resistance of some semiconducting oxides is also found to responds to the introduction of oxidizing gases, such as chlorine and nitrogen dioxide (NO$_2$), in air. These gases react with surface oxygen ions as:

\[ \text{NO}_2 + e^- \rightarrow \text{NO}_2^- \]  

and \[ \text{Cl}_2 + 2e^- \rightarrow 2\text{Cl}^- \]  

According to the discussions, materials can be classified as n-type or p-type according to whether they show a decrease or an increase of resistance when they are exposed to a reducing gas in an atmosphere of fixed oxygen partial pressure (air). On the basis of reaction, such as these, it would be expected that the responses would take place in the opposite sense to those with reducing gases and the consistent pattern of response type would be as shown in Table 1.3.

Table 1.3: Material-resistance profile.

<table>
<thead>
<tr>
<th>Material</th>
<th>Reducing gas</th>
<th>Oxidizing gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-type</td>
<td>Resistance decreases</td>
<td>Resistance increases</td>
</tr>
<tr>
<td>p-type</td>
<td>Resistance increases</td>
<td>Resistance decreases</td>
</tr>
</tbody>
</table>

Both p-type and n-type semiconductor have used in sensors. In n-type semiconductor, electrical resistance changes from high to low (electrical current changes from low to
high) in the presence of the gas being sent (for a p-type semiconductor, the change in resistance is the reverse). The resistance of semiconducting oxide may be modified as a result of gas reaction producing water molecules as:

\[ \text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O} + 2e^- \quad \text{(16)} \]

There may be contribution to the resistance response made by this reaction product as well as by release of electrons. In summary there are number of ways in which semiconducting oxide provide resistance responses to impurity gases into air ambient (in temperature range 100-450 °C).

### 1.10 Adsorption-desorption kinetics

Gas molecule arriving at the semiconducting oxide surface adsorb preferentially at some specific sites due to the thermodynamics driving force of lowering of free energy. A molecule can spend a long time on the surface and the residence time \( \tau \) depends on the adsorption energy \( \Delta H_{\text{ads}} \) as:

\[ \tau = \tau_0 \exp \left( \frac{\Delta H_{\text{ads}}}{RT} \right) \quad \text{(17)} \]

where \( \tau_0 \) is the surface atom vibration time, \( T \) is the temperature and \( R \) is the gas constant [31].

The surface concentration of the gas molecules (expressed as coverage) can be determined by the product of the flux of the incident gas atoms \( F \) and residence time \( \tau \),

\[ \theta = F \tau \quad \text{(molecules/cm}^2) \quad \text{(18)} \]

\[ \theta = (3.5 \times 10^{22} \text{P(torr)}/\sqrt{M(\text{g/mole})T} \tau_0 \exp (\Delta H_{\text{ads}}/RT)) \quad \text{(19)} \]

where \( F = (3.5 \times 10^{22} \text{P(torr)}/\sqrt{M(\text{g/mole})T} \), \( P \) is the pressure, and \( M \) is the molecular weight of the gas. Thus, \( \theta \) is directly proportional to the pressure, varies exponentially with the adsorption energy and has a complex dependence on \( T \).

At constant temperature, \( \theta \) should be directly proportional to \( P \). However, this relationship is not always valid and hence it is much useful to express coverage as a function of gas pressure. This relation at constant temperature is known as the adsorption isotherm.

The most commonly used adsorption isotherm is the Langmuir type isotherm, where it is assumed that the adsorption is terminated upon the formation of a monolayer and that
adsorption to one site is dependent on the occupancy condition of the adjacent site. The degree of coverage ($\theta$) is estimated from the Langmuir equation as:

$$\theta = \frac{bP}{1+bP} \quad \text{(20)}$$

where, $b$ is a constant and $P$ is the gas pressure at constant temperature. There are significant studies regarding the adsorption of gases on metals as well as oxide surface, where the Langmuir adsorption isotherm can be fitted. For example, the adsorption studies of sulphated Ru (001) surface indicated Langmuir type of kinetics. The adsorption kinetics of H$_2$ on a clean partially sulphated Ru (001) surface [32] is described by:

$$\frac{d\theta_H}{d\varepsilon} = S_0[(1-\theta_s)-\theta_H]^2 \quad \text{(21)}$$

where, $\varepsilon$ is exposure of gas, $\theta_s$ is fraction covered by sulfur, $\theta_H$ is fraction of surface covered by H$_2$ and $\theta_s$ is the sticking coefficient. From this expression, the sticking coefficient is found to be 0.1.

However, the Langmuir isotherm has several limitations due to the unrealistic assumptions and several other isotherms such as Temkin, Frumkin, Freundlich. Dubinin-Raduschkevich are modeled which fit well with most of the studies.

1.11 Sensing material: Zinc oxide (ZnO)

(i) Crystal and surface structure of ZnO

The structure can be visualized as Zn$^{2+}$ ions in half of the tetrahedral holes of a hexagonal close-packed oxide lattice; the structure with the longitudinal axis (c-axis) is shown in Fig. 1.5(a-c). Zinc oxide is an important semiconductor which has been studied for many decades. It has a wide band-gap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature [33]. Polycrystalline ZnO has attracted intensive research effort for its unique properties and versatile applications in ultraviolet (UV) light emitters, short-wavelength nano-lasers, and piezoelectric devices, ultrasensitive, spin electronics, field-effect transistors, and field emitters. ZnO, like ZnS, has the wurtzite structure type, which is the thermodynamically stable phase under ambient conditions. The ZnO wurtzite structure has a hexagonal closed-packed unit cell, with dimensions $a = 3.25$ Å and $c = 5.12$ Å [34].
Fig. 1.5: ZnO crystal (a, b) wurtzite structure and (c) plane geometry.

In this crystal structure, both zinc and oxygen ions are coordinated with four ions of the opposite charge with strong ionic binding. Due to the size differential of the ions, the ions fill about 44% of the total volume in a ZnO crystal, and leaving a relatively large free volume.

Some typical properties of ZnO are listed below in Table 1.4.
(ii) Properties of ZnO

Table 1.4: Properties of ZnO.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice parameters at 300 K:</td>
<td></td>
</tr>
<tr>
<td>$a_0$</td>
<td>3.2498 Å</td>
</tr>
<tr>
<td>$c_0$</td>
<td>5.2069 Å</td>
</tr>
<tr>
<td>$a_0/c_0$</td>
<td>1.602 (1.633 for ideal hexagonal structure)</td>
</tr>
<tr>
<td>Density</td>
<td>5.606 g/cm$^3$</td>
</tr>
<tr>
<td>Stable phase at 300 K</td>
<td>wurtzite</td>
</tr>
<tr>
<td>Melting point</td>
<td>1975°C</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>0.6, 1-1.2</td>
</tr>
<tr>
<td>Linear expansion coefficient ($^\circ$C)</td>
<td>$a_0=6.5 \times 10^{-6}$, $c_0=3.0 \times 10^{-6}$</td>
</tr>
<tr>
<td>Static dielectric constant</td>
<td>8.656</td>
</tr>
<tr>
<td>Refractive index</td>
<td>2.008, 2.029</td>
</tr>
<tr>
<td>Energy gap</td>
<td>3.4 eV (direct)</td>
</tr>
<tr>
<td>Energy gap at room temp.</td>
<td>3.37 eV</td>
</tr>
<tr>
<td>Cohesive energy</td>
<td>1.89 eV</td>
</tr>
<tr>
<td>Heat of fusion</td>
<td>4,470 cal/mol</td>
</tr>
<tr>
<td>Intrinsic carrier concentration</td>
<td>$&lt;10^{6}$ /cm$^3$</td>
</tr>
<tr>
<td>Exciton binding energy</td>
<td>60 meV</td>
</tr>
<tr>
<td>Electron effective mass</td>
<td>0.24</td>
</tr>
<tr>
<td>Hole effective mass</td>
<td>0.59</td>
</tr>
<tr>
<td>Electron Hall mobility at 300 K</td>
<td>200 cm$^2$/V s</td>
</tr>
<tr>
<td>for low $n$-type conductivity</td>
<td></td>
</tr>
<tr>
<td>Hole Hall mobility at 300 K</td>
<td>5-50 cm$^2$/V s</td>
</tr>
<tr>
<td>for low $n$-type conductivity</td>
<td></td>
</tr>
</tbody>
</table>

ZnO is a typical n-type semiconductor, in which the density of holes in the valence band is exceeded by the density of electrons in the conduction band; the major charge
carrier in ZnO semiconductors is electrons in the conduction band. The formation of oxygen vacancies leads to a higher electron density; donor bands from vacancies in the band gap lead to a substantial increase in the conductivity of the oxide.

1.12 Choice of materials for solid-state gas sensors

(I) Sensing material choice through their surface properties

It is known that operating characteristics of solid-state gas sensors, especially sensitivity, are controlled by three independent factors such as receptor (recognition) function, transducer function and peculiarities of sensor construction. Receptor function provides the ability of the oxide surface to interact with the target gas, and transducer function provides the ability to convert the signal caused by chemical interaction of the oxide surface into electrical signal [35]. Surface of metal oxides is responsible for receptor function of solid-state gas sensors [36-43], and therefore this section will be devoted to brief overview of some surface properties of metal oxides important for gas sensor operation.

(i) Density of surface states

The density of native surface states is metal oxide surface parameter, which has special importance for solid-state gas sensors. If we want to achieve effective operation of solid-state gas sensors, the concentration of those states should be minimized. Only in this case the surface Fermi level will not be pinned. Indicated surface’s property creates a condition for modulation of surface potential of semiconductor at the change of surrounding atmosphere, because the charge of native. The same correlation with concentration of native surface states was observed for Schottky barrier heights at the metal–semiconductor interface [44, 45].

(ii) Electronic structure of gas-sensing metal oxides

Metal oxides exhibit a very wide range of electro-physical properties [45-48]. Their electrical behavior ranges from the best insulators (e.g., Al₂O₃ and MgO) through wide-band gap and narrow-band gap semiconductors (TiO₂, SnO₂ and Ti₂O₃, respectively) to metals (V₂O₃, WO₃, and ReO₃), and superconductors (including reduced SrTiO₃). The
range of electronic structures of oxides is so wide that metal oxides were divided into two following categories:

- Transition-metal oxides (Fe$_2$O$_3$, NiO, Cr$_2$O$_3$, etc.) and
- Non-transition-metal oxides, which include
  - pre-transition-metal oxides (Al$_2$O$_3$, etc.) and
  - post transition-metal oxides (ZnO, SnO$_2$, etc.).

Transition-metal oxides with $d^0$ and $d^{10}$ electronic configurations find their real gas sensor application. Pre-transition-metal oxides (MgO, etc.) are expected to be quite inert, since they can neither be reduced nor oxidized easily due to this they are not promising material for resistive gas sensors. Post-transition-metal oxides ZnO, SnO$_2$, and $d^0$ transition-metal oxides may be reduced, but not oxidized. The post-transition oxides ZnO, In$_2$O$_3$, SnO$_2$, as well as majority of transition-metal oxides are active in “redox” reactions since the electron configuration of the solid may be altered. However, the reaction with oxidizing species such as O$_2$ is expected only with samples that have been bulk reduced or where the surfaces have been made oxygen deficient [49]. At that the reduction of post-transition oxides as a rule leads to the formation of free carriers, which greatly increase the metal oxide conductivity, a fact that is crucial for sensor applications.

(iii) Adsorption/desorption parameters

In a lot of research it was shown that for effective operation of chemisorption sensor the gas-sensing materials should have specific combination of adsorption/desorption parameters for oxygen and detecting gases [50-54]. It is known that the smaller is the activation energy of chemisorption and the higher is the activation energy of desorption, the bigger is gas-sensing effect of adsorption type sensors [55-57]. At the same time we have to take into account that excessively big activation energy of adsorbed species desorption might lead to a considerable increase of recovery time after the change of surrounding atmosphere, which is not acceptable for practical applications. Research presented in [58, 59] have shown that the processes of electron exchange between conduction band of metal oxides and adsorbed species for most studied materials such as SnO$_2$ and In$_2$O$_3$ already at $T > 100 \, ^{\circ}C$ are fast, and, therefore, they do not limit the kinetics of sensor response. According to [59, 60] just adsorption/desorption of oxygen
and water controls kinetics of conductivity response of gas sensors on the base of these materials. That is why for chemisorption type gas sensors a material with optimal activation energy of desorption for given work temperature is needed. Otherwise for recovery time reducing it would be necessary to increase operating temperature, which could lead to a sharp drop of sensor’s reliability and durability. In accordance with estimations, conducted for operating temperature 300°C, the activation energy of oxygen desorption, equaled ∼1.0 eV, is optimal.

The main method of the influencing on electronic parameters of adsorbed species is the change of composition of metal oxide films, i.e. the transition from simple binary metal oxides to multi-oxide films, and metal oxide surface doping by additional catalyst particles [61-65].

The analysis of gas detection reactions indicates that material for gas sensors should also be stable to surface poisoning, i.e. it should have acceptable desorption energy of catalytic reaction products. In other case these products could be accumulated at the surface of sensitive element, and gas sensor parameters could be worsened. “Sulfur poisoning” can be referred to such a type of poisoning [66-68]. Another source of poisoning is the one from other compounds, reducible to metals and elements under reaction conditions. These ones, such as As, Fe, P, etc., may alloy with the catalytically active metal and metal oxides, and reduce its effectiveness. In this context one should note that metal oxides are more resistant to certain poisoning (especially by halogens, As, Pb, and P) than noble metals.

**(iv) Catalytic activity**

In many gas sensors the conductivity response is determined by efficiency of catalytic reactions with detected gas participation, taking place at the surface of gas-sensing material. Catalytic reactions, involving surface oxygen, can change both the surface potential and concentration of point defects, which control electro-physical properties of poly- and nanocrystalline metal oxides [69-71].

Results of experiments directed on simultaneous control of sensor response and efficiency of detected gas conversion are confirmations of this statement [72]. Therefore it is considered that high catalytic reactivity of the surface and especially selectivity of
this reaction to detected gas are important advantages of sensor material. Because of that fact the control of catalytic activity of new material is often used as the main method for a preliminary estimation of its suitability for gas sensors elaboration, and for determination of sensor’s operation temperatures. As a rule, a position of maximum of sensor response on a temperature dependence $S (T_{\text{oper}})$ coincides with a temperature, corresponding to 50% conversion of detected gas [73]. At the same time we have to admit that a choice of metal oxide as additive for properties’ modification of other metal oxides is often connected with catalytic properties of those oxides [74, 75]. For example, the catalytic activity to selected gas is the most important parameter for application in membranes, used for sensor response’s selectivity improvement [63]. Room temperature (RT) gas sensors are other possible field for catalytic active metal oxide applications. In [76], it was found that RT work-function sensors on the base of catalytically active oxides.

**II) Sensing material choice through their electro-physical properties**

(i) Band gap

Pretty big band gap ($E_g$) and small activation energy of the centers, responsible for metal oxide conductivity, is an optimal combination of parameters for the materials designed for semiconductor solid-state gas sensors. Such correlation of activation energies is necessary in order to avoid sensor’s operation in the region of self-conductance. In this case the influence of surrounding temperature on sensor parameters is reduced. At that, as a rule, the higher operation temperature is, the bigger should be $E_g$. As it follows from experimental results, for solid-state gas sensors, operating at the temperatures exceeding $T > 300^\circ$C, the optimal band gap must be higher than 2.5eV. Analyzing data, presented in [77-79], Moreover, for example for room temperature work function sensor with small $E_g$ may be advantageous.

It is necessary to note that an opportunity to operate at higher temperature is an important advantage of solid-state gas sensors, because this fact allows reducing considerably the influence of air humidity on gas-sensing characteristics. It was established that, as a rule, the lower operating temperature is, the greater is the sensitivity of the sensor’s parameters to relative air humidity [61, 68].
(ii) Electroconductivity

No doubts that a variety of metal oxides make possible their use in all types of gas sensors. However it does not mean that oxides do not have any limitations in application. For example, for chemisorptional conductometric gas sensor the sensing material should be conducting one, i.e. the concentration of point defects in metal oxides should be pretty high. As experiment shows, the optimum lies in the range $10^{17}$ to $10^{20} \text{ cm}^{-3}$.

To high concentration of point defects, i.e. high electroconductivity reduces the influence of the surface on the concentration of charge carriers in the grains and electroconductivity of gas-sensing material. Because of this fact a metals usually are not being used for sensors design. However, results of the recent years have shown that metals also be used for this purpose [80-83]. Metals in this case should be in the form of super thin films with thickness less than 20-40 nm.

(iii) The type of conductivity

It is known that gas-sensing materials can have either n or p-type of conductivity. Semiconductors of p-type have inverse direction of conductivity’s change at interaction with the same gases, which is very important fact for their application. For materials with p-type the conductivity rises with oxygen pressure’s growth, whereas for n-type oxides it drops.

The analysis of main gas-sensing materials in respect to their conductivity type shows that all the most effectively working gas sensors of chemisorption type are designed on the base of metal oxides of n-type conductivity, such as ZnO, SnO$_2$, TiO$_2$, WO$_3$ and In$_2$O$_3$, providing the opportunity of oxygen’s chemosorption. Previous research has shown that, in general, all n-oxides are thermally stable and have possibility to work at lower oxygen partial pressure in comparison with well known p-type oxides, for example such as CuO [78]. It is known [61] that many p-type oxides are relatively unstable because of the tendency to exchange lattice oxygen easily with air. Besides, the interaction with reducing gas decreases the resistance of n-type oxides. This is the preferred direction for sensor’s resistance change during detection of reducing gases, contributing to simpler compatibility with peripheral measuring devices, and better reproducibility of output signal.
However, it does not mean that p-type materials are not applicable for sensor design. For example, the last research has shown that metal oxide Cr$_{2-x}$Ti$_x$O$_3$ ($x < 0.4$) (CTO), prospective for gas sensors design, is p-type material [84, 85]. Stable perovskites, for example ReCoO$_3$ (Re = La, Nd, etc.), promising for chemical sensor application, are p-type as well. CuO and ferrum oxides also have p-type conductivity. These oxides are effective additives to both tin and indium oxides for forming of nano-composite-based sensors with extremely high conductivity response to H$_2$S and series of other specific gases [86, 87]. Besides that materials with p-type conductivity are being successfully used in adsorption type gas sensors and gas sensors of electro-chemical type.

(vi) Oxygen diffusion in metal oxides

Depending on used type of solid-state gas sensor there are needed materials with extreme properties, i.e. with very high coefficients of bulk diffusion of oxygen and point defects, or with very low ones. The first type of materials is necessary for gas sensors, which work is based on the change of bulk properties of materials. In such sensors the change in bulk conductivity is a reflection of the equilibration between the oxygen activity in the oxide and oxygen content (oxygen partial pressure, $P_{O_2}$) in the surrounding atmosphere. Usually for their behavior explanation the following equation is used [88, 89]:

$$G = G_0 \exp (-E_a/kT) P_{O_2}^{\pm 1/n} \quad \text{(22)}$$

where $G_0$ is a constant and $E_a$ is the activation energy for conductivity. The value and sign of $1/n$ are determined by the type of dominant bulk point defect, involved in the equilibration process. The positive and negative signs of $1/n$ correspond to p-type and n-type conduction, correspondingly. The sensitivity of a semiconducting gas sensor is determined by the value of $1/n$. The higher the value of $1/n$ is, the greater is the sensitivity of the sensor. High diffusion coefficient in such devices provides a decreasing of both operation temperatures and response time.

At lower temperatures, the change in ambient gas concentration does not necessarily lead to equilibration of bulk properties of metal oxides and gas surrounding. Gas surrounding affects electrical properties through surface reactions. It means that for the attainment of good exploitation parameters of such sensors at their design it is necessary
to use materials, in which the constant of oxygen diffusion is minimized. For sensors of
chemosorption type the diffusion of oxygen in the bulk of crystallites is a source of
temporal parameters’ drift [90].

(v) **Other parameters important for gas-sensing materials**

Taking into account that at present a large variety of optical methods may be used in
gas sensors, including ellipsometry, luminescence, fluorescence, phosphorescence and
Raman spectroscopy, interferometry, surface plasmon and so on, one can conclude that
for gas sensor design on the base of these methods, parameters, such as refractive index,
absorbance and fluorescence properties of analyte molecules or a chemo-optical
transducing elements will have definite importance. For example in order to shift the
operating point of the surface, plasmon resonance gas sensors towards aqueous
environment, a thin high refractive index dielectric overlayer can be employed [91]. The
use of overlayer with higher refractive indexes allows for thinner overlayer and
potentially better sensor sensitivity.

(III) **The role of parameters’ stability in sensing material choice**

(i) **Thermodynamic stability**

Materials, destined for gas sensors, working at high temperature, have to possess high
thermo-dynamic stability. The better material’s thermo-dynamic stability is, the higher
are temperatures, at what chemical sensor with this material is able to work especially at
the presence in atmosphere of reducing gases. The thermal program reduction (TPR)
technique may be used to probe the stability of different metal oxides.

(ii) **Chemical activity**

Used gas-sensing materials should be characterized by high chemical stability. This
property provides lack of corrosion at interaction with gases and solutions, i.e. an
opportunity to work in corrosive mediums. Chemical activity of materials is an important
problem of gas sensor application in medical purposes as well. Sensing element, as well
as construction elements of sensor, often contacts patient blood; therefore, a prevention of
patient’s infection is an important task in widely spread application of gas sensors in
medicine for express control. From this point of view, metal oxides are the most preferable materials for gas sensors. As it is known, metal oxides have the minimum chemical activity in comparison with metals and covalent semiconductors.

(iii) Long-term stability of gas sensors

Gas sensor, in spite of the absence of encapsulation and high operation temperature, should provide long-term of exploitation, even at their being in corrosive mediums. It means that long-term stability of gas sensor’s output signal is one of the most important factors determining the practical use of such device. In general, it is required that, for example, any gas-sensing device should exhibit stable and reproducible signal for the period of at least 2–3 years (17,000–26,000 h). Taking into account this goal we have to introduce some sufficient corrections in evaluation of availability of sensing material for practical application in gas sensors.

As it was established [92, 93], the main reasons for long-term instability of solid-state gas sensors are the change of the metal oxide parameters, caused by the following processes:

i) microstructural and morphology changes of sensing element (the change of the crystallite size, number and distribution of grains and intergranular boundaries), a consequence of insufficient pre-aging by tempering;

ii) irreversible reactions with gas phase, i.e. metal oxide reduction during interaction, or reactions with active gases, such as SO₂, Cl₂, etc., with creating new phases;

iii) the reactions with the substrate.

(iv) Sensitivity to humidity of surrounding atmosphere

Gas sensors should work in atmosphere, containing water vapors. As we know, relative humidity of surrounding atmosphere could reach 100%. One can judge about the importance of water vapor influence on the sensor parameters, analyzing the results of research, given in [94, 95]. It was established that adsorption of water is a dominant factor in the surface characteristics forming, both with respect to adsorption of other species and to surface catalysis. In [96, 97] it was shown that there is a competitive
adsorption between \( \text{O}_2 \) and \( \text{H}_2\text{O} \) related surface species, and as a result, different sensing mechanism can be observed for gas detection in dry and wet atmospheres.

(IV) The role of structure and technology in gas-sensing material choice

The metal oxides with morphology and crystallographic structure optimal for achievement maximum gas-sensing effect are important factor for application of this material in solid-state gas sensors.

(i) Manufacturability of sensing materials

The good manufacturability of sensing material, i.e. an opportunity to produce under control and with high reproducibility powders, films, and ceramics with required structural properties, is an important criterion for selection of materials for gas sensor [98-104].

However it is necessary to note that at present there are not great technological problems of fabrication any binary oxides and standard semiconductors with specified electro-physical and structural properties. In the literature one can find a great deal of works, devoted to elaboration of both deposition and synthesis technologies of various binary oxides in the form of thin, thick, epitaxial films and ceramics using different methods [105-107]. Considering more complicated oxides and binary oxides, modified by different additives, polymers and organic semiconductors, one can conclude that here there are much more problems. For example, during polymer sputtering with use of electronic beam their chemical decomposition is possible, which naturally limits an opportunity of such materials’ application.

An important aspect of good manufacturability of sensing material is an opportunity of its adaptation in modern micro-electronic technology, for example during fabrication Simicromachined microhotplate array structures [98-108]. These devices can be adapted for a variety of applications by tuning both the composition of multiple types of active films and the temperature cycles programmed for individual elements within an array. As last research has shown, this problem becomes especially evident in the area of micro-miniaturization of high temperature gas sensors. It was established that difficulties here are connected with agglomeration of very fine metallic electrode structure on oxide
surface at high temperatures, and with film cracks due to thermal expansion mismatch between thin film and substrate.

Therefore while choosing a material for solid electrolyte gas sensor in microelectronic design; one should take into account this specificity. According to [109], for microelectronic design such solid electrolytes as \((\text{Al, Sc})_2((\text{Mo, W})\text{O}_3)_3\) were found to be the most appropriate. They have low thermal expansion coefficients and good chemical compatibility with silicon technology.

It can be conducted that the choice of a suitable material for gas sensors should be based on good gas response, low sensitivity to air humidity, high selectivity, low hysteresis, high stability of parameters over the time, all range of operation temperatures, thermal cycling, and on exposure to the various chemicals likely to be present in the environment [61, 104, 110]. Therefore desired efficiency of reactions, responsible for gas sensors’ sensitivity, it is necessary to achieve, taking into account the necessity of an attainment of maximum chemical, structural, and long-term stability of the device’s parameters.

(ii) Structural parameters of sensing materials

At present, considering sensing materials, we may select five types of material’s state, differing by its structural properties. These are amorphous state, glass-state, nanocrystalline state, polycrystalline state, and single crystal state. Every state has its own specific peculiarities, and materials in any of these states may be used for gas sensor’s design. However, in practice, nanocrystalline and polycrystalline materials have found the greatest application in gas sensors. Exactly nanocrystalline and polycrystalline materials have the most optimal combination of such properties as enough developed surface, cheap design technology, and necessary stability of both structural and electro-physical properties.

As it is known a specific surface area is sharply increased with decrease of grain size. A high specific surface area and comparability of grain size \((D)\) with the thickness of surface space charge layer \((L_S)\) can take great advantage for the development of high-sensitive gas sensors [63, 111, 112].
Fig. 1.6: Diagram showing the possible directions of gas sensor’s parameters optimization through various parameters.

Regarding amorphous and glassy materials, they are not stable enough, especially at higher temperatures. Single crystalline and epitaxial materials have maximum stability of characteristics. However their application is limited by high cost and difficulty of technological process of their deposition. At present, various kinds of one-dimensional nanomaterials such as Si, Ge, MgO, CaO, GaN, SiC, In₂O₃, TiO₂, Fe₂O₃, ZnO, SnO₂, etc., were synthesized as nanowires, nanotubes, nanospheres, nanorods, nanoparticles, and nanobelts [113-119]. However, there are much more research of quasi-one-dimension structure synthesis, than attempts of these materials application in gas sensors.

This review has also shown that there is no universal decision for simultaneous optimization of all sensors parameters. As a rule, an improvement of one parameter is accompanied by worsening of another one. Therefore, one should always seek a compromise between high sensitivity, high stability and high selectivity of designed devices (Fig. 1.6). Such a situation allows making a conclusion that development of sensors for more specific or focused applications, rather than design multi-purpose devices targeted at all markets. The last aspect is important because it can help decrease
research and development expenses, elevate the acceptance level of solid state sensors and promote further development for specific sensors for use in various environments.

(A) Nanomaterials and Nanotechnology

Nanomaterials are defined as materials having at least one of its dimensions smaller than 100 nm. “Nano” comes from the Greek word for small and it is used to indicate one-billionth of a meter. The scale of things ranging from nm to mm is demonstrated in Fig. 1.7. As shown, the diameter of human hair is around 60 µm to 120 µm, which is about ten thousand times larger than 1 nm. Nanostructures can be categorized into zero dimensional (0-D), one dimensional (1-D) and two dimensional (2-D). For 0-D structures, such as quantum dots, the x, y, z dimensions are all nanometer in length. Using a quantum dot as an active material, various types of nanoscale devices have been fabricated. These include, for example, single electron transistors [120], memory units [121], optical detectors [122], light emitting diodes [123,124] and gas sensors [125]. 1-D structures refer to those materials with two dimensions which are nanometer in length, and for materials with only one dimension within the nanometer range, are known as 2-D structures.

Wires, rods, belts and tubes constitute the important class of 1-D nanostructures; they can potentially play important roles both as interconnects and functional units in miniaturized electronic, optoelectronic, electrochemical devices. Moreover, they provide a good system for investigating the relationship between the dimensionality of the system and the electrical, thermal transport or mechanical properties [126]. Owing to the unique applications of 1-D nanostructures in mesoscopic physics and fabrication of nanoscale devices, intensive research has been focused in this area. 1-D nanostructures can be fabricated using a “top down” strategy through a number of advanced nanolithographic techniques [124], such as electron beam or focus ion beam (FIB) writing [127,128], proximal probe patterning [129,130], and X-ray or extreme −UV lithography [131,132].
Fig. 1.7: The scale of things.

However, arriving at practical routes of producing large quantities of 1-D nanostructures in the form of thin film and powder at a reasonably low cost, is still a great challenge to researchers. Therefore, unconventional methods based on ultrasonically synthesis have attracted much attention recently because it can be an alternative strategy for generating 1-D nanostructures (thin film and powder form) in terms of material diversity, cost, throughput and the potential for high volume production [133]. In the past few years, a variety of inorganic materials with 1-D nanostructures has been successfully synthesized and characterized using the “bottom up” approach.

Nanotechnology is the study of the manipulation of matter on the molecular scale and promises to have a significant impact in many different fields. In the electronics industry,
it provides the next step in the future miniaturisation of electronic devices and it will open up the possibility for the development of novel devices. In medicine, nanotechnology may lead to better drug delivery systems [134] and imaging techniques [135]. Nanotechnology is also expected to provide solutions to our increasing energy demands by leading to more efficient lighting [134], solar energy conversion [137], and energy storage [138]. One of the key aspects of nanotechnology is the study of the unique properties of nanomaterials. The nanoscale marks the point where materials are no longer in their bulk form; it is where quantum confinement and surface effects begin to be significant [139]. As a result, the properties of materials become size dependant and can differ dramatically from their bulk form. For instance, metals can become semiconductors [140] and the melting points of solids typically decrease with size [141].

The high surface to volume ratio of nanomaterials makes them particularly chemically active. For example, aluminium in bulk form is relatively inert, but on the nanoscale it becomes combustible [142]. This is the reason why many nanoparticles have been found to make very effective catalysts [143]. Nanomaterials can be used as very sensitive gas sensors because surface reactions dominate their electrical properties [144].

Many of the problems we face in nanotechnology today are related to harnessing these properties of nanomaterials and using them in workable devices. For instance, carbon nanotube transistors have been built that show promising performance [145]. However, there is no fast and easy way to control the placement of the carbon nanotubes to form dense complex circuits. In addition, the high surface to volume ratio of nanomaterials can also be a hindrance to the fabrication of devices as it increases the driving force behind diffusion, which can lead to unwanted coalescence between nanomaterials that are in close proximity.

**(B) The world of oxide nanomaterials**

Metal oxides play a very important role in many areas of chemistry, physics and materials science [146-151]. The metal elements are able to form a large diversity of oxide compounds [152]. These can adopt a vast number of structural geometries with an electronic structure that can exhibit metallic, semiconductor or insulator character. In technological applications, oxides are used in the fabrication of microelectronic circuits,
piezoelectric devices, fuel cells, coatings for the passivation of surfaces against corrosion, as catalysts and sensors. In the emerging field of nanotechnology, a goal is to make nanostructures or nanoarrays with special properties with respect to those of bulk or single particle species [153-157]. Oxide nanoparticles can exhibit unique physical and chemical properties due to their limited size, a high density of corner or edge surface sites and high surface to volume ratio.

(C) Problems with conventional (bulk) MOS

Conventional type semiconductor oxide gas sensors have major problems:

i) They have relatively less selectivity to a particular gas among the mixture of gases.

ii) Many gas sensors work at high temperature.

iii) They respond to the higher gas concentration above threshold limit value for polluting gases and above lower explosive limit (LEL) value in case of inflammable gases.

iv) They require and consume larger power.

v) The speed of reacting the target gas is relatively low.

vi) Slower recovery was obtained.

vii) Thermal stability was observed to be lower.

viii) Difficulty rose for long term exposure of target gas.

ix) Difficult in handling for its relatively larger size.

(D) Merits of nanocrystalline MOS over bulk oxide

i) Sensitivity is strongly increased in materials composed of grains with size close to the space charge region size nanomaterials.

ii) Large specific surface areas and a large fraction of atoms are available for chemical reaction.

iii) Large surface to volume ratio.

iv) Homogeneous particle size distribution.

v) Maintained their stability over long-term operation at high temperature.
vi) Dimensions comparable to the extension of surface charge region, superior stability owing to the high crystallinity.

(E) Need of nanocrystalline semiconductor metal oxide (MOS) gas sensors

Nowadays, there is great interest in using sensing devices to improve the environmental and safety control of toxic gases. There is also a great need for these kind of sensors for optimizing combustion reaction in the emerging transport industry, and domestic and industrial applications. An alternative to using metal oxides in the form of thin and thick films for gas sensing is to use them in their nanocrystalline form. With their crystalline structure and high surface to volume ratio, they are expected to be more stable and sensitive than their bulk counterparts [158]. In addition, the ability to control their dimensionality enables the possibility of tuning their gas sensing properties.

1.13 Nanomaterials based gas sensors

In order to improve commercial gas sensors, many approaches have attempted to modify the sensing properties of metal oxide semiconductor gas sensors in order to achieve higher sensitivity and selectivity. Enhancements of the sensing properties of MOS sensor materials can be achieved by the development of sensors with nanoscale sizes and structures, such as nanoparticles, nanowires, nanorods etc [159]. Quasi-one-dimensional MOS nanostructures, such as nanowires and nanorods, are expected to show higher sensitivity than bulk gas sensor for the following reasons: first, quasi-one-dimension nanostructures have a large surface-to-volume ratio, which means a significant fraction of the atoms in such systems are surface atoms that can participate in surface reactions, thus resulted into extremely sensitive to species adsorbed on their surfaces. Second, the radius of MOS nanowires is comparable to the Debye length $\lambda_D$ through a wide temperature range, which causes their electronic properties to be strongly influenced by processes at their surfaces. Finally, semiconducting oxide nanowires are often stoichiometrically well defined and have a greater level of crystallinity than multi-granular oxides [159]. As the dimension of the semiconductor material shrinks down to the nanometer scale, some of their physical properties undergo changes known as quantum size effects. For example, quantum confinement increases the band gap energy.
of quasi one-dimensional ZnO structures. Understanding the fundamental physical properties is crucial to the rational design of functional devices. Investigation of the properties of individual MOS nanostructures is essential for developing their potential as the building blocks for future nanoscale gas sensors.

Fig. 1.8 shows the relationship of Debye length and diameters of the sensors. When the size of the structure is larger than the Debye length $\lambda_D$ (\(\sim 30\) nm for ZnO), only atoms in the space-charge region participate in the surface reactions. Thus atoms in the core of ZnO crystals are not involved in the sensing response. Decreasing the size of a ZnO nanowire should thus result in a much larger portion of the ZnO wire which interacts with an analyte gas, which should increase the sensitivity of the sensor. When the size of ZnO nanowires is similar or smaller than the Debye length of ZnO, the sensitivity of the ZnO should increase dramatically. With reducing diameter, the surface/volume ratio increases; and when the size of the wires is close to or even smaller than the Debye length, the whole wire can be treated as a surface. For the sensors based on the In$_2$O$_3$ nanowires, sensitivities up to $10^5$-fold greater than those of comparable solid film devices have already been reported [160]. The signal-to-noise ratio obtained indicated that \(\sim 103\) molecules can be reliably detected on a 3 \(\mu\)m-long device. By shortening the conductive channel length to \(\sim 30\) nm, the adsorption of as few as 10 molecules could, in principle, be detected [160, 161].

![Fig. 1.8: Schematic description of size effect on the sensitivity of ZnO sensors.](image)
(I) Gas sensing mechanism of nanocrystalline MOS gas sensor

The gas response of any metal oxide semiconductor to a particular gas increases with decrease in the size of crystallites/grains [162] due to increase in surface to volume ratio and therefore the reactivity. Crystallite/grain sizes and microstructures of the sensor affect the gas sensing performance of the sensor. It was found that, if the grain size of the sensor material is sufficiently small, the area of active surface sites is larger, and the sensitivity and selectivity for a particular gas enhances largely. Several recent research reports have confirmed the benefits of “nano-scale materials” on sensor performance [163, 164]. The sensor showed good response by controlling its’ particle size below 10-60 nm. It was also observed that the response was decreased with increasing the particle size by sintering at high temperature [165, 166]. Proper control of grain size remains a key challenge for high sensing performance.

Nano-ZnO material would be expected to show much better gas sensing performance [167, 168] as compared with the sensor fabricated from conventional methods such as thick film, thin film, pellets, etc. It was reported that the competitive sensor using ZnO of with nano-sized grains in LPG and ethanol sensors improves their sensitivity [168]. These examples highlight the improvements which can be made through nanotechnology research and development. At this stage the use of nanoparticles is limited and still under development, but the possibilities are limitless. It is therefore, a key objective of researchers in this field is to create and use structures, devices and systems that have novel properties and functions because of their small and/or intermediate size. It may be, due to the smaller grain sizes (< 100 nm) of oxides, arranged in the manner so that, the effective surface area becomes undoubtedly, explosively largest.

(II) Gas sensing mechanism of nanograins consisting of MOS thick and thin film gas sensor

The resistance of the nanocrystalline materials decreases as gas flows into the test chamber and is subsequently adsorbed on the surface of the nanocrystalline material. However, as shown in Fig. 1.9(a), when a thick film, consisting of small grains, is surrounded by air, the conduction electrons in the nanocrystalline materials in the form of thick film cannot be depleted completely, as the air molecules are unable to enter
effectively into the inner parts of the film. When exposed to gas, as shown in Fig. 1.9(b), the thick film (nanocrystalline materials) will gain electrons from the reaction between the target gas and adsorbed oxygen. Even though, at this time, the carrier-depleted layer of the nanocrystalline materials (film) becomes thinner, the resistance of the nanocrystalline materials film will not be reduced to any large extent because the carrier-depleted layer is electronically connected in parallel with the remaining part of the materials on the film, which remains highly conductive. In Fig. 1.9(c), when a nanocrystalline thin film consisting of fine grains is exposed to air, the depletion layer would extend throughout the entire layer of nanocrystalline materials on the film, and its resistance becomes strikingly large. In a target gas environment (see Fig. 1.9(d)), the depleted layer will shrink quickly as it obtains conduction electrons from the gas-adsorbed oxygen reaction, and the resistance of the nanocrystalline materials would experience a large change.

However, there are many challenges in preparing thin enough nanocrystalline film to form an entirely depleted layer when exposed to air, the nanocrystalline thin film with multi-microstructures is shown in Fig. 1.9(e and f) maybe a solution. Because of the many channels formed in the materials, when exposed to air, the air could freely enter the inner parts of the film, and the electrons of the whole materials are almost completely depleted, as shown in Fig. 1.9(e). In contrast, when exposed to gas, as seen in Fig. 1.9(f), the entire nanomaterials film will be rich in conduction electrons, and the resistance of the film will diminish abruptly.
Fig. 1.9(a-f): Schematic diagram of all kinds of nanocrystalline thin and thick films exposed to air and target gas.

(III) Why do nanocrystalline materials give better gas sensing performance?

Fig. 1.10(a, b) represent the channel width in the absence and in presence of the target gas respectively. The mechanism for gas detection in nanomaterials is based on reactions that occur at the sensor surface, resulting in a change in the concentration of adsorbed oxygen $O^{-}$ ions. Oxygen ions adsorb onto the material’s surface, remove electrons from the bulk, building a potential barrier of depth $\delta$, that decreases the channel width $L_c$ of passage of electrons through a nanoparticle of diameter $D$ (Fig. 1.10(a)) and hence electron movement and conductivity decreases.
where \( L_c = D - 2 \delta \)

If the particle size is reduced up to nanometer level (< 100 nm), the channel width would be almost blocked (Fig. 1.10(a)) and the initial resistance of the sensor would be infinitely high in air ambient.

![Diagram](image1.png)

(a)

![Diagram](image2.png)

(b)

**Fig. 1.10:** Conduction channel due to potential barrier (a) blocked in air ambient, and (b) open on exposure of target gas.

On exposure, the target gas would consume oxygen atoms to oxidize, liberating electrons behind it on the surface. Desorption of oxygen from the surface of the sensor, would decrease the potential barrier height which broadens the channel width for migration of electrons (Fig. 1.10(b)). Thus nano-scale materials offer the grain sizes where the depletion layer has about the same dimensions as the particle radii. The charge
transfer is, therefore, predominantly grain controlled. When reactive (reducing) gases combine with this oxygen, the barrier height is reduced, broadening the passage of electrons and hence conductivity increases. This change in conductivity is directly related to the amount of a specific gas present in the environment, resulting in a quantitative determination of gas presence and concentration. To maximize the opportunities for surface reactions, a high ratio of surface area to volume is needed. As an inverse relationship exists between surface area and particle size, nano-scale materials, which exhibit very high surface area, are highly desirable.

1.14 Growth of nanostructured materials

Nanocrystalline materials can be classified into different categories depending on the number of dimensions that are nanostructured (with dimensions lower than 100 nm); we will follow one of the possible classification: i.e. zero dimensional for clusters, mono dimensional for nanowires and two dimensional for films.

There are two different approaches to the production of 1D structures: top-down and bottom up technologies. The first one is based on standard micro fabrication methods with deposition, etching and ion beam milling on planar substrates in order to reduce the lateral dimensions of the films to the nanometer size. Electron beam, focused ion beam, X-ray lithography, nano-imprinting and scanning probe microscopy techniques can be used for the selective removal processes. The advantages are the use of the well developed technology of semiconductor industry and the ability to work on planar surfaces, while disadvantages are their extremely elevated costs and preparation times. A few classes of these new nanostructures with potential as sensing devices are summarized schematically in Fig. 1.11.
Fig. 1.11: A schematic summary of the kinds of quasi-one-dimensional metal oxide nanostructures

The Fig. 1.11 is the schematic summary of the kinds of quasi-one-dimensional metal oxide nanostructures: (a) nanowires and nanorods; (b) core-shell structures with metallic inner core, semiconductor, or metal-oxide; (c) nanotubules/nanopipes and hollow nanorods; (d) heterostructures; (e) nanobelts/nanoribbons; (f) nanotapes; (g) dendrites; (h) hierarchical nanostructures; (i) nanosphere assembly; (j) nanosprings and (k) nanoparticles.

In the top-down approach highly ordered nanowires can be obtained \cite{169-172}, but at the moment this technology does not fulfill the industrial requirements for the production of low cost and large numbers of devices. Furthermore the 1D nanostructures produced with these techniques are in general not single-crystalline.

The second approach, bottom-up, consists of the assembly of molecular building blocks or chemical synthesis by vapor phase transport, electrochemical deposition, solution-based techniques or template growth. Its advantages are the high purity of the nanocrystalline materials produced, their small diameters, the low cost of the experimental set ups together with the possibility to easily vary the intentional doping and the possible formation of junctions. The main disadvantage regards their integration on planar substrates for the exploitation of their useful properties, for example transfer and contacting on transducers can be troublesome.
The bottom-up approach allows low cost fabrication although it could be very difficult to get them well arranged and patterned [173]. Furthermore more control and insight into the growth process must be achieved for their fruitful integration in functional devices. The most promising approach to produce functional nanowires will be the combination of the two preparation technologies.

Numerous one-dimensional oxide nanostructures with useful properties, compositions, and morphologies have recently been fabricated using bottom-up synthetic routes. Some of these structures could not have been created easily or economically using top-down technologies.

A nomenclature for these peculiar structures has not been well established. In the literature a lot of different names have been used, like whiskers, fibers, fibrils, nanotubules, nanocable, etc. The definition of these 1D nanostructures is not well established. A few classes of these new nanostructures with potential as sensing devices are summarized schematically in Fig. 1.11. The geometrical shapes can be tubes, cages, cylindrical wires, rods, nails, cables, belts, sheets and even more complex morphologies. When developing 1D nanocrystals the most important requirements are dimensions and morphology control, uniformity and crystalline properties. In order to obtain one-dimensional structures a preferential growth direction with a faster growth rate must exists. Achieving 1D growth in systems with an isotropic atomic bonding requires a break in the symmetry during the growth and not just stopping the growth process at an early stage (0 and 2D).

In the past years the number of synthesis techniques has grown exponentially. We can divide these growth mechanisms in different categories, first of all catalyst-free and catalyst assisted procedures and then we can distinguish between vapor and solution phase growth. As far as metal oxides are concerned the most used procedure is the vapor phase one. But solution phase growth techniques provide a more flexible synthesis process with even lower production costs. There are different growth mechanism depending on the presence of a catalyst, i.e. vapor–liquid–solid, solution–liquid–solid or vapor–solid process.
1.15 Methods for the growth of nanostructures

There are various methods for synthesis of nanostructures in the form of thin film and powder.

(I) Thin films preparation methods

In literature, many researchers are reported several methods for deposition of thin films of different materials. These methods are categories as follows.

(i) Thermal deposition in vacuum / resistance heating

It is the most commonly used technique adopted for the deposition of many compounds. This involves the evaporation or sublimation of the materials in vacuum by thermal energy and allowing the vapor stream of the charge to condense on a substrate so as to form a continuous and adherent deposit of desired thickness. The quality and the characteristics of the deposit will depend on the rate of deposition, substrate temperature, ambient pressure, geometry of the evaporant source and its distance from the substrate.

(a) Thermal evaporation

The thermal evaporation deposition technique consists in resistive heating of materials, which evaporates in the form of vapor and deposited on to the substrate. A thermal evaporator uses an electric resistance heater to melt the material and raise its vapor pressure to useful range. Low pressures are used, about $10^{-6}$ or $10^{-5}$ Torr, to avoid reaction between the vapor and atmosphere. At these low pressures, the mean free path of vapor atoms is the same order as the vacuum chamber dimensions, so these particles travel in straight lines from the evaporation source towards the substrate. Only materials with a much higher vapor pressure than the heating element can be deposited without contamination of the film. The equipments available in the laboratory use resistance heating (Joule effect). The metals used as heating resistance (Boat) are tantalum (Ta), Molybdenum (Mo) and wolfram (W) etc.

(b) Flash evaporation

This method is generally adopted when a material has a tendency to decompose or dissociated during evaporation. Basically the process is similar to the thermal evaporation
techniques with the difference that only a small amount of the charge in powder form is fed at a time to a white hot boat of tungsten, molybdenum or tantalum so that an instantaneous evaporation of the total charge takes place without leaving any residue because of the high temperature of the boat. Hence the composition of the gaseous phase will be more or less the same as that of the charge and it is expected that on condensation the deposits will retains the composition of the evaporant.

There is no accumulation of the charge on the heated boat before the arrival of the next charge. The charge in powder form is fed from a reservoir or a hopper to the heated boat through a chute and the feeding rate can be made continuous or intermittent by using a vibrator or suitable cam arrangement. For some oxides often a part of the molten charge is maintained over the heated boat which is then constantly fed by a small amount of fresh charge depending on the rate of evaporation. Using this method a constant composition film can be produced.

(c) Multi evaporation

In this technique several sources are simultaneously used for the evaporation of the constituent species or depositions are made sequentially i.e one after another from different sources on the substrate to form the desired composite films. The rate and the time of deposition of each species will generally determine the film composition. These deposits are then heat treated in vacuo for homogenization, for ensuring a complete reaction between the constituent elements and also removing excess of more volatile components from them. This technique is particularly suitable for film composition especially non-stoichiometric ones which cannot be easily prepared by the conventional method. The simultaneous deposition process from different sources is known as “co-evaporation” technique.

(d) R.F. / Inductive heating

It is also possible to melt the charge by R.F or induction heating and the evaporation takes place as in the case of thermal heating. In this technique it is possible to avoid contamination of the charge. However, the method is not suitable for general applications.
(ii) Electron beam method

The technique is based on the heat produced by high-energy electron beam bombardment on the material and material gets melted and goes into vapor state, which is to be deposited on the substrate. The electron beam is generated by an electron gun, which uses the thermionic emission of electron produced by an incandescent filament. Emitted electrons are accelerated towards an anode by a high difference of potential. The crucible itself or a near perforated disc can act as the anode. A magnetic field is often applied to bend the electron trajectory, allowing the electron gun to be positioned below the evaporation line.

(iii) Sputtering/cathodic sputtering

Sputtering is the process of ejection of atoms from solid target materials due to bombardment of high energetic ions. Sputtering was first observed by Grove in 1852 and Pulkerin 1858 using von Guericke-type oil-sealed piston vacuum pumps. Sputter deposition of films was first reported by Wright in 1877. It is useful for compounds or mixtures, where different components would otherwise tend to evaporate at different rates.

(a) Glow discharge

Glow-discharge sputtering means the energetic particles used to strike target is generated by glow-discharge. Glow-discharge is created by tube filled with argon, neutral, no charged particles between cathode and anode. The pressure of the chamber should be about $10^{-1}$ to $10^{-3}$ torr.

(b) Low pressure sputtering

Low pressure sputtering normally carried out at or below $10^{-3}$ torr gas pressure and in some cases as low as $10^{-6}$ to $10^{-7}$ Torr. This technique has a fine control of sputtering rate that can be made by adjusting the magnetic field.

(c) Reactive sputtering

One of the effects of ion bombardment is to affect the reaction processes, occurring in reactive sputtering, and it is necessary to consider this technique. Commonly the
admission of the reactive gas in a reactive sputtering process is done by control of the flow, with a simple mechanical valve or an electronic feedback device which can indicate the magnitude of that flow. In reactive sputtering with a planar magnetron consumption of the reactive gas by the process is greater than that being pumped by the system and conditions are often created where the process is unstable, switching between "metallic" and "oxide" sputtering modes without allowing access to the intermediate point, which is the one generally required.

(d) R.F sputtering

In RF sputtering method an impedance matching between the power supply and the discharge tube is necessary. This technique is useful for the deposition of dielectric materials. The RF sputtering process has some advantage in terms of: simple low-cost deposition system, absence of toxic/pyrophoric gases from the process and the possibility of sequential deposition of different films in the same system.

(iv) Chemical deposition

(a) Electrodeposition

When a current is passed through an aqueous solution of the some metal salts between two electrodes of the same or different metals, the deposition of metal from aqueous solution takes place at the cathode surface. In this method, the dissociation of metal salts to anions and cations the deposition of the latter at the cathode surface and consequent neutralisation of their charges to form metallic films. Bath composition, pH, current density, temperature conditions have been suitably controlled to get the desired quality of the deposits.

(b) Electron plating

In this process metal films can be deposited without passing any current and the film thickness can be built up to in order of micron or more. The substrates can be both metals and non conductors. Its main advantage is that uniform deposition can be made even to intricate parts and deep recesses of any design where the normal electro deposition
method may not be suitable. This technique is now being used for the preparation of specialized films required for electronic and other purpose.

(c) Chemical displacement

This process depends on the difference in the relative electrode potentials of two metals in their aqueous salt solutions. If a lower electrode potential metal is dipped in a salt of a higher electrode potential, then due to the difference on their solution pressures, the later metal gets deposited on the surface. The films prepared by this technique are generally porous, non-adherent and inhomogenous.

(d) Chemical bath deposition

The most used solution technique and also one of the oldest methods for thin film growth is chemical bath deposition (CBD) or chemical solution deposition (CSD). CBD has been widely used for the deposition of chalcogenides for various applications. In CBD all the precursor ions are present at the same time in the reaction vessel. Typically CBD has a so-called terminal thickness indicating a point where the growth of thin film is stopped due to depletion of precursors in the solution. The precursor molecules are metastable releasing slowly ions for the deposition reaction. The product has low solubility, but due to limited number of free ions a direct homogeneous precipitation in the solution is prevented. For metal sources complexed ions are usually utilized. Generally sulphur and selenium sources are decomposable molecules, like thiourea or thioacetamide and selenoure, respectively.

(e) Sol-gel

Sol-gel processing is widely used in the synthesis of inorganic and organic-inorganic hybrid materials and capable of producing nanoparticles, nanorods, thin films, and monolith. Sol-gel methods for oxide coatings were reviewed by Francis. Prior to sol-gel transition or gelation, sol is a highly diluted suspension of nanoclusters in a solvent, and typically sol-gel films are made by coating sols onto substrates. Most commonly used methods for sol-gel film deposition are spin- and dip-coatings; though spray and ultrasonically pulverized spray were also used.
(v) **Chemical vapor deposition/ vapor plating**

Chemical vapor deposition is the process of chemically reacting volatile compounds of a material to be deposited, with other gases, to produce a non-volatile solid that deposited atomistically on a suitably placed substrate.

(a) **Vapor phase reaction**

In this method constituent species in the gaseous phase react in the presence of inert, oxidizing or even some reducing atmosphere to form the desired product. Thus films can be produced by the reaction of precursor vapors.

(b) **Vapor transportation method**

In this method vapors of two reacting constituents are passes over the substrate kept at a high temperature region where the reaction take place to form the desired films. This technique is often used for the preparation of very thick films and wafers and even flat shaped crystals of several mm sizes.

(c) **Thermal decomposition/ pyrolysis**

In thermal decomposition techniques the nebulizer is used to inject very small droplets of precursor solution and decomposes at particular temperature. It is also known as aerosol decomposition synthesis. The conversion droplet-to-particle is achieved by this technique. Reaction takes place in solution in the droplets, followed by solvent evaporation.

(d) **Spray pyrolysis**

Spray pyrolysis, one of the chemical techniques applied to form a variety of thin films, results in good productivity from a simple apparatus. A solution containing starting compounds is atomized by a pneumatic spraying system (spray gun) at particular air pressure. The droplets are transported onto a heated glass substrate with the compressed air. The solution is atomized not consecutively but intermittently, since the substrate temperature is lowered by the spraying. It thus takes several tens of seconds for the next spray until the substrate temperature has recovered.
(II) Powder preparation methods

There are several methods for preparation of nanocrystalline powder such as:

(a) Aqueous solution method

Aqueous solution is particularly well suited to prepare ultrafine powders, so it is widely used to prepare many kinds of metal powders.

(b) Citrate gel method

This process can avoid complex steps such as refluxing of alkoxides, resulting in less time consumption compared to other techniques. This process involves complexation of metal ions by poly functional carboxyl acids such as citric acid or tartaric acid having one hydroxyl group. On heating this mixture, the solvent (water) evaporates resulting in increased viscosity. On complete removal of water, the mixture is a polymeric gel and its constituents mixed at atomic level. This resin on heating at higher temperature produces the respective oxides. The citrate gel process offers a number of advantages for the preparation of fine powders of many complex oxides.

(c) Co-precipitation method

Co-precipitation is one of the more successful techniques for synthesizing ultrafine ceramic powders having narrow particle size distribution. This process can avoid complex steps such as refluxing of alkoxides, resulting in less time consumption compared to other techniques. The only drawback of this method is that all the cations should have similar solubility product.

(d) Gas phase synthesis

The gas phase synthesis technique is an aerosol technique for powder synthesis. The technique is used to generate a large variety of micro, nano particles of interest. In this process, the appropriate precursor vapor /gas is mixed with a fuel (e.g. Acetylene or Methane) and oxygen. The mixture is burnt through a specially designed burner. The precursor decomposes in the flame and nano particles are nucleated. The synthesized particles are then collected by using a suitable method of capture. By proper choice of precursors the different nano materials that may be synthesized.
(e) **Hydrothermal synthesis**

Hydrothermal synthesis includes the various techniques of crystallizing substances from high-temperature aqueous solutions at high vapor pressures; also termed "hydrothermal method". It can be defined as a method of synthesis of single crystals that depends on the solubility of minerals in hot water under high pressure. The crystal growth is performed in an apparatus consisting of a steel pressure vessel called autoclave, in which a nutrient is supplied along with water. A gradient of temperature is maintained at the opposite ends of the growth chamber so that the hotter end dissolves the nutrient and the cooler end causes seeds to take additional growth.

Possible advantages of the hydrothermal method over other types of crystal growth include the ability to create crystalline phases which are not stable at the melting point. Also, materials which have a high vapor pressure near their melting points can also be grown by the hydrothermal method. The method is also particularly suitable for the growth of large good-quality crystals while maintaining good control over their composition. Disadvantages of the method include the need of expensive autoclaves, and the impossibility of observing the crystal as it grows.

(f) **Pechini process**

One of the more successful technique for high-quality ceramic powder synthesis which is a solution-polymerization route. In general, the process relies on the ability of certain organic acids (e.g., citric acid) to chelate metal ions. Then, with the help of a polyhydroxy alcohol (e.g., ethylene glycol), the chelates undergo polyesterification when heated. The polyesterification reaction results in a polymerized resin that has the various cations distributed uniformly in stoichiometric proportions. The polymerized resin that contains the chelated cations is the preceramic powder, which can then be calcined to obtain the target ceramic powder.

(g) **Sol-gel**

The sol-gel process, also known as chemical solution deposition is a wet-chemical technique widely used in the fields of materials science and ceramic engineering. Such methods are used primarily for the fabrication of materials (typically a metal oxide)
starting from a chemical solution (or sol) that acts as the precursor for an integrated network (or gel) of either discrete particles or network polymers. Typical precursors are metal alkoxides and metal chlorides, which undergo various forms of hydrolysis and polycondensation reactions.

(h) **Spray pyrolysis**

Spray pyrolysis is a promising technique for producing various materials in a wide range of composition, size and morphology. Powders and films can be successfully prepared. Spray pyrolysis involves passing an aerosol of a precursor solution through a graded temperature reactor, in which the individual droplets are thermally decomposed to form oxide particles. The aerosols may be generated by pneumatic or spray gun.

(i) **Flame spray pyrolysis**

The process of flame spray pyrolysis is a variant of aerosol techniques used for powder synthesis. This process involves the introduction of finely subdivided liquid precursor droplets into the flame instead of injecting the precursor vapors. These droplets are subsequently transported through the flame, in which the solvent evaporates and the dissolved species react to form product particles. It thus allows the use of precursors having high vapor pressures and expands the scope of flame synthesis to using a variety of precursors and in turn producing a variety of new materials.

1.16 Previous work done on nanocrystalline ZnO, NiO and Ni-doped ZnO

Table 1.5: Survey of: nature of powders, preparation techniques and sizes.

<table>
<thead>
<tr>
<th>Nature of ZnO</th>
<th>Preparation technique</th>
<th>Size (nm)</th>
<th>Reference</th>
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<tbody>
<tr>
<td>Nanopowder</td>
<td>aqueous solution</td>
<td>33</td>
<td>[174]</td>
</tr>
<tr>
<td>Nanopowder</td>
<td>microwave-assisted solution approach</td>
<td>30</td>
<td>[175]</td>
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<td>Nanopowder</td>
<td>solvothermal synthesis</td>
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<td>[176]</td>
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<td>50-100</td>
<td>[177]</td>
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<td>ultrasonic mist-chemical vapor deposition</td>
<td>50-100</td>
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**NiO**

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**Ni-doped ZnO**

| Microspheres           | solvothermal                             | 1.5–2.0 µm | [203] |
### Table 1.6: Survey of: materials, structure synthesis method, tested gas, operating temperature and response.

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(III) Nanocrystalline ZnO based sensors

Table 1.6 shows the work done by various researchers on nanocrystalline ZnO based sensors.
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### 1.17 Objectives of the present study

There is a great deal of contemporary concern about developing nanocrystalline chemical sensors for conventional gases and due to their prominent role in safety, industrial process monitoring and pollution control. There is currently lot of interest in the development of nanocrystalline materials as possible sensors. The search for preparation of nanocrystalline sensing materials and developing the sensor properties to sense the conventional gases has become an active research field.

The major objectives of the present research work are:

i. to prepare nanocrystalline ZnO powders by chemical and hydrothermal route,

ii. to prepare nanostructured ZnO thin films by spray pyrolysis technique,

iii. to prepare nanocrystalline NiO and Ni-doped ZnO nanorods by hydrothermal route,

iv. to prepare thick films of as prepared nanostructured material by screen-printing technique,

v. to study the structural, microstructural, electrical, optical and optical properties of above prepared nanocrystalline ZnO, NiO, Ni-doped ZnO powders and ZnO thin films,

vi. to study gas sensing properties of as prepared thin/thick films for various conventional gases at different operating temperatures.
vii. to characterize these powders by various analytical techniques such as: XRD, SEM, TEM, EDAX UV-vis spectroscopy, Photoluminence spectroscopy and sensor specification.

The ultimate aim of the present work is to find out best sensor composition in terms of sensing characteristics for detection of conventional gases.

1.18 Definition of the problem

With comprehensive and critical survey of the literature it is decided to study on “Synthesis and gas sensing performance of nano ZnO thick film resistors”.
References


[34]. O. Madelung, U. Rössler, M. Schulz, Zinc oxide (ZnO) crystal structure, lattice parameters, DOI: 10.1007/10681719 286.


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