

# CHAPTER 1

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## Introduction and Literature Review

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This chapter describes the brief introduction of gas sensors and their classification, applications along with literature review. Motivations, objectives and organization of thesis have also been discussed in this chapter.

### 1.1 Introduction

Hydrogen has received much attention due to its potential use as a “clean” energy source, aiding the reduction of environmental concerns such as pollution and global warming. Furthermore, hydrogen has many important applications in many industries such as chemical, petroleum, food, semiconductor and metallurgy. However, there are number of safety concerns regarding use of hydrogen. Its low mass and high diffusion coefficient ( $0.61\text{cm}^2\text{s}^{-1}$ ) makes it extremely difficult to store [Hord J. (1978); Eichert H. and Fischer M. (1986)]. It is highly flammable in concentrations ranging from 4% to 90% by volume, with its lowest explosion limit being 4.1% [Sax N. I. (1975)]. The low ignition energy having value  $20\mu\text{J}$  and large flame propagation velocity ( $3.46\text{ms}^{-1}$ ), further aggravate the condition by making it extremely explosive and hence dangerous. Hydrogen gas is anticipated to be used as the next generation’s fuel and from the basic energy infrastructure that will provide power to the future societies. Hydrogen powered vehicles could diminish the green house gas emission and improve air quality. However safety issues are one of the most important challenges in the progress of hydrogen energy.

In addition to hydrogen, hydrocarbons are another class of gases that have tremendous potential to be used as fuel. Hydrocarbons are commonly found in exhaust gases, largely due to incomplete combustion, predominantly from automobiles. They react in the atmosphere to form ground-level ozone, a major component of smog and also contribute to the formation of green house gases. They are widely used in preparation of various products like pesticides, solvents and plastics. Hydrocarbons may also pose several health risks, with short- term exposure possibly resulting in dizziness, intoxication, irritation and anaesthesia. Thus monitoring hydrocarbons not only provides a route for process control monitoring, but it is also an effective tool towards

current stringent pollution control. The detection of volatile organic compounds or smells generated from food or household products has also become increasingly important in food industry and in indoor quality.

H<sub>2</sub>S is another gas which is very toxic if present even at very low concentration in environment. It is colorless, very poisonous, ignitable gas with the characteristic of foul odor of rotten eggs. It is mainly used for the production of elemental sulphur and sulphuric acid, the manufacture of heavy water and other chemicals. For agriculture purpose, it is used as a disinfectant. It often results from the bacterial breakdown of organic matter in the absence of oxygen, such as in swamps and sewers. Other sources are craft paper mills, tanneries, coal mines, petroleum refineries etc. since, it is a chemical asphyxiate, which affect human's nervous system and could cause an individual to lose consciousness even at a very low concentration.

The sensors are similar to human sensory organs, optical sensors are similar to eye, pressure sensors are similar to skin as it senses the touch. Similarly, gas sensors are also analogous to human nose. The realization of these sensors depends on different transduction principles in accordance with the requirements that have to be detected. The basic transduction principles are piezoelectric effect, photoelectric effect, Hall effect, Seebeck effect and chemical effect etc.

Therefore, efficient and reliable sensors are required for monitoring and leak detection [Trinchi *et al.* (2008)]. Applications of gas sensors in different fields are summarized in Table 1.1.

Conventional gas sensing instruments such as Mass Spectrometer (MS), Gas Chromatograph (GC) etc. are very cumbersome, costly and need a careful maintenance by skilled personnel. In addition, most analysis requires sample preparation, so that on-line, real-time analysis is difficult. As a result there has been a drive to establish a device for rapid and inexpensive detection of gases which does not require skilled personals. Ideally, the device should be portable, allowing direct online or offsite measurements.

The solid gas sensors are cheap solution to the problems associated with conventional gas detection instruments. Further, the miniaturization of chemical sensors was made possible by silicon processing which leads to opportunities for mass production of

inexpensive sensors with low power consumption, fast responsive and increased sensitivity to small amounts of chemical species [Majoo *et al.* (1996)].

## 1.2 Applications of Gas Sensors in Different Fields

The major applications of gas sensors have been given in Table 1.1.

**Table 1.1:** Applications of gas sensors [Capone *et al.* (2003)]

S.No.	Fields	Applications
1.	Environment and Pollution control	<ul style="list-style-type: none"> <li>• Weather stations</li> <li>• Pollution monitoring</li> </ul>
2.	Medicine	<ul style="list-style-type: none"> <li>• Disease detection</li> <li>• Breath analysis</li> </ul>
3.	Industrial Production	<ul style="list-style-type: none"> <li>• Fermentation control</li> <li>• Process control</li> </ul>
4.	Safety	<ul style="list-style-type: none"> <li>• Personal gas monitor</li> <li>• Boiler control</li> <li>• Toxic/flammable/explosive gas sensors</li> <li>• Leak detection</li> <li>• Fire detection</li> </ul>
5.	Food Processing	<ul style="list-style-type: none"> <li>• Process control</li> <li>• Food quality control</li> <li>• Packaging quality control</li> </ul>
6.	Automobiles	<ul style="list-style-type: none"> <li>• Filter control</li> <li>• Car ventilation control</li> <li>• Alcohol breath tests</li> </ul>

### 1.3 Semiconductor Gas Sensors and Literature Review

A micro gas sensor is a transducer that converts chemical interaction into an electrical signal. Generally, semiconductor gas sensors are gas sensitive resistors and are fabricated by either thin [Seiyama *et al.* (1962)] and thick film technology [Taguchi (1972)]. Depending on the various microelectronics technologies used for the development of gas sensors, there are basically following types of solid state gas sensors which are classified as follows:

i) Thin film sensors

ii) Thick film sensors

iii) MOS sensors

A brief description and review of sensors is described below:

#### 1.3.1 Thin Film Sensors

Thin solid films are involves depositing individual atoms on a substrate. A thin film is defined as a low-dimensional material created by condensing, one by one, atomic/ionic/molecular species of matter. The thickness is typically less than several microns [Wasa *et al.* (2004)]. Thin film sensors consist a pair of electrodes underneath the gas sensing layer, which are fabricated by vacuum evaporation technique [Ogawa *et al.* (1981); Baciocchi *et al.* (1990)], sputtering [Fleischer *et al.* (1992); Hubner and Drost (1991); Demarne *et al.* (1992)], chemical vapour deposition [Laluzé *et al.* (1991)] and high temperature vapour hydrolysis [Geatches *et al.* (1991)].

Thin film technology has been found more suitable for fabrication of gas sensors as it allows the control of material composition at a monolayer level which eventually causes the tremendous improvement in the sensitivity and the long term stability of the sensor [Sberveglieri (1995)].

Seiyoma *et al.* [Seiyoma *et al.* (1970); (1962)] fabricated the first thin film semiconductor gas sensor. A thin film of SnO<sub>2</sub> or ZnO is deposited on glass, alumina or silicon substrates for sensor applications, different techniques have been used. In such types of sensors, a very low percentage of noble metals such as Pd and Pt are

considered as promoters of the reaction between the gas and the semiconductor surface. The addition of these metals has been known to be effective in improving the sensitivity and selectivity to specific gases.

Tesfamichael [Tesfamichael (2009)] has fabricated the electron beam evaporated nanostructured tungsten oxide ( $\text{WO}_3$ ) and iron-doped tungsten oxide ( $\text{WO}_3:\text{Fe}$ ) thin film gas sensors for detection of  $\text{NH}_3$ ,  $\text{CO}$ ,  $\text{CH}_4$  and  $\text{CH}_3\text{CHO}$  gases. Pure  $\text{WO}_3$  sensor has been shown good sensitivity at low concentrations (1-10 ppm) of these gases and at operating temperature between  $100\text{ }^\circ\text{C}$ - $250\text{ }^\circ\text{C}$  while Fe-doped  $\text{WO}_3$  sensor showed some sensitivity to acetaldehyde only. To make the  $\text{WO}_3$  sensor workable at low temperatures ( $50\text{ }^\circ\text{C}$  -  $100\text{ }^\circ\text{C}$ ), the sensor surface was photo activated with blue-LED and the appreciable improvement in the sensitivity was obtained.

Jeong *et al.* [Jeong *et al.* (2010)] have been reported the Indium tin oxide (ITO) based thin film gas sensor for detection of methanol. A sandwich structure of ITO/ Au/ ITO (IAI) multilayer films was fabricated on the glass substrate and effect of Au interlayer (5 nm) on the methanol sensitivity has been studied by comparing its response with the ITO single- layer film sensor. ITO/Au/ ITO (IAI) multilayer film sensor was found to exhibit higher sensitivity than conventional ITO film sensor at room temperature.

### **1.3.2 Thick Film Sensors**

The principle of operation of thick film sensor is based on the concept of change in conductance due to the adsorption of gases on the surface of a semiconductor. Thick film sensor consists a closely spaced electrode pair those are connected via a gas sensitive layer. Thick film technology has been developed primarily for producing miniaturized and robust electronic circuit in an extremely cost effective manner [Matsura *et al.* (1993); Arkinson *et al.* (1991)] as it leads to mass production and automated techniques hence allowing significant economies of scale to be achieved on large production runs.

Taguchi [Taguchi (1970;1991)] made revolution in the area of gas sensor by utilizing the concept of change in conductivity due to adsorption of a gas on the surface of semiconductor. He made the first sensor using ZnO. Tin oxide has become more popular because it is more sensitive to large number of oxidizing as well as reducing

gases. In addition, the sensitivity towards specific gas (selectivity) could be enhanced/modified [Cobos (2001); Vlachos *et al.* (1997)] by the addition of catalyst to the oxide layer.

Oyabu *et al.* [Oyabu *et al.* (1982)] reported the sensing characteristics of doped tin oxide thick film gas sensors. They have developed the device by screen printing method with Pd and Pt doped tin oxide as base material. They observed that the mass production and sufficient mechanical strength of the sensor can be achieved by using screen printing method.

Kohl [Kohl (1990)] has discussed the role of the noble metals (Palladium) in tin oxide based sensor in the chemistry of solid state gas sensors. He demonstrated the role of chemisorbed as well as lattice oxygen on oxide and noble metals in detection of hydrogen.

Gopel [Gopel (1990)] has discussed the atomistic models and research trends in solid state chemical sensors. Firstly, he presented a brief survey about the thermodynamically and kinetically controlled sensing mechanism, atomistic models and research trends of solid state chemical sensors. In the same work discussed the future work involving new technologies of interface analysis controlled to dimensional physical chemistry at interface, new materials, new technologies, new micro-structured devices and pattern recognition approaches. He concluded that the concept and definitions of analytical chemistry make possible a quantitative characterization of sensitivity and selectivity. He has also reported the effect of doping on performance of tin oxide based thick sensors.

Watson *et al.* [Watson *et al.* (1990)] had reported a tin oxide based CO (0-100 ppm CO in air) selective sensor interfaced with a microprocessor- controlled instrument. A relevant electronic design procedure has been proposed which demonstrate the linearity of sensor response in terms of the instrument output as a function of CO concentration.

Mishra *et al.* [Mishra *et al.* (1994)] have studied SnO<sub>2</sub> based pure and doped thick film sensors and sensor arrays for H<sub>2</sub>, CO, CH<sub>4</sub> and LPG and they have observed that doping and selection of electrode materials show significant effect on response and selectivity of the sensor.

Srivastava *et al.* [Srivastava *et al.* (1998)] fabricated Pd-doped tin-oxide gas sensor with improved performance at room temperature. They observed that plasma processing improves the sensitivity of the sensor.

Wei *et al.* [Wei *et al.* (2010)] had reported the copper oxide/ tin oxide thick film gas sensor for detection of H<sub>2</sub>S. Sol-gel dialectic technique was used for preparation of tin oxide powder and CuO was doped by deposition-precipitation method. The polycrystalline powder of CuO/SnO<sub>2</sub> was utilized in fabrication of thick film gas sensor. The fabricated sensor exhibited the good sensitivity with fast response and recovery to H<sub>2</sub>S at 160 °C and 210 °C operating temperature.

Kashyout *et al.* [Kashyout *et al.* (2010)] had reported ZnO based thick film gas sensors for detection of O<sub>2</sub> and CO<sub>2</sub> gases. Sol-gel technique was used to prepare ZnO and Sb-doped ZnO nano powder and subsequently film gas sensors were fabricated with these nanopowders. ZnO was doped with different concentrations (3, 5, 7 and 10 wt %) of Sb and their effect on material properties and gas sensing characteristics were studied. The gas sensitivity was higher for O<sub>2</sub> gas than CO<sub>2</sub>, and the sensitivity improved after Sb doping with maximum value at Zn: Sb= 93:7 wt%.

Kim *et al.* [Kim *et al.* (2012)] reported the La-doped SnO<sub>2</sub> thick film sensor for the detection of CO<sub>2</sub> and the effects of mechanical milling of SnO<sub>2</sub> powders on the CO<sub>2</sub> sensitivity of a SnO<sub>2</sub> thick film sensor were also studied. It was found that after the exposure of 1000 ppm CO<sub>2</sub>, the sensitivity of SnO<sub>2</sub> thick film sensor improves from 1.14 to 1.52 with increasing the La<sub>2</sub>O<sub>3</sub> doping concentration from 0 mol% to 2.2 mol%. Furthermore, enhanced sensitivities of 1.45 to 1.51 were obtained for the thick film sensors processed with mechanically milled SnO<sub>2</sub> powders.

Auroutonion *et al.* [Auroutonion *et al.* (2013)] investigated the multi-walled carbon nanotubes (MWCNTs) coated with SnO<sub>2</sub> nanoparticles using both hydrothermal process and sol-gel technique under different solvent conditions. Gas sensor structures were developed on the base of these materials. It was observed that the Ru nanocomposite thick film sensor structures having the ratio of the components 1:8 and 1:50 possess the high response to methanol and ethanol vapour as well as i-butane gas at 200 °C operating temperature. Furthermore, the structure having 1:4 ratio of components exhibited the best selectivity toward methanol and ethanol vapors. Though the sensor comprises porous pellets of SnO<sub>2</sub>, and usually containing a

precious metal catalyst, offer a high degree of sensitivity combined with a light weight, simple construction, high stability and a low cost, but the non-selectivity, high operating temperature (300 °C to 400 °C) and a significant power requirement, are the main disadvantages of these thick film sensors.

### 1.3.3 MOS Sensors

MOS sensors consist of a thin catalytic metal layer; generally noble metals like platinum (Pt), palladium (Pd), Iridium (Ir) etc deposited on the surface (top) of an insulating oxide layer, usually SiO<sub>2</sub> on silicon (Si) substrate. These sensors are very small in size. They occupy less area which is of the order of few (mm)<sup>2</sup>. MOS gas sensors have been come in existence for more than three decades and are a promising device for monitoring hydrogen and hydrogen containing gases in a wide range of commercial applications [Lundstrom (1996)]. In 1975, Lundstrom *et al.* had first fabricated and reported the MOSFET based hydrogen sensor. The basic principle of operation of these devices has been proposed by Lundstrom and co-workers [Lundstrom (1981); Lundstrom and Soderberg (1981); Fogelberg *et al.* (1995); Fogelberg and Petersson (1996); Eriksson *et al.* (1997)]. According to their models, molecular H<sub>2</sub> dissociates into atomic H<sub>2</sub> on the catalytic metal gate. These H<sub>2</sub> atoms are diffused through porous Pd layer (gate) to the Pd-insulator interface. At the interface H<sub>2</sub> atoms form a dipole layer which decreases the effective work function of Pd metal which results in decrease in flat band voltage of the MOS sensor. The decrease in flat band voltage can be measured as either a shift in the capacitance-voltage (C-V) curve of capacitor, or in the current-voltage characteristic of a MIS diode or transistor [Lundstrom (1981)].

Lundstrom *et al.* [Lundstrom *et al.* (1976(a))] developed a hydrogen-sensitive Pd-gate MOS-transistor to detect small amounts of hydrogen in smoke. It had been found that the device can be used to detect a fire before it has started and therefore has a potential application as a fire alarm.

Lundstrom *et al.* [Lundstrom *et al.* (1977)] reported that metal-oxide-semiconductor structures those can be used to study catalytic reactions on metal surfaces (like Pd and Pt surfaces). The flat band voltage shift induced by hydrogen at the metal-oxide interface is a measure of the amount of hydrogen in the metal, which in turn reflects the chemical reactions on the surface. The Pd mos sensor is tested towards hydrogen



in the argon and in air ambient and experimental results are compared with absolute reaction rate theory. The agreement between theory and experiments is surprisingly good.

Yamomoto *et al.* [Yamomoto *et al.* (1980)] found that the current through a schottky barrier formed at the interface between Pd film and n-type titanium oxide (TiO<sub>2</sub>) single crystal is sensitive to H<sub>2</sub> or other reducing gases in the ambient. They explained this effect by taking account of the diminished barrier height at Pd and TiO<sub>2</sub> interface caused by the action of gases, changing the work function of Pd metal. The change in Pd work function estimated from the result is confirmed by the direct measurements of the metal surface potentials by use of a vibrating capacitor method. Similar electrical properties have been investigated for junctions of TiO<sub>2</sub> with Pt, Au, Ni, Al, Cu, Mg and Zn and of ZnO, CdS, GaP, and Si with Pd.

Ackelid [Ackelid (1980)] reported that Pd gate MOS sensors can detect the ethanol vapour at about 150 °C. The mechanism believed to be the catalytic dissociation of ethanol yielding H<sub>2</sub> atoms, which in turn possesses a similar response to that of hydrogen.

Dobos *et al.* [Dobos *et al.* (1980; 1983)] studied a different CO sensitive MOSFET in which the gate contact was made by TiO<sub>2</sub>. The sensing mechanism of such device was correlated to the change in the Fermi energy of the diode on the adsorption of CO. The device was shown to respond well to CO, but had poor base line stability, due to the poorly conducting nature of the TiO<sub>2</sub>, required for high gas sensitivity.

Lundstrom *et al.* [Lundstrom *et al.* (1983)] have described the properties of gas-sensitive field-effect devices with catalytic metal gates. They demonstrated that how the selectivity of these sensors depends on parameters such as the choice of catalytic metal, the structure of the catalytic metal film and the operation temperature of the device. The sensitivity towards molecules like hydrogen, ammonia, ethanol and ethylene had been demonstrated. The selectivity pattern of devices with catalytic metal gates had also been discussed in relation to the fabrication of multisensor arrays and the development of 'artificial olfactory senses'

Dobos *et al.* [Dobos *et al.* (1984)] reported that hydrogen induced drift problems of Pd/SiO<sub>2</sub>/Si hydrogen sensor can be eliminated by introducing a thin layer of thermally

oxidized alumina layer between the Pd metal gate and the SiO<sub>2</sub>. It has also been shown that sputtered metal oxide such as alumina, Ta<sub>2</sub>O<sub>5</sub> and LPCVD silicon nitride exhibit the similar behavior towards hydrogen induced shift.

Maclay [Maclay (1985)] reported a Pd gate MOS sensor employing an ultra thin layer (30 Å) of Pd. The MOS sensors were fabricated on n-type and p-type silicon wafers with thermal oxide layer ranging in thickness from 66 Å to 269 Å. A 350 Å layer of gold was also deposited to have a continuous electric contact. The fabricated devices exhibited much faster response and recovery at room temperature than that of sensors fabricated with thick layer (300 Å) of Pd. He concluded that sensors fabricated on p-type silicon exhibited faster response than the sensors fabricated on n-type silicon.

Lundstrom *et al.* [Lundstrom *et al.* (1986)] reviewed the properties of gas sensitive semiconductor devices with catalytic metal gate. They emphasised on H<sub>2</sub> containing molecules like H<sub>2</sub>, NH<sub>3</sub>, H<sub>2</sub>S, alcohols, ethylene etc. sensitive FET structures. A brief review of some of the developed device structures is given. The principles of hydrogen sensors with Pd gates are described in some detail. Ammonia sensitive field effect devices with thin catalytic metal gates are discussed. Applications of gas sensitive field effect devices had been reviewed for medical diagnosis, leak detectors, and biosensors etc..

Ross *et al.* [Ross *et al.* (1987)] reported the response to ammonia of silicon-based MOSFET devices having either evaporated or sputtered Pt gate electrodes. A measure difference in ammonia sensitivity was observed between these two types of device, which is thought to be related to differences in morphology between the two types of gate electrode, devices having evaporated Pt gate electrodes, which are non-continuous, are very ammonia sensitive, whereas devices having sputtered Pt gates, which are thick, are not ammonia sensitive

For MOS sensor to be sensitive towards other gases like CO, Alcohols, NH<sub>3</sub> and wide range of hydrocarbons, the morphology of the metal gate should consist high concentration of cracks [ Jelly and Maclay (1987); Flippov *et al.* (1995); Lofdahl *et al.* (2001)].

Dobos *et al.* [Dobos *et al.* (1985)] reported the performance of PdO-Pd-multilayer gate MOSFET sensor for detection of CO which was fabricated with holes in gate

electrode. They suggested that “hole-gate” structure facilitates the CO molecules to penetrate through the metal. The sensor exhibited the high sensitivity to CO and also the good electrical control of the transistor. The performance was also compared with the commercial SnO<sub>2</sub> based CO sensor and it was found that MOS transistor showed lower cross sensitivity for methane, butane and ethanol for MOS sensor to be sensitive towards other gases like CO, alcohols, NH<sub>3</sub> and wide range of hydrocarbons, the morphology of the metal gate film should consist high concentration of cracks [Jelly and Maclay (1987); Flippov *et al.* (1995); Lofdahl *et al.* (2001)].

Formoso *et al.* [Formoso *et al.* (1990)] studied the admittance of ultra thin (25 Å) Palladium (Pd) gate MOS capacitor as a function of hydrogen and CO gas concentration. The ultrathin gate is a porous film in the form of partially connected islands. Bias scan conductance method at fixed frequency has been employed for evaluate the interface state density (Nit). They observed that Nit increases with increase in hydrogen concentration in the range of (3 ppm to 1% ) while Nit was found to decrease with increasing concentration of CO in the range of (100 ppm to 10,000 ppm).

Kobayashi *et al.* [Kobayashi *et al.* (1994; 1995)] reported sensing mechanism of hydrogen on Pd/SiO<sub>2</sub>/Si MIS tunnelling diodes. They reported the variation of I-V and G-V characteristics of device upon exposure to hydrogen voltage shift of the I-V curves for Pt/ SiO<sub>2</sub>/ Si MIS tunnelling diodes following the introduction of hydrogen are caused mainly due to (i) the decrease in the effective Pt work function, (ii) the internal field dependent movement of hydrogen ions in the SiO<sub>2</sub> film, (iii) the formation of interface states. They have also reported interface states formation of hydrogen induced interface states in Pt/SiO<sub>2</sub>/Si MOS sensor and found that the diffusing species through SiO<sub>2</sub> layer results in the interface states in form of proton and not hydrogen atoms.

Lundstrom *et al.* [Lundstrom *et al.* (1995)] reviewed some of the ongoing studies at their laboratory of gas-sensitive field-effect devices with catalytic metal gates. Particularly, they discuss the use of such devices in so-called electronic noses due to the possibility of changing the selectivity patterns of the devices by the selection of catalytic metal and operation temperature. So many examples of the application of e-noses consisting of field-effect devices in combination with metal oxide-based sensors

are given. A summary is given on some remaining scientific problems and studies related to the understanding and development of gas-sensitive field effect devices.

Fillipov *et al.* [Fillipov *et al.* (1995)] observed the effect of porous gate structure on ammonia response of Pd/SiO<sub>2</sub>/Si MOS structure. They found that hydrogen cyclic treatment (HCT) modifies the structure of evaporated Pd film due to pore formation. They concluded that Pore formation is mainly responsible for ammonia and CO sensitivity of MOS gas sensor.

Fillipov *et al.* [Fillipov *et al.* (1997)] studied the physiochemical properties of Pd/SiO<sub>2</sub>/Si based MOS gas sensor with external catalytic element towards methane and propane. The temperature of sensitive element was kept constant (463 K) while the CE (platinum coil) which was mounted above the sensor could be heated in wide temperature range from 1100 K in air to 700 K in helium. The sensor was found to be sensitive to saturated hydrocarbons in air as well as oxygen atmosphere. They observed the linear relationship between the sensor's signal (initial rate of flat band voltage) and the chosen hydrocarbons (propane and butane) concentration in air ranging from 100 ppm to 2000 ppm.

Alexe [Alexe (1998)] has investigated interface trap density distributions within Si for metal-bismuth titanate-silicon capacitors fabricated by chemical solution deposition. The interface trap density was measured by a G-V technique at room temperature and a value in the order of 10<sup>11</sup>-10<sup>12</sup> eV<sup>-1</sup> cm<sup>-2</sup> was found depending on the ferroelectric crystallization temperature. An increase in the annealing temperature results in an increase in the interface trap density.

Fakuda *et al.* [Fakuda *et al.* (2000)] reported the sensing behaviour of MOSFET gas sensor with porous Pt-SnO<sub>2</sub> gate for detection of CO. The sensor responded well in an operating temperature range of 27 °C to 100 °C, much lower than, the range of operation for conventional noble metal gate MOSFET gas sensors. At 27 °C, even low concentration (54 ppm) of CO gas could be detected with response time of less than 1 minute. A model comprising of adsorption of CO on thin porous catalytic layer of Pt and a subsequent spill-over onto SnO<sub>2</sub> was also proposed to support the sensing mechanism.

Kunimoto *et al.* [Kunimoto *et al.* (2000)] reported NO<sub>x</sub> sensing behaviour of heterojunction structure consisting of Pt/SnO<sub>2</sub>/n-Si/p<sup>+</sup>-Si/Al having porous SnO<sub>2</sub>. The sensor was found to be extremely sensitive for NO<sub>x</sub> detection in a low concentration level of 1 ppm at room temperature. The barrier height or conductivity change of SnO<sub>2</sub> sensing layer was assumed to be responsible for this high sensitivity behaviour. The Sensors fabricated with n-Si, p-Si or P-Si/n<sup>+</sup>Si substrate gave no response to NO<sub>x</sub>.

Dwivedi *et al.* [Dwivedi *et al.* (2000)] studied the performance of a palladium-gate MOS hydrogen sensor by conductance method. Structure of the device was fabricated on a n-type <100> silicon wafer having resistivity of 1-6 Ω cm using plasma technology. Sensitivity and response-recovery time of the fabricated sensor have been studied for different concentration (1480±11840 ppm) of hydrogen with different signal frequency (500 Hz, 10 KHz and 100 kHz) at room temperature. Hydrogen-induced interface-trapped density (N<sub>it</sub>) has been also evaluated as a function of gas concentration using a bias scan conductance method. Obtained results show that device performance is improved (i.e., high sensitivity and low response recovery time) and further it has been concluded that implementation of plasma technology (i.e., dry plasma cleaning of Si surface and in-situ RF anodization of silicon in oxygen plasma near room temperature) may be a future step towards fabrication of MOS-based sensors and integrated arrays with improved performance at room temperature.

Filippine *et al.* [Filippine *et al.* (2000)] have reported the Au- gate MOS gas sensor for the detection of nitrogen dioxide (NO<sub>2</sub>) in concentration range of 15 ppm to 200 ppm. The sensing properties were found to be strongly dependent on the gate morphology and grain size. The response mechanism has been explained by considering the permeation of gas along the grain boundaries.

Lofdahl *et al.* [Lofdahl *et al.* (2001)] attempted to correlate the morphology and selection of gate material with the response of field effect gas sensor towards H<sub>2</sub>, NH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>OH, C<sub>2</sub>H<sub>4</sub> and CH<sub>3</sub>CHO. Palladium, Platinum and Iridium respectively were used as the gate material. Instead of fabricating the various samples (of particular gate material) with different morphology a single sample where the morphology over the gate area can be varied continuously was fabricated while the measurements were performed by utilizing the scanning light pulse technique [SLPT] at different points of the gate area. The crack coverage and the sensitivity was found

to be independent only in case of  $\text{NH}_3$ . The observed results were explained through dissociative mechanism.

Abom *et al.* [Abom *et al.* (2002 (a))] have attempted to modify the catalytic activity at the gate surface of Pt-gate MOS sensor by depositing the thin film of oxides ( $\text{SnO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  respectively) over the gate metal. The response of the sensors towards  $\text{H}_2$ ,  $\text{NH}_3$ , propane,  $\text{CH}_3\text{OH}$ , CO and  $\text{NO}_2$  was measured. The sensors with very thin layer (<10nm) of  $\text{SiO}_2$  or  $\text{SnO}_2$  over Pt-gate were found to be highly selective towards  $\text{NH}_3$ , whereas for thicker film (of  $\text{SiO}_2$  or  $\text{SnO}_2$ ), sensor showed a very poor response. In addition, the sensitivity of the sensor was not much affected by using thin film of  $\text{Al}_2\text{O}_3$  over gate metal.

Abom *et al.* [Abom *et al.*(2002 (b))] observed the effect of growth parameters of gate metal film on hydrogen response of field effect sensor by using the d.c magnetron sputtering and evaporation technique for deposition of Pt film. The parameters such as substrate temperature, film thickness and energy of impinging metal atoms were investigated and correlated with morphology of the growth film. The obtained results illustrate that growth parameters significantly affect the morphology, crystallinity and quality of metal/oxide interface and consequently the gas response of the sensor.

Weidemann *et al.* [Weidemann *et al.* (2003)] compared the hydrogen response of in-situ (oxide free interface) and ex- situ (with oxide) deposited Pd-Schottky contacts on Si-doped GaN layer. The hydrogen sensitivity of ex-situ fabricated sensor was found to be approximately 50 times higher than in-situ deposited diodes, as intermediate oxide layer was believed to provide more adsorption site for atomic hydrogen as compared to in-situ deposited Pd-Schottky diode.

Liu. *et al.* [Liu *et al.* (2004)] reported the large area Au/ $\text{Al}_2\text{O}_3$ / n-Si (MIS) sensor for the detection of ethylene and oxygen. It was found that only MIS structures exhibit detection capability for the gases having low adsorption energy. The variation of the sensitivity of the sensor towards chosen gases (ethylene and oxygen) with the insulator ( $\text{Al}_2\text{O}_3$ ) thickness was also studied. The sensitivity of the sensor for oxygen was observed to be decreasing rapidly with increase in the oxide thickness whereas for ethylene the sensitivity increases from zero in the absence of oxide and attain maximum value (nearly 30 pA) at approximately 6 nm oxide thickness and was found

to decrease with further increase in oxide thickness. However, the sensor exhibited higher sensitivity to ethylene in thickness range of 2.5-8 nm in comparison to oxygen.

Casals *et al.* [Casals *et al.* (2005)] reported the Pt/TaSi<sub>x</sub> gate MOS sensor based on 6H-SiC substrate for sensing CO and NO<sub>2</sub>. MOS capacitors with 40 nm thermal oxide and 100 nm thick gate while tunnel MOS diode with an interfacial layer of 1 nm and 20, 40 and 100 nm thick gates were fabricated and annealed. The sensors based on MOS capacitor showed no response before annealing. However, a significant improvement in the electrical stability as well as sensitivity to CO and NO<sub>2</sub> was observed after annealing MOS capacitor in propane for some hours. The tunnel diode however, with thick Pt gate after annealing at 700 °C in air provided the best response, through the response of the tunnel diode structure was lower as compared to annealed MOS capacitor.

Erikson *et al.* [Erikson *et al.* (2005)] observed the effect of choice of insulator on the hydrogen sensing properties such as saturation concentration, saturation response and detection limit of the field effect gas sensor. They fabricated the MOS capacitor with different insulators like SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, SiN<sub>4</sub> and Ta<sub>2</sub>O<sub>5</sub>. They concluded that the gas response is proportional to the concentration of surface oxygen atoms at the insulator surface and the oxygen concentration of insulator surface also determines the size of saturation response

Zamani *et al.* [Zamani *et al.* (2005)] fabricated the NO<sub>2</sub> gas sensor by combining the MIS structure with a solid electrolyte (NaNO<sub>2</sub>). The sensing mechanism was based on shift in flat band voltage on NO<sub>2</sub> exposure. The flat band voltage was found decreasing linearly with an increase on NO<sub>2</sub> concentrations on logarithmic scale

Li *et al.* [Li *et al.* (2006)] studied the effect of polyimide (PI) deposition on the surface of Pd/SiO<sub>2</sub>/Si MOS capacitor to the hydrogen selectivity. The PI coated sensor exhibited the improved selectivity to hydrogen in mixture consisting of CO<sub>2</sub>, O<sub>2</sub> and mixed hydrocarbon streams (CO, acetylene, ethylene, methane). The effect of the PI thickness on the sensing behaviour was also observed and the response time was found to be dependent on the thickness of the coating.

Balyuba *et al.* [Balyuba *et al.* (2006)] studied the effect of thermal annealing on the sensitivity and response time of Si-based MOS sensors towards H<sub>2</sub> and NH<sub>3</sub> exposure.

The sample annealed at 200 °C exhibited the higher sensitivity towards hydrogen as compared to ammonia whereas for annealing temperature above 300 °C the decreasing trend in the sensitivity for both the gases was observed. However, decrease in hydrogen response was more rapid as compared to NH<sub>3</sub>. Besides this response time for NH<sub>3</sub> was found to be decreasing with increase in annealing temperature and for H<sub>2</sub> the response time was found unaffected.

Lu *et al.* [Lu *et al.* (2007)] fabricated the hydrogen sensor based on Ni/SiO<sub>2</sub>/Si MOS capacitor. Fabricated sensor was tested for various hydrogen concentrations (50 ppm-1000 ppm) at an operating temperature of 140 °C. The highest response was observed at the same bias voltage (-0.4 V) for all the concentration levels. The response/recovery time of the low cost Ni- based sensors was similar to that of the Pd-based hydrogen sensors. The observed sensing phenomenon has been explained on the basis of Langmuir isotherm model and the experimental results were found to be in good agreement.

Nakagomi *et al.* [Nakagomi *et al.* (2007)] proposed floating gate field effect gas sensor for hydrogen sensing in oxygen atmosphere at room temperature. Hydrogen exposure in presence of O<sub>2</sub> caused the variation in V<sub>DS</sub> (drain source voltage) and V<sub>GS</sub> (gate-source voltage) at constant current and these changes are recorded as sensing signals. V<sub>GS</sub> exhibited a unique behaviour with change in the H<sub>2</sub> concentration by showing initial rising trend with increase in hydrogen concentration, reaching a peak point, followed by decreasing trend with increase in hydrogen concentration. It has also been reported that presence of water vapour prevents the hydrogen.

Salchi *et al.* [Salchi *et al.* (2007)] fabricated the Ni/n-Si schottky diode. They also compared the hydrogen sensing properties of magnetic and non magnetic Ni/ n-Si schottky contacts. The sensitivity of the magnetic Ni/Si sensor was found to be higher (62% at 80 °C while 51% at room temperature) than non magnetic sensor. The Sensor with thin layer of Ni were found to exhibit a better sensitivity for hydrogen.

Tan *et al.* [Tan *et al.* (2008)] have reported the high-yield synthesis of SnO<sub>2</sub> nanoparticles via a facile, economical and easily scalable solid-state molten salt synthesis method. The inorganic additive, molar ratios of chemicals and annealing temperature were found to control the size and porosity of the SnO<sub>2</sub> nanoparticles. The synthesized SnO<sub>2</sub> nanostructures were uniform, well dispersed and exhibited high



crystallinity. Hydrogen sensors fabricated by the SnO<sub>2</sub> nanoparticles exhibited high sensitivity and stability. Other than tailoring the material's structure in terms of size and porosity, another potential method of enhancing the gas sensitivity is functionalization with Pd metal.

Rahman *et al.* [Rahman *et al.* (2008)] reported the MIS (Pd/AlN/SiC) hydrogen sensor capable of operating in dual mode as rectifying diode and also as a capacitor. The sensitivity was measured in terms of shift in forward bias voltage and observed to be nearly same ( $\Delta V_{FB}=0.35V$  for 100ppm) for both the modes of operation. They concluded that existence of large band gap and the presence of small concentration of shallow donors in AlN is mainly responsible for the dual behaviour of sensor.

Tsaltin [Tsaltin (2008)] studied the hydrogen sensing characteristics of Pd/ anodically grown native nitride/n-GaAs structure at different temperature (50, 90 and 130 °C). He has also studied the effect of thickness of nitride on the sensitivity and observed the tremendous improvement in sensitivity and detection limit of the sensor with thicker layer of native nitride.

Shafiei *et al.* [Shafiei *et al.* (2008)] reported material and gas sensing properties of Pt/SnO<sub>2</sub> nanowires/SiC MOS devices towards hydrogen. The SnO<sub>2</sub> nanowires were deposited onto the SiC substrates by vapor-liquid-solid growth method. The material properties of the sensors were investigated using SEM, TEM and X-ray photoelectron spectroscopy. The I-V characteristics have been carried out. The measure change in the barrier height for 1% hydrogen was found to be 142.91 meV. The dynamic response of the sensors towards hydrogen at different temperatures has also been studied. At 530°C, voltage shift of 310 mV for 1% hydrogen was observed.

Tang *et al.* [Tang *et al.* (2008)] studied the hydrogen sensing properties metal-insulator-SiC (MISiC) schottky diodes and evaluated the thickness of insulator layer on the hydrogen sensitivity. The results showed that sensitivity is a direct function of the oxide layer thickness. The layer change in the barrier was observed for thick oxide layer on hydrogen exposure.

Ryzhikov *et al.* [Ryzhikov *et al.* (2008)] reported the sensing properties of MIS structure Pt/Al<sub>2</sub>O<sub>3</sub>/Si towards reducing gases (1000 ppm H<sub>2</sub>, 300 ppm CO, 1000 ppm CH<sub>4</sub>) at operating temperature of 100 °C and 200 °C. Al<sub>2</sub>O<sub>3</sub> was doped with various

concentrations (3% and 6%) of noble metals Pt and Rh respectively. Micro structural analysis of the dielectric layer showed the existence of large number of grain boundaries and the porosity. The sensitivity and selectivity of the sensor was found to be higher than conventional MIS structure and attributed to the presence high density of surface states in  $\text{Al}_2\text{O}_3$  and at the interface of  $\text{Al}_2\text{O}_3/\text{Si}$ .

Boureane *et al.* [Boureane K. *et al.* (2008)] reported the effect of thickness of porous SiC layers on the sensing behaviour of Pt/SiC-pSi schottky diodes towards  $\text{H}_2$  and Acetylene and compared it with the sensing behaviour of schottky diode with non-porous SiC. The schottky diode with porous SiC (PSC) layer was found to possess higher sensitivity ( $\Delta I/I=90\%$ ) and sensitivity at low voltage (below 1Volt) than the diode with non porous SiC. In addition, the sensor with thin layer of porous SiC layer was found to perform better and the behaviour was independent of chosen catalytic metals (Pt, Pd).

Chiu *et al.* [Chiu *et al.* (2009)] reported the hydrogen sensing properties of metal-semiconductor-metal (MSM) sensor employing a Pd-mixture (Pd and  $\text{SiO}_2$ )-Pd triple layer structure on GaN substrate. The fabricated sensor biased with constant voltage (giving sensing current as output) exhibited high sensitivity nearly equal to  $8.7 \times 10^4\%$  at 49.1 ppm  $\text{H}_2$  while it exhibited a very high voltage shift of 17 V when biased by constant current (giving voltage as output) at same concentration  $\text{H}_2$ . The formation of double dipole layer formed at Pd-GaN interface and inside the mixture (Pd and  $\text{SiO}_2$ ) was assumed to be responsible for improvement in performance in comparison to Pd deposited GaN sensor.

Chang *et al.* [Chang *et al.* (2009)] studied the sensing response of Pd/ $\text{SiO}_2$ /AlGaIn based MOS diode towards hydrogen. It was found that response of the Schottky diode improves on deposition of intermediate  $\text{SiO}_2$  layer at the metal/ semiconductor interface. The performance of MOS diode at the room temperature was observed to be almost same as that of MOS diode at 150 °C. High reaction rate at Pd/ $\text{SiO}_2$  was assumed to be responsible for the better sensitivity and lower response time of MOS diode.

Kim *et al.* [Kim *et al.* (2009)] reported the MIS diode structure with Pd/  $\text{TiO}_2$ /  $\text{SiO}_2$  /heavily doped Si wafer/Al layer for detection of  $\text{CO}_2$  gas (in the range of 2.5% - 12.5%) at room temperature. The role of the quality and hence the surface properties

of Pd-TiO<sub>2</sub> sensing layer in improving the sensing performance of sensor has been investigated and performance of the sensor was observed to be significantly influenced by the surface characteristics of Pd-TiO<sub>2</sub> film.

Lombardi *et al.* [Lombardi *et al.* (2010)] investigated the chemical response of Pd-gate and Au-gate MOS sensors towards H<sub>2</sub> and NO<sub>2</sub> respectively by employing the pulse illumination technique. The gates were provided with the open windows to produce stronger pulsed photo current signals and to allow the direct access of the gases to dielectric. Above threshold voltage ( $V_T$ ), the Pulsed photocurrent versus the bias voltage curves of the Pd gate MOS capacitor shifted ( $\Delta V$ ) towards negative side on H<sub>2</sub> exposure while that of Au-gate MOS capacitor curve shifted towards positive side upon NO<sub>2</sub> exposure. In addition, it was found that observed shift in the bias voltage were reversed if the devices were operated below  $V_T$ .

Andringa *et al.* [Andringa *et al.* (2010)] fabricated a gas sensor based on self assembled monolayer field effect transistor (SAMFET) to sense the biomarker nitric acid (NO) acting as a neurotransmitter useful in asthma treatment. The SAMFET sensors were fabricated using iron porphyrin as a specific receptor for NO detection. The sensor exhibited high sensitivity towards NO (in ppb concentration). The high sensitivity of SAMFET sensor was attributed to the fact that semiconductor being only molecule thick proved the easy access of the analytic as the analytic and the active channel are separated by only one monolayer.

Kanungo *et al.* [Kanungo *et al.* (2010)] reported the influence of porosity on the hydrogen sensing performance of surface modified porous silicon (PS) sensors. Different samples of PS with different porosities were prepared by electrochemical anodization of p-type Si wafer using an electrolyte solution of HF and ethanol in different ratio. These samples were chemically modified by Pd and then Pd-Ag and Al electrodes were deposited on the top of PS samples to obtain Pd-Ag/PS/Si/Al MIS structure. The result showed that chemical surface modification with Pd metal improved the stability, sensitivity and also the response time of the hydrogen sensor. The unmodified PS sensors exhibited the increase in sensitivity with increase in porosity and attained the saturation while Pd modified PS sensors exhibited the optimum performance (84% sensitivity and minimum response and recovery time(8

sec and 207sec ) at 55% porosity. Further increase in porosity showed the decreasing trend.

Skucha *et al.* [Skucha *et al.* (2010)] reported the palladium/nanowire Schottky barrier based nano sensor for detection of hydrogen gas. Nano sensor was fabricated by growing SiNW (Si nanowire) arrays on a separate Si substrate and then transferring them on the top of SiO<sub>2</sub>/Si substrate through contact printing technology with subsequent evaporation of Pd contact. The reported nanosensor showed higher sensitivity (6.9% at 100 ppm hydrogen) than nanosensors based on other sensing principles. The sensor achieved a drift limited LOD (lower limit of detection) of only 5 ppm.

Kim *et al.* [Kim *et al.* (2010)] reported the MIS (Pd/TiO<sub>2</sub> nanoporous/SiO<sub>2</sub>/Si) gas sensor employing the nanoimprinting method for detection of toluene. Catalytic Pd-TiO<sub>2</sub> thin film was chosen as the gas sensing layer. The nanoporous thin film of titania (TiO<sub>2</sub>) was obtained by spin coating the titania sol-gel solution on SiO<sub>2</sub>/Si. The fabricated sensor was capable to detect the different concentration of toluene (50 ppm to 200 ppm) at room temperature.

Pandey *et al.* [Pandey *et al.* (2010)] studied the combined effect of RF and microwave plasma on the performance of Pd/SiO<sub>2</sub>/Si MOS sensor for hydrogen at room temperature. It was observed that sensitivity of MOS sensor increases with plasma exposure time. The sensitivity can be attributed to the fact that oxygen plasma treatment provides the availability of higher no. of adsorption sites and modification in the surface state density.

Kim *et al.* [Kim *et al.* (2010)] reported the electrical characteristics of the metal-insulator-semiconductor (MIS) structure of low-dielectric-constant SiOC(-H) films. SiOC(-H) thin films were deposited on p-Si(100) substrates by using a plasma-enhanced chemical vapor deposition (PECVD) system. The frequency dependence of the capacitance-voltage (C-V) and the conductance-voltage (G/ω-V) characteristics of the Al/SiOC(-H)/p-Si(100)/Al MIS structures was analyzed. C-V and G/ω-V measurements were carried out over a frequency range of 1 kHz to 5 MHz. Based on our analysis, the C-V and the G/ω-V characteristics confirmed that the surface states and the series resistance were important parameters that strongly affected the electrical properties of the Al/SiOC(-H)/p-Si(100)/Al MIS Structures.

Gupta *et al.* [Gupta *et al.* (2011)] have reported Interfacial characteristics of metal oxide-silicon carbide (MOSiC) structure with different thickness of SiO<sub>2</sub>, thermally grown in steam ambient on Si-face of 4H-SiC (0 0 0 1) substrate. Variations in interface trapped level density ( $D_{it}$ ) were studied employing high-low (H-L) frequency  $C-V$  method. It has been found that the distribution of  $D_{it}$  within the bandgap of 4H-SiC varied with oxide thickness. The calculated  $D_{it}$  value near the midgap of 4H-SiC remained almost stable for all oxide thicknesses in the range of  $10^9-10^{10} \text{ cm}^{-2} \text{ eV}^{-1}$ . The  $D_{it}$  near the conduction band edge had been found to be of the order of  $10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$  for thicker oxides and for thinner oxides  $D_{it}$  was found to be the range of  $10^{10} \text{ cm}^{-2} \text{ eV}^{-1}$ . The process had direct relevance in the fabrication of MOS-based device structures.

Irokawa *et al.* [Irokawa *et al.* (2011)] reviewed his recent results in investigating hydrogen sensors using nitride-based semiconductor diodes, focusing on the interaction mechanism of hydrogen with the devices. Effects of interfacial modification in the devices on hydrogen detection sensitivity have been discussed. Surface defects of GaN under schottky electrodes do not play a critical role in hydrogen sensing characteristics. However, dielectric layers inserted in metal/semiconductor interfaces are found to cause drastic changes in hydrogen sensing performance, implying that chemical selectivity to hydrogen could be realized. They observed that the work function change in the schottky metal is not responsible for hydrogen sensitivity. The interface between the metal and the semiconductor plays a critical role in the interaction of hydrogen with semiconductor devices. The low-frequency  $C-V$  characterization is used to investigate the interaction mechanism of hydrogen with diodes. It is suggested that the formation of a metal/semiconductor interfacial polarization could be attributed to hydrogen-related dipoles. In addition, using low-frequency  $C-V$  characterization leads to detection of 100 ppm hydrogen even at room temperature where it is difficult to detect hydrogen by using conventional current-voltage ( $I-V$ ) characterization, suggesting that low-frequency  $C-V$  method would be effective in detecting very low hydrogen concentrations.

Yadava *et al.* [Yadava *et al.* (2012)] fabricated Pd/TiO<sub>2</sub>/Si MOS gas sensor to detect hydrocarbons such as acetone, ethanol and trichloroethylene. The sensitivity measurements have been carried out in various ambient (O<sub>2</sub>, N<sub>2</sub> and Ar) at room

temperature which revealed that fabricated structure showed maximal response for acetone in contrast to other vapors examined. The study of ambient-effect on the device shows that its performance is outstanding in oxygen ambient. A catalytic oxidation mechanism for detection of acetone with a model based upon Langmuir law of adsorption and Frenkel-Poole theory of electronic emission for the description of sensing behavior and vindication of experimental results have been proposed.

Andersson *et al.* [Andersson *et al.* (2013)] fabricated enhancement and depletion type MISFET sensors with different gate dimensions and two different gate metallization, Pt and Ir. I/V- characteristics have been obtained under exposure to various concentrations of H<sub>2</sub>, NH<sub>3</sub>, CO and O<sub>2</sub> at different bias conditions. The influence of gate dimensions and bias conditions on the sensitivity and dynamic range had been Investigated. The long term stability has also been studied and compared b/w different devices and bias conditions for conceptually different gas compositions. The results show that the depletion type devices offer better possibilities for tuning of sensitivity and dynamic range as well as improved long term stability properties, whereas enhancement type require much less control of the processing to ensure good repeatability and yield.

Aval *et al.* [Aval *et al.* (2015)] fabricated the four Ni/SiO<sub>2</sub>/Si mos sensor with different SiO<sub>2</sub> film thickness (28 nm, 40 nm, 46 nm, 53 nm). The influence of SiO<sub>2</sub> film thickness on the sensor response speed, response (R%), and flat band voltage (V<sub>FB</sub>) has been investigated at 140 °C and 100 KHz. Using MOS C-V measurement under the bias thermal stress (BTS) technique, the trapped charges were measured. The highest response was observed for thin SiO<sub>2</sub> film (28 nm) MOS sensor. The response decreases with the increase of SiO<sub>2</sub> film thickness. Experimental results demonstrate that the sensor is highly sensitive to SiO<sub>2</sub> film thickness, which can be used for response, response/recovery time and V<sub>FB</sub> studies of MOS capacitance gas sensors.

Konduru *et al.* [Konduru *et al.* (2015)] used a gas sensor array, consisting of seven SnO<sub>2</sub> and WO<sub>3</sub> Metal Oxide Semiconductor (MOS) sensors. These are sensitive to a wide range of organic volatile compounds. This array was developed to detect rotten onions during storage. These MOS sensors were enclosed in a specially designed Teflon chamber equipped with a gas delivery system to pump volatiles from the onion samples into the chamber. The electronic circuit comprised a microcontroller, non-

volatile memory chip, trickle-charge real time clock chip, serial communication chip, and parallel LCD panel. User preferences are communicated with the on-board microcontroller through a graphical user interface developed using Lab VIEW. The developed gas sensor array was characterized and the discrimination potential was tested by exposing it to three different concentrations of acetone (ketone), acetonitrile (nitrile), ethyl acetate (ester), and ethanol (alcohol). The gas sensor array could differentiate the four chemicals of same concentrations and different concentrations within the chemical with significant difference. Experiment results also showed that the system was able to discriminate two concentrations (196 ppm and 1964 ppm) of methylpropyl sulfide and two concentrations (145 ppm and 1452 ppm) of 2-nonanone, two key volatile compounds emitted by rotten onions. As a proof of concept, the gas sensor array was able to achieve 89% correct classification of sour skin infected onions. The low-cost gas sensor array could be a useful tool to detect onion postharvest diseases in storage.

The use of plasma technology is common place in today's semiconductor production lines as an integral part of the integrated circuit fabrication process, simply because it proved to be a better technology for etching, ashing and growth/deposition of insulating films. Also, this technology (implemented in present study) eliminates the demerits of conventional method upto some extent. Environment impact is also reduced due to reduction in the use of the wet chemicals in etching and cleaning, leading to reduction in waste disposal. Therefore, in present work an effort has been made for the development of Pd-gate MOS gas sensor with improved performance at room temperature. A comparative study has been made on the performance of Pd-gate (Pd/SiO<sub>2</sub>/Si) gas sensors based on conventional fabrication process and plasma technology implemented in the present study. Obtained results show the implementation of plasma technology may be a valuable step towards future development of MOS based gas sensors and its integrated arrays with improved performance at room temperature.

#### **1.4 Motivation and Objectives of the Present Work**

Based on above literature survey, MOS sensors having either Pd or Pt as a gate with SiO<sub>2</sub>/TiO<sub>2</sub> as an insulator on Silicon substrate have widely been studied for the detection of hydrogen, hydrocarbon and hydrogen containing gases. Lundstrom *et al.*

[Lundstrom *et al.* (1975(a) & 1975(b))] reported SiO<sub>2</sub>/TiO<sub>2</sub> based mos sensors. Their studies were based on C-V and G-V characteristics of the device with varying gas concentration and frequency. It was concluded that Pt shows the better selectivity but less sensitivity as compared to Pd towards the H<sub>2</sub>. The sensitivity response of Pt gate MOS sensor was found one third as compared to Pd gate towards hydrogen detection [Solomonsson *et al.* (Solomonsson *et al.* (2005))]. Further it has been observed that growth of SiO<sub>2</sub> is relatively easier as compared to TiO<sub>2</sub> on Silicon substrate. Besides this, sensors made by SiO<sub>2</sub> show better sensitivity as compared to TiO<sub>2</sub> [Pandey *et al.* (2010)]. The gridded gate structure/discontinuous gate structure as compared to ungridded gate structure/ Thick gate structure has an advantage of providing a the larger effective surface area due to inner side wall of gridded gate, which results larger dissociation of H<sub>2</sub> molecules in atomic form [Dobos *et al.* (1980), Soderberg *et al.* (1980), Tan *et al.*(2008)]. Due to high selectivity of Pt over Pd and easy growth of SiO<sub>2</sub> on silicon substrate and higher dissociation capability of gridded gate structure towards H<sub>2</sub> containing gases it has been decided to fabricate a gridded gate Pt/SiO<sub>2</sub>/Si MOS sensor, which may be highly sensitive and more selective towards H<sub>2</sub> containing gases. Keeping above mentioned points in view, therefore a detailed study has been carried out on gridded Pt/SiO<sub>2</sub>/Si MOS sensor. The performance of gridded Pt gate MOS sensor has been evaluated by using C-V and G-V response with various gas concentrations of H<sub>2</sub>, NH<sub>3</sub>, CH<sub>4</sub> and H<sub>2</sub>S, for various frequencies (15 KHz, 25 KHz and 50 KHz) and it has been found that, low frequency G-V method provides more accurate information about interface parameter in such devices.

The use of plasma technology has become a very promising technology in silicon industry for integrated circuit fabrication process, simply because it is widely used during etching ashing and deposition of insulating films. Also, this technology (implemented in present study) eliminates the demerits of conventional method up to some extent. Undesired impact in the surrounding is also reduced due to reduction in the use of the wet chemicals in etching and cleaning, leading to reduction in waste disposal. This has become an essential component in the present day scenario for minimizing the environmental pollution. Therefore, in present work an effort has been made for the development of Pt-gate MOS gas sensor with improved performance at room temperature. A comparative study has been made on the performance of Pt-gate (Pt/SiO<sub>2</sub>/Si) gas sensors based on conventional fabrication process and plasma



technology implemented in the present study. Obtained results show the implementation of plasma technology may be a valuable step towards future development of MOS based gas sensors and its integrated arrays with improved performance at room temperature.

The objectives of the present research work are-

1. To develop the gridded Pt gate MOS sensor (Pt/SiO<sub>2</sub>/Si) for the detection of gases like hydrogen, ammonia, methane and hydrogen sulphide.
2. To study the surface morphology (through SEM and AFM analysis) of gate material and to determine the effect of porosity and cracks present in the gate film on the sensing characteristics of the MOS gas sensor.
3. To determine the gas sensing response, electrical characteristics such as C-V, G-V characteristics and evaluation of fixed charge density and interface trap charge density ( $N_{it}$ ) of the fabricated MOS sensor as a function of gas concentration and measurement frequency.
4. To investigate the combined effect of surface treatment of SiO<sub>2</sub> by oxygen plasma with RF power on the hydrogen sensing performance of MOS gas sensor.

### **1.5 Organization of Thesis**

In the present thesis, the entire work has been organized and presented in six chapters:

Chapter 1 discussed the needs of gas sensors, their classifications and applications. This chapter also presents the detailed review on MOS sensors. Based on the literature survey and keeping in view of various aspects in the area of MOS sensors, the objectives and outlines of the work have been discussed in the end of this chapter.

Chapter 2 describes the structure, electronic behaviour and various interaction mechanisms between gas and solid surface like gas adsorption processes, Physisorption, Chemisorptions and adsorption isotherm, gas sensing mechanism of MOS sensor.

Chapter 3 deals with the available facilities for the fabrication and characterization of MOS sensor and the fabrication process of gridded gate Pt/SiO<sub>2</sub>/Si MOS sensor. This chapter also describes the fabrication process of plasma treated SiO<sub>2</sub> MOS sensor.

Chapter 4 includes the surface characterization (SEM, AFM analysis), electrical characterization of gridded gate MOS sensor towards H<sub>2</sub>, NH<sub>3</sub>, CH<sub>4</sub> and H<sub>2</sub>S. Interface Trap charges have been calculated for all above said test gases.

Chapter 5 describes the effect of RF plasma on the performance of gridded gate Pt/SiO<sub>2</sub>/Si MOS sensor. Comparative study has been carried out between plasma treated and non plasma treated sensor. The surface characterization has been done by using AFM. The electrical characterization is carried out towards H<sub>2</sub> exposure at room temperature. The fixed oxide charge density has also been evaluated for H<sub>2</sub>.

Chapter 6 includes the summary and conclusion of the entire investigation done. The major findings of the present work are summarized in this chapter. Lastly, an outline on the future scope of research in related areas considered in the thesis is also presented in this chapter.