A sensor is a device that measures a physical quantity and converts it into a signal which can be read by an observer or by an instrument. Sensors are broadly classified into physical sensors and chemical sensors. Physical sensors measure various physical quantities such as pressure, temperature, velocity, acceleration, flow, liquid level, magnetic field etc. Gas sensors are a type of chemical sensor able to convert the chemical properties of a volatile gas into detectable electrical signals.

1.1 Need for a Gas Sensor

With the massive industrialization there is an increase in pollutants and toxic gases in our environment. To preserve our environment there is an impelling demand of improved tools for monitoring chemical vapour in our ambience. A few of the areas where we need reliable gas sensors are listed below (Parthangal (2007)).

1. Detectors for chlorofluorocarbons and greenhouse gases; air quality measurement based on industrial and automobile wastage for environmental safety.

2. Detection and control of carbon monoxide, nitrous oxides, ammonia and volatile organic compounds (VOCs) like LPG for domestic and industrial safety.
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3. Breath analysis for diabetes and gastrointestinal disorders; alcohol detector for checking drunken drivers.

4. Aroma sensors during baking, roasting processes, freshness monitors for medical diagnostics of food processing zones.

5. Detectors for chemical and biological warfare agents like phosgene, chlorine, sarin, tabun etc. for national security and defense.

6. Hydrogen sensors, oxygen detectors, NO\textsubscript{x} and VOC detectors for aerospace applications.

1.2 Desirable Sensor Characteristics

The desired sensor characteristics of any material are given below:

1. Sensitivity: Sensor should be able to respond to minute concentration of gases.

2. Stability: Results should be reproducible with continuous operation for long time periods.

3. Selectivity: Sensor should be able to differentiate between the different gases.

4. Response: Response and recovery should be quick with the changes in the environment.

In addition to these requirements, commercial sensors should be cost effective, low power consuming and reliable as well (Parthangal (2007)).

1.3 Chemical Gas Sensors

Chemical gas sensor is a device that measures change in its conductance upon interaction with chemical vapour or gas. All chemical gas sensors detect, identify and measure gas concentration through electrical or optical signals. Human nose is a good sensor, it can detect and differentiate a large number of gases easily. However, it is unable to sense very low concentration of certain gas species as well as odourless gases, which demands the gas sensing device to fulfill the requirement.
1.3 Chemical Gas Sensors

1.3.1 Types of Chemical Gas Sensors

Chemical gas sensors are broadly classified as: solid state, catalytic bead, electrochemical, infrared and piezoelectric sensors. Solid state sensors consist of a semiconducting material deposited between two metallic electrodes on a substrate embedded with a heater which detect adsorbed gases on the surface of sensing element. Catalytic bead sensors employ a catalytic surface maintained at high temperatures around a temperature sensor, wherein rapid combustion of flammable gas molecules on the catalyst surface result in observable temperature changes. Electrochemical sensor consists of a sensing electrode and a counter electrode immersed in an electrolyte, where interaction of gas molecules with the sensing electrode results in a change in the measured current between the electrodes. Infrared sensors use IR radiation to thermally excite gas molecules and sense gases based on their absorption spectra. Sensors based on piezoelectric effect undergo a change in surface mechanical oscillation frequency upon interaction with gases. Each type of sensors has its own advantages and disadvantages depending upon the application. Solid state sensor having advantage for domestic and industrial safety; catalytic bead sensors in high temperature and harsh environment; electrochemical sensors for toxic gas detection; IR detectors for volatile organic compound (VOC) and surface acoustic wave (SAW) devices for chemical warfare agents etc. (Parthangal (2007)).

Since this thesis work focuses on the synthesis of zinc oxide (solid state metal oxide) gas sensors therefore, a detailed explanation of their design, sensing mechanism, advantages and applications will be discussed in the following sub sections.

1.3.1.1 Solid State Gas Sensor

During research work related to semiconductor p-n junctions, scientists found that these junctions were sensitive to environmental background gases. This was a problem at that time which was later on utilized to make a gas sensing device. In 1968, Taguchi marketed a simple semiconductor sensor for the detection of hydrocarbons, it was based on the powder of SnO₂. The intention was to provide an alternative to the catalytic bead sensor, which have the disadvantages like short life and burns out during process. In 1972, International Sensor Technology (IST) in Irvine, California introduced a solid state sensor for the detection of hydrogen sulfide in a range of 0-10 ppm. A few years later, IST developed the solid state sensors for more than 100 different harmful gases at low ppm levels which was a significant development in the field of sensors (Chou (2000)).
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kinds of sensors, solid state gas sensors are the most popular because of their excellent sensitivity, stability, vast range of detection, reliability, easy production and low manufacturing cost. Semiconducting metal oxides such as tin oxide $\text{SnO}_2$, tungsten oxide $\text{WO}_3$, zinc oxide $\text{ZnO}$, titanium oxide $\text{TiO}_2$ are widely used as the sensor element, owing to the fact that they present a chance for surface reactions involving molecular chemistry with a wide range of gases. Nowadays, solid state sensors are available for the detection of majority of harmful and toxic gases. Catalytic sensors consume the gas being detected during process and sensor eventually burns out. On the other hand in solid state gas sensor, gas simply adsorbs onto the sensor surface, which causes change in conductance of the material. When the gas disappears, the sensor returns to its original state. Thus no sensor material is consumed during the process and hence solid state gas sensors offer a long life. This is the main advantage of solid state sensor over the other sensor types which have short life span.

1.3.1.2 Conduction Model for Gas Sensing

It is a well known phenomenon that the adsorption and desorption of gas molecules on and from the surface of a metal oxide semiconductor causes a change in its electrical resistance, but the exact gas sensing mechanism is yet to be fully understood. The basic operational principle for conductometric gas sensor may be discussed as follows:

There exists a finite number of electron donors and acceptors on the surface of semiconducting metal oxide, adsorption of oxygen molecules from the environment result in an electronic charge transfer from the semiconductor forming oxygen species like $\text{O}^-$ and $\text{O}_2^-$. Due to this negative charge at the surface, a depletion region is created near the surface, which enhances the resistance of the semiconductor. When this semiconducting surface is exposed to gas, then interaction between the gas molecules and adsorbed oxygen ions modulates the conductivity of the space charge region, which is measured as an electric signal.

Figure 1.1(a) shows the schematic of a semiconducting metal oxide surface after adsorption of oxygen molecules from the surrounding medium. A few grains of powder in contact show the space charge region around the surface of each grain and in particular at the inter-granular contact. The space charge region being depleted of current carrier is more resistive than the bulk. Thus inter-granular contact provides most of the sample resistance.
1.3 Chemical Gas Sensors

Figure 1.1: Grains of semiconductor, showing how inter-granular contact resistance appears and is analyzed. Image adapted from Madou & Morrison (1995).

Figure 1.1(b) represents the band model of the same group of grains. It can be observed that the carriers must overcome the substantial energy barrier qV, in order to cross from one grain to other grain. Thus the current is proportional to the electron density $n_s$ with energy qV. Conductance $G$ is expressed as

$$G = G_0 e^{-qV/kT},$$

where $G_0$ is a proportionality constant accounting for all other less sensitive factors determining the conductance (Madou & Morrison (1995)).

The adsorption of oxygen molecules on the sensing surface is either through physisorption or chemisorption depending upon the operating temperature. At temperatures below 100°C physisorption occurs, with the weak van der Waal interaction between adsorbate and adsorbent. Most of the metal oxide gas sensors are operated at temperatures above 250°C in order to get noise free output. So, chemisorption is dominating at higher temperatures, wherein the oxygen molecules are connected via strong bonding to the semiconductor surface and form chemical bonds after electronic transfer. Every molecule approaching the surface can polarize and induce an equivalent dipole in the adsorbate to the surface. The energy of the system is represented as a function of adsorbate/adsorbent separation, d, by curve (a) in Fig. 1.2. This figure is Lennard-Jones representation of
physiosorption and chemisorption. In case of physiosorption, the system at zero energy with infinite $d$ develops a dipole-dipole attraction when adsorbate approaches the surface whereas develops a "billiard-ball" repulsion as $d$ approaches zero. Physiosorption, with its small heat of adsorption $\Delta H_{phys}$ represented by curve (a) in Fig. 1.2.

In Fig. 1.2, the curve (b) represents chemisorption. In this case adsorbate has substantial energy even at distance $d$, to account for the dissociation energy provided. However, when atoms approach the surface and strong chemical bonds are formed, the adsorbate energy becomes much more negative than that of physiosorption. The heat of chemisorption $\Delta H_{chem}$ can approach the heat of compound formation and in rare cases, exceed it.

Ionosorption is the process that predominately affects the phenomenon of gas sensing. In this case there is no local adsorbate-to-surface atom bonding, but the adsorbate acts as a surface state, capturing an electron or hole, and is held to the surface by electrostatic attraction. In gas sensors ionosorption of oxygen is very important, it can be ionosorbed in several forms: $O_2^-$, $O^-$ and $O^{2-}$. The high doubly charged adsorbed oxygen $O^{2-}$, is least expected for adsorbed species because such high charge on the ion may lead to instability unless the site
1.4 Role of Nanotechnology in Modern Research

Nanotechnology has opened the novel and challenging opportunities to the scientific fraternity for exploring new approaches to research. Nanotechnology has also encouraged interdisciplinary research due to several peculiar and attractive properties of nanostructures (structures that have at least one dimension between 1-100 nm). In electronic industry, with miniaturization of devices, millions
of components can be integrated into a single chip, reducing its cost, power consumption and provide faster operation. In the field of medical research nanotechnology is playing important role for curing patients, targeting and destroying cancer cells, and repairing damaged tissues. Nanoparticles of various kinds are regularly used in industrial processing for coating to prevent corrosion, chemomechanical polishing, fillers for conductive polymers and catalytic supports etc. There are several prototypes of nanoscale devices like sensors, actuators, lasers, transistors and optical sensors which have been successfully designed and fabricated. Still there are innumerable devices whose performance needs a face lift. So, it is necessary to develop innovative methods for nanoscale research in a cost effective manner (Parthangal (2007)).

1.4.1 Nanocrystalline Materials

The properties of any material decide its behaviour and application for which it is suitable. And the properties in turn are decided by its atomic structure, composition, microstructure, defects and interfaces of the material, which are regulated by the thermodynamics and kinetics during their synthesis. A recent paradigm of synthesizing and processing of advanced materials emphasizes the tailored assembly of atoms and particles, from the atomic or molecular scale to the macroscopic scale. Researchers show interest in nanostructured material because of its unique properties as compared to conventional material. Material in micrometer range have the same physical properties as that of the bulk materials. However, materials in the nanometer range may exhibit physical properties significantly different from that of bulk. For example, crystals in the nanometer range have a low melting point (the difference can be as large as 1000°C) and reduced lattice constants, since the number of surface atoms becomes a significant fraction of the total number of atoms or ions and the surface energy plays an important role in the thermal stability. Crystal structures stable at elevated temperatures can be stable at very lower temperatures in nanometer scale, so ferro-electrics and ferro-magnetics may lose their ferro-electricity and ferro-magnetism when the materials are shrunk to the nano-scale. Semiconductors can become insulators when the characteristic dimension is sufficiently small.

Nanomaterials can be made by top-down approach means from macroscale to nanoscale or by bottom-up approach means by assembly of atoms or particles. The bottom-up approach is indeed the strength of material chemistry. Therefore, the great attention has been paid to the chemical synthesis and pro-
cessing of nanostructured materials. There are three basic classes of aqueous reactions: acid/base, precipitation and reduction/oxidation reaction. The reactants of the materials can be solids, liquids or gases in any combination. A multi-element compound is called precursor and can be prepared by precipitation reaction. In precipitation reactions, solution of two or more electrolytes are mixed to form insoluble precipitate. In order to ensure the reproducibility of reactions, the synthesis parameters like temperature, pH, reactant concentration and time should be correlated with factors like supersaturation, nucleation and growth rates, surface energy, and diffusion coefficients. Chemistry is based on the manipulations of atoms and molecules, and chemical synthesis is used for the synthesis of nanostructured material very frequently. Bottom-up approach also promises a better chance to obtain nanostructures with less defects, more homogeneous chemical composition, and better short and long range ordering. This is because the bottom-up approach is driven mainly by the reduction of Gibbs free energy, so that produced nanostructures and nanomaterials are in a state closer to thermodynamic equilibrium state (Cao (2004)).

Nanostructures possess a large fraction of surface atoms per unit volume. The ratio of surface atoms to interior atoms changes dramatically if one successively divides a macroscale object to smaller pieces. This change might illustrate why changes in size to nanometer scale is expected to lead to unique changes in the physical and chemical properties of the materials. The total surface energy increases with the overall surface area, which is in turn strongly dependent on the dimensions of material. Enhancement in surface area of nanostructured materials, increases its surface energy tremendously and make them thermodynamically unstable. Surface energy reduction is one of the great challenges during the fabrication and processing of nanomaterials to prevent the growth in size of nanostructures. Thermodynamically a system can be stable only when it is in a state with the lowest Gibbs free energy. Therefore, there is a natural tendency for a solid or liquid to have minimum total surface energy. There are various mechanism to reduce the overall surface energy. For a given surface with a fixed surface area, the surface energy can be reduced through:

1. Surface relaxation in which the surface atoms or ions shift inwardly which occur more readily in liquid phase than in solid surface due to rigid structure in solids.

2. Surface restructuring i.e. through combining surface dangling bonds into strained new chemical bonds.
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3. Surface adsorption i.e. through chemical or physical adsorption of terminal chemical species onto the surface by forming chemical bonds or weak attraction forces such as electrostatic or van der Waals forces.

4. Composition segregation or impurity enrichment on the surface through solid-state diffusion.

At the overall system level, mechanisms for the reduction of overall surface energy include:

1. Combining individual nanostructures together to form large structures so as to reduce the overall surface area, if large enough activation is available for such a process to proceed.

2. Agglomeration of individual nanostructures without altering the individual nanostructures.

Specific mechanisms for combining individual nanostructures into large structures include:

1. Sintering, in which individual structures merge together.

2. Ostwald ripening, in which relatively large structures grow at the expense of smaller ones.

In general, sintering is negligible at low temperatures including room temperature, and becomes important only when materials are heated at high temperatures, typically 70% of the melting point of the material. Ostwald ripening occurs at a wide range of temperatures, and proceeds at relatively low temperatures when nanostructures are dispersed and have an appreciable solubility in a solvent (Cao (2004)).

Latest research is focused on the development of sensors with improved sensing capabilities, miniaturization of devices for low power consumption, improvement of data analysis method and low cost of production. The significance of nano-material in gas sensors research is that they have high surface to volume ratio which provides high surface area interaction with the gases, they have unique electronic properties enable rapid detectable signal changes and they can be integrated into miniature devices which will consume less power. There are many types of nanostructures of various metal oxide materials which have been studied
1.4 Role of Nanotechnology in Modern Research

for gas sensing applications including nanocrystalline thin films, porous membranes, one-dimensional structures such as nanorods, nanowires, nanotubes and nano belts etc. and have better sensing characteristics than the existing sensors (Parthangal (2007)).

1.4.2 ZnO and its Applications

Zinc Oxide has recently gained a lot of attention from scientific fraternity as a prospective future material. Now a days a lot of industrial manufacturing and fabrication is based on this material. This semiconducting metal oxide is a widely studied transition metal oxide owing to its peculiar properties which makes it useful for a number of applications.

Moreover, it is bio-safe and bio-compatible and is preferred in biomedical applications. Zinc oxide has been synthesized in a variety of morphological distinct nanostructures. Its properties not only depend on the nanoscale dimensions but also on the morphology of the material. The combination of these morphologies may give the interesting results (Jagadish & Pearton (2006)).

1.4.2.1 Crystal Structure and Properties

Zinc oxide has a hexagonal wurtzite structure as shown in Fig. 1.3.

**Figure 1.3:** The hexagonal wurtzite structure of ZnO. Image adapted from Jagadish & Pearton (2006).
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<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>0.324 nm</td>
</tr>
<tr>
<td>$c_0$</td>
<td>0.520 nm</td>
</tr>
<tr>
<td>$a_0/c_0$</td>
<td>1.602</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$^\circ$C</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>0.6, 1-1.2</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>3.37 eV</td>
</tr>
<tr>
<td>Exciton binding energy</td>
<td>60 meV</td>
</tr>
</tbody>
</table>

Table 1.1: Properties of wurtzite ZnO (Pearton (2005)).

In the hexagonal wurtzite structure of ZnO, O atoms are shown as large spheres, Zn atoms as smaller black spheres. One unit cell is outlined for clarity. This hexagonal lattice is characterized by two sub-lattices of Zn$^{2+}$ and O$^{2-}$, such that each Zn ion is surrounded by a tetrahedra of O ions, and vice-versa. This tetrahedral coordination leads to polar symmetry along the hexagonal axis. This polarity is a background of number of properties of ZnO, such as its piezoelectricity and spontaneous polarization, and is also responsible for crystal growth, etching and defect generation. The tetrahedral coordination also indicates the $sp^3$ covalent bonding in the compound. However, the Zn-O bond also possesses very strong ionic character, and thus ZnO lies on the borderline between covalent and ionic compound. In addition to wurtzite phase, ZnO is also known to crystallize in the cubic zinc blende and rocksalt structures (Jagadish & Pearton (2006)). The basic properties of zinc oxide are given in Table 1.1.

1.4.2.2 Applications

ZnO is a widely used material, it is used in manufacturing process of paints, cosmetics, pharmaceuticals, plastics, batteries, electrical equipment, rubber, soap,
1.5 Literature Survey

textiles, floor coverings etc. ZnO based nanostructures like nanowire arrays have
great applications including flat screen displays, field emission sources, gas sen-
sors, biological sensors and UV light emitters and switches (Jagadish & Pearton
(2006)). Epitaxial layers and single crystals are important for the development
dof piezoelectric, optoelectronic and spintronic devices. ZnO as a transparent
thin films is important for solar cells, gas sensors, displays and wavelength se-
lective applications. ZnO nanoparticles have successfully been used as improved
sunscreens, paints and coating etc. (Jagadish & Pearton (2006)). Moreover, its
irradiation hardness makes it a suitable candidate for space research applications.
Thus, future where ZnO based devices become part of our daily lives is already
approaching reality.

1.5 Literature Survey

1.5.1 Historical Background

Research in the field of chemical gas sensors was initiated in the 1950s, Brattain
and Bardeen and Morrison have observed the change in conductance of semi-con-
ductors due to variation in surrounding gases [Brattain & Bardeen (1953), Morri-
son (1953), Morrison (1955)]. However, it was not taken seriously because results
were not reproducible. In 1962, Seiyama and co-workers reported the change
in electrical conductivity due to adsorption and desorption of gas molecules in
case of polycrystalline zinc oxide thin films (Seiyama et al. (1962)). And it was
Taguchi, who successfully made the first commercial tin oxide based gas sensor
in 1960s which is still very popular (Taguchi (1971)). He chose SnO\textsubscript{2} as a sensor
material because it is chemically inert and avoids oxidation in air and other re-
actions. Results obtained by him, were reproducible and stable as compared to
germanium etc., where oxidation would slowly change the device characteristics.
This sensor is marketed by Figaro Inc. Since 1970, there has been a number of
reports on novel sensing techniques and development of technologically advanced
sensing techniques for various applications.

1.5.2 Different Approaches for Gas Sensing

There are different approaches available for gas sensing such as amperometric
gas sensors, acoustic wave sensors, optical fiber sensors, polymer film gas senors,
bioanalytic gas sensors and metal oxide gas sensors etc. [Seiyama (1988, 1990),
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1.5.3 Types of Metal Oxide Gas Sensors

Basically three types of metal oxide based sensors including sintered ceramic block, thick film type and thin film type have been introduced for the detection of harmful gases [Sayago et al. (1995), Jin et al. (1998), Dieguez et al. (1999)]. A conventional powder processing procedures is used for the fabrication of sintered ceramic devices (Baik et al. (2000)). The paste of SnO$_2$ powder, inorganic additives and organic binders is printed over an alumina ceramic tube having two gold electrodes and a heater is embedded in the tube, this is actually Taguchi-type sensor element (Taguchi (1971)). Sensor element can also be sintered into a pallet shape (Du (2007)).

Sintered ceramic sensors elements can be fabricated with a very low cost but they have disadvantages such as high power consumption and large sensor to sensor performance variation within production lots. To overcome these issues new thick film techniques for planar structure gas sensors have been developed. There are other reported techniques along with screen printing for thick films which include painting, tape casting and dip coating (Du (2007)).

The third type of sensors are of thin film type, where thickness of the materials is in the range of 5 nm - 1µm and particles are very closely packed [Jin et al. (1998), Ivanov et al. (2004)]. The basic requirements of good sensor such as portability, low cost, low power consumption and short response time are fulfilled by thin film gas sensors (Du (2007)). The reported techniques for the fabrication of thin films are thermal evaporation [Pan (2001), Dai et al. (2003)], sputtering [Poopova et al. (1990), Stedile et al. (1990), Soares et al. (1992)], ion plating (Minami (1999)), spray pyrolysis [Chen et al. (1995), Matko (1999)], metal organic chemical vapour deposition (Bruno et al. (1994)), rheotaxial growth and thermo oxidation [Sberveglieri et al. (1990), Bontempi et al. (2001), Comini et al. (2004)]
and sol-gel process [Presecatan et al. (1992), Turkov & Ivanda (1997), Morazzoni et al. (2001), Du (2007)] etc.

1.5.4 Types of Material States for Gas Sensing

Materials such as amorphous-like state, glass state, nanocrystalline state, polycrystalline state, and single crystalline state can be used as resistive type gas sensors [Sberveglieri et al. (1992), Eranna et al. (2004), Korotcenkov (2007b), Korotcenkov (2007a)]. Amorphous and glassy state materials are not favourable as a gas sensor at high temperature [Tsiulyanu et al. (2004), Korotcenkov (2007b)]. Among all types of materials, nanocrystalline and polycrystalline materials have the greatest importance because of their special properties like high surface area due to small crystallite size, low cost design technology, and stability [Sberveglieri et al. (1992), Schierbaum et al. (1992), Gopel & Schierbaum (1995), Barsan et al. (1999), Kohl (2001), Korotcenkov (2007b)]. Single crystalline materials are stable enough to be used as gas sensors but due to high cost and technological challenges related to their deposition their use in gas sensors is limited (Korotcenkov (2008)).

1.5.5 The Role of Sensor Geometry and Contacts

In literature many sensor geometries have been reported to measure the sensing response of semiconductor metal oxide. Compressed pellet with metal electrodes on each face have been reported by McAleer et al. (1987) and Blaser et al. (1999). In case of thin/thick film on a substrate, number of planar shapes of electrode assemblies have been reported such as rectangular, inter-digital and circular etc. [Williams & Pratt (1995), Vilanova et al. (1998), Capone et al. (2001), Schmidt-Zhang & Guth (2004) and Toohey (2005), Korotcenkov (2008)].

The choice of metal for making electrical contacts for sensing is very important for a good sensor. Platinum and gold are the widely used metals for electrical contacts since they have good ohmic contact with most of the metal oxides (Faglia et al. (1998)).

Vilanova et al. (1998) have reported that the sensitivity of a sensor increases with the electrode spacing if the electrodes were underneath the film, however decreases with the electrode spacing if the electrodes are deposited over the film. In their study, they also concluded that if electrode spacing is reduced to less than the film thickness, it is possible to detect a less reactive gas. Williams &
Pratt (1995) have reported that if two or more pairs of contacts with different separations are made on the sensor, then the conductance measured between any two pairs under a given set of conditions will be related by a known function, even though the individual values, will of course change with the test gas concentration.

1.5.6 The Role of Grain Dimensions for Gas Sensing

Yamazoe and others showed that by reducing crystallite size, performance of ceramic type sensors increases [Xu et al. (1991), Yamazoe (1991b), Yamazoe (1991a), Sakai et al. (2001), Rothschild & Komem (2004), Abe et al. (2005), Kaur et al. (2005), Timmer et al. (2005)]. A sensor consists of grains interconnected to neighbours by necks. Adsorbed oxygen molecules on the surface of the grains extract the electrons from the conduction band and trapped electrons at the surface in the form of ions producing band bending and an electron depleted region called space charge layer. When the dimension of particles is close to or less than double the thickness of the space charge layer, the sensing response of the sensing material enhances significantly. Xu et al. (1991) explained the phenomena by semiquantitative model, which is depicted schematically in Fig.1.4. In semiconducting metal oxide thick film gas sensors, the part of resistance produced is due to the intergranular contacts. The effect of particle size on gas sensing response has been reported by many researcher at various times. The resistance contribution from the inter-granular contacts is of three types; grain boundary control, neck control and grain control. The conductance is controlled by the grain boundary, if the particle diameter (D) is much greater than twice the Debye length (L) i.e. $D \gg 2L$. Then conductivity depends upon the inner mobile charge carriers. In this case the conductivity is not sensitive to the charges acquired from surface reactions. The conductance is controlled by the necks, if the particle size is decreased i.e. $D \geq 2L$. In this case space charge layer region around neck forms a conduction channel. The conductivity depends upon the boundary barriers as well as cross section area of these channels. So, it is sensitive to reaction charges. Hence, particles are sensitive to environment gases. The conductance is controlled by the grain, if the particle diameter becomes comparable to the Debye length i.e. $D < 2L$. In this case particles are fully depleted of mobile charge carriers. Few charges from surface reactions change the conductivity significantly. In the other words, if the size is small then material becomes very sensitive (Sun et al. (2012a)). Xu’s model, is used to propose new materials with good sensing performances (Xu et al. (1991)).
Figure 1.4: Schematic model of the effect of crystallite size on the sensitivity of the metal oxide gas sensors. Image adapted from Du (2007).
1.5 Literature Survey

1.5.7 The Role of Morphology and Porosity

Wang and co-workers reported thick film sensors based on nanorods. The nanorod sensors can detect very low ppm of ethanol and H$_2$S. According to them sensing response depends upon the amount of active sites for oxygen and the reducing gases on the surface of the sensor materials (Wang et al. (2006a)). Numerous efforts have been made to improve the sensitivity of gas sensors. The rate of diffusion, depends on the porosity of the surface so it plays a critical role in improving the sensitivity (Sakai et al. (2001)). Although many methods have been reported to synthesize monodisperse nanoparticles of metal oxides [He et al. (1990), Gu et al. (2003), Ahn et al. (2004), Jiang et al. (2005), Vuong (2005)] but small size of nanoparticles are not stable which may easily congregate and grow up under heating conditions (Yin et al. (2009)). Also during film coating they are compacted too much which decreases diffusion rate. The porous nanostructures of nanowires, nanorods, nanospheres etc. can overcome this problem. Porous materials give excellent performance in gas sensing because they have large surface area, relatively more reactive sites and formed loose film structures (Sun et al. (2012b)).

In conductometric gas sensor, one dimensional metal oxides have the advantages like high surface to volume ratio, Debye length is comparable to the lateral dimensions and providing a long semiconducting channel. Nanowires are one dimensional nanostructures which have diverse applications [Kolmakov & Moskovits (2004), Wang & Song (2006)]. Nanowires of ZnO [Wan et al. (2004), Liao et al. (2007b), Ahn et al. (2008)], SnO$_2$ [Choi et al. (2008), Qin et al. (2008), Wang et al. (2008a)], In$_2$O$_3$ [Xu et al. (2008b), Moon et al. (2009)] and TiO$_2$ [Francioso et al. (2008), Thanh Le et al. (2009)] etc. are highly potential sensing materials. Nanowires can be smooth or porous, but porous nanowires have advantages over the smooth one, because they have high surface to volume ratio which allows adsorption not only on the surface but also throughout the bulk. Porous nanowires of SnO$_2$ have been prepared and exhibited wonderful sensing behaviour towards ethanol, CO and hydrogen [Wang et al. (2003b), Jiang et al. (2004), Sun et al. (2012b)]. Guo et al. (2008) have prepared the nanowires of CdO for gas sensing application, due to their porous structure, response of these nanowires was really quick, they are capable of detecting even few ppm, high signal to noise ratio and they were selective to nitrogen oxide.

Another kind of one dimensional nanostructures, which is widely applied in various fields including gas sensor is nanotubes. Nanotubes have a large sur-
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face area and porosity because of their hollow structures (Levy-Clement et al. (2009)). Synthesis of nanotubes is relatively complicated as compared to that of nanowires. Basically metal oxide nanotubes can be prepared by hydrothermal method [Hoyer (1996), Kasuga et al. (1998)], anodizing process or template method [Lee et al. (2006), Lee & Smyrl (2008)], and sol-gel process (Wang et al. (2008c)). Nanoporous nanotubes of SnO$_2$ have been synthesized by sol gel template synthetic technique. Although the nanotubes produced have excellent sensing responses but their synthesis is complex and production is limited. Multiwall carbon nanotubes (MWCNT) are used as the template in the synthesis of SnO$_2$ nanotubes by wet chemical method (Sun et al. (2005)) and these nanotubes have more porosity than the nanotubes prepared by sol gel template (Jia et al. (2009)).

Although the single crystalline materials have low response as compared to polycrystalline material, but have more stability than the polycrystalline material. So there is a demand of the material which can make a balance between the high sensing response and stability. Nanosheets, which are porous have the characteristic of single crystalline structure and have high surface area [Liang et al. (2004), Zhang et al. (2007), Sun et al. (2012b)]. Therefore we can use these porous nanosheets as a gas sensor for good sensing response and for good stability. Single crystalline nanowires can be a good balance between high response and stability, but its production is difficult at large amount. However, porous nanosheets are relatively easy to synthesize, have reported the single crystalline ZnO nanosheets which shows good sensitivity, stability, and quick response and quick recovery time (Liu et al. (2009)).

Porous and hollow oxide structures are considered as a suitable for gas sensing because of its good diffusion rate [Zhang (2006), Gou et al. (2008)]. As porous nanospheres may adsorb the gases on the outer and inner surfaces, therefore have been widely used in gas sensing [Li (2004), Park et al. (2009), Sun et al. (2012b)]. Wang et al. (2003a) and Guo et al. (2008) have reported the hollow nanospheres of SnO$_2$ and In$_2$O$_3$ respectively for gas sensing application.

1.5.7.1 Agglomeration

In case of nano materials agglomeration and aggregation are expected to occur everywhere in nature. Metal oxides are usually agglomerated during synthesis [Barsan et al. (1999), Korotcenkov (2005)]. In gas sensing studies effect of agglomeration has not been studied properly. Agglomeration is well observed during the synthesis of thin film and bulk. In many cases smaller particles of powder
agglomerates into big particles during synthesis (Chabanis et al. (2003)). They observed that during ceramic synthesis agglomerates are more porous and larger in size than those formed during thin film synthesis. Agglomeration formation in ceramic as well as in thin film metal oxides are the two types of emerging aggregations (Gadomski et al. (2005)). In case of ceramic materials there is diffusion controlled aggregation, in which the attachments of particles and clusters occur instantaneously at first contact. Whereas, in thin film it is chemical reaction controlled aggregation (Korotcenkov (2008)). Anderson & Lekkerkerker (2002) suggested that the incorporation takes place in the form of a particle or some cluster of particles with different types of microstructures.

1.5.8 ZnO Based Gas Sensor

Semiconducting oxides such as ZnO, SnO$_2$, TiO$_2$ and ZnS exhibit improved properties in their nanosize structures [Wang et al. (2003a), Liu et al. (2005), Jing & Zhan (2008), Fang et al. (2009)]. Among these ZnO nanostructures attracted the most of the attention because of their low toxicity, good thermal stability, good oxidation resistibility, good biocompatibility, large surface area and high electron mobility [Wei (2008), Gupta et al. (2010)]. ZnO has the ability to have lot of variation in their morphology. It can be morphed into interesting morphologies like nanorods, nanotubes, nanobelts, nanoneedles, nanoparticles, nanocombs, and nanodisks etc. simply by the variation in their synthesis recipes [Wang & Muhammed (1999), Kong & Wang (2003), Wei et al. (2006), Bhatti et al. (2006), Zhou et al. (2008), Chang et al. (2009), Wei et al. (2011)]. ZnO nanostructures have been used widely in various applications including, field-effect transistors, light emitters, lasers, solar cells and gas sensors [Fang et al. (2009), Zhang et al. (2009), Gullapalli et al. (2010), Pachauri et al. (2010)]. Several properties are favourable for gas sensing and are widely used. Gas sensors are based on the conductance change due to adsorption on surface of ZnO nanomaterials (Kim & Yong (2011)). Wang and co workers observed that pressure sensor are based on piezoelectric property of ZnO (Wang et al. (2008b)). Due to bio-compatibility and non-toxicity of ZnO, it is also used as biosensors (Ahmad et al. (2010)).

Environment and human life is tremendously effected by the volatile organic compounds (VOCs) in the ambiance. Exposure to VOCs can cause number of health related problems such as throat and lung problem, eye irritation and cancer etc. Therefore, for human safety several attempts have been tried to overcome these problems. Therefore many thick and thin films gas sensors have been fab-
1. Introduction and Literature Review

ricated to detect these VOCs like ethanol, methanol, acetone, hydrocarbon and LPG etc. (Kanan et al. (2009)). Researcher have reported various high sensing results, but high selective response still remains a great challenge.

Heiland (1982) has reported the gas sensing behaviour of ZnO. It has been observed that the conductivity of thin layers of ZnO in vacuum is more than in an atmosphere. Therefore conductivity changes on the surface of ZnO crystals has been used as the gas sensors. The electrical conductivity changes of ZnO single crystals in gas air mixtures at 300-500°C using a constant voltage source has been reported by Bott et al. (1984). The sensing response of single crystal of ZnO for H₂ and CO were maximum at 400°C. ZnO single crystal was found insensitive to CH₄ (Bott et al. (1984)) but conductivity of polycrystalline oxide was more affected by CH₄ (Jones et al. (1984)). Rao & Rao (1999) have reported the thick film of zinc oxide as a gas sensor. The pure and doped ZnO have been deployed as thick films for the ammonia sensing. Among these palladium doped zinc oxide exhibited good sensitivity and response time to ammonia at room temperature. Mitra et al. (1998) have reported the gas sensing response of chemically deposited zinc oxide thin film. As grain size is the major factor which affects sensing properties, some groups have synthesized nano sized zinc oxide and used it for gas sensing. Dong et al. (1997) have reduced the operating temperature of a sensor and enhanced the sensitivity of ZnO by using arc plasma method for the synthesis of nano-ZnO. It was found that nano-ZnO showed higher sensitivity to LPG and C₂H₂ than H₂ and CO. Fe and Ag doped nano-ZnO showed excellent sensitivity and selectivity to H₂ against C₂H₂, CO and LPG and response time with less than 15 sec at 150°C. Chang et al. (2002) have reported the effect of film thickness on the sensing response. They used rf sputtering for the thin film deposition and deposited different thickness of the material on SiO₂/Si wafer. The best sensing response was observed for the thinnest film (65 nm). Physical and chemical properties of the materials can be altered by the introduction of dopant. Dopant creates defects in the material which influences the gas sensitivity and selectivity of the semiconducting oxides. Thus, various researchers have reported numerous papers on the effect of doping on gas sensitivity of zinc oxide nanostructures. Aluminium is one of the important dopant to enhance the performance of zinc oxide gas sensor. Nanto et al. (1993) have used the Al doped ZnO to check the freshness of seafood. Sputtered thin film of Al doped ZnO was effective for sensing seafood odour selectively. Mukhopadhyay et al. (1996) has used Al doped ZnO as a H₂ sensor. In literature dopant like Tin (Nanto et al. (1996)), Molybdenum (Dayan et al. (1998)), Calcium (Inoue & Miyayama (1998)) and
## 1.5 Literature Survey

<table>
<thead>
<tr>
<th>Detecting Object</th>
<th>Sensitivity</th>
<th>Detection Limit</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trimethylamine</td>
<td>7</td>
<td>1 ppm</td>
<td>Nanto et al. (1992)</td>
</tr>
<tr>
<td>O₃</td>
<td>-</td>
<td>49.8 Pa</td>
<td>Martins et al. (2004)</td>
</tr>
<tr>
<td>Alcohol</td>
<td>50 ppm</td>
<td>8.5</td>
<td>Jiaqiang et al. (2005)</td>
</tr>
<tr>
<td>Butane</td>
<td>-</td>
<td>100 ppm</td>
<td>Mazingue et al. (2005)</td>
</tr>
<tr>
<td>H₂</td>
<td>2.6 %</td>
<td>10 ppm</td>
<td>Wang et al. (2005)</td>
</tr>
<tr>
<td>LPG and Ethanol</td>
<td>ppm</td>
<td>1</td>
<td>Baruwati et al. (2006)</td>
</tr>
<tr>
<td>H₂S</td>
<td>78.7 %</td>
<td>0.05 ppm</td>
<td>Wang et al. (2006b)</td>
</tr>
<tr>
<td>NO₂</td>
<td>1 ppm</td>
<td>1.8</td>
<td>Ghimbeu et al. (2007)</td>
</tr>
<tr>
<td>H₂S</td>
<td>-</td>
<td>100 ppm</td>
<td>Liao et al. (2007a)</td>
</tr>
<tr>
<td>LPG</td>
<td>0.2 vol.%</td>
<td>31%</td>
<td>Shinde et al. (2007)</td>
</tr>
<tr>
<td>CO</td>
<td>-</td>
<td>2 ppm</td>
<td>Wagner et al. (2007)</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>1.6</td>
<td>100 ppm</td>
<td>Jing &amp; Zhan (2008)</td>
</tr>
<tr>
<td>NO</td>
<td>-</td>
<td>100 ppm</td>
<td>Farmakis et al. (2008)</td>
</tr>
<tr>
<td>LPG</td>
<td>200 ppm</td>
<td>2700 %</td>
<td>Navale et al. (2008)</td>
</tr>
<tr>
<td>Acetone</td>
<td>3.8</td>
<td>1 ppm</td>
<td>Qi et al. (2008)</td>
</tr>
<tr>
<td>NO₂</td>
<td>10</td>
<td>0.5 ppm</td>
<td>Ahn et al. (2009)</td>
</tr>
<tr>
<td>NO₂</td>
<td>100</td>
<td>0.2 ppm</td>
<td>Jun et al. (2009)</td>
</tr>
<tr>
<td>Ethanol</td>
<td>11</td>
<td>1 ppm</td>
<td>Li et al. (2009)</td>
</tr>
<tr>
<td>LPG</td>
<td>17 %</td>
<td>0.1 vol %</td>
<td>Lokhande et al. (2009)</td>
</tr>
<tr>
<td>CO₂</td>
<td>22.5</td>
<td>1000 ppm</td>
<td>Lupan et al. (2009)</td>
</tr>
<tr>
<td>Triethylamine</td>
<td>6</td>
<td>1 ppb</td>
<td>Lv et al. (2009)</td>
</tr>
<tr>
<td>NH₃</td>
<td>-</td>
<td>60 ppb</td>
<td>Wang et al. (2009)</td>
</tr>
<tr>
<td>CH₄</td>
<td>-</td>
<td>100 ppm</td>
<td>Wang et al. (2009)</td>
</tr>
<tr>
<td>CO</td>
<td>32,000 %</td>
<td>-</td>
<td>Wei et al. (2009)</td>
</tr>
<tr>
<td>Methanol</td>
<td>-</td>
<td>10 ppm</td>
<td>Zhang et al. (2009)</td>
</tr>
<tr>
<td>O₂</td>
<td>0.15</td>
<td>1.4 ppm</td>
<td>Park et al. (2010)</td>
</tr>
</tbody>
</table>

*Table 1.2: Gas sensing literature of ZnO (Wei et al. (2011)).*
1. Introduction and Literature Review

Lanthanum (Stambolova et al. (2000)) have also been studied for improving the gas sensing performance. For highly sensitive and good selective measurement of ethanol, Nanto et al. (1996) used SnO$_2$ doped ZnO thin films. Sensing response of Mo doped thick films towards H$_2$, CO and CH$_4$ has been investigated by Dayan et al. (1998). A small literature survey about ZnO nanostructure based sensors is shown in Table 1.2.

1.6 Outline of Current Thesis

A large volume of literature is available on gas sensing materials, their processing and applications. In spite of that there is enough scope for study on gas sensors related to processing of material and improvement in sensor performance. Nature of material, crystallite size, morphology, additives etc. are some of important parameters which effect the performance of a gas sensor. In case of pure materials, crystallite size and morphology play crucial role in controlling the sensor behaviour.

In this thesis work my prime aim is to synthesize the various morphologies of ZnO for improving its gas sensing characteristics. More specifically in this work I have altered the morphology for the improvement in gas sensing, by varying various parameters like reaction temperature, sintering temperature, pH of the solution, precursor solution and surface activation of oxide material. The detail of layout of my thesis work is listed in the following text.

1. The focus of 2$^{nd}$ Chapter is on the experimental details and characterization techniques. When material is synthesized then it is necessary to analyze its structural and morphological properties. I have discussed briefly about characterization techniques such as XRD, FESEM and TEM, a gas sensing chamber and a testing unit. All components of gas testing unit like gas sensing chamber, sensor heater and sensor holder have been designed and developed in the lab.

2. 3$^{rd}$ Chapter deals with the chemical synthesis of zinc oxide nanostructures by varying reaction temperature during precipitation. The effect of sintering on nanostructure growth have also been investigated. The material characterization results clearly indicate that the formation of zinc oxide nanorods and nanoparticles is reaction temperature dependent. The sensors fabricated out of these powder indicated their response to be dependent on morphology and particle size.
3. In the previous chapter the effect of morphology and particles size on the gas sensing behaviour has been investigated. 4\textsuperscript{th} Chapter deals with the change in morphology by varying pH of the solution. I have morphed the nanorods into nanoparticles by varying pH of the solution from pH 8 to pH 11. From pH 8 to pH 10 nanorods of different dimensions have been found and at pH 11 these nanorods completely changed to nanoparticles. It was found from this study that the sensing behaviour is different for different morphology of ZnO.

4. In 5\textsuperscript{th} Chapter I have investigated the effect of precursor solution viz. zinc nitrate, zinc chloride and zinc acetate on the morphology of zinc oxide. By changing precursor solution I have observed that nanorods morphed into hexagonal prism geometry. Further I have investigated the sensing behaviour of synthesized morphologies.

5. High energy nuclear irradiations cause damage in the bulk of material through which they traverse. Semiconductor devices are prone to irradiation damage and devices become dis-functional if damage is irreversible. To check the ruggedness of fabricated ZnO sensor it was subjected to high energy ion irradiation. In 6\textsuperscript{th} Chapter I investigated the effect of 100 MeV of O\textsuperscript{7+} ion with different fluences on the sensing behaviour of the zinc oxide nanorods. In this investigation it was found that sensing behaviour is stable after irradiation.

6. In 7\textsuperscript{th} Chapter an attempt was made to modify the surface of zinc oxide nanorods for sensor improvement. I have activated the surface of zinc oxide nanorods with different percentages of tin oxide. With this activation I have found a change in its morphology which enhances its gas sensing response significantly.

All these issues are elaborately discussed in the following chapters.
1. Introduction and Literature Review