1.1 Sensor

Sensor is a device that produces a measurable change in their output for a particular input stimulus. The variation in output signal is typically proportional to the strength or concentration of input stimulus.

Determined by the type of input stimulus, sensors can be broadly classified into three. They are:-

1) Physical sensors, for physical stimulus like temperature, pressure, flow rate, stress, strain, position, particles or force etc.

2) Chemical sensors for chemical stimulus including both quality and quantity of a chemical substance like ethanol, carbon monoxide, gasoline, or other molecules, in either solid, liquid or vapour state.

3) Biosensors for biologically active substances, cellular like toxic plague bacteria or anthrax spores; supra-molecular like flu viruses etc. Sometimes biosensors are considered a subset of chemical sensors.
There are six sensor categories, typically classified according to the energy transduced by it. They are optical (radiation), mechanical, thermal, magnetic, electrical, electronic, chemical and biological. There is not a single sensing technology that can successfully detect everything of interest in all possible environments. Instead, selecting the optimum sensing scheme from a group of technologies could be the best to deal with a sensing need.

Sensor technology is now relevant in almost all aspects of life including safety, precaution, scrutiny, monitoring, production, industry, medicine, purity and understanding. Sensors could have an important role in the intelligent automatic control of a large number of processes ranging from microwave cooking to the efficient combustion of cryogenic engines. They are initially developed in Japan for devices such as gas leak alarms and measuring instruments. They are also central to public health wherein utilised for diagnostic, monitoring and critical care. The successful implementation of a sensor is determined by the performance, cost, reliability, long term stability, repeatability etc.

1.1.1 Gas Sensor

Gas sensors are transducers that detect the presence of particular gas molecules in its ambient by producing a physical or chemical change – magnitude of change generally proportional to the concentrations of the gas and or time of exposure.

The main features of a gas sensor are:

- Sensitivity – showing large response to a typical gas under consideration
- Selectivity – showing response only to a predetermined gas
Introduction

- Swiftness – showing immediate response on exposure to a gas
- Chemical inertness – not creating any physical or chemical change on the stimulant gas
- Stability – towards ageing, frequent use, operating temperature, humidity etc.

However, it is observed that all the practical sensors lack many of these features to a certain extent. Even some type of gas sensors get impaired after a single use. Loss of accuracy, corrosion, noise, gain error, etc are some other common problems faced by real sensors.

The idea of gas sensor was first materialised during 1910. The development of sensor technology has been in a slow pace until the recent decades. Owing to recent consciousness in environmental pollution, there is a growing need for reliable and inexpensive gas sensors and monitoring systems for industrial process and production areas.

Gas sensors have variety of objectives like the detection of humidity (Padmanathan et al, 2010), ethanol (Mishra et al, 2002), methanol (Patel et al, 2003), and gases like ozone (Aguir et al, 2002), H₂ (Antonin et al, 2013), N₂, chlorine, O₂, CO, NO₂ (Rakesh et al, 2010), H₂S (Ramesh et al, 2013), acetone vapour (Marco et al, 2010), inflammable organic gases like methane, LPG (Mishra et al, 1998), butane (Sumati et al, 2013; Boon and Soon_Don, 2005, p 125-129), pentane, and also for monitoring air pollutants, smoke (Yuan Liu et al, 2013) and automobile expellants (Viricelle et al, 2012).
Earlier gas sensors were based on catalytic beads. The catalytic bead sensor (Krebs et al, 1993) consist of two coils of fine platinum wire each embedded in a bead of alumina, connected electrically in a Wheatstone bridge circuit. One of the coils is impregnated with a special catalyst which promotes oxidation while the other is treated to inhibit oxidation. Current is passed through the coils so that they reach a temperature at which oxidation of a gas readily occurs at the catalysed bead (500-550°C). Passing combustible gas raises the temperature further which increases the resistance of the platinum coil in the catalysed bead, leading to an imbalance of the bridge. This output change is linear for most gases up to and beyond 100% LEL and response time is a few seconds to detect alarm levels around 20% LEL. At least 12 % oxygen by volume is needed for the oxidation.

The main disadvantages with catalytic type sensors are

i. Catalyst poisoning – because of the direct contact of the gas with the catalytic surface it may get deactivate in certain gas ambiance and

ii. Sensor drift – decreased sensitivity may occur depending on operating and ambient conditions.

Later infra-red point sensor (David et al, 1992) came into scene where the presence of combustible gas will reduce the intensity of the sample beam in comparison with the reference beam. The difference between intensity of these two signals being proportional to the concentration of gas present in the measuring path is utilised for gas detection. The system is very complicated and is not giving much qualitative idea on the gas being sensed.
Now there are a large number of technologies and materials utilised for sensing gases. They include methods like thermal conductivity (Pascal et al., 2004), capacitance (Tatsumi et al., 1998), work function (Burgmair et al., 2003), optical (Martucci et al., 2003) and infrared absorption, photo ionisation (Ashih et al., 2003).

Material categories include ceramic type (Ralf et al., 2013), single crystal semiconductor (Manmeet et al., 2008), electrochemical cell (Werner W., 1987), dye and pigments (Jin H.B. et al., 2008), solid state- pellet type (Ji Haeng Yu et al., 2001), solid state- thin and thick films, polymer type (Chi-ju et al., 2013), acoustic method (Arsat R. et al., 2009) and carbon nanotubes (Marek T., 2006).

Apart from these the gas chromatographs that use analytical columns, mass spectrometers that identify molecules through characteristics variable deflections from a magnetic field etc are some complex methods for identifying gases.

All of the methods mentioned above have advantages as well as disadvantages. Many of them have limitations like high maintenance cost, slow response time and huge size. Newer sensors built by micro-fabrication technique have the advantage of small size, light in weight and low power consumption. Another important factor that determines the viability of a sensor is the production cost.

Some major advantages and disadvantages of common gas sensor materials are given as table 1.1 (Xiao Lin et al., 2012). The major fields of their applications are also mentioned.
Table 1.1 Advantages and disadvantages of common gas sensor materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Application fields</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal oxide semiconductors</td>
<td>Low cost</td>
<td>Relatively low selectivity</td>
<td>Both industrial and domestic use</td>
</tr>
<tr>
<td></td>
<td>Short response time</td>
<td>Sensitive to environmental factors</td>
<td></td>
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<tr>
<td></td>
<td>Wide range of target gases</td>
<td>High energy consumption</td>
<td></td>
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<tr>
<td></td>
<td>Long life span</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>High sensitivity</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>Reversible</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Detect few ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>Polymer</td>
<td>High sensitivity</td>
<td>Instability due to ageing</td>
<td>Chemical industries,</td>
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<tr>
<td></td>
<td>Low fabrication cost</td>
<td>Irreversibility</td>
<td>storage places,</td>
</tr>
<tr>
<td></td>
<td>Simple design</td>
<td>Poor selectivity</td>
<td>indoor air monitoring</td>
</tr>
<tr>
<td></td>
<td>Low power consumption</td>
<td></td>
<td></td>
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<tr>
<td>Carbon nanotubes</td>
<td>Ultra sensitive</td>
<td>Complicated fabrication</td>
<td>Detection of partial discharge</td>
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<tr>
<td></td>
<td>Large adsorptive capacity</td>
<td>High cost</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Quick response</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>High surface-volume ratio</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>Miniature</td>
<td></td>
<td></td>
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<tr>
<td>Moisture absorbing material</td>
<td>Low cost</td>
<td>Irreversible in high humidity</td>
<td>Humidity monitoring</td>
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<td></td>
<td>High stability to water vapour</td>
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<tr>
<td>Optical methods</td>
<td>Long life time</td>
<td>High cost</td>
<td>High end scientific applications</td>
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<tr>
<td></td>
<td>No environmental factors</td>
<td>Tidious fabrication</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Stable</td>
<td>Heavy in size</td>
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<tr>
<td>Calorimetric methods</td>
<td>Stable</td>
<td>Poor selectivity</td>
<td>Petrochemical plants and</td>
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<tr>
<td></td>
<td>Low cost</td>
<td>Risk of catalyst poisoning</td>
<td>industrial environment</td>
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<tr>
<td>Gas chromatography</td>
<td>Excellent sensitivity and selectivity</td>
<td>Very high cost</td>
<td>Research analysis</td>
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<td></td>
<td></td>
<td>Not portable</td>
<td></td>
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<tr>
<td>Acoustic methods</td>
<td>Long life time</td>
<td>Low sensitivity</td>
<td>Remote sensing applications</td>
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<tr>
<td></td>
<td>No secondary pollution</td>
<td>Environmental factors</td>
<td></td>
</tr>
</tbody>
</table>

1.1.2 Solid State Gas Sensor

The term solid state gas sensor usually refers to thin / thick films of sensing materials formed on substrates like ceramic, glass or silicate. With
solid state sensors, the gas simply gets adsorbed onto the sensor surface, changing the resistance of the sensor material. The sensing mechanism involves an electrical conductance change caused by gas adsorption on the semiconductor surface, which is highly dependent on the surface stoichiometry. The mechanism was discovered by Brattain-Bardeen (Brattein et al., 1953) and Heiland (Heiland, 1954) in 1953. When the gas is desorbed, the sensor resistivity returns to the initial value. During sensing process nothing is consumed physically on solid state sensors. Hence properly manufactured solid-state sensors offer long life expectancy and repeated usage. The main feature with solid state sensor is that, the surface temperature of such a sensing material can be suitably tuned in order to make it more sensitive to a particular gas and less sensitive to other gases at a time. Versatility of solid state sensors to detect a wide variety of gases is an added advantage. There are several manufactures of solid state sensors, but each of them has different levels of performance and quality (Julian W. Gardner, 1999). The main advantage of a properly made solid state sensor is its durability, as the sensor lasts more than ten years in clean applications. It is not unusual to find fully functional sensors that were installed 30 years ago.

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 solid-state sensors for the detection of more than 100 different hazardous gases at low ppm levels. This was a significant development, since OSHA (Occupational Safety and Health Administration) was being formed at about the same time and began to regulate acceptable gas concentration levels for safety at the workplace.
In the early 1980s, Japan passed a law that required gas detectors to be installed in residential apartments where gas bottles were being used. For this huge market, the competition was between solid-state and catalytic bead sensors. While there were initial complaints about solid-state sensors that produced false alarms, they were outweighed by the long-life of the sensor. Because catalytic sensors burn the gas being detected, sensor material is consumed or changed in the process and the sensor eventually burns out. For domestic applications, the catalytic sensors have become less popular due to the need for frequent sensor replacement. With solid-state sensors, on the other hand, gas simply “adsorbs” onto the sensor surface, changing the resistance of the sensor material. When the gas disappears, the sensor returns to its original condition. No sensor material is consumed in the process, and hence the solid-state sensors offer long-life prospect.

Although the general principle of the detection mechanism with solid state sensors is appreciated, there are many problems associated with developing a satisfactory materials’ for devise advancement. The problems are concerned with achieving selectivity and sensitivity. The sensor characteristics are found to be dependent on the material, microstructure, method of preparation and to the addition of dopants.

Recently, emphasis is being given to the work on the nanostructure or nano-patterned to exploit the unique properties. As far as gas-sensing application is concerned, nanosized materials provide the advantages that the surface-to-volume ratio is much greater than for coarse materials, and the sensor tends to exhibit increasing sensitivity with decreasing the grain size.
1.1.3 Thin Film Gas Sensor (TFGS)

Thin films are the basis for a large number of technologies and are one of the most important tools for the preparation of novel materials. The technology and understanding of films less than one micron thickness have made tremendous advances in the last couple of decades, primarily because of the industrial demand for reliable thin film microelectronic devices to fulfill the urgent needs of the microelectronic era. Thin films studies, in addition to major contributions to a variety of new scientifically based technologies, have directly or indirectly advanced many new areas of research in solid-state physics and chemistry, which are based on phenomena unique in characteristic of the thickness, geometry, and structure of films (Chopra, 1979). Investigations on electrical behaviour of low and high resistivity film materials have been stimulated largely by the industrial demand for micro-miniaturised electronic components. The chief requirement for such a component are small size, low cost, high thermal, mechanical and aging stability, good control on the value of resistance, low TCR (temperature coefficient of resistance), low high-frequency losses and compatibility with the used substrate.

The end result in the design and manufacture of modern gas sensors is the transfer from ceramic (Figaro type) to thin film gas sensor (TFGS). This transfer provides new opportunities for micro-miniaturisation, power consumption and cost reduction of gas sensors (Korotchenkov et al, 1999). Some of the factors which determine the physical, electrical, optical and other properties of a thin film are rate of deposition, substrate temperature, environmental conditions, residual gas pressure in the system, purity of the material to be deposited, inclusion of foreign matter in the deposit, in-
homogeneity of the film, structural and compositional variations of the film in localised or wider areas (Goswamy, 1996; Maissel and Glang, 1983).

The first electrically conducting and semi-transparent CdO film was reported as early as 1907 by Badeker (Badeker, 1907). During the last few decades, these semi conducting transparent films of tin oxide, indium oxide and zinc oxide have been widely used in a variety of applications such as gas sensors, solar cells, heat reflectors, protective coatings, light transparent electrodes etc. The basic properties of these films include variations in morphology, structure, electrical conductivity and elevated optical transmission.

The recognition of the gas-sensing capability of a semiconducting oxide dates back to the 1950’s when it was observed that the adsorption of reducing gas on zinc oxide (ZnO) brought about a change in the electrical conductivity of the oxide. The practical significance of this was quickly realised leading to patents for gas-sensors. The first thin film semiconductor oxide gas sensors were reported by Seiyama in 1962 (Seiyama et al, 1962). Since then, there have been numerous studies concerning such oxide semiconductors as SnO₂ (Wan-Young Chung et al 1994, Korotcenkov G. et al, 1999; Niranjan et al, 2005), ZnO (Mitra et al, 1998), indium tin oxide (ITO) (Patel et al, 2003), In₂O₃ (Korotcenkov et al, 2004), TiO₂ (Ana et al, 2004) etc. Expert reasoning is mainly exercised in the development of new sensor materials and nowadays most of them are widely exploited in the detection of gases.

Highly conducting materials having positive temperature coefficient of resistance in the bulk form show negative temperature coefficient of resistance when in thin film state to behave as semi conducting films (Goswamy, 1996). Surface states of a film play a dominant role in
modifying the electrical properties of the thin film. In addition, because of a high surface to volume ratio in a film, a freshly formed film surface becomes highly reactive. Thickness plays an important role in the film properties. Thin film properties are sensitive to their structure, crystallinity, surface topography, nature of defects and imperfections, compositional variations and to some extent on the thickness. Most of the factors are associated with the growth process of films and can be controlled or optimised by taking appropriate precautions.

The electrical resistance of thin films changes because of absorption of gases and other impurities. Adsorption studies on thin films are clearly an important tool in the field of research. It is necessary to emphasise that the electrical conductivity of discontinuous or nearly conducting films is very sensitive to slight changes in the structural rearrangement due to aging, annealing and adsorption. This distinct change in sensitivity is due to the dependence of electrical conduction on the weak interaction between the discrete islands. Changes in the electronic structure of the surface of film due to adsorption can also alter surface scattering of electrons and thereby conductivity. Surface transport phenomena play an important role in the transport properties of semi conducting films. The surface conductivity of a semiconductor is very sensitive to surface contaminants, preparation techniques, contact effects and induced localised charges (Chopra, 1979).

In general, the semiconductor oxide gas sensors like SnO\textsubscript{2}, ITO, In\textsubscript{2}O\textsubscript{3}, TiO\textsubscript{2}, WO\textsubscript{3} (Aguir K. \textit{et al}, 2002) and ZnO have been widely studied due to their range of conductance variability and their response towards both the oxidising and reducing gases. They are used in the form of bulk material, thick film or thin films. Gas sensing is basically the surface
phenomenon and hence thin film sensors have advantages due to their higher surface to volume ratio (Niranjan et al., 2004).

1.1.4 Micro-Sensor

Among solid state sensors, those having sensing element as thin film with thickness less than 50 nm are classified as micro sensors. Diverse response characteristics are achieved by varying the material, processing techniques and operating temperature. Among the unique features of micro-sensors, their ability to detect low ppm level of gases has activated tremendous research in the field (Varfolomeev et al., 1992; Mishra and Agarwal, 1998; Tadashi Tadaka, 1998; Dae-sik Lee et al., 2002; Stankova et al., 2004; Wurzinger and Reinhardt, 2004; Tournier and Pijolat, 2005). In certain gases, often, the lower ranges need to be monitored for toxic concentrations while the same gases need to be monitored in the combustible range for explosive concentrations. Micro-sensors are capable of detecting gases in both ranges.

One common drawback of these sensors is that they read not only the presence of target gas but also other gases, designated by weak selectivity. Most sensors are sensitive to a group or family of gases. In order to achieve some degree of selectivity for practical applications, different techniques are frequently employed. In micro-sensors, for instance, the surface temperature of the sensor can be set differently in order to make it more selective to a particular gas. Another method is by doping with suitable impurities. Utilising different basic material, dopants, processing techniques and sensor operating temperatures, to a great extent we can achieve the varied requirements of response characteristics. As a result a micro sensor is to be
designed so that functionality (effectiveness), cost, quality size, weight, speed etc matches the requirements of the customer. Investigations are underway to process gas sensors with better stability, fast response at low operating temperature and rapid recovery. Efforts are also in progress to reduce the size of the sensors and to make them more efficient than at present (Julian W. Gardener, 1999).

To date micro-sensors do not exist for 100% selective to a gas. Achieving such selectivity requires the use of analytical techniques or instruments to identify gases. Examples of such instruments include Fourier transform infrared (FTIR), gas chromatographs, and mass spectrometers. (Sunu et al, 2004; Tournier and Pijolat, 2005; Feng Gu et al, 2003).

1.1.5 Semi Conducting Metal Oxide Micro-sensor

Micro sensors of semi conducting metal oxide (tin oxide, zinc oxide and indium oxide) thin films are widely studied for detection applications. Among them, tin oxide is the first transparent semi-conductor to have received significant commercialisation. It is an n-type semiconductor with a wide band gap of about 3.5 eV which can be manipulated by the materials’ formation. It has been observed that thin films of SnO$_2$ exhibit a higher degree of gas sensitivity compared to other forms (Mitra et al, 1998). Semiconducting solid state thin film gas sensors have been developed for wide range of reactive and non-reactive gases. (Chaudary et al, 1999; Yuta Matsuhima et al, 2003; Patel et al, 2003; Pancheri et al, 2004; Zhu et al, 2004; Niranjan et al, 2004). The ability of a semi conducting metal oxide to sense chemicals depends on the interaction between gas molecules and the surface of the sensing film, and is affected by factors such as temperature of
operation, gas being analysed, sensor geometry and sensor packaging etc. Also sensor responses tend to vary significantly when they are used over a long period, resulting in poor selectivity. Therefore it is necessary to fabricate more reliable and suitable sensors.

The changes in electrical conductivity depend on the relative energies of the electronic charge carriers before and after adsorption and these energies are dictated by the structure and composition of the bulk and surface of the semi conducting oxide. Since the electronic properties of oxides change significantly by the chemisorptions of gas species, a deliberate modification of the surface can be used effectively in controlling the gas sensing behaviour (Mishra and Agarwal, 1998). There are reversible chemisorptions of reactive gases at the surfaces of certain metal oxides, which are accompanied by reversible changes in conductance. Unlike metal films, where the conductance modulation due to absorption is very small and is caused by changes in mobility due to changes in surface scattering, the conductance changes in semiconductor materials are large and are caused primarily by changes in conduction-band electron or valence-band hole concentration.

The electron concentration in semiconductor sensors varies in the conduction band approximately linearly with pressure, while the variation in mobility is generally small. This suggests that gas chemisorptions on to the surface of the semiconductor material influence its electrical conductivity significantly. It is this large and reversible variation in conductance with active gas pressure that has made semiconductor materials attractive for the fabrication of gas sensing electronic devices (Hartnagel et al, 1995). In addition, it is recognised that together with atmospheric oxygen the presence
of humidity greatly influences the gas detection. Reaction between gases and the surface oxygen will vary depending upon the sensor element temperature and activity of the sensor materials. Dopants and additives can accentuate the changes, for particular target gases at constant concentration.

Considering the reducing gas-sensing characteristics of a semiconductor sensor, two reactions are important. One is the reaction between reducing gases and surface oxygen ad-ions, which results in a resistance decrease of the semiconductor, and another is the combustion of reducing gases with gaseous oxygen molecules that is catalysed by the sensing material. Both reactions are exothermic. The resistance decrease of semiconductor was sometimes accompanied by a temperature drop of the sensor, particularly for sensors that were less active for oxidation of reducing gases. This temperature drop has also been extensively studied as a method for gas identification (Tadashi Takada, 1998).

Semi conducting transparent coatings of some metallic oxides such as cadmium oxide, tin oxide (Korotcenkov et al, 2001; Sang Woo Lee et al, 2000), indium oxide (Golovanov et al, 2005; Korotcenkov et al, 2004, p 297-303), indium tin oxide (Salehi, 2002; Patel et al, 2003), zinc oxide (Mitra et al, 1998), Ag₂O (Jinzhong Wang et al, 2002), BaTiO₃ (Park and Seo, 2004) has known to be very promising material as gas sensors with high stability and reliability. Metal oxide semiconducting sensitive layers play roles in the detection of CO (Serventi et al, 2003; Korotcenkov et al, 2004, p 41-45), H₂S, NO₂ (Pancheri et al, 2004), SO₂, CO₂, CH₄, H₂ (Mishra and Agarwal, 1998; Jinzhong Wang et al, 2002), LPG (Mitra et al, 1998), ammonia and alcohol sensors (Teeramongkonrasmee et al, 2000). More recently there has been an upsurge in the use of silicon technology on
which there is possibility of integrating electronic circuitry on the same chip (Wan-Young Chung et al, 1994).

1.2 Undoped and Doped SnO₂ Films

Among the semi conducting metal oxides used for gas sensors, tin oxide is the most widely used material with respect to practical applications in domestic, commercial and industrial area due to its low cost (raw material and technological process), ease of production, rigid construction, compactness in size, long life and that it requires very simple measuring electronics and little maintenance is involved. SnO₂ is chemically inert, mechanically hard and can resist high temperature. They have commonly polycrystalline cassiterite structure and are composed of crystallites joined together by grain boundaries, which are transitional regions between different orientations of neighbouring crystallites. These boundaries between grains play a significant role in the scattering of charge carriers in polycrystalline thin coatings.

Tin oxide based sensors provide good response to various gases, both reducers and oxidants (Andreia Lopes et al, 2001). Most of the sensors known now are based on sintering thick tin oxide. But due to its higher dimension, low sensitivity and selectivity, degradation of performance with time, dependence on grain size, surface morphology and internal porosity, the use of this material in the form of thin film has set to attract a wide range of attraction (Andreia Lopes et al, 2001).

SnO₂ has been subjected to widespread research as a solid-state gas sensor (Wan-Young Chung et al, 1994; Ponce et al, 2003). Tin oxide exhibits high sensitivity at conveniently low operating temperatures brings
about the attention to concentrate on this material. So far, it is the most widely used solid-state device for gas-alarms on domestic and industrial premises. Recently, homogeneous semi conducting gas sensors utilising SnO$_2$ have been studied by many authors for detecting small concentrations of reducing gases such as CO, H$_2$ and CH$_4$ and are being commercially manufactured on a large scale.

The electrical conductivity of a semiconductor in the region of the space-charge layer is influenced by the gas surrounding the semiconductor surface (Klober et al, 1991). Several attentions have been put to improve its sensitivity and swiftness. Its electrical resistance depends on the oxygen vacancies in the lattice and the gases adsorbed on the surface. It is believed that sensor sensitivity can be improved by increasing the sensitive materials’ surface areas in order to provide more surface site available for more oxygen to be adsorbed on these sites and to make contact with the surrounding gases (Yude Wang et al, 2004). An n-type metal–oxide can adsorb oxygen from the atmosphere both in the O$^{2-}$ and in the O$^{-}$ species. The adsorption of O$^{-}$ is the most interesting process in sensors, because this oxygen ion is the more reactive and thus makes the material more sensitive to the presence of reducing gases. At relatively low temperature, the surface preferentially adsorbs O$^{2-}$ and the sensitivity of the material is consequently very small. As the temperature increases, the dominant process becomes the adsorption of O$^{-}$, and then the sensitivity of the material increases too (Yude Wang et al, 2004).

The gas sensing performance is strongly depending on the method of preparation of the thin film. This is one of the reasons why differently prepared films can be used for sensing different gases. Although the oxides themselves are catalytically active, they are rarely used in isolation as their
gas sensing characteristics are usually enhanced by using a small amount of noble metal catalysts such as palladium (Pd) (Korotcenkov et al, 2003) and platinum (Pt) (Bittencourt et al, 2004). Metal oxides such as Al₂O₃ (Tiwari et al, 2000), ThO₂ (Niranjan et al, 2004), Fe₂O₃ (Bose et al, 2005) not only promote gas sensitivity but also improves the response time (Niranjan et al, 2004; Mitra and Maiti, 2004). In doped tin oxide thin films, catalyst can create oxygen vacancies and defects in thin films that make the sensing performance even more complicated. The high sensitivity of thin films to gases is considered to be due to the large surface area and porous film structure. It has been reported that doping in SnO₂ changes film morphology and decrease both crystallite size and concentration of free charge carriers. The doping effect on conductivity is due to controlled valency mechanism (Thangaraju, 2002). Such changes in film parameters are important factors influencing the catalytic activity of the SnO₂ surface and promote a considerable increase in their gas response.

The results showed that the gas sensitivity is affected not only by the additive but also on the site to which it is added to the sensor material. Undoped and doped SnO₂ films can be fabricated by means of a number of techniques such as sputtering (Serventi et al, 2003), chemical vapour deposition (CVD) (Salehi, 2003), ultrasonic spray CVD, spray pyrolysis (Siebert, 1984; Vasu and Subrahmaniam, 1991; Thangaraju, 2002; Korotcenkov, 2003; Niranjan et al, 2004), thermal evaporation, ion beam deposition, sol gel (Dal Santos et al, 2003), pulsed laser deposition (Stanimirova et al, 2007), dip coating, r. f. magnetron sputtering (Yuheng Wang et al, 2005), r. f. reactive sputtering (Giulio et al, 1995), d. c. magnetron reactive sputtering (Snyders et al, 2001), wet chemical process (Mitra et al, 2004), chronoamperometry etc.
Commercially available SnO$_2$-based sensors typically contain a small quantity of noble metals such as Ag, Ti, Pd and Pt, which are dispersed on the oxide as activators or sensitisers to improve the gas selectivity and to lower the operating temperature. Recently it is found that the performance of SnO$_2$-based sensors can be improved by doping them with small amounts of non-noble metals like cesium (Radha K. K., Ph.D thesis, 2007), lanthanum and manganese (Stambolova et al., 2000). It was reported that Ca addition to SnO$_2$ thin film causes higher sensitivity towards CH$_4$ due to the crystallite growth inhibition (Bong-Ki and Soon-Don, 2005, p 119-124).

Although semiconductor gas sensors based on SnO$_2$ have already been in the market, the enhancements in the sensing properties are still under way to meet their ever-expanding demands in new applications. The sensor characteristics have been modified by using different catalysts and promoters and by tuning the operating temperature. In addition, the role of newer dopants with different ionic radii from non-noble metals has yet to be explored to evaluate the sensor performance.

1.3 Liquified Petroleum Gas (LPG)

LPG is discovered in 1912 by Dr. Walter Snelling. The term liquid petroleum gas (LPG) is applied to pressurised mixture of long-chain hydrocarbons of which the chief components are propane (C$_3$H$_8$) and butane (C$_4$H$_{10}$), with fractions of propylene, butylenes and ethylene. It is basically a fossil fuel and is normally obtained during primary distillation of crude oil. It can be also obtained by cracking reduced crude oil. It is stored at high pressure causing them a higher chance for leakage. At normal temperature and pressure it evaporates. LPG is heavier than air and settles in the lowest
areas facilitating them the need of a warning system to protect human life. The composition of bottled LPG may slightly vary in each bottling batch. If a particular gas is on high demand for other purpose, the ratio of that gas in the bottling batch will be less. A typical analysis of commercial LPG available in India is given in table 1.2 (Courtesy: M/s Bharat Petroleum Corporation Ltd., Kochi refineries, Kochi).

### Table 1.2 Typical analysis of components in commercially available LPG in India (M/s Bharat Petroleum Corporation Ltd., Kochi refineries, Kochi)

<table>
<thead>
<tr>
<th>Sl.No</th>
<th>Test</th>
<th>Test method</th>
<th>Typical Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Density @ 15°C gm/ml</td>
<td>P:76/D:1657</td>
<td>0.5630</td>
</tr>
<tr>
<td>2</td>
<td>Vapour pressure @ 65°C Kg/Cm²</td>
<td>P:71/D:1267</td>
<td>14.0</td>
</tr>
<tr>
<td>3</td>
<td>Water</td>
<td>Visual</td>
<td>No free entrained water</td>
</tr>
<tr>
<td>4</td>
<td>Copper Corrosion 1 Hr @ 38°C</td>
<td>P:D:1838</td>
<td>No.1</td>
</tr>
<tr>
<td>5</td>
<td>Total Sulphur %wt.</td>
<td>P:34</td>
<td>0.01</td>
</tr>
<tr>
<td>6</td>
<td>Hydrogen Sulphide</td>
<td>P:73</td>
<td>Nil</td>
</tr>
</tbody>
</table>

**COMPOSITION MOLE %**

| 7     | Ethane/ Ethylene GC                       |              | 1.3                     |
| 8     | Propane                                   | *            | 18.1                    |
| 9     | Propylene                                 | *            | 24.6                    |
| 10    | Iso-butane                                | *            | 20.7                    |
| 11    | N-butane                                  | *            | 14.3                    |
| 12    | 1-butene                                  | *            | 4.8                     |
| 13    | Iso-butene                                | *            | 6.4                     |
| 14    | t-butene                                  | *            | 4.7                     |
| 15    | c-butene                                  | *            | 3.6                     |
| 16    | Iso-pentane                               | *            | 1.2                     |
| 17    | n-pentane                                 | *            | 0.3                     |

Besides these, a very small concentration of Ethanethiol (commonly known as ethyl mercaptan, a colourless gas with a distinct odour which is an organosulfur compound with the chemical formula CH₃CH₂SH is intentionally added to LPG to impart an easily detectable smell to the odourless fuel.
LPG is at the present commercially used in industry and automobiles. It is commonly used as cooking gas, worldwide. MOS gas sensors are utilised widely in domestic gas leak detectors to produce an alarm at a given gas concentration. For the gas detection over the entire range, ideal and cost-effective sensing methods are yet to be established.

1.4 Methane Gas

Methane (CH₄) is a colourless, odourless gas with a wide distribution in nature. The main use of methane is as a fuel. It is the principal component of natural gas. At room temperature, methane is a gas, less dense than air. It melts at –183°C and boils at –164°C and cannot be liquified at ordinary temperature. It is not very soluble in water. It is combustible, and mixtures of about 5 to 15 percent in air are explosive. It is not toxic when inhaled, but it can produce suffocation by reducing the concentration of oxygen inhaled. A trace amount of smelly organic sulfur compounds (tertiary-butyl mercaptan and dimethyl sulfide) are added to give commercial natural gas a detectable odour to make gas leaks readily detectable. An undetected gas leak could result in an explosion or asphyxiation. Since it is a greenhouse gas, efforts to prevent or utilise methane emissions can provide significant energy, economic and environmental benefits.

1.5 Literature Review on Thin Film Gas Sensors for LPG and Methane

Among the metal oxides with gas-sensing behavior, particular interest has been obvious in SnO₂-based sensors because of their promising properties. Taguchi N. started making a simple solid-state semiconductor sensor for the detection of hydrocarbons in combustible ranges during 1962.
His intention was to provide an alternative to the popular catalytic bead sensor. Since then solid state gas sensors for monitoring inflammable and toxic gases were commercially manufactured and marketed. Different materials and different technologies have been employed all over the world to develop gas sensing materials to match the needs. Tin oxide gas sensors have been manufactured and sold by Figaro Engineering Inc. (Japan) since the early 1970s. The most successful 8-series sensor consists of a heater coil inside an alumina ceramic tube, which is coated with a thick sintered film of tin oxide (Julian W. Gardner, 1999). More recently, there has been an upsurge in the use of silicon technology to fabricate planar microelectronic sensors.

Pt doping on SnO$_2$ proved to impart excellent sensitivity towards organic and toxic gases. In 1994, Wan-Young Chung and his co-workers fabricated SnO$_2$:Pt micro-sensors that exhibit about 85% sensitivity to 5000 ppm C$_3$H$_8$ and 5000 ppm C$_4$H$_{10}$ (the main components of LPG) at an operating temperature of 250ºC with a rapid response less than 5s (Wan-Young Chung et al, 1994). Later Platinum-doped SnO$_2$ sensors were fabricated to detect LPG at an operating temperature 147ºC (Trivikrama Rao et al, 1995).

Keshavaraja and his co-workers observed that the sensitivity and selectivity of SnO$_2$ can be modified by the presence of sulphate species on the surface due to the formation of super acidic sites (Keshavaraja et al, 1995).

Later single element catalytic sensor based on SnO$_2$:Pt catalyst to detect LPG at ppm levels were manufactured by Rao (Rao and Rao, 1997).

Phani (India) investigated the gas response of palladium doped tin oxide as a means of improving the selectivity for LPG. The sample loaded
with Al₂Si₂O₇ (35 wt. %) and 1.5 wt. % Pd doped SnO₂, sintered at 800°C has shown a high sensitivity of 97% towards LPG with a negligible cross interference of CO and CH₄ at an operating temperature of 350°C (Phani et al, 1997&1999).

Mishra reported that palladium-doped SnO₂ possesses the highest sensitivity for H₂, LPG and CH₄, whereas platinum doped sensor enjoys the highest sensitivity for CO at an operating temperature of 350°C. The response time is found to be least for CO and maximum for H₂ while the recovery time is more for LPG (Mishra and Agarwal, 1998).

Mitra observed a high sensitivity (50-75%) for 0.4-1.6 vol% LPG in air and the degree of sensitivity could be varied by changing either the LPG concentration or operating temperature using chemically deposited ZnO thin films. A high sensitivity (75%), fast response (12 s) and swift recovery (4.5 min) for 80% LEL (lower explosive limit) LPG at 300°C makes the sensor attractive for domestic LPG alarms. A prototype electronic LPG alarm has been designed which exhibits stable continuous operation for one week at a stretch without any degradation (Mitra et al, 1998).

Pt doped SnO₂ thin films deposited by electron-beam evaporation exhibited their response to LPG and other common household gases (Madhusudhana and Chandorkar, 1999).

Chaudhary reported that ruthenated tin oxide showed a sensitivity enhancement for 1000 ppm LPG in comparison with pure tin oxide at an operating temperature of 300°C. At elevated temperatures, the potential barrier between the grains of tin oxide is increased due to adsorption of
oxygen. Ruthenium acts as a catalyst for oxygenation, as result of which the potential is further increased which enhances the reaction rate and accounts for the apparent increase in sensitivity (Chaudhary et al., 1999).

In the case of SnO₂ and SnO₂/Al₃Si₂O₇, when the samples are exposed to LPG, the SnO₂ is reduced to metallic Sn indicating adsorption-desorption process termed as chemical mechanism. Whereas for the SnO₂/Pd and SnO₂/Al₃Si₂O₇/Pd systems in addition to chemical mechanism, there is an additional contribution from the Pd, in which PdO₂ and PdO are reduced to PdO and Pd, respectively, attributed to electronic mechanism. Regarding the material, Phani argues that the electronic mechanism is more predominant when compared to the chemical one, in the gas sensing action (Phani et al., 2000).

Studies on La₂O₃ addition in SnO₂ revealed that increasing the doping level above 2 wt. % has no added advantage in improving its gas sensitivity towards LPG and CH₄ and in stabilising the SnO₂ surface (Gopal et al., 2000).

Response of oxygen, hydrogen, nitrogen and argon plasma treated tin oxide thick film gas sensors has been studied upon exposure to CCl₄, C₃H₇OH, CO, LPG, N₂O and CH₄. It is observed that the sensitivity of sensors treated in various gaseous plasmas is much higher at room temperature in comparison to untreated sensors (Chaturvedi et al., 2000).

Zylka used RGTO (Rheotaxial Growth and Thermal Oxidation) method to produce polycrystalline SnO₂ thin films and investigated the gas sensing properties towards LPG (Zylka 2000).

SnO₂ films doped with Al₂O₃ and lead borosilicate are used in monitoring of leakage of gases such as H₂, LPG, CO, CH₄, etc (Tiwari et al, 2000).
Niu noticed that sensors made from SnO$_2$, In$_2$O$_3$ have a high sensitivity and selectivity to LPG and ethanol, while the sensors made from ZnO, Fe$_2$O$_3$ have relatively poor sensitivity (Niu et al., 2002).

An array of sensors fabricated by thick film technology using tin oxide paste doped with Pd, Pt, CuO, ZnO, Cd and SnO$_2$ after annealing oxygen plasma for 15 minutes showed a good response towards CO, LPG, CCl$_4$, CH$_4$ and C$_3$H$_7$OH (Chaturvedi et al., 1999; Lee et al., 2002).

Wang fabricated a highly selective and reliable $\gamma$-Fe$_2$O$_3$ gas sensor to detect the leakage of coal gas or LPG in domestic appliances by doping with Ag$_2$O and modifying with the Al$_2$O$_3$ surface-coat doped with PtO. Sensitivity studies for reducing gas are carried out by Satyanarayana demonstrated that nanocrystalline nickel ferrite - Ni$_{1-x}$Co$_x$Mn$_x$Fe$_{2-x}$O$_4$, is highly sensitive and selective to LPG. The operating temperature as low as 180°C after 1 wt. % Pd incorporation is highly favorable from the commercial development of LPG sensors (Satyanarayana et al., 2003).

An abrupt fall in the electrical resistance of the material was observed by the interaction of the LPG gas with the surface of SnO$_2$ films prepared by modified sol-gel process, using tin tartrate as a precursor and hence can be used as LPG sensors (Dal Santos et al., 2003).

SnO$_2$ gas sensor based on dynamic measurement by Liu and showed that hazardous gas such as LPG can be obviously identified (Liu et al., 2004). Experimental results showed up different properties with the different concentrations of LPG.
A novel non-heating room temperature gas sensor was prepared from SnO$_2$, $\alpha$-Fe$_2$O$_3$, SiO$_2$, and ErO$_2$. The sensor showed high sensitivity to H$_2$, CH$_4$ and LPG (liquefied petroleum gas) at room temperature with low power consumption and low response and recovery times (Yan et al, 2004).

Antimony doped tin oxide thin films deposited by the spray pyrolysis technique show maximum sensitivity towards LPG with minimum response time at the operating temperature 400°C (Subramanian et al, 2004).

According to More, SnO$_2$:Cu (Cu = 9 wt.%) in the form of pellet is a high-performance temperature-selective composition for the detection of CO, H$_2$ and LPG gases at a concentration level of 1000 ppm (More et al, 2004).

In the case of MoO$_3$ pellet sensors with Pt electrodes, the LPG sensitivity of 61% at 673K increased with temperature which was insignificant below 553K (Sunu et al, 2004).

45Å Pt-covered SnO$_2$ thin film deposited by ion beam sputtering after annealed at 650°C shows excellent response to butane when operated at 400°C. But they are heavily affected by relative humidity (Bong-Ki Min et al, 2005).

Reasonably good sensitivity of Ru-doped nanostructured SnO$_2$ sensor for both H$_2$ and LPG reported in 2005 (Niranjan et al, 2005). In the same year, Ramgir reported the response of Ru-SnO$_2$ nanowires to NO$_2$ and LPG at an operating temperature of 250°C (Ramgir et al, 2005).

With ceria doped SnO$_2$ prepared by a sol-gel method and sintered at 600°C is reported to have good selectivity to ethanol in contrast to LPG, CH$_4$ and CO. At 350°C, the ceria-doped SnO$_2$ becomes more sensitive to CO and LPG (Pourfayaz et al, 2005).
SnO$_2$ doped with 10 wt. % Bi$_2$O$_3$ has been characterised by d.c. electrical measurements for different gases such as CO, LPG, H$_2$S and H$_2$ in dry air (Chaudhari 	extit{et al}, 2005).

An enhancement in resistance change ratio from 35% to 118% for 1000 ppm LPG gas is obtained to Srivastava from the SnO$_2$ powder derived by hydrosol process (Srivastava 	extit{et al}, 2005).

The SnO$_2$ nanocrystals synthesised by decomposing stable tin complex showed high sensitivities to LPG, petrol, alcohol and methanol, and the response and recovery times were much shorter than previously reported values (Zhang 	extit{et al}, 2005).

Nanosized tin oxide powders are obtained using microwave assisted synthesis procedure for their application on gas sensor technology. Enhancement in LPG and CNG gas sensitivity has realised after microwave irradiation to a hydrosol solution (Srivastava 	extit{et al}, 2006).

Dong reported that the biomorphic SnO$_2$ (fabricated using a biotemplate eggshell membrane (ESM) combined sol-gel approach) have a good selectivity for LPG with a working temperature above 300°C while for ethanol below 270°C (Dong 	extit{et al}, 2006).

Chaudhari fabricated a thick-film semiconductor sensor for liquid petroleum gas (LPG) detection using a nanosized WO$_3$-based mixed with different metal oxides (SnO$_2$, TiO$_2$ and In$_2$O$_3$) and doped with noble metals (Au, Pd and Pt). The WO$_3$-based mixed with 5 wt. % In$_2$O$_3$ and 0.5 wt. % Pd showed the higher sensing characteristic at low concentration of LPG sensor at an operating temperature 225°C (Chaudhari 	extit{et al}, 2006).
Iron doped tin dioxide (Chakraborty et al, 2006) can detect both methane and butane (present in CNG and LPG respectively) at a temperature of 350°C with selective detection of butane at 425°C.

Jain prepared Ni- and/or Al-doped and undoped SnO₂ thick film gas sensors using screen printing technique and tested for LPG sensitivity (Jain et al, 2006).

Multi-walled carbon nanotubes coated with SnO₂ exhibited fine responses to LPG and ethanol gas having rapid response and recovery time, responses being linear with the gas concentrations (Liu et al, 2006).

Pb doped SnO₂ sintered at 1000°C for 2 hr has shown high sensitivity to LPG at an operating temperature of 150°C (Senguttuvan et al, 2007).

Regarding methane sensing, Jae Chang suggest that alumina supported Pd catalyst SnO₂ sensor have good sensitivity to methane at 658K and posses an improved sensitivity at 573K by Ca incorporation (Jae Chang et al, 1997).

Osmium-doped tin oxide thin films, prepared by sol–gel technique are studied and compared to undoped SnO₂ thin films. Quaranta concluded that Os inclusion enhance methane sensing at a lower temperature of 270°C (Quaranta et al, 1999).

Takashi studied the interactions between methane and an O₂-exposed SnO₂ thin film using X-ray photoelectron spectroscopy (XPS) from room temperature to 473 K (Takashi et al, 2000).

Andreia Lopes done the Hall effect studies on SnO₂ thin film based methane sensors and reported the conduction mechanism in the presence of air and ambient gas (Andreia et al, 2001).
Soon-Don and Lee have compared the gas sensing behavior of K, Ca and Mg doped SnO$_2$ films and suggested that Ca doped films sintered at 700°C have a maximum sensitivity of 90 % in 5000 ppm of methane at an operating temperature of 400°C. In the Mg doped films, the sensitivity obtained for the same methane level is only 39 % but their mechanical stability is poor (Soon-Don and Lee, 2001).

Abbas achieved the multicomponent determination of CH$_4$ and NO$_2$, using a set of two tin oxide sensors, one is doped with Pd and working at 300°C selective for methane and the other doped with Pt and working at 150°C selective for nitrogen dioxide (Abbas et al, 2001).

Nandini Das (Nandini et al, 2006) prepared nanosized SnO$_2$ based powders containing antimony and palladium by ultra-sonic assisted precipitation for methane sensing. The powder composition has selected keeping in view of the role of Pd and Sb (an ‘n’ type dopant) catalysts going into solid solution with SnO$_2$ for lowering the sensor resistance within acceptable limit for real life applications.

Divya and Vinay reported that ultraviolet exposure on Pd doped SnO$_2$ films enhance methane sensitivity even at room temperature and are encouraging for commercial realisation of room temperature SnO$_2$ based thin film sensor for methane (Divya and Vinay, 2013).

Electro-physical and structural properties of the SnO$_2$ films showed that structural changes are caused mainly by incorporation of cobalt in the SnO$_2$ lattice which changes the SnO$_2$ gas sensing properties in ozone and hydrogen sensing (Korotcenkov et al, 2013).
A theoretical approach on the factors influencing sensing characteristics of sprayed SnO$_2$ films were done by Brinzari and his colleagues (Brinzari et al., 2001). A detailed theoretical study on structural and electronic properties of single crystal tin oxide surface highly oriented in (110) and (101) tetragonal phase in relation to their improved gas adsorption/desorption process is reported by Matthias and his colleagues (Matthias et al., 2005).

A brief review of the major results on doped SnO$_2$ sensors for LPG detection is given as table 1.3 (Sutichai Chaisitsak, 2011)

<table>
<thead>
<tr>
<th>Author, Year</th>
<th>Deposition method</th>
<th>Dopant</th>
<th>LPG ppm level</th>
<th>Sensing performance</th>
<th>Grain size</th>
<th>Operating Temp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reddy M et al, 1999</td>
<td>Electron beam evaporation</td>
<td>Pt, Pd</td>
<td>8000</td>
<td>75% Response time 23 s</td>
<td></td>
<td>400 °C</td>
</tr>
<tr>
<td>Gupta et al, 2004</td>
<td>Magnetron sputtering &amp; evaporation</td>
<td>Pd</td>
<td>3000</td>
<td>65% Response time 10 s</td>
<td></td>
<td>350 °C</td>
</tr>
<tr>
<td>Senguttavan et al, 2007</td>
<td>Conventional solid-state route</td>
<td>Pb</td>
<td>1000</td>
<td>48%</td>
<td></td>
<td>150 °C</td>
</tr>
<tr>
<td>Majumder et al, 2008</td>
<td>Sputtering</td>
<td>Si</td>
<td>1000–7000</td>
<td>59% Response time 30 s</td>
<td>90</td>
<td>300 °C</td>
</tr>
<tr>
<td>Vaishampayan et al, 2008</td>
<td>Pechini route</td>
<td>Pd</td>
<td>20 – 1000</td>
<td>75 – 95%</td>
<td>11</td>
<td>50 – 100°C</td>
</tr>
<tr>
<td>Boben et al, 2008</td>
<td>Spray Pyrolysis</td>
<td>Cs</td>
<td>1000</td>
<td>93.4%</td>
<td>18</td>
<td>345 °C</td>
</tr>
<tr>
<td>Babar et al, 2011</td>
<td>Spray Pyrolysis</td>
<td>Sb</td>
<td>1000 – 5000</td>
<td>40%</td>
<td>20</td>
<td>450 °C</td>
</tr>
<tr>
<td>Sutichai C., 2011</td>
<td>Dip Coating</td>
<td>F</td>
<td>50000</td>
<td>46%</td>
<td>4 - 6</td>
<td>300 °C</td>
</tr>
<tr>
<td>Nguyen et al, 2010</td>
<td>Thermal evaporation</td>
<td>undoped</td>
<td>500–4000</td>
<td>22%</td>
<td></td>
<td>400 °C</td>
</tr>
<tr>
<td>Abhilasha et al, 2007</td>
<td>Co-precipitation</td>
<td>Sb, Ca, ZnO, Pd</td>
<td>1000</td>
<td>17.2%</td>
<td>6</td>
<td>325 °C</td>
</tr>
</tbody>
</table>
1.6 Importance of the Problem

Due to rapid industrialisation accompanied by globalisation, developing countries like India are now facing grave environmental crisis. The increasing environmental pollutants, effluents, toxic and inflammable gases, radiation etc are posing a great threat to the healthy and sustained existence of flora and fauna all over the world. Air pollution is one of the most crucial current environmental problems, especially in urban areas. Never before have arisen a situation where a continuous monitoring and control of pollutant gases become inevitable. In order to regulate the emission of toxic or environmentally sensitive gases into the atmosphere, stringent safety regulations has been designed to create safer living and working conditions. This necessities a need for development of effective and sensitive pollution monitors (Desai et al, 2005).

The environmental regulations on inflammable and toxic gases have been tightened all over the world to control highly poisonous gases and much attention has been given to develop high performance sensors and systems for monitoring such gases in environment inside mines, gas leak inside residence and to control atmospheric pollution. There are already gas sensors commercially available for these gases, made by Riker Keiki (Japan), Korean, Chemautomatics (Russia) and others. These sensors based on different physical principles are primarily used for the protection of personnel and property against toxic and inflammable gases (Yamazoe and Miura, 1994) with various merits and demerits (Varfolomeev et al, 1992).

Difficultly in identification of a gas species of a particular concentration occurs when the gas concentration changes during
measurement. Moreover, each sensor shows different characteristics under various circumstances, including different temperature and humidity. This makes gas sensing more laborious (Tadashi Tadaka, 1998). However the production of new gas sensing materials with actual requirement still lags behind. Further, the gas sensing properties of presently investigated materials are found to be continuously increasing by simply changing various parameters like additive concentration / type, firing temperature, synthesis method, processing conditions etc. However, the correlation of the sensing mechanism and the microstructure of the sensing materials have not been clearly established yet. The lack of understanding becomes severe in case of film type sensors (Sang Woo Lee et al, 2000). This gives an innovative direction for searching the newer and newer materials for gas sensing applications. (More et al, 2004). Presently there are three types of semiconductor gas sensing devices viz. pellet type, thin film type and thick film types (Jayadev Dayan et al, 1998). Thin film type has been found quite attractive for the realisation of an intelligent Gas Sensor (More et al, 2004).

Currently available sensors are based on the chemical interactions between the gas and a specific material whose physical properties are modified by the gas. Two of the most important issues in those devices are sensitivity (detection of gas concentrations at the ppm level) and gas selectivity (detection of specific gases in a mixed gas environment). In addition to the target gas, numerous substances can be present at the surface of the oxide. These can result in a false measurement signal or even an imitation of the gas to be detected. One of the core objectives of the sensor design is therefore the selectivity of the system. Establishing sensor sensitivity for specific gases is difficult and challenging. Selectivity is
dependent on many parameters, such as adsorption and co-adsorption
mechanisms, surface reaction kinetics, and electron transfer to or from the
conduction band of the semiconductor.

For any gas sensor device to be useful, it should be able to detect the
active gas component in the presence of non-interfering background
constituents. Moreover, they should have controllable levels of sensitivity.
Semiconductor oxide gas sensors are extensively studied in order to
improve their sensing characteristics such as sensitivity, selectivity,
response rate to various kinds of gases to meet the increasing needs of
sensors in complicated systems under strict conditions (Hartnagel et al,
1995). The currently available gas warning systems do not fulfill the
reliability requirements needed for safety applications to realise a sufficient
acceptance of the market by satisfying the customer requirements.

Another disadvantage of semiconductor oxide sensors is that most of
the oxide semiconductor gas sensors usually operate at high operating
temperature (350 - 450°C) and therefore require an attached heating
element. Maintenance of sensor at high temperature increases power
consumption which reduces sensor life and complicates the design of the
sensor due to need for integration of heater with gas sensor (Thangaraju,
2002). Moreover, reactive gas vapours having low boiling point require care
to prevent the reaction and fire at a high operating temperature. Therefore
the lessening of operating temperature is one of the demanding factors of
viable gas sensor for the industrial applications (Patel et al, 2003).

Another major problem of such sensor is the lack of selectivity and
reliability with ageing, due to evolution of the gas sensitive material under the
influence of either the elevated operating temperature or the ambient humidity. The overall performance of a micro sensor can be described by a parameter called effectiveness. The important factors contributing the effectiveness of a micro sensor are the capability, reliability and availability (Julian Gardner, 1999).

The capability of a sensor is its capacity to perform the desired function under predefined conditions while the reliability is the ability to perform a required function within its technical specification over a prescribed period. The availability of a sensor is the capability of performing a required function when required to do so. Additionally it is defined by its failure and its repair-rate.

In order to enhance the effectiveness, the parameters influencing gas sensor characteristics have to be crucially controlled both during in-situ preparation and post modifications. The main physical parameters to be controlled are

1. Geometric and structural parameters of the film: Area, thickness and porosity of the film, effective size of grains or crystallites, area of inter-grain contacts and crystallography structure and orientation of grains (crystallites).

2. Electronic parameters of chemisorbed species: number of surface sites, adsorption/desorption energies, positions and distributions of local electronic levels in the band gap of semiconductor due to chemisorptions and so on

3. Composition, bulk and surface stoichiometry of the film. These parameters determine the electron concentration, initial surface
potential and own surface charge through the surface and bulk number of oxygen vacancies.

4. Parameters of the impurities and additives: type of impurity, effective size and surface density of clusters, bulk concentration, electrical activity etc.

The uncontrollable parameters include water in various forms, drift due to ageing, small concentration of carbon compounds and other interfering chemisorbed species, etc (Brinzari et al, 2001). Characteristically sensors have to be designed as if they can provide continuous or periodic real time, online point measurements.

Catalytic metallic additives such as palladium are often used to increase the selectivity and to enhance the response of these tin oxide based gas sensors. In recent years, the sensitivity of the semiconductor oxide materials has been improved by reducing the grain size, with greatly improved properties reported for sizes in the 5-50 nanometer range. Below the critical grain size, substantial improvement in sensor properties are observed influenced by oxide material in certain morphology with dopants added.

1.7 Objectives of the Present Work

The problem of optimisation is a key factor in the design of any technology. An accurate mechanism which could describe the gas sensing operation in metal oxide semiconductor thin film is not framed yet. Developing a long lasting sensor having large value for sensitivity at low concentrations of LPG or methane gas which could withstand multiple encounters of the target gas and humidity is aimed in this work. Investigations on the microstructural aspects that should be modified for
effective oxygen adsorption/desorption mechanism on the sensor surface favoring gas sensing operation is investigated by doping with Mg and B. The details of surface composition also have been analysed side by side for a better understanding.

In short, an attempt has been made herein to develop a reliable LPG sensing material with significant sensitivity to detect small amounts of gas in air with good humidity stability and relatively short response time.

The main objectives of the present studies can be summerised as follows:-

- To deposit pure SnO₂ thin films on glass substrate by spray pyrolysis technique. To compare the microstructure, morphology and composition of Magnesium (Mg) and Boron doped SnO₂ films with the undoped.

- To analyse resistance variation of films in the presence of LPG and methane at different operating temperatures. To modify the micro structural properties and composition to enhance the gas sensitivity and selectivity.

- To analyse the dependence of film thickness, crystal structure, crystallite orientation, deposition temperature, lattice strain, concentrations of dopants, and operating temperature of the films in relation to the gas sensing properties.

- To evaluate their characteristic variation in gas sensing and surface topography due to long-term ageing.