Chapter 2
Theoretical considerations

2.1 Thin film deposition technologies

The performance of metal oxide semiconducting materials as gas-sensing detectors depends strongly on structural and morphological factors. Thin film deposition techniques can readily control these factors. Thin-film gas sensor exhibits merits over other types of sensors by virtue of its simplicity in fabrication and feasible application. These types of gas sensors have potential advantages of fast response times, the miniaturization via integration with IC based technology leading to low power consumption, higher reliability via batch fabrication and improved selectivity through use of arrays and reduced costs.

Based on structural properties thin films can be divided into two different groups: single crystals and polycrystals. Monocrystalline thin films are not much used as gas sensors because they do not have grain boundaries and show only small variations of electrical resistance in the presence of oxidizing and reducing gases. Polycrystalline thin films are most suitable gas sensors. The effect of substrate cannot be ignored because surface condition of the substrate influences the characteristics of the film. Oxide, single crystals, ceramics, and metals and/or alloys have been tested as to their suitability for serving as substrate materials for superconducting thick and thin layers. Sufficient chemical and thermal stability are key properties of a substrate, i.e., it may not react chemically with the coating.

There are varieties of thin film deposition techniques which are divided into two broad categories, depending on whether the process is primarily chemical or physical. Chemical deposition includes liquid precursor techniques (plating, chemical solution deposition) and gas precursor techniques (chemical vapor deposition) whereas physical vapor deposition uses mechanical, electromechanical or thermodynamic means to produce a thin film of solid (thermal evaporation, sputtering, pulsed laser deposition etc). Thermal evaporation is one of the important techniques used for the deposition of high quality metal thin films. This
technique is carried out in high vacuum, to allow the vapor to reach the substrate without reacting with or scattering against other gas-phase atoms in the chamber, and reduce the incorporation of impurities from the residual gas in the vacuum chamber.

2.1.1 Thermal Oxidation technique

Thermal Oxidation is a simple, low cost technique which is considered as a novel method for preparation of metal oxide films. It comprises of two different steps. The first consist of deposition of thin metal film by means of a PVD technique (thermal evaporation, sputtering etc.) on substrates. The second step involves the thermal oxidation of thin film by keeping the metallic films at high temperatures for sufficiently long periods in air flow. First, the oxidation reaction of metal occurs at the surface where metal loses electron to form $M^{++}$ ions. Then, the electron from metal moves to the surface. The adsorbed oxygen molecule and the electron react to form oxygen ions on the surface. The adsorbed oxygen ions include $O^{2-}$ and $O^{-}$.

The diffusion across oxide layer owing to metal ion or oxygen ion is dependent on the domination of transport. The transportation of ions can be considered for four possible mechanisms as shown in above Figure 2.1. If oxygen ions are more mobile, the new metal-oxide is formed at the metal-oxide interface. On the contrary, if metal ions are more mobile than oxygen ions, the transportation of metal ions is interstitially without permanently displacing any of the matrix atom or through metal ion vacancies [Shewmon, (1989). The new metal-oxide is formed at oxide-oxygen interface.

Many researchers have reported about the growth of metal oxide nanostructures by thermal oxidation technique with different conditions such as temperature, time, catalyst, and gas flow. The list of some of metal-oxide nanostructures synthesized by thermal oxidation is shown in Table 2.1. Thermal oxidation under controlled conditions is one of the most efficient approaches for the fabrication of ZnO nanostructures also (Table 2.2).
Figure 2.1 Possible mechanisms of ion transportation in thermal oxidation
Table 2.1 List of nanostructures synthesized by thermal oxidation technique

<table>
<thead>
<tr>
<th>Materials</th>
<th>Temperature (°C)</th>
<th>Oxidation time</th>
<th>Morphology</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO</td>
<td>400-700</td>
<td>2-4 h</td>
<td>Nanowire</td>
<td>Jiang <em>et al.</em> (2002)</td>
</tr>
<tr>
<td>CuO</td>
<td>300-500</td>
<td>0.5-24h</td>
<td>Nanowire</td>
<td>Chen <em>et al.</em> (2008)</td>
</tr>
<tr>
<td>CuO</td>
<td>600</td>
<td>6 h</td>
<td>Nanowire</td>
<td>Raksa <em>et al.</em> (2008)</td>
</tr>
<tr>
<td>CuO</td>
<td>400</td>
<td>2 h</td>
<td>Nanowire</td>
<td>Nguyen <em>et al.</em> (2009)</td>
</tr>
<tr>
<td>CuO</td>
<td>400</td>
<td>4 h</td>
<td>Nanowire</td>
<td>Zeng <em>et al.</em> (2009)</td>
</tr>
<tr>
<td>CuO</td>
<td>400-800</td>
<td>4 h</td>
<td>Nanowire</td>
<td>Kaur <em>et al.</em> (2006)</td>
</tr>
<tr>
<td>CuO</td>
<td>500</td>
<td>1.5 h</td>
<td>Nanowire</td>
<td>Hansen <em>et al.</em> (2008)</td>
</tr>
<tr>
<td>SnO₂</td>
<td>600</td>
<td></td>
<td></td>
<td>Partridge <em>et al.</em> (2008)</td>
</tr>
<tr>
<td>TiO₂</td>
<td>650–800°C</td>
<td>30-180 minutes</td>
<td>Nanowires</td>
<td>Kaewsai <em>et al.</em> (2010)</td>
</tr>
<tr>
<td>TiO₂</td>
<td>650–650°C</td>
<td>30 minutes</td>
<td>Nanowires</td>
<td>Huo <em>et al.</em> (2009)</td>
</tr>
<tr>
<td>WO₃</td>
<td></td>
<td></td>
<td>Nanowire</td>
<td>You <em>et al.</em> (2010)</td>
</tr>
</tbody>
</table>
### Table 2.2 ZnO nanostructures made by thermal oxidation.

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature (°C)</th>
<th>Oxidation time</th>
<th>Morphology</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>300</td>
<td>5 min</td>
<td>nanowire and nanoflake</td>
<td>Hsueh &amp; Hsu (2008)</td>
</tr>
<tr>
<td>ZnO</td>
<td>600</td>
<td>24 h</td>
<td>Nanowire</td>
<td>Wongrat et al. (2009)</td>
</tr>
<tr>
<td>ZnO</td>
<td>300-600</td>
<td>1 h</td>
<td>Nanoneedle</td>
<td>Yu &amp; Pan (2009)</td>
</tr>
<tr>
<td>ZnO</td>
<td>500</td>
<td>1 h</td>
<td>Nanoplate</td>
<td>Kim et al. (2004)</td>
</tr>
<tr>
<td>ZnO</td>
<td>200-500</td>
<td>30 min</td>
<td>Nanowire</td>
<td>Schroeder et al. (2009)</td>
</tr>
<tr>
<td>ZnO</td>
<td>300-600</td>
<td>1 h</td>
<td>Nanowire</td>
<td>Fan et al. (2004)</td>
</tr>
<tr>
<td>ZnO</td>
<td>400</td>
<td>30 min</td>
<td>Nanowire</td>
<td>Ren et al. (2007)</td>
</tr>
<tr>
<td>ZnO</td>
<td>600</td>
<td>1.5 h</td>
<td>Nanowire</td>
<td>Sekar et al. (2005)</td>
</tr>
<tr>
<td>ZnO</td>
<td>400-600</td>
<td>1 h</td>
<td>nanowire and nanorod</td>
<td>Liang et al. (2008)</td>
</tr>
</tbody>
</table>

### Table 2.3 Gas sensing nanostructures prepared by thermal oxidation technique

<table>
<thead>
<tr>
<th>Materials</th>
<th>Gas</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>H₂ and NO</td>
<td>Hung et al. (2009), Hung et al. (2010)</td>
</tr>
<tr>
<td>ZnO</td>
<td>Ethanol</td>
<td>Wongrat et al. (2009)</td>
</tr>
<tr>
<td>ZnO</td>
<td>H₂</td>
<td>Hardan et al. (2009)</td>
</tr>
<tr>
<td>ZnO</td>
<td>Ethanol</td>
<td>Hsueh et al. (2008)</td>
</tr>
<tr>
<td>SnO₂</td>
<td>C₄H₁₀</td>
<td>Shim et al. (2002)</td>
</tr>
<tr>
<td>SnO₂</td>
<td>H₂</td>
<td>Partridge et al. (2008)</td>
</tr>
<tr>
<td>TiO₂</td>
<td>H₂</td>
<td>Jun (2005)</td>
</tr>
<tr>
<td>CuO–SnO₂</td>
<td>H₂S</td>
<td>Lee (2005)</td>
</tr>
<tr>
<td>Cu₂O</td>
<td>Methane</td>
<td>Jayatissa et. al. (2009)</td>
</tr>
<tr>
<td>CuO</td>
<td>Ethanol</td>
<td>Raksa et. al. (2009)</td>
</tr>
</tbody>
</table>
2.2 Surface modification

Surface modification is the act of modifying the surface of a material by bringing physical, or chemical characteristics different from the ones originally found on the surface of a material. This modification is usually made to solid materials. Solids are composed of a bulk phase covered by a surface phase. The surface phase of a solid interacts with the surrounding environment. Surface modification involves altering the properties of the surface phase in order to achieve different goals. The modification can be done by different methods with a view to altering a wide range of characteristics of the surface, such as: roughness, hydrophilicity, surface charge, surface energy, biocompatibility and reactivity. Surface engineering techniques are being used in the thin film field to develop a wide range of functional properties, including physical, chemical, electrical, electronic, magnetic, mechanical, wear-resistant and corrosion-resistant properties at the surfaces. Almost all types of materials, including metals, ceramics, polymers, and composites can be coated on similar or dissimilar materials. This thesis discusses and analyzes two techniques used to modify the surface of thermally oxidized In$_2$O$_3$ and ZnO films to be used for gas sensing applications:

1. Surface modification by dip coating technique
2. Ion beam surface modification

2.2.1 Surface modification by dip coating technique

In dip coating process a substrate or film surface is dipped into a liquid coating solution which can produce excellent and high quality coatings on the surface. Via high quality surface modification one can synthesize nanocrystals and incorporate some functional groups on the surface. It has proven to be a popular way to modify the surface of thin films to make them susceptible for sensing a particular gas. Depending on both the concentrations of additives and crystallization parameters, a simultaneous structure modification can take place, accompanied by the grain size change, appearance of second phase in base oxide, i.e. heterostructures of various forms, and the change of electrophysical and surface properties of metal oxides.

During dip coating, additives reside in intergranular region of host material which increases the effective surface area and form misfit regions uniformly over the surface. Usually the modified surface has larger number of adsorbed oxygen ions.
For indium oxide this technique is exploited for the detailed investigation of its properties by few groups. Lee et al. (1996) have characterized In$_2$O$_3$ thin films prepared by this technique deposited on several substrates while Das et al. (1996) have carried out investigations on the optical and electrical properties of thermally oxidized Indium films. The influence of oxidation and preparation conditions on In$_2$O$_3$ films have also been studied by Gritan et al. (2000). Oztas et al. (2006) have studied structural and optical Properties of nanocrystalline In$_2$O$_3$ films prepared by Thermal Oxidation of In$_2$S$_3$ Films.

The metal oxide films made by thermal oxidation have proved to have good gas sensing properties. The incorporation of oxygen in the lattice during oxidation increases the volume, causing interconnection of agglomerates and creating percolating path for current flow. Thus the surface of semiconductor film after thermal oxidation consists of porous agglomerates and a porous surface is well suited for gas absorption. There are examples where this technique has been exploited to prepare gas sensitive metal oxide structures (Table 2.3).

The technique of thermal oxidation has proven to be very useful for the development of efficient ZnO and In$_2$O$_3$ gas sensing films. Law et. al. (2008) has tuned the carrier concentration with the help of thermal oxidation which greatly influenced the sensitivity of ZnO nanowires.

Hardan et al. (2009) also exploited this technique to increase the gas response of ZnO film towards H$_2$. They showed that higher concentration of oxygen in film yielded more response to gas under test. Hung et al. (2009) and (2010) also synthesized wire like ZnO films by thermal oxidation for hydrogen gas and NO sensing application. Comini et al. (2000) has also utilized thermal oxidation for the development of indium oxide films for CO and NO$_2$ gas sensing applications at room temperature. Thus this technique has already proven to be useful for the deposition of gas sensitive ZnO and In$_2$O$_3$ films. But still more research efforts are necessary to tailor the porosity, grain size, oxygen content and carrier concentration of ZnO and In$_2$O$_3$ films using the technique of thermal oxidation.

have explained the sensitivity of CuO activated ZnO films to LPG on this theory [Patil et al. (2006)]. The introduction of additives may also lead to the formation of new donor or acceptor energy states or influence the grain size and
growth mechanism [Patil et al. (2006)]. The characteristics or behavior of gas can also be a clue for enhancing gas sensitivity of the metal oxide material. For example, sensitivity to acidic gases or basic gases can be increased by incorporation of a corresponding basic or acidic oxide respectively in metal oxides by surface modification. Ethanol experiences two routes of decomposition reactions i.e., dehydration and oxidative dehydrogenation at elevated temperature, depending on the acid-base properties of the oxide catalysts doped [Kohl (1989)]

\[
\begin{align*}
\text{C}_2\text{H}_5\text{OH} & \rightarrow \text{C}_2\text{H}_4+\text{H}_2\text{O} \quad \text{(acidic oxide)} \\
\text{C}_2\text{H}_5\text{OH} & \rightarrow \text{CH}_3\text{CHO}+\text{H}_2 \quad \text{(basic oxide)}
\end{align*}
\]

When an acidic catalyst (e.g. Al$_2$O$_3$) is added into SnO$_2$, ethanol decomposes forming ethylene (C$_2$H$_4$) after the initial dehydration step. When a basic catalyst (e.g. La$_2$O$_3$) is added, however, acetaldehyde (CH$_3$CHO) is also observed as a major intermediate form of ethanol after the initial dehydrogenation. CH$_3$CHO is known to have a much higher molecular sensitivity to a semiconductor gas sensor than C$_2$H$_4$.

Cr$_2$O$_3$-activated ZnO sensor has shown high selectivity for NH$_3$ at room temperature [Patil et al. (2007)] because Cr-oxide is well known to generate the solid acidity on solid bases such as ZrO$_2$ and ZnO. The solid acidity on the sensor surface would form NH$_4^+$ cations, which constitutes the proton conductivity leading to a crucial decrease of the resistance. Hence a basic catalyst like Lanthanum oxide can promote the basicity while acidic oxide like Al$_2$O$_3$ can be helpful for promoting the acidity of metal oxide surface.

Sometimes p-n heterojunctions are fabricated by forming a contact between a p-type and an n-type semiconductor during surface modification. Heterocontact sensors based on p-type and n-type ceramics have been shown to exhibit a high sensitivity to gas species. For example CuO (p type) modified SnO$_2$ nanoribbons (n-type) are very sensitive to H$_2$S at room temperature [Kong and Li (2005)]. CuO modified ZnO films have also been used for room temperature sensing of chlorine. When CuO–ZnO comes in contact with chlorine gas, lattice oxygen would be replaced by chlorine rupturing the heterojunctions and the resistance drops down suddenly [Patil and Patil (2007)].

**2.2.2 Surface modification by swift heavy ion irradiation**

The understanding of irradiation induced surface modification in metal oxides is also an outstanding topic due to many different applications of these materials in
various fields involving the interaction with energetic particles. Swift heavy ions are a special form of particle radiation. They are accelerated in particle accelerators to very high energies, typically in the MeV or GeV range and have sufficient energy and mass to penetrate solids on a straight line. In many solids swift heavy ions release sufficient energy to induce permanently modified cylindrical zones, so-called ion tracks.

Swift Heavy Ions (SHI) of various species in the energy range of 50 MeV to 250 MeV provided by the 15 million volt Pelletron at Inter university accelerator centre, New Delhi (IUAC) are being used for materials modification and characterization. Irradiation of materials at these high energies gives rise to highly excited states of lattice atoms with negligible contribution from elastic collisions.

Figure 2.2 shows the schematic of the 15 UD Pelletron accelerators. Negative ions are generated in the SNICS (source of negative ions by cesium sputtering) ion source. The sputter source uses accelerated cesium ions, striking a cold cathode, to produce a negative ion beam of cathode material. A thin layer of cesium condensed over the cathode surface enhances negative ion production. These ions are extracted from the ion source by applying a positive injection voltage (generally $V_{\text{inj}}=220$ kV). These singly charged ions are then mass analysed (by injector magnet) and are accelerated towards the Pelletron accelerator which is set with a positive terminal voltage of V. It will then acquire an energy, $E_1 = V$, (since $q=1$). Now the ‘charge stripper’ stripes off the electrons from the ions to make the ions multiply charged positive ions. These positive ions are again accelerated with positive potential V so that the energy becomes, $E_2 = q V$, (where $q$ is the charge state of the multiply charged ion). Ions with a total energy $E = E_{\text{inj}} + V + q V$, are then taken away to different beam line for irradiation studies, after the mass analysis [Sreekumar (2008)].

The Monte Carlo simulation (SRIM) has been widely tested and accepted as an accurate benchmark to generate accurate predictions about ion-solid interactions, penetration depth at arbitrary energies and incidence conditions, stopping ranges and sputter yields. SRIM is a group of programs which calculate the stopping and range of ions (10 eV - 2 GeV/amu) into matter. This calculation is made very efficient by the use of statistical algorithms which allow the ion to make jumps between calculated collisions and then averaging the collision results over the intervening gap. During the collisions, the ion and atom have a screened Coulomb collision, including exchange
Figure 2.2 Schematic of 15 UD Pelletron accelerator
and correlation interactions between the overlapping electron shells. The ion has long range interactions creating electron excitations and plasmons within the target. These are described by including a description of the target's collective electronic structure and interatomic bond structure when the calculation is setup (tables of nominal values are supplied).

The charge state of the ion within the target is described using the concept of effective charge, which includes a velocity dependent charge state and long range screening due to the collective electron sea of the target.

Swift heavy ion irradiation is a unique post deposition treatment which can create new defects in some materials and anneal out pre-existing defects in some others, through the intense interaction of incident ions with the target atoms. The control of defects and associated charge carriers is of paramount importance in applications that exploit the wide range of properties of gas sensing metal oxides.

The irradiation will not change the chemical composition of the semiconductor, but produces structural defects which can change the concentration of the adsorption centres of each given type and the capacity of adsorption on the surface of the semiconductor, these factors causes the change in resistance of thin films. When a high-energy ion beam passes through a material, it loses its energy in two distinct pathways; namely, nuclear and electronic energy losses. The nuclear energy loss dominates at lower energies, whereas higher energy beam results in electronic excitation of the target material. By suitable control of the irradiation parameters such as energy and fluence of the ion beam, it is therefore possible to tailor structural, electrical and optical properties of the target material.

There are several reports on structural and microstructural phase transformation due to irradiation using high-energy heavy ion in metals, semiconductors, insulators and polymers [Nakao et al. (1996), Benyagoub et al. (2001), Gilbert-Mougel (2001) and Kanjilal (2001)]. High electronic energy released by the ion beams in a very short interval of time produces significant excitation of the lattice, causing changes in the structural, electrical and optical behaviour of the materials. A few preliminary studies related to gas sensing properties and nano-crystallization has been reported by Medrignac et al. (1992) and Mohanty et al. (2006) respectively. Sanju Rani et al. has reported the effect of swift heavy ion irradiation on structure, optical, and gas sensing properties of SnO₂ thin films [Rani et. al. (2008)].
Comparative Study of irradiated and annealed ZnO thin films for ammonia gas sensing at room temperature is done by Kshirsagar et al. (2008).

### 2.3 Working principle of gas sensor

When an n-type semiconductor is placed in an oxygen atmosphere, oxygen is adsorbed onto the semiconducting metal oxide surface (SMO), forming a potential barrier at the grain boundaries. The interaction of atmospheric oxygen with the SMO surface forms charged oxygen species $\text{O}_2^-$, $\text{O}^-$, $\text{O}_2^-$, which trap electrons from the bulk of the material thus decreasing the concentration of the number of charge carriers near the surface giving rise to a depletion region. The layer of charged oxygen at the surface repels other electrons from interacting with the bulk of the film, creating a region depleted of electrons which results in an increased potential barrier at the grain boundaries. This impedes the flow of electrons and thus increases the resistance. When the sensor is exposed to an atmosphere containing a reducing gas, the SMO surface adsorbs the gas molecules and lowers the potential barrier, allowing the electrons to flow easily and thus reducing the electrical resistance. In this manner, the sensors act as variable resistors whose value is a function of gas concentration. Conversely, an oxidising gas serves to deplete the sensing layer of charge carrying electrons, resulting in an increase in resistance.

In case of a p-type semiconductor where positive holes are the majority charge carriers; hence, the opposite effects are observed. The adsorption of atmospheric oxygen on surface of the material causes ionization of atom yielding a positive hole.

$$\frac{1}{2}\text{O}_2 \leftrightarrow \text{O}^+ + \text{p}^+.$$  

When the sensor is exposed to an oxidizing gas, number of positive holes increases showing an increase in conductivity and vice versa for reducing gas, where the negative charge introduced in to the material reduces the positive (hole) charge carrier concentration [(Fine, et al. (2010)]. The gas sensing property of gas sensors is relative to the surface absorption and contact to atmosphere.

### 2.3.1 Sensor parameters

#### 2.3.1.1 Sensor response

One of the important parameters of gas sensors is the sensitivity or response of the sensor. This parameter has been attracting the researchers and much effort has been made to enhance it. There is not a uniform definition for gas sensitivity
(response) now. Usually, response can be defined as ratio of change in resistance of a sample upon exposure to gas to the original resistance in air i.e

\[ R = \left( \frac{R_g - R_a}{R_a} \right) \times 100 \% \quad (2.1) \]

where \( R_a \) stands for the resistance of gas sensors in the reference gas (usually the air) and \( R_g \) stands for the resistance in the reference gas containing target gases. Both \( R_a \) and \( R_g \) have a significant relationship with the surface reaction(s) taking place. In this thesis, we have focused on various methods resulting in the increase of gas response.

2.3.1.2 Selectivity

Selectivity refers to characteristics that determine whether a sensor can respond selectively to a group of analytes or even specifically to a single analyte. Currently, two general approaches exist for enhancing the selective properties of sensors. The first one is aimed at preparing a material that is specifically sensitive to one compound and has low or zero cross-sensitivity to other compounds that may be present in the working atmosphere. To do this, the optimal temperature, doping elements, and their concentrations are investigated. Nonetheless, it is usually very difficult to achieve an absolutely selective metal oxide gas sensor in practice, and most of the materials possess cross-sensitivity at least to humidity and other vapors or gases.

Another approach is based on the preparation of materials for discrimination between several analytes in a mixture. It is impossible to do this by using one sensor signal; therefore, it is usually done either by modulation of sensor temperature [Nakata et al. (2006), Huang et al. (2006)] or by using sensor arrays [Sysoev et al. (2007), Rock et al. (2008)]. In the former case, such discrimination is possible because of the different adsorption and reactivity properties of analytes. In the latter case, N signals are obtained simultaneously from N sensors, which usually differ in some way (e.g. doping element, doping ratio, grain size, or temperature). These kinds of devices are usually referred to as "electronic noses." In both cases, signals are typically analyzed by an artificial neural network.

2.3.1.3 Response time

Another parameter taken into account while checking the efficiency of the sensor is the response and recovery time. Response time is defined as the time
required for 90% of total change in resistance. The recovery time is defined as the
time taken to get back 90% of the original resistance in air. The response and recovery
times of sensor device depend on adsorption/desorption kinetics between the surface
and the gas phase which is ultrafast in case of nanowire devices. Recent reports of
ethanol vapour detection by ZnSnO$_3$ nanowires show the response and recovery time
to be as fast as 1 s [Xue et al. (2005)]. Rapid response implies more efficient sensor.

2.3.1.4 Robustness

Robustness at the sensor level refers to the ability of the sensor to perform its
function over a range of ambient condition e.g. humidity, temperature etc. and over a
range of times in the presence of drift and stability variations. Unfortunately, the
parameters of a chemical sensor technology that can be adjusted to improve
robustness are often the same parameters that result in a decrease in sensitivity and
selectivity [Tsujita et al. (2005)]. For example, the most sensitive chemical sensor is
often one whose reactions are totally irreversible. A fine balance between the
robustness and sensitivity can be overcome by using both engineering and science.

2.4 Factors influencing performance

There are several factors which effect the performance of a gas sensor. Some
of them have been discussed below.

2.4.1 Baseline drift

As a result of harsh environmental conditions, of hardware limitations and of
olfactory pollution specificities, odor real-time monitoring is always a real challenge.
The sensor has to automatically compensate the time drift and the influence of
ambient parameters such as temperature or humidity. Sensor drift is a first serious
impairment of chemical sensors. The sensors alter over time and so have poor
repeatability since they produce different responses for the same odor. Sensor
replacement is generally required to address such issue, but, after replacement, odors
should still be recognized without having to recalibrate the whole system. But
commercial sensors are rarely reproducible.

2.4.2 Sensor poisoning

In highly polluted atmosphere, another major problem encountered is a sensor
failure or an irreversible sensor poisoning. For example some gases like H$_2$S can
block the catalytic activity of Pd on ZnO surface. The usual way of minimising drift effect is to consider as useful response the difference between the base line, obtained by presenting the sensor array to pure reference air, and the signal obtained after stabilisation in the polluted atmosphere. The early metal oxide-based sensor materials possessed a number of unpleasant characteristics, such as high cross-sensitivity, sensitivity to humidity, long-term signal drift and, slow sensor response. In order to improve sensor performance, a series of various metal-oxide semiconductors have been tested [Meixner et al. (1996)].

2.5. Ways to improve sensors

Conducted research have shown that gas sensing effect in metal oxides is very complicated phenomenon, which depends on all metal oxide parameters, such as thickness, grain size, porosity, grain faceting, agglomeration; bulk conductivity, surface architecture, grain network, surface stoichiometry, catalytic reactivity, band gap and so on. Carried out analysis has shown that influence of above mentioned parameters on gas sensing characteristics takes place through the change of such parameters as effective area of intergrain and inter-agglomerate contacts; energetic parameters of adsorption/desorption processes; number of surface sites; concentration of charge carriers; initial surface potential; coordination number of metal atoms on the surface, gas penetrability of sensing matrix, etc. Conventional ways to improve the sensor selectivity are to adjust the microstructure of the sensor material to each particular gaseous species, to optimize the analysis temperature, and to introduce carefully chosen dopants.

2.5.1 Grain size effect

Two of the most important issues in gas sensing devices are gas sensitivity (detection of gas concentrations at the ppm level) and gas selectivity (detection of specific gases in a mixed gas environment) [Gopel (1994), Yamazoe (1991)]. Sensitivity is generally enhanced either by doping, which modifies the carrier concentration and mobility, or by microstructural changes such as reduction of the oxide particle size to the nanometer scale. In recent years, the sensitivity of semiconductor oxide materials has been improved by reducing the particle size, with greatly improved properties reported for sizes in the 5-50 nanometer range. It has pointed out that the gas sensitivity increases sharply as the diameter of tin oxide
crystallites becomes smaller than twice of the depth of the space-charge layer (3 nm) [Xu et al. (2006), Baik et al. (2000), Dolbec et al. (2003), Yan et al. (1998)]. Actually gas sensing is a surface property and the electron exchange between the surface states and bulk takes place within the surface layer with the thickness on the order of the Debye length which is expressed as

\[
L_D = \left( \frac{\varepsilon_0 k T}{e^2 n_b} \right)^{1/2}
\]

where \(\varepsilon, k, T, e, \) and \(n_b\) are the dielectric constant, Boltzmann constant, temperature, electron charge, and charge carrier density, respectively [Ogawa et al. (1982)]. In particular, if diameter of grain is comparable to the debye length, the surface effect becomes more pronounced in charge carrier dynamics, and significantly changes the conductivity of nanostructures, resulting in enhanced gas sensing performance [Niranjan et al. (2010)]. The surface condition has the most significant influence on the electrical properties of the material if \(l/2 < L\), where \(l\) is the grain size and \(L\) is the thickness of the depletion layer, typically from 3 to 10 nm, depending on the oxide. Therefore, the gas detection ability dramatically increases with decreasing grain size and the surface-to-volume ratio limits the maximum sensitivity. Nanowire/nanobelt diameter is usually on the order of several nanometers and is comparable to the Debye length and this often results in much larger sensitivity than their thin film or bulk counterparts. It is essential that while decreasing the grain size, efforts must be put to minimize the agglomeration and maximize the porosity so that sensitivity can be enhanced.

There are many examples where diameter of the sensing materials has been reduced, making it close to or smaller than the space-charge length \((L_d)\) [Kim et al. (2005), Chen et al. (2005)]. Recently, Huang et al. (2010) found that the SnO\(_2\) nanorods with a diameter of 7 nm showed enhanced sensitivity to CO at a low temperature of 250°C. Kim et al. (2005) used WO\(_{2.75}\) to detect 100 ppm NH\(_3\) even under ambient conditions. The results above suggest that the reduction of the size of 1D MOS nanostructures is a very efficient way to realize the sensors operated in low-temperature environments. There are some more examples of metal oxide-based nanostructures which were capable of detecting volatiles at room temperature because of reduced grain size [Lupan et al. (2007), Deshpande et al. (2007), Espinosa et al. (2007)]. Many single nanowire devices using SnO\(_2\), TiO\(_2\), ZnO, In\(_2\)O\(_3\) and WO\(_3\)
nanowires have been fabricated and their performances have been investigated in terms of operating temperature, sensitivity and response time [Chu et al. (2004), Fan et al. (2005), Francioso et al. (2006), Kalinin et al. (2005), Kim et al. (2009), Kolmakov et al. (2005), Wan et al. (2004), Wan and Wang (2005), Zhang et al. (2003)]. In the case of single nanowire devices, an excellent review [Kolmakov (2004)] proposed that a small change in the chemical state of the surface can cause depletion/accumulation of electron/holes not only near the surface but also in the entire volume of the nanostructure. However, the fabrication of single nanowire devices and parallel nanowire array devices require cumbersome post-growth processing [Yun et al. (2004), Fan and Lu (2005), Kolmakov et al. (2005), Shaw et al. (2005), Sysoev et al. (2006)]. On the other hand, thin films containing nanowires in a highly networked fashion could probably be used for making gas sensing devices with behaviour similar to that of single nanowire devices without much post-processing effort. This is possible only when the individual nanowires within the mat are covalently bonded to each other and the mat closely resembles that of two- and three-dimensional networks of nanowires. In a recent paper, synthesis of a nanowire thin film containing branched tungsten oxide nanowires was reported that simulated a type of three-dimensional nanowire network [Ponzoni et al. (2006)]. The sensors made using such films yielded promising gas detection performances. Hence we can see that grain size is an important factor affecting the gas sensing performance of a semiconductor oxide material.

2.5.2. Operating temperature

Besides grain size, another extrinsic factor like operating temperature is also very important affecting the gas sensing properties. The gas-sensor reactions typically occur at elevated temperatures, requiring the sensors to be internally heated for maximum response. The working temperature, at which these devices work, varies depending on the specific target gas in the ambient and on the selected sensor material in conjunction with its properties in every case. As this working temperature ranges usually from 200 to 400°C, it is necessary to implement a heating element in sensor device. However, if the processing temperature is too high, substantial grain growth can occur, coupled with a rapid decrease in open porosity, resulting in a marked decrease in sensor response. To further complicate matters, many metal oxides of interest to sensor research can assume multiple oxidation states, each of which can behave very
differently when exposed to gases. Thus high temperature would change the surface morphology and microstructure of thin films after long time use, leading to decrease in sensitivity and stability [Comini et al. (2001)]. To decrease the operating temperature, the feasible approaches include doping the metal oxide with noble metals [Kolmakov et al. (2008)], applying the electrostatic field [Zhang et al. (2011)] and using UV radiation [Comini et al. (2001), Comini et al. (2000)] during the gas sensing.

2.5.3. Use of catalyst/dopants

Semiconductor oxides suffer mostly from a lack of gas selectivity. Metal oxide-based gas sensors are normally sensitive to more than one chemical species in air and usually show cross-sensitivities. This non-specificity of the response to chemical species whose presence, identity and concentration in air have to be determined is by now considered an intrinsic property of metal oxide-based gas sensors. It’s easy to understand that it represents a real problem when different reactive gases are present simultaneously in the same atmosphere and interference effects between them can occur. Selectivity cannot be eliminated completely but it can be improved in different ways, the way of promotion can be different depending on the properties of the gases to be detected, like: (i) the use of filters [Park et al. (2002)] or chromatographic columns to discriminate between gases on the basis of their molecular size or other physical properties [Hebrle et al. (2000)](ii) the use of catalysts and promoters or more specific surface additives [Yamazoe et al.(1984), Vlachos et al.(1997)], the main effect of the additives introduced is the variation of the electrical properties resulting from the modifications of surface conditions (iii) the selection of the material for the sensing layer [Meixner and Lampe (1996), Moseley (1992)] and its physical preparation, (iv) the analysis of the transient sensor response [Distante et al. (2002)], (v) the selection of a fixed temperature to maximize sensitivity to a particular analyte gas [Capone (2001)] or (vi) the use of temperature modulated operation mode [Lee et al. (1999)]. Because of the complexity of gas sensing mechanism, the main method of giving suitable selectivity is implemented generally by altering the operating temperature, using effective gas filters, and adding catalytically active dopants. Morrison (1987) has proposed two mechanisms of catalyst control in gas sensors, the Fermi level energy control mechanism and spill over mechanism. “Fermi energy control” simply means that the adsorbed oxygen will remove electrons from the catalyst and catalyst will effectively remove from the
semiconducting film. In this effect the sensor signal is determined mainly by the electronic contact of the semiconductor with the catalyst, which results in alignment of the Fermi energy of the metal oxide with the additive. Since gas reacts with the metal oxide via the catalyst, the chosen catalyst can strongly change the selectivity.

In the “spill over” mechanism, the catalysts will dissociate the molecule and then the atoms will spill over the surface. Spillover is a well-known effect in heterogeneous catalysis and is probably most active with metal catalysts such as platinum. The Pt catalyst dissociates the oxygen molecules, numerous of oxygen ions (O\(^+\)) can spill over onto the surface of the semiconductor support. There is evidence that the O\(^+\) species is far more reactive than the O\(^2-\) species and the reaction rate of CO with O\(^+\) was higher than that with O\(^2-\). So that we can suppose that Pt particles dispersed on the surface of the thin films enhanced the gas-sensing properties.

2.5.4 Thickness of gas sensing films

The physical and sensing properties of semiconductor gas sensors are directly related to their preparation e.g. particle size, sensing film morphology, and sensing film characteristics as well as film thickness. There are many examples in which the effect of film thickness on the sensing characteristics of sensing films is reported. The sensitivity and response time of ethanol drastically increased and decreased with decreasing the film thicknesses of ZnO film [Liewhiran et al. (2007)]. The study of thickness and operation temperature on ZnO: Al thin film CO gas sensor revealed that the grain sizes were enhanced as the film thickness was increased, which resulted in decrease in the total surface area and as a result a low sensing sensitivity [Chang et al. (2002)]. In case of CdO thin films the response was found to be decreased at higher thicknesses [Salunkhe et al. (2008)]. The effect of density and film thickness of SnO\(_2\) films on H\(_2\) gas sensing properties revealed that lower density films were more sensitive [Yamazaki et al. (2005)]. They have shown that the sensor characteristics of sensing films are affected by the film structure, morphology, and film thickness, which are determined by the film preparation procedure. Becker et al. (2001) showed that thin and thick film devices of nominally the same material exhibit widely different gas sensitivity versus temperature profiles which can be explained on the basis of a simple diffusion reaction model. According to this model the different levels of gas penetration into porous tin oxide films are attributed to different kinetic barriers for triggering the individual detection reactions. Due to diffusion warming
thick film materials exhibit lower kinetic barriers for triggering detection reactions. The term “thick film” does not relate so much to the thickness of the film but more to the kind of deposition. Thick films are made by low-priced processes such as doctor (dr) blading, screen-printing, or spraying methods, etc. The preparation of thick films of ceramic material by these methods generally implies a processing sequence of the following steps: preparation of the oxide powders; preparation of pastes and slurries; painting/printing, etc. of the pastes onto a suitable substrate; drying at low temperature; and sintering at high temperature to get a consolidated layer. In the literature, one finds values for thicknesses of “thick films” that start with nanometers and go up to millimeters; normally, one finds 10–200 μm values, sometimes the values extend to mm.