SUBHASHIS ROY

DESIGN AND REALIZATION OF SENSORS AND SENSOR BASED SYSTEMS

Thesis submitted by

SUBHASHIS ROY

Doctor of Philosophy (Engineering)

Department of Electronics & Telecommunication Engineering

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1. Subhashis Roy, Anup Dey, Bikram, Biswas and Subir Kumar Sarkar, "Investigation of Pt and Pd modified WO_3 and ZnO based Thin Film Sensors for Ethanol Sensing" Journal of Materials Engineering and Performance, Springer, vol. 27, no. 6, pp. 2635–2642, 2018. DOI: https://doi.org/10.1007/s11665-017-3105-9.
2. Subhashis Roy, Anup Dey, Bikram Biswas, and Subir Kumar Sarkar, "Analytical Modeling of Voltage to Time Conversion Circuit for Gas Sensing System and Some Experimental Studies", Journal of Nanoelectronics and Optoelectronics, American Scientific Publishers, vol. 12, pp. 1–8, 2017. DOI: https://doi.org/10.1166/jno.2018.2215.
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4. Bijoy Kantha, Subhashis Roy and Subir Kumar Sarkar, "Implementation of Pd modified WO_3 thin film gas sensing system with Bulk-CMOS and SOI-CMOS for monitoring leakage of hydrogen gas" Journal of Nanoelectronics and Optoelectronics, American Scientific Publishers, Vol. 10, pp-1-8, 2015.DOI: https://doi.org/10.1166/jno.2015.1692.

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2. Subhashis Roy, Anup Dey, Bikram Biswas, Sudhabindu Ray, and Subir Kumar Sarkar "Influence of annealing Temperature on H_2 Sensing Properties of Solgel Spin Coated Pd-ZnO-Si Thin Film Sensor" IEEE international Conference on Electrical, Electronics, Computers, Communication, Mechanical and Computing (EECCMC), Tamil Nadu, 2018.
3. Subhashis Roy, Bikram Biswas, Anup Dey, Bijoy Kantha and Subir Kumar Sarkar, "A Proposal for Detection Ethanol Leakage using WO_3 Thin Film Sensor with RFID Technology" First International Conference (Springer) on Computational Intelligence, Communications, and Business Analytics (CICBA-2017) Calcutta Business School,India. March 24-25, 2017. DOI: 10.1007/978-981-10-6427-2_35
4. Subhashis Roy, Bijoy Kantha and Subir Kumar Sarkar "Study the Effect of Catalytic Metal Contacts on Ethanol Vapour Sensing Performance of WO_3-Si Hetero-Structure Sensor", Springer International Conference on Computational Science and Engineering (ICCSE), Kolkata, 2016. ISBN 978-1-138-02983-5.
5. Subhashis Roy and Subir Kumar Sarkar "RFID Based Real Time System For Early Detection of Avian Influenza For Poultry Based Industry" IEEE Microelectronics, Computing and Communication (MicroCom), NIT Durgapur, 2016. DOI:10.1109/MicroCom.2016.7522460

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2. Subhashis Roy, Bijoy Kantha and Subir Kumar Sarkar "Study the Effect of Catalytic Metal Contacts on Ethanol Vapour Sensing Performance of WO_3-Si Hetero-Structure Sensor", Springer International Conference on Computational Science and Engineering (ICCSE), Kolkata, 2016. ISBN 978-1-138-02983-5.
3. Subhashis Roy and Subir Kumar Sarkar "RFID Based Real Time System For Early Detection of Avian Influenza For Poultry Based Industry" IEEE Microelectronics, Computing and Communication (MicroCom), NIT Durgapur, 2016. DOI:10.1109/MicroCom.2016.7522460

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CERTIFICATE FROM THE SUPERVISORS

This is to certify that the thesis entitled **"DESIGN AND REALIZATION OF SENSORS AND SENSOR BASED SYSTEMS"** *submitted by* ***Shri. Subhashis Roy,*** *who got his name registered on* ***28/06/2016*** *[****D-7/E/471/16****] for award of Ph.D. (Engg.) degree of Jadavpur University is absolutely based upon his own work under the supervision of* ***Prof. Subir Kumar Sarkar and Prof. Sudhabindu Ray*** *and that neither his thesis nor any part of the thesis has been submitted for any degree/ diploma or any other academic award anywhere before.*

[Prof. Subir Kumar Sarkar]
Signature of the Supervisor and date with office seal

[Prof. Sudhabindu Ray]
Signature of the Supervisor and date with office seal

Dedicated to

My Parents Shri. Sujit Kumar Roy and Smt. Mala Roy

&

My Sister Mrs. Sarmistha Ray

&

My grandfather Late Ramesh Chandra Roy

&

My grandmother Smt. Lila Saha

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ABSTRACT

The sensor is a transducing device that converts the change in physical conditions such as temperature, pressure etc. into the measurable electrical responses. Now-a-days sensors are becoming part of our daily lives. At present with the speedy progress in technology, sensors gain its popularity day by day.

Semiconducting Metal-Oxides show potential as an attractive sensing material to detect different hazardous gases like ethanol, hydrogen, methane etc. The important characteristics of these gas sensors are photo-catalytic properties, high reliability and low cost. In the present work, fabrication of ethanol sensor with WO_3 material by Pt and Pd modulation is carried out to achieve low power, high sensitivity, low temperature sensor. The sensitivity is measured from the gas concentration variation to sensor resistance variation. The sensing performances of two different ethanol sensors (Pd modulated and Pt modulated WO_3) are investigated. The effects of noble metal like Pd, Pt on the sensing properties are also studied using Scanning Electron Microscopy and X-Ray Diffraction methods. Present analysis shows that Pt modulated WO_3 sensor gives enhanced performance than other sensors. Further to study the enhancing methods of the sensors' sensitivity, the effects of annealing temperature and the effects of hetero junction structure on gas sensor are investigated. The ZnO and WO_3 type materials are chosen for the application of sensing H_2 gas for this study. The formation of heterostructure structure sensor is done by using these two materials. On the other hand the study of annealing temperature is carried out during the fabrication process of the sensor. The direct effect of annealing temperature on the grain size of fabricated sensor is studied using Scanning Electron Microscopy and X Ray Diffraction methods.

The detection of toxic as well as inflammable gases is necessary for improving the quality of the environment. Generally sensor with the signal conditioning unit is essential to detect different inflammable gases. Hence the voltage to time conversion circuit with fabricated sensor to detect hydrogen (H_2) and methane (CH_4) gas is proposed based on a bridge circuit, an instrumentation amplifier and a timer circuit. Normally in real time applications if the sensor's output data i.e. the analog form of

sensing data is send without proper signal conditioning then there may be huge degradation in quality and quantity of the signal. Hence in the present work a signal conditioning circuit is tested with fabricated gas sensor and the result is studied thoroughly. Further a proposal using RFID based system for early leakage detection of ethanol with RFID tags as sensors is presented. Now-a-days the RFID technology which is better than available bar code technology is gaining more attention because of its attractive features like low cost, reusability, and stability. Hence in the present work the main RFID component which is RFID tag is used as sensing device to detect leakage of ethanol gas % from 0.15% to 0.5%.

Chapter 1

INTRODUCTION AND ORGANIZATION OF THE THESIS

1.1 Introduction

1.2 Organization of the thesis

References

1.1 Introduction

There are different hazardous gases like toxic gases which that are harmful to humans when inhaled in various quantities. This includes gases such as ammonia, chlorine, sulfur, ethanol and many others. Another hazardous group of gas is flammable gas capable of burning in certain concentrations at presence of oxygen which need proper attention while using in different application areas. Other hazardous gas is combustible gases. This category of hazardous gas includes all gases that can explode in certain concentrations. Like flammable gases, combustible gas requires the presence of oxygen. These kind of gases are produced by different industries like coal factories, cement factories, alcohol production factories and many more. Hence many researchers around the globe are working in the area of detection these kinds of gases using different materials; different fabrication techniques and showing improvement day by day towards more enhanced gas detection sensors and sensor based systems.

A sensor is a device used for the detection and measurement of the physical phenomena like pressure, temperature, resistance etc. [1.1-1.5]. The sensors are widely utilized in various applications like domestic appliances, process industries, defense equipment and environmental monitoring. Depending on the input physical parameters different types of sensors such as a gas sensor, pressure sensor, biosensor and temperature sensor are present. In literature many types of gas sensors are developed using different types of sensing materials and methods. The gas sensors can be classified as electrochemical, catalytic combustion, solid electrolyte, infrared absorption, thermal conductive and Semiconductor Metal Oxide (SMO) type sensors [1.6-1.10] on the basis of physical parameter to be measured. On the basis of sensing methods gas sensors can also be classified into two groups i.e. sensors varies its electrical properties like conductivity in presence of sensing parametrs like SMO sensors, sensors varies its other properties like magnetic, optic, and acoustic like optical, biosensors. Thus in literature varites of process or varities of materials are used to make gas sensors. The challenge is to make more efficient, cost effective, long life time based sensor fabrication which can be done with SMO based sensors. The

SMO based sensors offers attractive features like smaller size, repeatable, cheap, low power-consuming and many more.

The scalability of CMOS devices makes the remarkable contributions in the advancements and achievements of microelectronics technology. It has been realized by implementing complex functions on silicon wafers in a batch process that the introduction of micro-fabrication and integrated circuit (IC) technology boosts up the performance of the devices. Hence these lead to significant cost reduction and mass production of IC chips [1.11-1.15]. Apart from cost the other two important factors which are key to the IC chip fbrication are size and speed which are also improving in terms of high speed and smaller size respectively. However there exists the greatest challenge to design the most optimized circuit and system in the semiconductor industries [1.16-1.22]. Thus in the field of designing the sensor and sensor based system, the designer need to comply to all the necessary conditions to find the most optimized cicuit.

As the gas sensors are mostly fabricated in nano scale region thus it requires different types of analytical tools to properly characterize its molecular structure. Different types of tolls are present for this purpose like Atomic Force Microscope (AFM), Scanning Tunneling Microscope (STM), and Field Emission Scanning Electron Microscope (FESEM).These tools are enabled the researchers to work more precisely towards nanotechnology [1.23-1.24]. Nanotechnology can be applied on different types of substrates like GaAs, sapphire, ITO coated glass, n-Si, p-Si and many more and can be fabricated using diverse fabrication technologies like Pulsed Laser Deposition (PLD), Molecular beam epitaxy (MBE), Chemical Vapour Deposition (CVD), Metal Organic CVD (MOCVD), RF Sputtering, Solgel [1.25-1.30].

The semiconducting metal oxide has recently engrossed much interest as the key component for gas sensors. The sensitivity is studied by the change of electrical conductivity of the metal oxide in the presence of target gas. The general application areas of metal oxide gas sensors are sensor networks, automobiles, environmental monitoring, domestic safety, public security, medical, spacecraft and personal safety and amny more. So the development of a portable sensor with highl sensitivity, low

manufacturing cost, simple operatation technique, and chemically highly selective is very required for these applications. The mostly studied properties of different semiconducting metal oxides are SnO_2, ZnO, TiO_2 and WO_3. Among several semiconducting metal oxide WO_3 is a very popular as a sensing material because of its various advantages such as wide band gap, fast response, high sensitivity and low cost. The selectivity and stability of the metal oxide are improved with the incorporation of noble metals such as Pt, Au, Pd and Ag [1.31-1.35]. Currently the challenge is to fabricate stable nanodevices having small grain size at low operating temperature. Initially, the thick film technology was involved to prepare the first generation sensor devices. Then the thin film technology was introduced in place of thick film technology due to shortcomings of thick film technology like high power dissipation, less sensitivity, short life time. In this technology different fabrication processes such as chemical vapour deposition, electron beam method, solgel process presents several advantages like higher reproducibility, good compatibility, long life time, easy to work on silicon technology and many more. With the improvement of the thin film technology a lower grain size particles could be fabricated with low porosity and high surface to volume ratio. As a result, the gas sensing performance of the device is improved. Grain size modification is responsible for the variation of the electrical properties in both technologies i.e. thick and thin films. These effects are a serious issue for lower temperature application. However the modulation of grain size of nano devices could be a source of amalgamation of molecules at higher temperature. So, different steps are introduced to improve the stability of the nanodevices i.e. adding the element with the nanodevices and the formation of different semiconductor stable nanodevices like nano-wires, nano tubes, nano belts and many more. These stable nanodevice provides improved sensing properties and stability.

In the recent years, the device size minituarization becomes a trend of research of VLSI industries. The feature size of the CMOS devices are reducing day by day. Hence different researchers around the glode are continuously trying to make new structure of devices [1.36-1.42]. Different new technologies are coming into the market like Radio frequency identification (RFID). It becomes an emerging

technology that is gaining popularity due to easy implementation, cost effective, reusability, wide range of application area. The RFID technology is far better than available bar code technology because the RFID technology does not required any line of sight communication which is essential in bar code technology and it can be used in three different frequency applications, i.e. low frequency (125-134 KHz), high frequency (13.56 MHz) and ultra high frequency (860-960 MHz). Also there is a provison of using three different RFID tags, i.e. passive tag, semi passive tag, active tag. Hence the researhers are using the RFID technology in different domains to solve many real life problems [1.43-1.49] . One of the important area is supporting logistics and supply chain processes where RFID technology plays the key role to to identify, trace and track information throughout the supply chain. This leads to a lot more easy and comfortable position for manufacturers, suppliers, distributors and retailers to precisely control their products in real time. This accurate knowledge of the inventory would result in lower labor cost, simplified business processes and improved supply chain efficiency. In recent times the researchers are also using the RFID technology as a sensing device as this technology is very cost effective and easy to use [1.50-1.58]. The thin film gas sensors can be used to sense very low concentration of hazardous gases which can be used with RFID technology for sending the sensor data accurately in time.

In view of the above declaration I have been inspired to design and implement some gas sensors and sensor based system as there are still dearth of scope for works in this area.

1.2 Organization of the Thesis

In this thesis work, some important aspects of metal oxide semiconductor (SMO) based sensor structures are studied and some sensor based systems are proposed. The Radio Frequency Identification (RFID) based tags are also studied as sensor device to solve real life problem like Avian Influenza. In the present work, The sensing properties of WO_3, ZnO based homojunction sensors and WO_3-ZnO based hetero-junction sensor towards hydrogen, ethanol are also investigated. The sensor based system i.e. voltage to time conversion circuit is also proposed for

sending the proper sensor signal to distant location. This section presents a brief overview of the research work in the various chapters.

Chapter 2 describes the basis of the thesis work which includes concept of low dimensional sensor device structure like homojunction, hetero-structure, thin film devices. This chapter also presents brief idea about RFID base technology which is very competent to use as a sensor device to solve many real life problems. In the present chapter, a brief overview of different methods to improve the sensitivity, selectivity of semiconductor metal oxide sensors are also discussed.

Chapter 3 describes the comparative study of WO_3 based sensor with Platinum (Pt) and Palladium (Pd) modified WO_3 based sensor structures in terms of different sensing parameters i.e. operating temperature, sensitivity, selectivity, response time. The improvements of WO_3 microstructure due to addition of noble metals Pd, Pt are thoroughly studied by scanning electron microscopy method (SEM) and X-ray diffraction (XRD) method. The fabricated sensors are tested for wide range ethanol concentration. The key effluents released by the industries to the environment are organic pollutants. Not only industries, the organic pollutants are also broadly used in daily life. The ethanol is the most common organic pollutant among the various organic pollutants, which also effects the environment, human health, aquatic system due to their toxicity and hazardous effect. Hence using the cost effective and accurate fabrication technique i.e. solgel method the proposed sensors structure are fabricated and tested for ethanol. The p type Si substrate is chosen to work with.

In chapter 4, the effects of annealing temperature and the effects of hetero junction sensor structure on the sensitivity of a gas sensor are studied. The activity of the low dimensional thin film sensor device structure based on ZnO type material is examined through the application of sensing H_2 gas. A sol gel grown ZnO-WO_3 thin film sensor is fabricated on p-Si<100> substrate to form the hetero-junction device. The change in microstructure of the bare WO_3 and the bare ZnO based sensor due to formation of heterostructure structure sensor directly enhances the sensitivity of the sensor. Theoretically it is due to the trapping of molecules at the interface between ZnO and WO_3 which increases the surface to volume ration of molecules with

respect to normal WO_3 , ZnO structure. On the other hand the annealing temperature directly controls the grain size i.e. the diameter of the fabricated nano particle of the sensor. The smaller grain size enhances the surface to volume ratio that controls the sensitivity of the sensor. These theoretical concepts are examined in this chapter by experimental work. The Pd-Ag alloy contacts are used on the both sides of the fabricated sensors. The structural characterizations of the devices are analysed by XRD and SEM methods.

In chapter 5, the voltage to time conversion circuit with fabricated sensor to detect hydrogen (H_2) and methane (CH_4) gas is proposed. Now the research trend increasingly showing interest to integrate thin film or MEMS based nanostructured sensor device with signal conditioning circuit for storing, calibrating, transmitting the sensor data properly to the desired location. There are different types of sensor's output data like resistive, capacitive or inductive. In the present work WO_3 and ZnO based sensors are fabricated for detecting the H_2 and CH_4 gas with reliable signal conditioning circuit based on a bridge circuit which helps to precisely detect a very small change in sensor's resistance in contact with target gas; a instrumentation amplifier for amplifying the small voltage to a desired range, and a timer circuit that converts the voltage change to equivalent time change signal. Normally in real time applications if the sensor's output data i.e. the analog form of sensing data is send without proper signal conditioning then there may be huge degradation in quality and quantity of the signal. Hence in the present work a signal conditioning circuit with nanocrystalline gas sensor is presented.

In chapter 6, a proposal for developing a RFID based system for early leakage detection of harardous gas like ethanol, methane with RFID tags as sensors is presented. In present day the RFID technology a booming technology which is far better than bar code technology. RFID technology does not require line of sight communication as well it is cheaper, reusable, and stable. However there are some limitations like reader collision, tag collision etc. In spite of these limitations, the RFID technology is used in logistics, supply chain, bio medical, animal husbandry and many more. Thus in the present work the main RFID component that is RFID tag is used as sensor device to detect lekage of ethanol hazardous gas at an early

stage. Ethanol is a key element in many industrial activities where production and maintenance process are the key parameters. Ethanol is volatile, flammable, colorless element (in vapour form) having the lower and upper explosive limits are 3.3 percent and 19 percent respectively which makes it highly combustible gas. Hence a RFID based system is proposed which mainly made of by RFID reader, RFID tag, weighing machine and basic stamp processor. The proposed system will work on the basis of leakage % of ethanol i.e. from 0.15% to 0.5%.

Finally in Chapter 7, the contributions of the research work are summarized. The performance of WO_3 or ZnO based sensor can be improved by adding noble metals like Pd, Pt or by controlling the annealing temperature or by forming hetero structure device. These types of sensors can also be used for detection of ethanol, hydrogen or methane gases. Low power, low cost and easy implementable sensor interfacing circuit can be designed using simple bridge, amplifier and voltage to time conversion circuits which is helpful to send undistorted sensors output signal to a desired location. RFID tags can also be used as proper sensor device to solve real life problem like detection of ethanol leakage which is useful for ethanol industries and mankind.

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Chapter 2

BASICS OF THESIS WORK

2.1 Introduction

The ever-increasing demands of industrial electronics for obtaining high speed & low power circuits encourage the researchers of microelectronics industry to move from Large Scale Integration (LSI) to Very Large Scale Integration (VLSI) and finally to Ultra Large Scale Integration (ULSI) circuits having billion of electronic devices. Due to the improvement of speed and reduction of both power consumption and device size, the performance of these modern systems gets improved. Moreover, the revolutionary development of fabrication techniques enables the researchers to study the ULSI citcuit component like nano structure metal oxides based semiconductor gas sensor more precisely and accurately in nano scale region [2.1-2.11]. Modern fabrication techiques are also advances that makes researchers to work with divesre fabrication techniques like the advance crystal growth techniques such as Molecular Beam Epitaxy (MBE), Metal Organic Chemical Vapour Deposition (MOCVD), thin film technology, and fine line lithography [2.12-2.17]. Nanostructure based semiconducting metal oxides are the key material for development of different types of gas sensors like resistive, capacitive and inductive. Recently this field of research has attracted much attention for their ability to solve many real life probems and compatibility with industry based applications. Mostly these sensors are used in the mining industries, in the field of defense application, environmental monitoring, supply chain management system, food industries and many more. The major key features of a good metal oxide are higher band gap energy, type of conductivity, easily fabricable or not, stability, compatibility with Si based technology. Depending these features the WO_3 and ZnO become promising material to be used as a sensing layer [2.18-2.23] . There main featuresof these materials are low cost, wide band gap, absence of toxicity and the fast speed of response to different gases. However ther are huge scope for further improvement in the field of fabrication to design more efficient gas sensor system even RFID technology can be used as a good sensing device. RFID is far more better technology than present satate of art technology like bar code technology. RFID does not need line of sight communication. It can also work in difeerent frequency domain like low frequency (LF 125-134 KHz), high frequency (HF 13.56 MHz), ultra high frequency

(UHF 860-960 MHz) according to the mode of application [2.24-2.38]. This technology is also user friendly, easy to install and maintain besides its life time is quite long. Thus research trend also moves to a direction where sensors are tied with RFID technology to resolve the critical problems more efficiently mainly in food industries, transport systems, tracking systems and many more.

2.2 Basics of metal oxide based gas sensors

In both domestic and industrial environments the detection of toxic, odorless and flammable gases is a very important research domain. The basc metal oxides which are extensively used in nano scale are mostly WO_3, TiO_2, SnO_2, NiO and ZnO [2.39-2.42]. Generally they are two types depending on the conductivity i.e. n-type or p-type. The electrons are mostly interacting molecules with target gas in case of n-type gas sensor like SnO_2, ZnO, WO_3. On the other side holes are the interacting molecules for p-type gas sensor.

2.2.1 Types of metal oxide gas sensors

The researchers have been working in the filed of metal oxide gas sensors from last two decades. To match the growing interest in the dufferent kinds of structures of metal oxide gas sensors have been proposed. Among them the important structures are discussed below.

(a) Resistive type sensors:

The most popular family of gas sensors comprises the metal oxide semiconductor based sensors that work based on the principle of changing conductivity [2.39-2.41]. The direct measurement capability, easy fabrication process, stability are the features of this kind of sensors.

(b) Schottky junction type sensors:

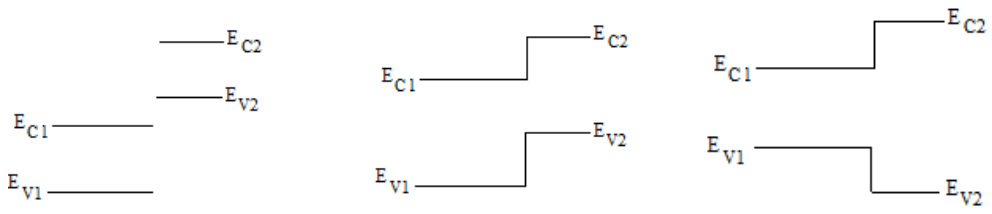
The Schottky junction based sensors are fabricated with catalytic metals contact both side of the gas sensors. These type of sensors gives better response magnitude and response time in presence of target gas than the resistive type sensors [2.43].

(c) Homo-junction gas sensors:

The metal oxides are normally n-type semiconductors like SnO_2, WO_3, TiO_2, ZnO but there are a few p-type conductivity metal oxides also presents like CuO, NiO, Co_3O_4, Cr_2O_3, In_2O_3, V_2O_3. Using single metal oxide the homo junction sensor are made and this are also highly sensitive to reducing or oxidizing gases [2.44-2.46].

(d) Hetero-junction gas sensors:

The hetero-junction gas senosrs are made of two dissimilar metal oxides with different band gap. The band difference at the conduction as well as valence bands at the metallurgical junction rises due to the differences in the energy band gap and electron affinity between the two semiconductors. The conduction process in heterojunction devices is influenced by the band offsets of the conduction and valence bands. The hetero junction devices can be sub divided into three groups depending on the energy band alignment, i.e (i) Broken gap (ii) Staggered and (iii) Straddedas shown in fig. 2.1.



Broken gap Type Staggered Type Stradded Type

Figure 2.1: Different kinds of energy band alignments [2.247]

In literature many such structure are fabricated and tested for different types of gases [2.4,2.47] like ZnO-p Si for sensing methane.

2.2.2 Working principle of metal oxide gas sensors

There are two important factors which determines the sensing performances of the sensors. They are the receptor and transducer functions. Receptor function is the ability of gas sensor's surface to interact with the target gas. The electrochemical reaction between the target gas and the surface of the gas sensor enhances the sensitivity of the sensor. The transducer function concerns about the capability to transform the generated signal from the gas sensor surface into electrical signal (chemical energy to electrical energy).

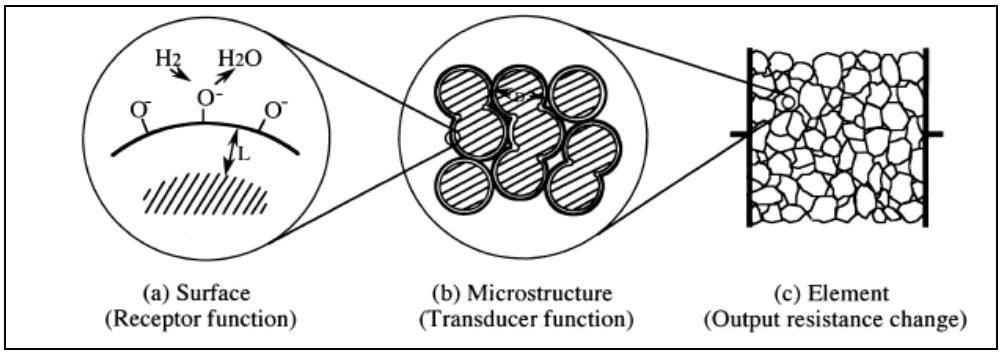


Figure 2.2: Oxygen adsorption on thin film Surface [Ref-2.11].

The adsorption of oxygen from the ambient air on the oxide surface due to strong electron affinity of the adsorbed oxygen causes dissociation and pulling of the electrons from the surface towards itself. Finally that results an O^- layer of the surface of the metal oxide sensor. Hence the Debye length that is a depletion layer of thickness (L) is increases due to pull out of electrons from the conduction band of the sensor. Finally the conductivity of the film reduces due to depletion of electrons as shown in fig.2.2. Now the reducing gas like hydrogen when reacts with the surface, breaks up to H^+ ions. Then it chemically bonded with the adsorbed O^- and produces H_2O. This process causes an increase in conductivity of the material as two electrons are given back to the oxide surface during this chemical process. This phenomenon happened in resistive metal oxide gas sensor. However in case of heterojunction sensor where two different metal oxides are involved there different phenomenon occurs. There exiss a depletion layer as well as accumulation layer at each side of heterojunction interface [2.47]. This causes energy band bending at the interfaces as shown and forming either stragared or stradded type heterojunction. In ambient air, the adsorbed oxygen species at grain boundaries of hetero junction shielded the interface regions so that conducting electrons are trapped and the resistance of composite material increases grater in amount in case of resistive/ homo junction sensor. Now in presence of H_2 gas surface reaction occurs and electrons will be generated. These electrons will flow along the interface with shrinking the depletion layer which decreases in overall resistance in presence of H_2 gas. The change in resistance in this structure is much higher than simple metal oxide sensors because of involvement of more carriers.

The basic characteristics of any type of gas senosrs can be shown as in fig. 2.3.

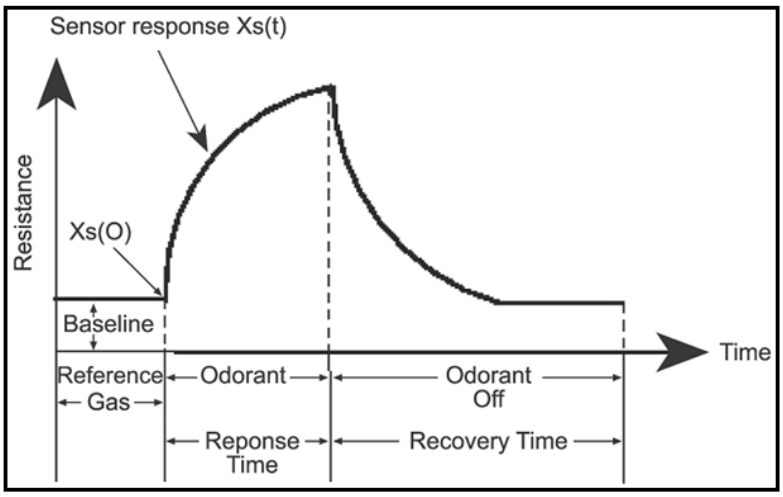


Figure 2.3: Sensor Response in existence of reducing gas [Ref- 2.12].

This is plot of sensor's resistance vs. time where R_a is sensor's resistance at air, R_g is sensor's resistance at sample gas. Gas-in is that time when smaple Gas is applied and Gas-out is that time when sample gas is off. Sensing properties of any gas sensor is characterized by the following properties:

- Sensitivity: The ratio of the change in the electrical resistance in the air and test gas

  $\Delta R = R_A - R_V$, to its resistance in the dry air R_A.

$$\text{Sensitivity (S\%)} = \frac{R_A - R_V}{R_A} * 100$$

- Selectivity: It is expressed in terms of a dimension that compares the concentration of the corresponding interfering gas that produces the same sensor signal. It is expressed as ratio of sensitivity towards interfering gas to sensitivity towards desired gas.
- Response Time: It is the time interval over which resistance of the sensor material attains a fixed percentage (using 90%) of the final value when sensor is exposed to full scale concentration of the gas. Small value in response time is mostly desirable in real time application.
- Recovery Time: It is the time interval over which sensor resistance reduces to 10% of the saturation value when target gas is switched off and sensor is

placed in reference air. A sensor should have small recovery time so that it can be ready for next detection.

- Stability: It is the ability of a sensor to maintain its sensing properties when operated continuously during its lifetime. Sensors are designed to have long term stability that lasts upto several years with showing very little drift in its performance.

2.2.3 Fabrication method of metal oxide gas sensors

The sensor material's morphology plays very important role in metal oxide gas sensor. Thus preparation of the metal oxide material plays very important role. As discussed in previous section, the transducer function is broadly dependent on the grain diameter and sensitivity is dependent on the transducer function. Thus using proper deposition technique the grain size can be controlled to achieve high sensitivity. Basically thin film sensors can be fabricated by wet chemical process and vapour deposition process. Now wet chemical process can be sol gel type and spray pyrolysis type. On the other hand the vapour deposition process can be chemical vapour deposition etc. In this thesis work the wte chemical sol gel process is taken to fabricate all the sensors. It is a wet chemical technique that uses either a chemical solution or colloidal particles to produce an integrated network(gel). Metal oxides and metal chlorides are typical precursor. They undergo hydrolysis and polycondensation reactions to form a colloid, a system composed of nanoparticles dispersed in a solvent. Then an inorganic continuous network containing a liquid phase (Gel) is formed. The formation of a metal oxide involves connecting the metal centers with oxo (M-O-M) or hydroxo(M-OH-M) bridges therefore generating metal oxo/ metal hydroxo polymers in solution. After a drying process, the liquid phase is removed from the gel. Then a thermal treatment (calcination) may be performed in order to favor further polycondensation and enhance mechanical properties [2.3,2.21,2.23]. Sol gel dispersion of colloidal particles typically sized 1-100nm in a liquid. The precursor sol can be deposited on a substrate to form a film e.g. by dip coating method or spin coating method. The main advantages of sol gel method It is cheap and low temperature technique that allows fine control on the product's

chemical composition. It can easily shape materials into complex geometries in a gel state. It can produce high purity products because the organo-metallic precursor of the desired ceramic oxides can be mixed, dissolved in a specified solvent and hydrolyzed into a sol, and subsequently a gel, the composition can be highly controllable. It can produce thin bond coating to provide excellent adhesion between the metallic substrate and the top coat. It can produce thick coating to provide corrosion protection performance. It can have low temperature sintering capability, usually 200-600^{0}C.

2.3 Improvement of metal oxide gas sensor

There are different factors which controls the sensivity and the other parameters of the gas sensors. The mosly valuable property is grain size of nano particles, effect of incorporations of noble metals, operating temperatue, sensitization and many more. Some of the important parameters are discussed in the following sections.

2.3.1 Grain size modulation

A nanocrystalline material is a polycrystalline material with a crystallite size of only a few nanometers. That is at least one of the dimension of 1 nm to 100nm size. Dfferent types of defects such as dangling bonds and vacancies of carriers are play a vital role in the transportation properties of electrons of nanoparticles [2.7,2.50-2.55]. This is mainly when the fraction of atoms at the grain boundary increases and generate defects. The conductivity depends on both neck control, i.e. cross section area of those channels and the grain boundary control. In existence of reducing gases, the variation of conductivity is very large thus decreases conductivity through the junction thereby yielding a high response. The working temperature of the gas sensors can be further reduced by nanocrystalline metal oxides. Interfacial or surface tension was reported to decrease with decreasing particle size by F. Ren et al. [2.48].

It has been observed that for a particular target gas and sensing material combination, there exist an optimal value for the grain size.

2.3.2 Noble metal addition

By incorporating noble metal additive into the semiconducting metal oxides, the performance of gas sensing can be enhanced. The rate of chemical reactions is increased in the presence of noble metal. As a result, the performance of gas sensor is improved. Using the noble metal as an electrode contact onto the metal oxides applications are reported [2.21,2.23, 2.54-2.55]. The Pd-Ag thin film has been also found to be effective for use in gas sensors because the rate of hydride formation is very little for Pd-Ag alloy compared to pure Pd and higher rates of hydrogen adsorption can be attained.

2.3.3. Nano particles with higher surface to volume ratio

It is already established that nanocrystalline materials present higher surface to volume ratio compared to any other materials. It is reported that with the reduction in the particle size from 30nm to 10nm,there is 25% increment in the percentage of atoms present on the surface that is from 5% to 30 % which ultimately results in exponential increment of the surface energy along with the formation of the huge number of dangling bonds on the surface of the material. Thus, there is a noticeable increment in the effective, sensitive area and thereby improvement in the sensitivity by a great deal.

2.3.4 Operating temperature:

The temperature controls the activation energy of carrier of gas sensor and even the grain size of nano particles. A gas sensor can operate at its maximum efficiency for a particular target gas at a particular operating temperature. That means the operating temperature is fixed for a particular material and for a

particular target gas. When temperature increased above it, there is a possibility of amalgamation of nano particles at the surafec of the gas sensor. This causes decrease in surface to volume ration and also decrease in sensitivity of the sensor. Finally it can be concluded that there is lowering of the operating temperature of the sensor with the lowering of activation energy for gas-adsorption [2.54]. As, for example, in case of ordinary thick film microcrystalline sensors, the operating temperature is quite high (350^0C) compared to that for nano-crystalline materials (about 200^0C).

2.3.5 Sensitization

Usage of catalysts as keenly correlated with surface science, have already been adopted by scientists to originate the optimal sensor. Platinum and Paladium, with their zero reactivity to those commonly used chemicals and gases, are utterly the conventional catalysts. In addition to this, Schottky barriers are formed at the interface which incorporates modulation of barrier resulting higher sensitivity. Plenty of defects prevailing at the above mentioned nano-crystalline surface act as recombination center consequently reduce the current conduction. To counter this, noble metals can be used for passivation over those barriers hindering conduction.

Energizing target gas, H^+ ions are adsorbed by the metal surface which is then followed by a spillover of those ions to the nanocrystalline oxide surface. Cations react with anionic O^- and subsequently generates water molecules which evaporate at elevated temperature. The formation described thus, is vividly noticed at the edges of the catalyst nano-cluster. Hence, noble metals undoubtedly enhances the adsorption of hydrogen with a faster chemical kinetics resulting from increased entropy lowered activation enthalpy. In another case of electronic sensitization, the electrons are accepted from the oxide, which is done by the additive. Hence, there is an induction of a surface space charge layer where the electrons are strongly depleted strongly in the oxide nearer to the interface. With the application of the target gas, the additive gets reduced and by electron compensation back to the oxide,

there is relaxation in the space charge layer. Owing to the metal oxide work function difference between the oxidized and reduced state, there is an improvement in the response of the sensor towards the target gas as shown in fig. 2.4.

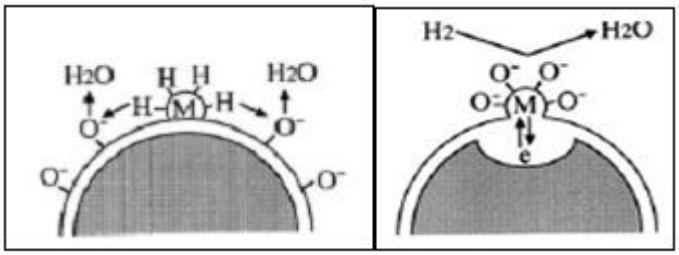


Figure 2.4: Chemical & electronic sensitization mechanism [Ref-2.12].

2.4 Signal conditioning systems of gas sensors

The gas sensors' outputs need to be conditioned properly for real life applications areas such as environmental monitoring and other industrial application. From the beginning of old micromachined silicon devices to present day wireless integrated Microsystems, all have integrated sensors that is complete sensor based system. Artificial neural network (ANN) based sensor arrays as proper conditioning circuit is used due to the lack of selectivity of most common chemical sensors. One of the principal problems in signal-processing methods for sensor arrays is the time-dependent behaviour of gas sensors. Short-term drift effects and compensation of sensor rise time are an important improvement in the treatment of these aforesaid time dependent processes. A simple signal conditioning circuit based on relaxation oscillator for resistive sensor has been proposed by T.Islam et al. in [2.55]. The circuit utilizes Op-amp based active bridge to convert the resistance change into frequency or duty cycle. The change in frequency is directly proportional to the change in resistance of the sensor. However there are still a huge scope available to design optimum sensor based system towards which different researchers are still working.

2.4 RFID techonology as a sensing device

Radio Frequency Identification (RFID) is the most reliable technique to electronically identify, data capture, control, track, and inventory items using RF communication. In the recent times RFID is having a very wide use but most of the time such systems are invisible or are not recognized by the users. The basic RFID system consists of a reader and a tag. The reader or transceiver acts as the master and provides the RFID tag with energy in case of passive tags and triggers the communication signals to force the tag to execute the desired action. The reader can be controlled either via a computer terminal or by the automatic execution of program codes stored in the internal memory of the reader's processors unit. Like recognizing friend or foe, backscatter radiation from a passive RFID tag can make visible what is otherwise invisible. One of the key learnings to emerge from the application scenarios that flow is that new processes must often be created to harness RFID information, as proposed in early research at MIT in this area. This scheme emerged from the Technology Day @ MIT that the auto ID Labs hosted for the EPCglobal Board of Governors further described how companies were breaking apart the brittle centralized manufacturing models of the industrial revolution to design more flux able business processes and tighter supplier collaboration to meet local market conditions [2.24,2.28,2.33-2.38]. RFID research and development program requires a balance between physics and electrical engineering, between computer science and business inside, in answering the question as to how best RFID data add value. As it is pointed out correctly in mastering the dynamics of innovation, new technologies often exist for decades before their true potential is discovered. Making the invisible visible is an opportunity that RFID makes available. How these can best be accomplished and in what application areas. This technology now integrating with sensors to provide more advanced solution to real life problems. Hence in this thesis work the RFID technology has been used as sensing device to solve problem like leakage of hazardous gas like methane or ethanol using simple fabricated gas sensor with RFID tag, RFID reader and interfacing circuit.

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Chapter 3

FABRICATION OF Pt AND Pd MODULATED WO_3 SENSOR AND ITS APPLICATION IN ETHANOL SENSING

3.1 Introduction

The semiconductor metal oxides (SMO) having wide band gap energy play key role in detection of variety of oxidizing and reducing gases [3.1-3.3]. WO_3 is broadly studied semiconductor type metal oxides among various substances with excellent gas-adsorption properties for the fabrication of solid state devices [3.4-3.6]. WO_3 is generally an n type compound substance having electron its majority carriers and it has a wide band gap (~2.6 – 3.6 eV at room temperature) [3.4]. WO_3 thin film can be developed on different platform (substrates like Si, quartz, optical fiber) using a variety of processes like electro spinning [3.7], thermal evaporation [3.8-3.9], chemical vapour deposition [3.10-3.11], hydrothermal [3.12-3.13], sol-gel technique etc. Among these various techniques the sol–gel is a low cost, highly accurate and CMOS compatible process for preparing nanoparticles. In recent times it is also reported that the sol–gel technique gives good control over the nano-particle size and thickness of the n-type metal oxide.

Different kinds of SMOs such as SnO_2, TiO_2, WO_3, ZnO, etc. are used as the sensing layers [3.14-3.20]. These devices are power efficient, less costly with good sensitivity and highly responsive [3.2]. Further improvement of sensing function is done by using noble metals such as gold, silver, platinum and palladium. The sensitivity of WO_3 based thin film sensors can be modulated using these noble metals which can detect different volatile organic compounds (VOC). The applications area of ethanol which is one of the important VOC in domestic and industrial zone includes space application- where it is used as fuel or fuel additives, alcohol industries – where it is used as the prime component, chemical industries – where it is used as precursor or solvent to produce different organic compounds [3.21] and many more. Even the concentration of alcohol consumed by drunken driver is checked in real time using the breath analysis. Hence the accurate and fast detection of low concentration ethanol is an important issue in those areas to maintain proper safety and security. The fabricated ethanol sensors must be stable and repeatable with good response time and high sensitivity. The operating

temperature of the sensor must be low to achieve low power consumption and long life time.

In this chapter the effects of modulation of WO_3 by Platinum (Pt) and Palladium (Pd) are studied as ethanol sensor. The important parameters of the fabricated sensor like operating temperature, sensitivity, selectivity, response time and effects of modulation are thoroughly studied. The solgel method is adopted to fabricate WO_3 thin film sensor on Si substrate by spin coating method and the sensor is tested for ethanol concentration 500-5000 PPM range.

3.2 Literature Survey

Nowadays the monitoring and detection of different toxic gases/vapours like ethanol, methane, ammonia, hydrogen is very important with respect to energy savings and environment [3.22-3.23]. So different types of gas sensors are fabricated to achieve the goal [3.22].

In literature many types of gas sensors are developed using different types sensing materials and methods. These gas sensors can be classified as electrochemical, catalytic combustion, solid electrolyte, infrared absorption, thermal conductive and SMO type sensors [3.24]. On the basis of sensing methods gas sensors further classified into two groups [3.25] (a) Sensors varies its electrical properties like resistance for SMO sensors and (b) Sensors varies its other properties (like magnetic, optic, and acoustic). Further the gas sensors may be classified according to the measurement methods as (1) Field Effect Transistors (FET) based gas sensors (2) Photo-luminescence based gas sensors (3) DC conductometric gas sensors [3.25]. Among these gas sensors SMO sensors are smaller size, cheap, repeatable and low power-consuming. Generally the SMO sensors exhibit a surface depleted of electrons in the presence of adsorbed oxygen from the atmosphere at its operating temperature zone. The size of depletion region reduces by leaving the chemisorbed oxygen in existence of the reducing type gases like: methane, hydrogen, ethanol at the grain boundaries of the semiconductor surface. This change in the depletion region noticeably influences the sensing phenomenon of the sensor.

In presence of oxidizing gas like carbon monoxide, oxides of nitrogen, carbon di oxide, oxygen the reverse phenomenon occurs at the surface of SMO sensors. The resistance of the SMO sensors changes due to adsorption of gas at the surface of the sensors. This sensing phenomenon is analysed to detect different flammable and toxic gases in the environment. The analysis of the sensor is done by two functions: the receptor function and transducer function [3.25]. Receptor function is stated as the capability of the SMO gas sensor surface to interact with the target gas. The electrochemical reactions between the target gas and the surface of the SMO enhance the sensing behaviour of the metal oxide. This function can be modulated by the addition of an additive like basic or acidic oxide, noble metal [3.21-3.23]. The response magnitude of the sensing device is changed largely due to these additives. Transducer function concerns about the capability to transform the generated signal from the SMO surface into electrical signal.

In literature the rigorous efforts are in progress to find more suitable materials to achieve better quality sensors. SMO gas sensors are generating huge interest due to fulfilment of the basic requirements of an ideal sensor. Recently the SMOs with nanoparticle size 1 nm–100 nm are being increasingly used for gas sensing application due to their size dependent properties like mechanical, optical, electrical, catalytic and magnetic properties. Two important factors i.e., high surface areas per unit mass and high surface to volume ratio of SMO based sensors control the sensitivity of the sensor. Further, different physical, chemical properties, the movement of electrons and holes in nanomaterials are also affected due to size reduction in nano scale [3.24-3.25]. High crystalline structure, doping of different noble materials and easy production rate increase the demand of research to develop different nanoparticle based SMO gas sensors [3.26] in the field of detection of ethanol vapour. Ethanol sensors like chromatographs, specific ionization and mass spectrometers gas pressure sensors exist in literature. They have some distinct limitations like large size, high cost, high response time, high operating temperature [3.27-3.29]. So different sensors are produced which are commercially available like electrochemical, semiconductor, thermoelectric, metallic, optical and acoustic etc. The SMO technology are the best one among them having different features [3.30-

3.32] due to which these sensors are used as promising materials as highly sensitive VOC sensors. In literature the mostly studied ethanol sensors are based on TiO_2, ZnO, WO_3 based SMO structures. These structures are different types like thin film, nanorod, nanotube, nanofiber and many more. Different fabrication processes are used for different structure devices like chemical vapour deposition (CVD), e-beam evaporation, hydrothermal, solgel and many more. Every structure has its own advantages and disadvantages. The thin film structure provides best result with respect to cost and easy fabrication process among different structures. On the other hand the solgel technique results good accuracy with highly cost-effective. The TiO_2 based nanotube structure was fabricated by Kwon et al., [3.24] for ethanol detection purpose. They found high sensitivity at presence of 1000 PPM ethanol at temperature 250°C. However, the response time of the sensor was high 110 sec. Thus, in another work p type TiO_2 sensor having good recovery kinetics and high accuracy for ethanol sensing has been fabricated by Kim et al. [3.25]. The high operating temperature causes safety hazards and the cross sensitivity to other gases are the most disadvantages of these types of sensors. A different kind of SMO device fabrication is also popular as hetero-junction sensors. Here the hetero-junctions are created using two dissimilar semiconducting metal oxides with different band gap [3.26-3.29]. In the beginning, ZnO/CuO hetero-junction based sensing device has reported for sensing of alcohol by researchers. Then, Z. Ling has reported a different class of hetero-junction sensor which is the combination of ZnO and p-type mixture of $BaTiO_3$/CuO/La2O_3 [3.27]. However these structures have different pros and cons associated with them. Then research trend moves towards new material WO_3 based different structures for detecting different VOC compounds by exploring different kind of structures like thin film, nanorod, nanoflower, 1D, 2D, heterostructures and many more. Thin film WO_3 for LPG detection is carried out in [3.28], flower like WO_3 by CVD process fabricated in [3.29] for detection of butanol. Further WO_3 nanoplates and WO_3 spheres are also fabricated and investigated for detection ethaylacetate, methanol and ethanol [3.30-3.31]. In literature many processes have been used to synthesize WO_3 like thermal evaporation [3.32-3.33], chemical vapour deposition [3.34-3.35], template assisted growth [3.36-3.37],

hydrothermal method [3.38-3.41] and so on. Each method has a series of parameters to control in order to obtain WO_3 with different morphologies such as in hydrothermal method reaction temperature [3.40], PH value [3.38], reaction time can be modulated. The WO_3 material has some inherent advantage over other materials like CuO, $Fe2O_3$, $In2O_3$ like compatibility with Si technology, highly sensitive toward different gases (like NH_3, CO) & volatile compounds like ethanol, acetone. Having high specific surface area and novel electron transportation properties, smaller gain size also increases the demand of WO_3. However, these types of sensors also suffer from selectivity issues [3.12]. Now researchers are trying to use different technology like RFID as sensing device to overcome the limitations [3.42-3.50]. RFID provides no line of sight communication, different frequency of applications, cost effective way of implementation of work. However further performance improvement is essential.

From the view of current research trend and research status it can be concluded that more research can be done with WO_3 material for efficient detection of ethanol. Thus fabricating the ethanol sensor with WO_3 material by Pt and Pd modulation to achieve low power, high sensitivity, low temperature sensor is the main focus of this chapter.

3.3 Fabrication of the Sensor

The fabricated sensor schematics is shown fig.3.1 and the detail steps for fabrication are described in the following sections.

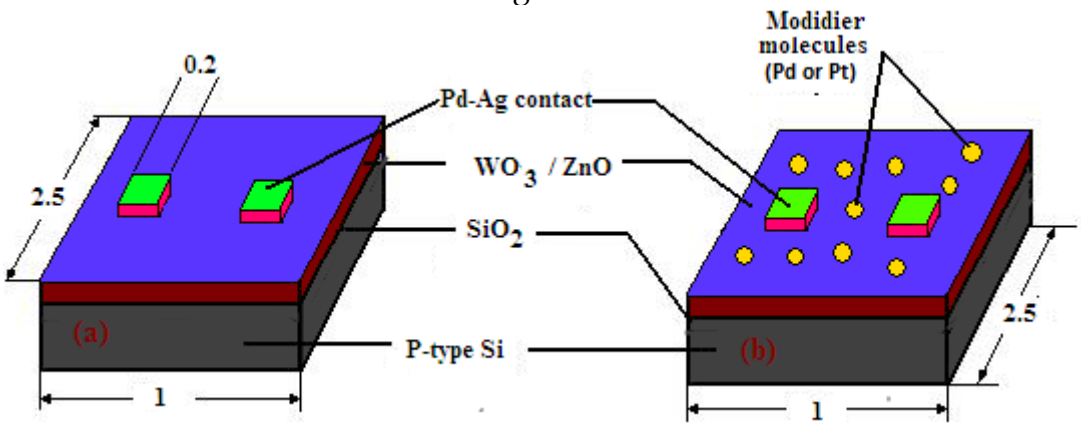


Figure 3.1: The schematic Structure of fabricated sensor (unmodified (a) and modified (b)) (not to scale).

3.3.1 Preparation of WO_3 thin film sensor

The thin film of WO_3 has been fabricated by sol-gel method using Tungsten hexa-choloride as a precursor. The thin film was prepared by the sol–gel process. The sol–gel method has emerged as one of the most promising processing route as it is particularly efficient in producing thin, transparent, homogeneous, multicomponent oxide films of many compositions on various substrates at low cost and it allows the tuning of the thickness of the film by varying synthesis parameters. As a starting material WCl_6 was used as a precursor to prepare WO_3 thin film. WCl_6 was dissolved in isopropanol at a ratio of 10g/150ml and stayed in dry air for 3 days. Then the sol was deposited on the substrate by spin coating method (3000rpm, 30s) and the substrate was dried in air at 150^0C for 30 minutes. Post deposition heat treatment (annealing) at 600^0C for 2 hours was carried out to improve microstructure and crystalline properties of the deposited thin film. Then Pd-Ag contact (0.2µm) was deposited for metallic contact formation by thermal evaporation technique.

3.3.2 Preparation of Pd-surface sensitized WO_3 thin film Sensor

For Pd sensitization, an aqueous solution of 0.01 (M) $PdCl_2$ is prepared and the sol-gel grown WO_3 thin films are dipped in the solution for 10s and annealed at 125^0C for 15 minutes. The mechanism of formation of Pd nano-clustered from $PdCl_2$ is investigated with oxidation reduction reactions in solution. In such solution, $PdCl_2$ dissolved easily Pd^{++} and Cl^- ions. The Pd++ ion took two electrons from the surface of WO_3 thin film to form Pd. E-beam vacuum evaporation technique is used to deposit pd-Ag (70%) electrodes (2mm X 2mm) with a thickness of 0.2µm on top surface and back surface of Pd-surface sensitized WO_3 thin film using Al mask.

3.3.3 Preparation of Pt-surface sensitized WO_3 thin film Sensor

1 ml of 80 mM H_2PtCl_6 solution in ethylene glycol was rapidly added to 8 ml ethylene glycol at 160°C that contained 0.08g Polyvinylpyrrolidone K-30 (PVP) under continuous stirring. The black colour Pt nanoparticles formation could be observed

during the reaction. Then using acetone and ethanol the black solution was washed continuously two or three times. Then the Pt nanoparticles were obtained after centrifuging and drying at 60°C under vacuum for 8 hour. The solution of Pt nanoparticles (0.8 mg) and deionized water (10 ml) is prepared and were mixed with WO_3 solution. Finally using this solution the Pt modified WO_3 thin film sensor was fabricated by calcining at 600°C in air for 2 h. Table 3.1 describes the detailed description of the fabricated samples.

Table 3.1: Description of the fabricated samples.

Sample Number	Description		
	Substrate	**Sensing Layer**	**Top Contact and Bottom Contact**
S1	p-Si <100>	un-sensitized WO_3	Pd-Ag (70%)
S2	p-Si <100>	Pd surface sensitized WO_3	Pd-Ag (70%)
S3	p-Si <100>	Pt surface sensitized WO_3	Pd-Ag (70%)

3.4 Structural Characterization

The grown nanocrystalline's average size is achieved by XRD results. It is calculated by the Scherer's equation as follows [3.13-3.14]

$$D = \frac{k\lambda}{\beta \cos\theta} \qquad \text{eq. (1)}$$

Where K: 0.9 (constant) λ: X-ray wavelength θ: Bragg angle β: full width of the diffraction line at the half of the maximum intensity. Based on the equation the average crystalline size of only WO_3 (S1), Pd modified WO_3 (S2), Pt modified WO_3

(S3) are 11.8nm, 6nm and 5.4nm respectively calcined under 600°C. The Scanning Electron Microscope (SEM) experimental images are shown in fig. 3.2 (a-c) for WO_3 based sensor with Pd and Pt modified and the XRD result is shown in fig 3.2(d) for fabricated sensors.

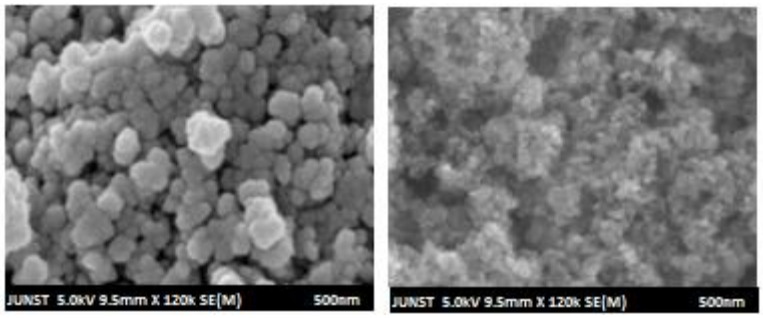
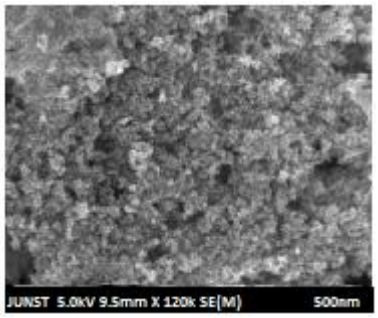


Figure 3.2 (a) SEM of WO_3 (b) SEM of Pd-WO_3



(c) SEM of Pt-WO_3

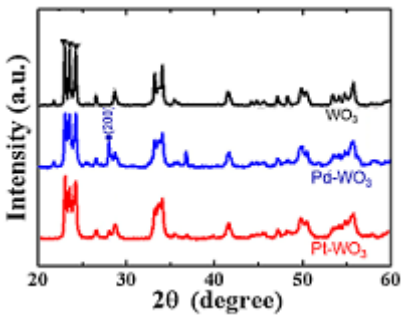


Figure (d) XRD of WO_3 based sensors

3.5 Measurement setup

Figure 3.3 shows the schematic of measurement set up for ethanol vapour sensor. The cylindrical sensor chamber is made of glass (length 25cm and diameter 3.5cm).The thin film sensor is inserted into the chamber (by contact connection). The temperature controller (TC) was used to attain the operating temperature.

Temperature controller was operated by resistive heating coil (≈ 8cm of constant heating zone, with temperature accuracy ±1˚C). The gas flow and mixing ratio were precisely monitored and controlled with the help of mass flow controller (MFC), Mass Flow Meter (MFM) (Alicat scientific, M-50SCCM-D) for air (reference gas). The homogeneous mixture carrying the desired percentage of the target vapour was fed into the chamber with a flexible PVC pipe. During the testing the gas pressure on the sensor was 1atm. Figure 3 shows that schematic diagram of experimental set up.

The sensitivity (S) is defined as:

$$\text{Sensitivity (S\%)} = \frac{R_A - R_V}{R_A} * 100 \qquad \text{eq.(2)}$$

where R_A is the sample resistance in N_2 (i.e. at 0% ethanol vapour) and R_V is the sample resistance at a given concentration of ethanol vapour. The operating temperature of the sensors is the critical parameter as it directly determines the stability and longevity of the sensors. The experimental work has been carried out to find out accurate operating temperature for all the sensor samples. The response time and recovery time of the sensor is other very important parameters to observe. Response time is the time interval over which resistance of the sensor material attains a fixed percentage (using 90%) of the final value when sensor is exposed to full scale concentration of the target gas/vapour. On the other side recovery time is the time interval over which sensor resistance reduces to 10% of the saturation value when target gas/vapour is removed and sensor is placed in reference air. Small value in response time and recovery time is mostly desirable in real time application.

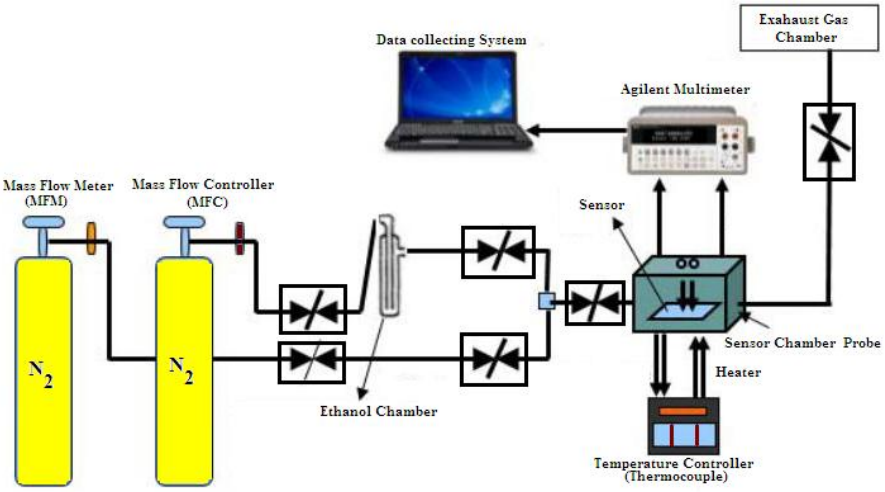


Figure 3.3 Experimental set up

3.6 Results and Discussions

The effects of noble metal modification (Pd, Pt) on sensors are examined. The operating temperature, response-recovery times and the sensitivity are the most important parameters where the improvement is reflected. The operating temperature is measured at ethanol vapour concentration 500ppm (0.05%) by varying the temperature from 100˚C to 350˚C and calculating the sensitivity according to eq. (2). The fig 3.4 shows the variation of sensitivity of the sensors with respect to variation of temperature. The operating temperature of WO_3 based sensors with Pd and Pt modified are 300˚C, 210 ˚C, 170 ˚C (for WO_3) (as shown Table 3.2). The influence of noble metals is prominent with this respect which shows better result with respect to ref [3.11] where Y. Kwon et al. have worked towards enhancing the ethanol sensing properties at temperature 250˚C and in ref [3.14] where CuO based fabricated sensor via solgel has been used with operating temperature 220°C.

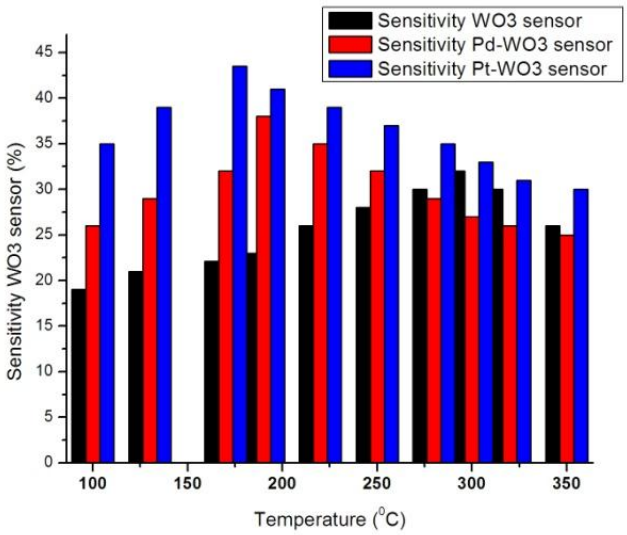


Figure 3.4 Sensitivity of WO_3 sensor vs. temperature

Further the sensitivity of the sensors is enhanced with modification of Pd and Pt for both the materials WO_3 and ZnO. Figure 3.5 shows the change of sensitivity of different sensors according to eq.(2) with respect to change of ethanol concentration at each sensor's respective operating temperature. The reason for enhancing the

sensitivity lies in the fact that the addition of noble metals creates more space for interactions between ethanol vapour molecule and sensing layer. The noble metal additives with high effective oxidation catalytic enhance the spillover effect. Besides, the surface to volume ratio is further enhanced as the diameter of the nanoparticles

Table 3.2: Experimental result for calculating operating temperature (OT (^{0}C)) for different sensors using sensitivity (S%)

Ethanol Concentration	WO_3 sensor		WO_3-Pd sensor		WO_3-Pt sensor	
	OT (^{0}C)	S (%)	OT (^{0}C)	S (%)	OT (^{0}C)	S (%)
500 PPM	300	30.1	210	35.3	170	45.2

is reduced by the effect of noble metals such that is for unmodified WO_3 to Pt modified WO_3 is 11.8nm to 5.4nm whereas for unmodified ZnO to Pt modified ZnO is 20nm to 11nm. It causes more nanoparticles to be accommodated at surface level and thus increasing the surface to volume ratio. Finally more vapour molecules interact at the sensor surface and the sensitivity increased. When the sensitive layer is heated at the operating temperature for the respective sensors, based on the amount of the ethanol vapour concentration present inside the test chamber the resistance of the sensing layer decreases, and the sensitivity increases. The temperature plays a vital role because the adsorption and desorption processes are temperature activated process which are the key processes for chemical reaction between the sensor and ethanol. However over the operating temperature the small nanoparticles try to agglomerate into large particles, decreasing both surface to volume ratio and catalytic properties of the sensor material which finally decreases the sensitivity of the sensor. The relation between the sensitivity and concentration shows a positive correlation with increasing the ppm value of ethanol vapour. The electrical conductivity variation of the sensors is controlled by the ethanol vapour and chemisorbed oxygen particles on the surface of the sensors at their respective operating temperatures. Oxygen molecule present in air environment adsorbed on the top surface of WO_3 or ZnO sensors and extract electron from their conduction

band (CB) hence initial resistance increases of the sensors. Then chemisorbed oxygen molecules react with the ethanol vapour and donate electron and thereby increasing the electron concentration and decreases the resistance of the sensing film. The following chemical process is followed at absence of ethanol:

O_2 (gas) → 2O (adsorbed)

O (adsorbed) + e- (from sensor's CB) → O-(ads)

Then at presence of ethanol vapour the following chemical process is followed:

C_2H_5OH (vap) + O-(ads) → CH_3CHO (ads) + H_2O (vap)+ e-

CH_3CHO (ads) + O (lattice) → CH_3CHO (vap) + VO

The fig. 3.5 represents the sensitivity vs. ethanol concentration graph for each sensor at their respective operating temperature. The maximum sensitivity achieved for Pt modified WO_3 is 77.2% and Pt modified ZnO is 74.6% towards highly pure (99.5%) ethanol vapour. The selectivity is another important property of any gas sensor and it determines that the sensor is only sensitive to a particular gas with respect to presence of other gases. The selectivity of the fabricated sensors are measured by measuring the sensitivity of each sensors at their respective operating temperature in presence of three different elements ethanol, methanol and methane. Figure 3.6 shows that both types of sensors are highly selective to ethanol whereas for other gases the sensitivity is quite low.

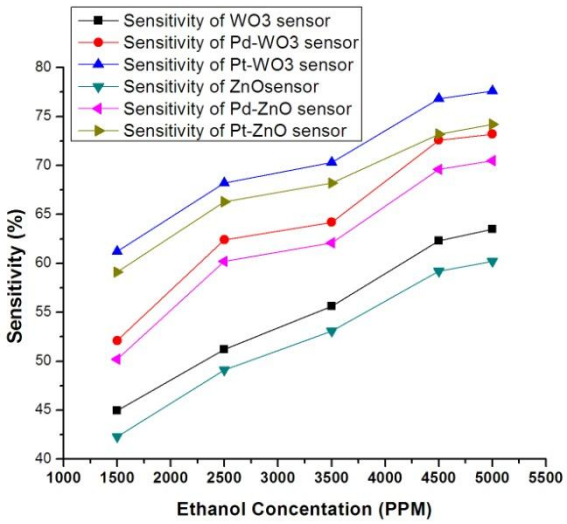


Figure 3.5 Sensitivity vs. ethanol concentration graph for different sensors (at their respective operating temperature)

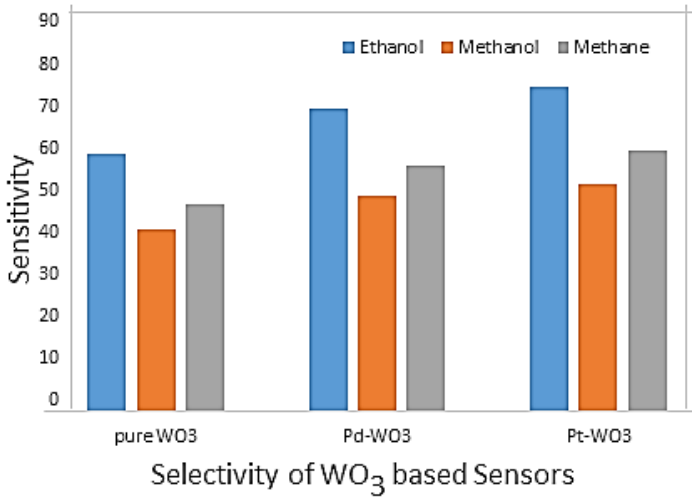


Figure 3.6 Selectivity of WO_3 Sensors

The current voltage characteristic for the fabricated highly sensitive ethanol sensors is shown in the fig. 3.7. It is found that forward current of fabricated sensor devices changes significantly with respect to forward applied voltage whereas insignificant current change occur in reverse applied voltage. Thus rectifying type contact has been formed for sensors and Pt modified sensors show higher current driving capability. The experimental study is carried out to calculate response time (TRES in seconds) and recovery time (TREC in seconds) of the fabricated samples at their respective operating temperature. Below table 3.3 shows variation of response and recovery time with change in ethanol vapour concentration. Figure 3.8-3.9 depicts the graphical representation of the response and recovery time for all the samples. It directly proves that addition of noble metals enhances these properties of the sensors.

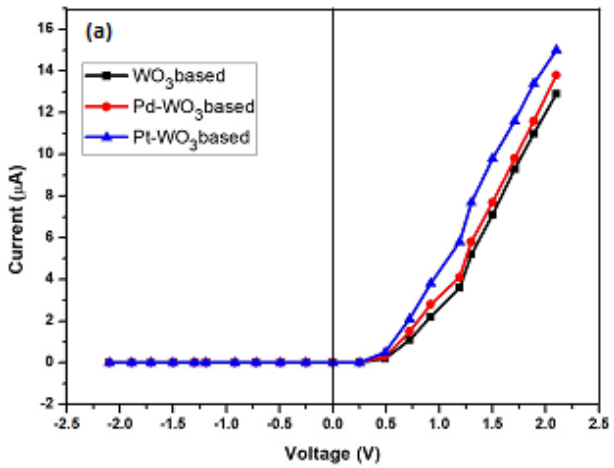


Figure 3.7 I-V characteristics of WO_3 based sensors

Table 3.3 Response and recovery time calculation(sec.) for different sensors

Ethanol (PPM)	Sample 1 (WO_3)		Sample 2 (Pd-WO_3)		Sample 3 (Pt-WO_3)	
	T_{RES}	T_{REC}	T_{RES}	T_{REC}	T_{RES}	T_{REC}
500	68	72	54	57	48	51
1500	59	86	48	68	41	62
2500	46	102	37	82	32	71
3500	33	115	27	92	25	82
4500	26	128	21	102	19	91

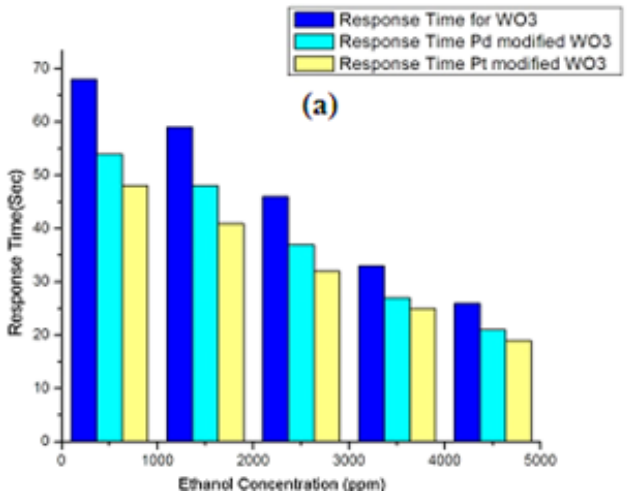


Figure 3.8 Response time vs. ethanol concentration

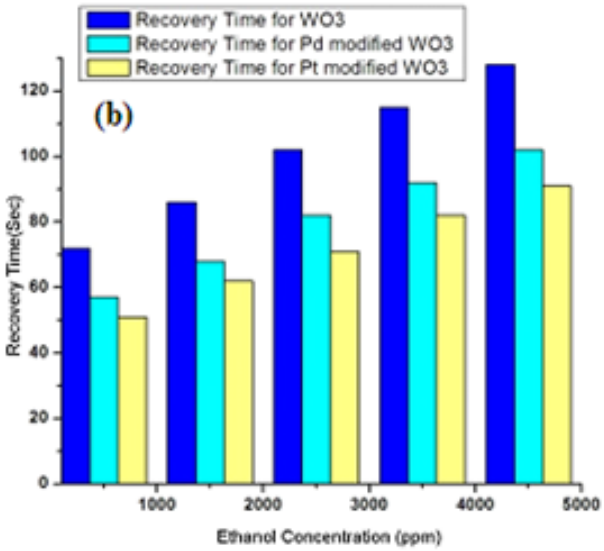


Figure 3.9 Recovery time vs. ethanol concentration

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Chapter 4

Study the effects of annealing temperature and heterostructure on solgel spin coated ZnO thin film sensor

4.1 Introduction

The thin film gas sensors play very significant role in detection of different gases. The key features of thin film gas sensor are sensitivity, selectivity, response time, recovery time and stability. The influential factors which directly control these key features of thin film gas sensors are structure of the sensor device like homojunction, heterojunction, capacitive, fabrication process parameters like annealing temperature, pressure, chemical ingredients, chemical additives etc. In recent times ZnO based thin film sensor is used in many applications like electronic, optoelectronic, MEMS based gas sensors etc. The key features for which ZnO is commercially used for gas sensing application are band gap (3.37eV), binding energy (60-65 meV) and n type conductivity. It can be fabricated on different types of substrate like GaAs, sapphire, ITO coated glass, n-Si, p-Si and many more using diverse fabrication technologies like Pulsed Laser Deposition (PLD), Molecular beam epitaxy (MBE), Chemical Vapour Deposition (CVD), Metal Organic CVD (MOCVD), RF Sputtering, Solgel [4.1-4.5]. Surface to volume ratio of nanoparticle ZnO plays very important role in sensing applications. The size of nanoparticle ZnO sensor can be modulated by varying annealing temperature during fabrication process. Si based substrate always preferred for fabrication ZnO based sensors using solgel process where annealing temperature plays very important to control the average nanoparticle size of ZnO sensor, crystalline structure and other physical parameters.

Another key challenge of thin film based sensor is its selectivity in presence of many gases in addition to target gas. The researchers are working towards thin direction and found electric nose to solve this problem. Electronic nose simultaneously analyse several sensors' signal at once i.e. up to 26 or more [4.6-4.7]. But it requires complex structure, complex algorithms. Thus further enhancementis till on in research area. Next researchers found composite materials. They show great enhancement towards selectivity and sensitivity parameters of thin film sensors. Composite metal oxide gas sensor results from physical interface between two different materials. When Fermi energy level equilibrates to the same energy the

charge transfer and depletion region formation happened. This unique feature increases sensors performance parameters like sensitivity, selectivity, operating temperature etc.

Thus in this chapter the effect of variation of fabrication process parameter (annealing temperature) and effect of hetero junction device structure for ZnO thin film sensor are studied for detection of hydrogen gas.

4.2 Review of recent work

The most investigated group of sensors is conductometric metal oxide gas sensors. This huge attention of these gas sensors are mainly because of low cost, flexibility in production, large number of detectable gases. These sensors reflect change in conductivity, capacitance, work function, optical characteristics etc. in presence of different target gases. The researchers have successfully shown that the detection process of conductometric sensor is reversible and stable. One of the important factor of the gas sensor selectivity with sensitivity has been taking more attention in recent time. This basic factor may be influenced by factors like chemical composition-heterojunction structures, noble metals-surface modifier, microstructure etc. The more recent works focus on composite materials, such as SnO_2-ZnO, Fe_2O_3-ZnO, ZnO-CuO [4.8-4.12] etc. These structures provide good control over adsorption ability, catalytic activity, sensitivity, thermodynamic stability of sensor. In addition to these binary oxides there exist ternary, quaternary and complex metal oxides [4.13-4.14]. Researchers also integrate the combination of metal oxides with other components like organic and carbon nanotubes [4.15-4.18]. The synergistic effect between the two components of composite materials or heterostructure device raises the sensitivity as well as selectivity of the sensors. Apart from synergistic effect the heterojunction interface between two or more components also enhances of the composite gas sensor's sensitivity-selectivity [4.19-4.22]. Next process is sensor's surface modification by adding noble metals as catalytic factors. The catalytic reactions with detected gas molecules take place at the surface of gas-sensing material. So by controlling the catalytic activity of sensor

material the sensitivity-selectivity of gas sensors can be increased. However, the widely used gas sensing materials like TiO_2, ZnO, SnO_2, Cu_2O, Ga_2O_3, Fe_2O_3, are the least active with catalytic point of view [4.23] whereas noble metals are highly catalyst and this makes them a prominent material for gas sensor surface. There are different ways to introduce noble metals such as impregnation, sol-gel, sputtering and thermal evaporation [4.24-4.34]. Due to the addition of noble metals the depletion zones are formed around the modified particles and the modulation of the nano-Schottky barriers occurred which causes enhancement of sensing behavior. Besides as the noble metals are also catalytically active and better oxygen dissociate which further enhances the overall sensitivity of thin film sensor. The receptor and transducer functions of the thin film gas sensor determine how fast sensor cans response to the target gas. Receptor function is stated as the capability of the thin film gas sensor surface to interact with the target gas. The electrochemical reactions between the target gas and the surface of the sensor enhance the sensing behaviour. Thus it is very important to optimise the sensor particle morphology and crystallographic structure as surface to volume depends on these factors. As the s-v ratio increases the particle size decreases. There exists a limitation towards the size of the particle of gas sensor that is smaller crystal size of nanocrystals does not necessarily mean the enhancement of gas sensor performance. Nanocrystals which are very small in size tend to agglomerate into large entities that give reverse result such as instability, distortion of catalytic properties of the material [4.35-4.49]. The annealing temperature variation during solgel fabrication process gives good control over nanoparticle size modulation.

From this view of current research trend to achieve more sensitivity and selectivity for MOS based gas sensor

- The effect of noble metal addition with annealing temperature variation to modulate microstructure of ZnO based SMO sensor is thoroughly studied in this chapter.
- The effect of chemical composition by forming heterostructure of ZnO- WO_3 is also thoroughly studied in this chapter

4.3 Fabrication and Characterization of Sensor

The fabrication process is carried out to fabricate

- Pd modified ZnO sensor at different annealing temperature
- Hetero structure sensor based on ZnO-WO_3

4.3.1 Fabrication of Pd modified ZnO sensor

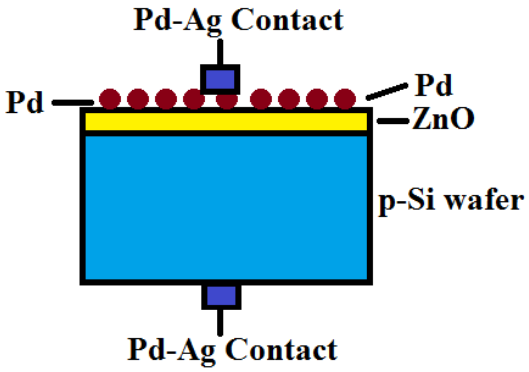

Figure 4.1 The schematic Structure of fabricated sensor

The schematic structure of the fabricated sensor is shown in fig4.1 with Pd-Ag contacts on both sides. The process of solgel fabricated Pd modified ZnO thin film sensor is described in fig.4.2. Three Pd modified ZnO sensors (PZ1, PZ2 and PZ3) annealed at different temperature 350˚C, 500˚C and 650˚C for 2 hours are fabricated. The crystalline property of the fabricated sensors is investigation by X-Ray Diffraction (XRD) process. The crystalline structure of differently annealed sensors studied by XRD is shown in fig. 4.3. The grown ZnO thin film without annealing has no clean peaks whereas multiple peaks with higher intensity exist for other fabricated sensors. The fig 4.3 confirms the presence polycrystalline nature of grown structure. The crystalline size of the ZnO thin films can be determined by analyzing XRD result and using following equation [1].

$$D = \frac{c\lambda}{\beta \cos\theta} \qquad (1)$$

where D is the crystalline size, c is correction factor, wavelength of X-ray is λ, β (in radian) is the full width at half maximum value of a peak in the XRD spectra and θ is the peak position angle in degree. Two other important parameters i.e. lattice parameters ‘a’ and ‘c’ of ZnO are calculated by following equation

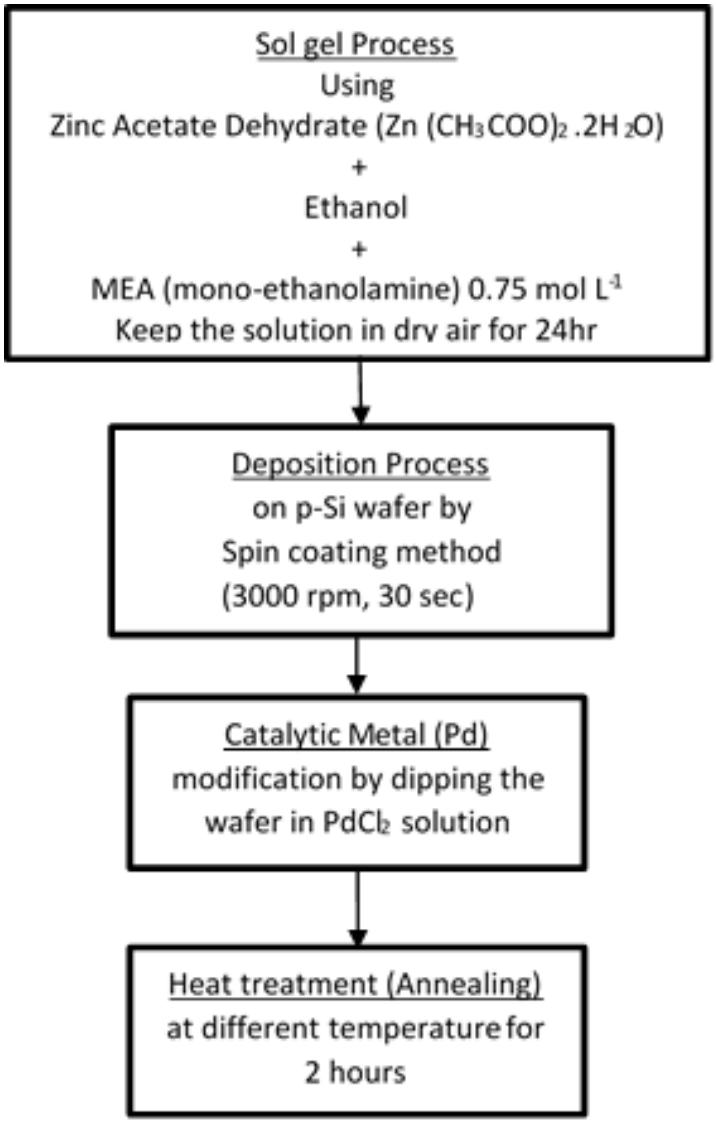

Figure 4.2 Fabrication process of ZnO thin film sensor

$$a = \sqrt{\frac{1}{3}}\ {}^{\lambda}/_{\sin\theta} \quad (2)$$

$$c = {}^{\lambda}/_{\sin\theta} \quad (3)$$

The values of crystalline size and parameters are calculated from XRD results as shown in fig.4.3 and tabulated in Table I for 350˚C, 500˚C and 650˚C annealing temperature.

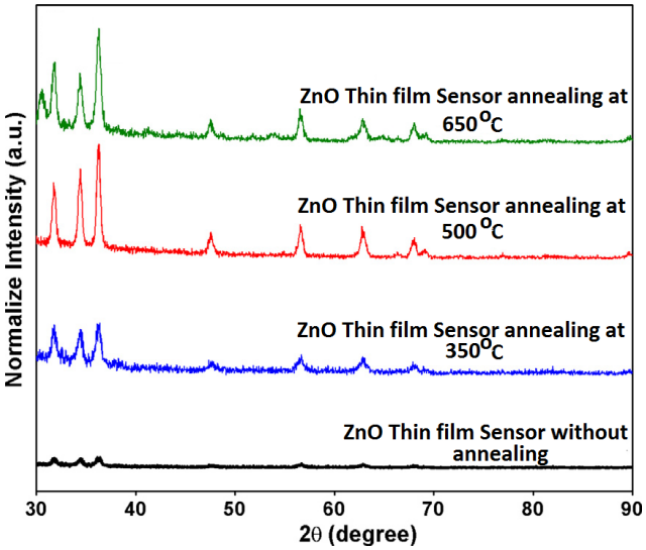

Figure 4.3 XRD spectra of fabricated different ZnO thin film sensors

TABLE 4.1 The crystalline size and lattice parameters of thin films for different annealing temperature range 350˚C to 650˚C

Annealing temperature (˚C)	Crystalline size along different planes (nm)				Lattice Parameter (Å)	
	(100)	(002)	(101)	Average	A	C
As grown	9.2	7.5	8.7	8.46	4.0705	7.0503
350	14.4	8.8	11.3	11.5	4.0504	7.0155
500	19.2	17.6	18.9	18.56	4.0471	7.0098
650	20.3	14.8	14.1	16.4	4.0432	7.0030

It is observed that the post fabrication annealing process has influenced the important parameters of thin film sensor like peak position, peak intensity, crystalline size and lattice constants. The minimum values of average crystalline size of the ZnO thin film is obtained for 350˚C annealing temperature. However with increasing the annealing temperature the particles try to agglomerate so the average particle size increases for higher temperature.

4.3.2 ZnO-WO_3 Heterostructure Sensor

In the present study four sensors are fabricated with different structures. They are (i) WO_3 based Sensor (WZ1) (ii) ZnO based Sensor (WZ2) (iii) heterostructure based Sensor (WZ3) and (iv)Pd modified heterostructure based Sensor(WZ4). Sol-gel

based synthesis process has been used to fabricate the sensors. The ZnO sol (milky white colour) is prepared using a precursor material zinc acetate dehydrate which is dissolved in a mixture of ethanol and mono-ethanolamine solution with a concentration of 0.80 mol L^{-1} and stirred for one hour. Similarly using WCl_6 as precursor material WO_3 sol (yellowish colour) has been prepared. Initially WCl_6 is dissolved in isopropanol at a ratio of 10g/150ml and stayed in dry air for 3 days.

After preparation of the sols, the sensor WZ1 is fabricated by direct spin coating method (3000rpm, 30sec) on well cleaned Si wafer using WO_3 sol. Post deposition heat treatment (annealing) is used at 350°C for 2 hours to improve microstructure and crystalline properties of the sensor material. Similar process is adopted for fabricating the sensor WZ2 using ZnO sol. For fabricating the sensor WZ3 the sol of WO_3 spin coated on Si wafer and dried at 150°C for 30 minutes. Then ZnO sol is sprayed over the WO_3 layer and then annealing is used to obtain microstructure of heterojunction materials taking both sol 1:1 ratios. Similarly for fabricating the sensor WZ4 the process of sensor WZ3 preparation is followed and before heat treatment the sample is dipped into $PdCl_2$ solution. Finally Palladium Silver (70%-30%) contact is deposited method on both side of each sample.

The prepared thin film is characterized by two experimental processes. The Scanning Electron Microscopy (SEM) method is used to find the surface structure of all the thin film sensors as shown in the fig. 4.4-4.5. The average grain size is about 70-90 nm. Then the X Ray Diffraction (XRD) fig. 4.6-4.7 results are examined to check detail of materials in the thin film sensors. Table 4.2 describes the detailed description of the fabricated samples.

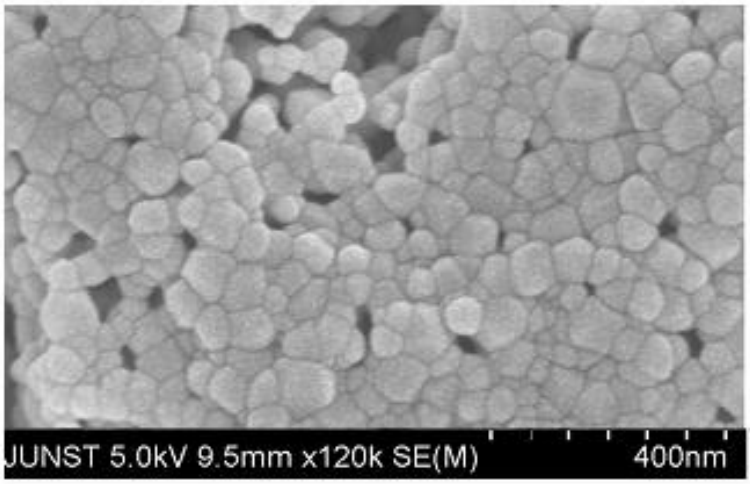

Figure 4.4 SEM image of WO_3 sensor

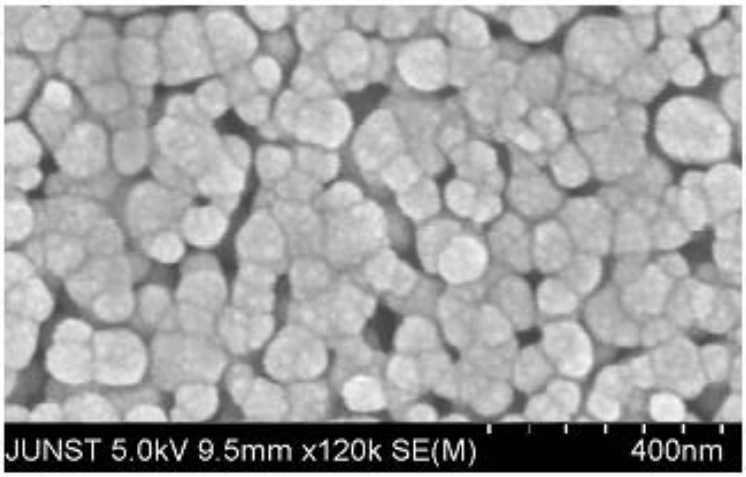

Figure 4.5 SEM image of ZnO sensor

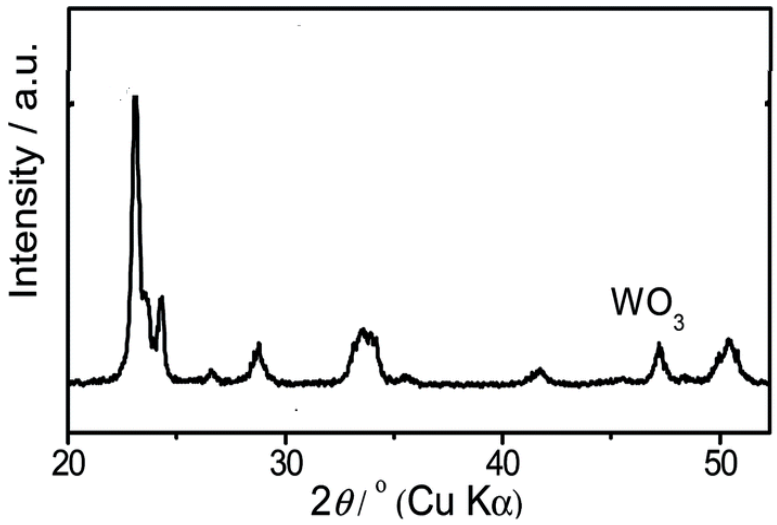

Figure 4.6 XRD image of WO_3 sensor

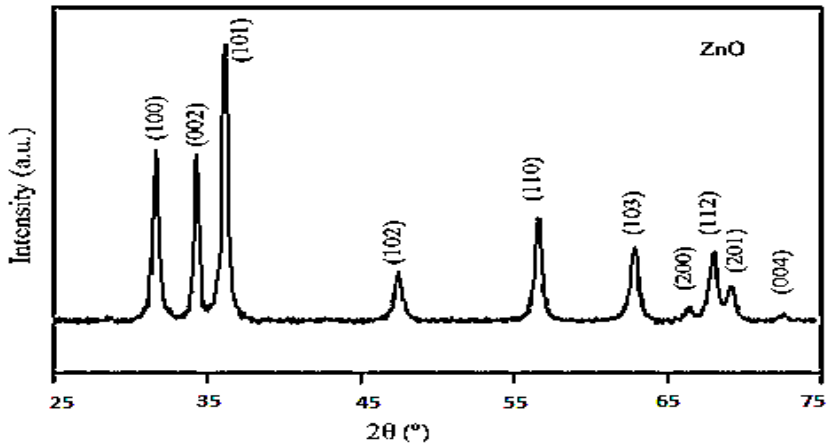

Figure 4.7 XRD image of ZnO sensor

Table 4.2: Description of the fabricated samples.

Sample Number	Description			
	Substrate	**Sensing Layer**	**Annealing Temperature (^{0}C)**	**Top Contact and Bottom Contact**
PZ1	p-Si <100>	Pd surface sensitized WO_3	350	Pd-Ag (70%)
PZ2	p-Si <100>	Pd surface sensitized WO_3	500	Pd-Ag (70%)
PZ3	p-Si <100>	Pd surface sensitized WO_3	600	Pd-Ag (70%)
WZ1	p-Si <100>	un-sensitized WO_3	350	Pd-Ag (70%)
WZ2	p-Si <100>	un-sensitized ZnO	350	Pd-Ag (70%)
WZ3	p-Si <100>	ZnO-WO_3	350	Pd-Ag (70%)
WZ4	p-Si <100>	Pd surface sensitized ZnO-WO_3	350	Pd-Ag (70%)

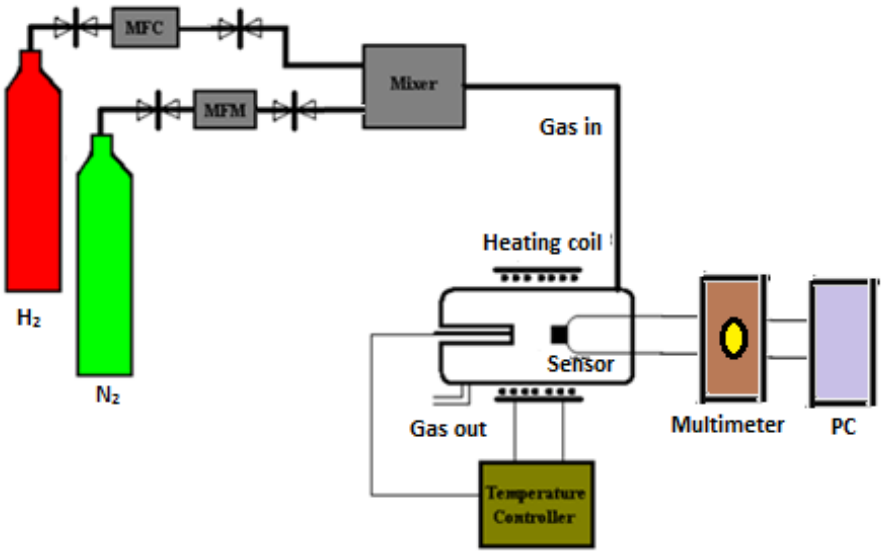

Figure 4.8 Experimental setup for measuring the sensor resistance change with H_2 concentration

Figure 4.8 shows the experimental set up for the hydrogen sensor. The sensor is placed into the sensor chamber. The chamber is made of glass having length 30cm and diameter 4cm. As the sensor works in a particular operating temperature the temperature controller is used to attain that. The temperature controller is resistive heating coil having length ≈ 8cm of the constant heating zone with precise temperature accuracy $\pm 1^0$C is used. The H_2 gas with purity (99%) is used in this work and the gas flow is precisely controlled by mass flow controller (MFC). The N_2 gas is used in this work as reference gas. The resistance across the sensor in presence of reference gas (N_2) and in presence of mixture of H_2 and N_2 is directly measured by multimeter and PC. During testing, the gas pressure on the sensor is maintained at 1atm.

In resistive type metal oxide gas sensor of the oxide layer may increase or decrease in presence of reducing or oxidizing gas. Initially at operating temperature the adsorption and desorption process of analytic gas molecules occur. O_2 molecule present in air environment adsorbed on the top surface sensor and extract electron from their conduction band hence initially resistance increases. Then chemisorbed O_2

molecules react with the target gas's molecules and donate electron. Hence the electron concentration increases that causes decrease in resistance of the sensing film.

$$O_2(gas) \rightarrow 2O(adsorbed) \quad \text{eq.(3)}$$

$$O(adsobed) + e^-_{(from\ ZnO)} \rightarrow O^- \quad \text{eq.(4)}$$

$$H_2 + O^- \rightarrow H_2O + e(to\ WO_3) \quad \text{eq.(5)}$$

Now for composite WO_3-ZnO based heterojunction sensor the sensing mechanism for reducing gas is greatly enhanced. n-n heterojunction is formed between WO_3 –ZnO materials having 5.2eV and 4.41 eV work function respectively. At the interface of hetero junction electron will start to flow from high energy conduction band to low energy conduction band till Fermi level equilibrium. Figure 4.9(a) shows energy band diagram of WO_3 –ZnO sensor before thermal equilibrium.

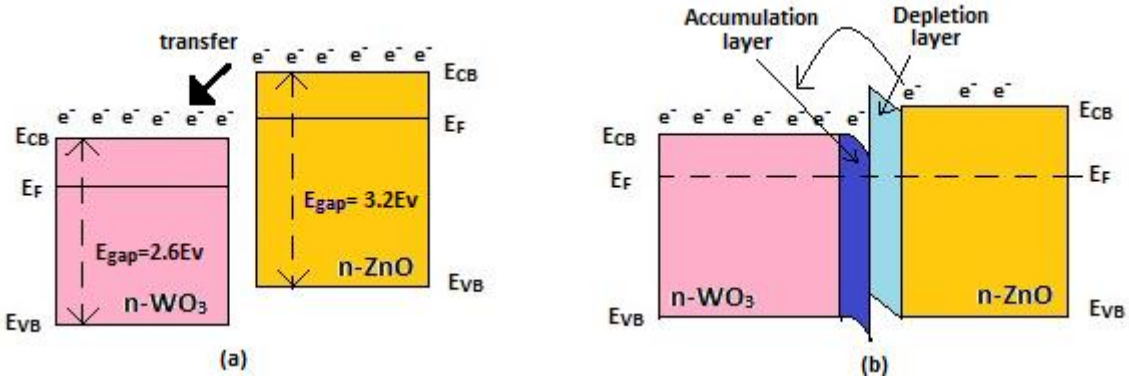

Figure 4.9 Band structure of WO3-ZnO heterostructure sensor (a) before thermal equilibrium (b) after thermal equilibrium

The depletion and accumulation regions are created at WO_3 side and ZnO side respectively. This causes energy band bending at the interfaces as shown in fig 4.9(b). In ambient air, the adsorbed oxygen species at grain boundaries of WO_3-ZnO shield the interface regions so that conducting electrons are trapped and the resistance of composite material increases. Now in presence of H_2 gas surface reaction occur and electron will be generated. These electrons will flow along the WO_3/ZnO interface with shrinking the depletion layer and barrier height. This

results decrease in overall resistance in presence of H_2 gas. The change in resistance in this structure is much higher than simple WO_3 or ZnO structure. The further decrease of resistance is achieved when Pd modifier is used for its catalytic effect.

The response magnitude (S) is defined as:

$$(S\%) = \frac{R_N - R_G}{R_N} * 100 \qquad \text{eq.(6)}$$

where R_N is the sample resistance in N_2 and R_G is the sample resistance at a given concentration of H_2. The operating temperature of the sensors is the critical parameter. It directly determines the stability and lifetime of the sensors. The experimental work has been carried out to find out accurate operating temperature for all the sensor samples. Response time is the time interval over which resistance of the sensor material attains a fixed percentage (using 90%) of the final value when sensor is exposed to full scale concentration of the target gas (H_2). On the other side recovery time is the time interval over which sensor resistance reduces to 10% of the saturation value when target gas (H_2) is removed and sensor is placed in reference air (N_2). Small value in response time and recovery time is mostly desirable in real time application.

4.4 Results and Discussions

At first the effect of annealing temperature is tested for the fabricated sensors PZ1, PZ2, and PZ3 for H_2 gas as shown in fig. 4.10. The maximum sensitivity is achieved for lowest crystalline size sensor i.e. PZ1 which is annealed at 350°C with respect to other sensors annealed at 500°C and 650°C. The surface to volume ratio of sensing material plays an important role for H_2 sensitivity. As the lowest crystalline size sensor offers highest surface to volume ratio so PZ1 sensor gives highest H_2 sensitivity 78% with respect to other sensors PZ2 and PZ3.

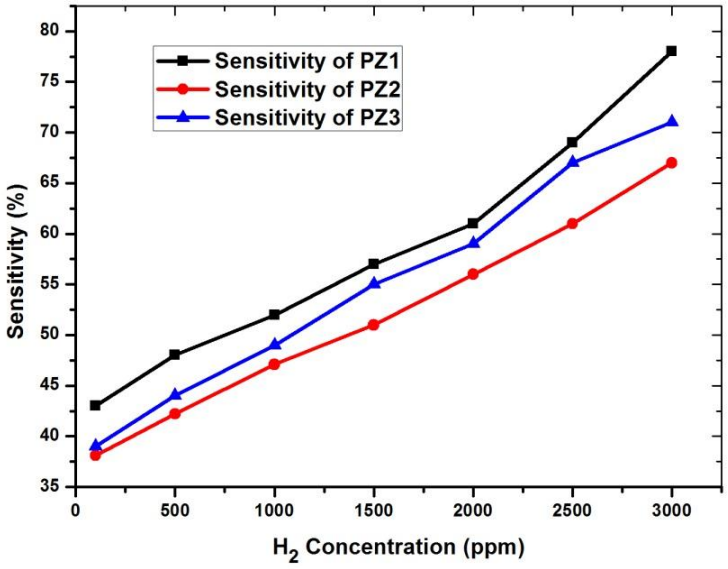

Figure 4.10 Sensitivity vs. H_2 concentration

Next the effect of heterostructure device of sensor is studied for measuring different parameters of sensors. The operating temperature is measured in terms of the sensor resistance change with varying the temperature at presence of target gas. With increasing temperature the resistance of the sensor decreases then increases. Temperature has direct effect on charge concentration, carrier thermal velocity, debye length and work function of the sensor material. The charge carrier's thermal velocity achieves an optimum value with proper debye length at operating temperature that enhances the sensitivity. Further the adsorption, desorption processes are also temperature activated process which are key factors of sensing mechanism. But very high temperature causes more charge carrier excitation that finally leads to e decrease in debye length and increase in overall resistance of the sensor beyond operating temperature point. Figure 4.11 shows this effect in terms of sensor response magnitude (sensitivity) vs. temperature.

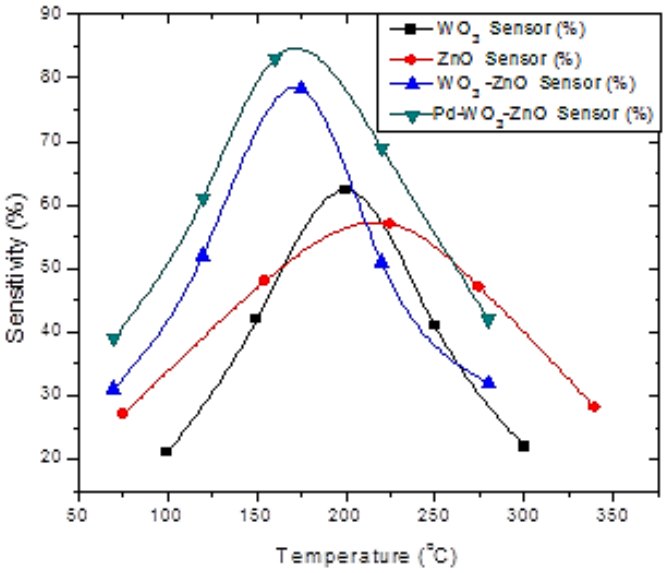

Figure 4.11 Sensitivity vs. temperature graph for different sensors

The Pd modified composite sensor provides the lowest operating temperature 160˚C where the operating temperature of ZnO based sensor is 230˚C. This result shows that the heterostructure sensors are more prominent in sensing application with respect to bare sensors as they offer more interaction space with target gas molecules. The variation of gas concentration with sensitivity of sensors is shown in fig.4.12. Further enhancement of sensitivity comes from Pd modification due to its catalytic effect.

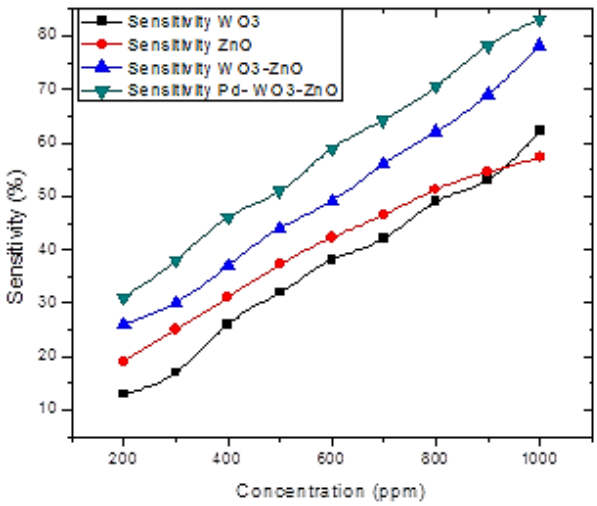

Figure 4.12 Sensor's sensitivity vs. H_2 gas concentration graph

The fast response and recovery time is always preferable for any sensor. In present work better timing results are found for modified heterostructure sensor with compare to other sensor as shown in fig.4.13-4.14.

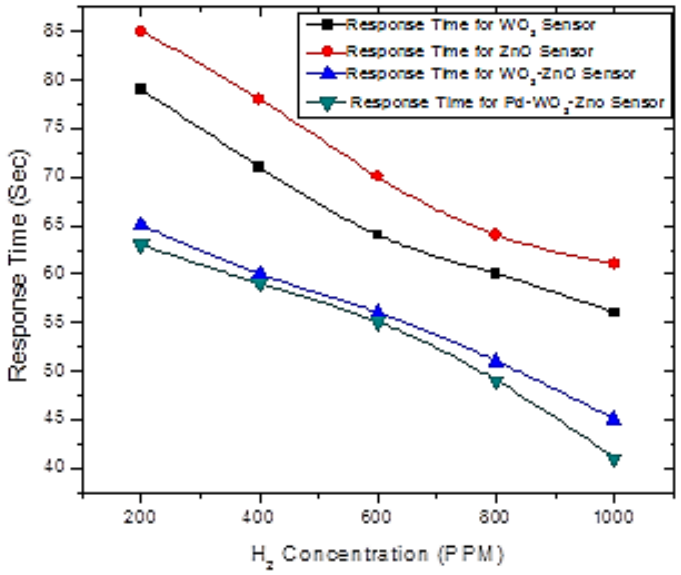

Figure 4.13 Response Time vs. H_2 concentration graph

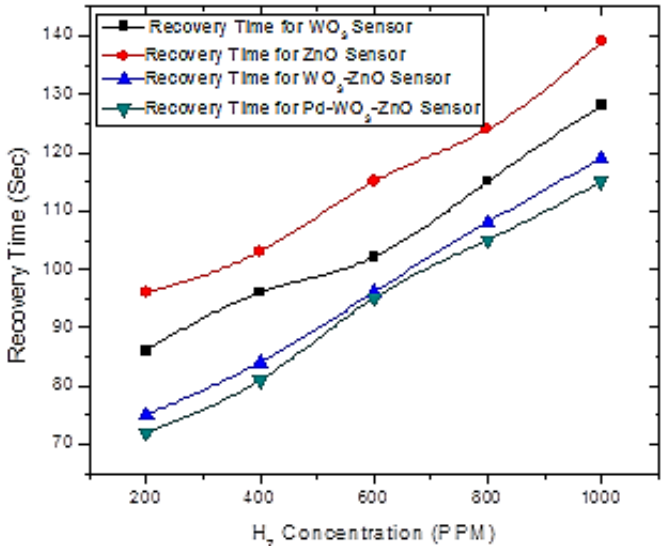

Figure 4.14 Recovery Time vs. H_2 concentration graph

The response time of Pd modified WO_3-ZnO sensor is 38sec whereas for ZnO based sensor is 64 sec. This clearly shows improvement in heterostructure devices as compared to other sensor devices. The cross selectivity of the sensors is measured with respect to other potentially hazardous gas like methane, methanol and ethanol as shown in fig. 4.15. Further the Pd modified composite sensor exhibits high

response towards H_2 with low response to other interfering gases. A comparison of the present work with previously reported H_2 sensor is summarized in table 4.3.

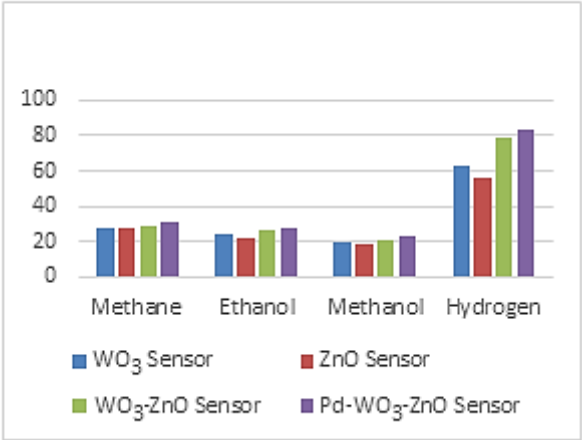

Figure 4.15 Selectivity of different fabricated sensors in presence of different toxic gases

Table 4.3 Comparison of present work with the earlier reported H_2 sensors

Structure	Fabrication Process	Operating Temperature (˚C)	Response Magnitude (%)	Detection Range (ppm)	Ref.
Pd modified WO_3	Solgel dip coating	200	71.85 @10,000ppm	1000-10,000	[18]
SnO_2-ZnO	PECVD	350	18.4 @ 100ppm	NA	[19]
TiO_2-NiO	DC Sputtering	200	70 @10,000ppm	500-10,000	[20]
ZnO (Mg doped)	PLD	150-300	50@5000ppm	5000	[21]
Pd-WO_3-ZnO	Solgel spin coating	160	83.1@1000ppm	200-1000	present work

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Chapter 5

Experimental studies with voltage to time conversion circuit in gas sensing circuit

5.1 Introduction

The applications of Micro Electro Mechanical System (MEMS) based smart sensor [5.1-5.3] devices are increasingly finding scope in a number of fields like robotics, automobile, civil, military aviation, biomedical, manufacturing control [5.4-5.6]. Other important uses of these sensors are in variation monitoring of rotating machinery like microscopic pressure sensors embedded in automobile tires have led to huge saving in oil, piezoelectric acoustic sensors for both audible and high frequency sensing, low cost highly reliable tiny blood pressure sensors for medical applications. Now the researchers increasingly showing interest to integrate MEMS based nanostructured sensor device with signal conditioning circuit for ease of data handling like data storing-calibrating-transmission-reception. The available sensors normally show different electrical properties like resistive, capacitive or inductive as widely studied in [5.7-5.15]. Normally in real time applications transmitting sensing data to a distant location is the main aim. In this aspect, the analog form of sensing data without proper signal conditioning may give severe degraded result in quality and quantity. Thus on board smart sensors with interfacing circuit will be the next useful solutions in near future.

The two important gases that widely used in industries and in domestic appliances are Hydrogen and Methane [5.16-5.21]. These gases are colorless, odorless and tasteless. Thus can't be detected easily. Besides these gases are easily flammable and explosive because of low ignition energy (0.017mJ for H_2) and wide flammable range (4-75% for H_2) and therefore accurate and rapid detection is the solution for proper monitoring these gases. The semiconductor metal oxide (SMO) gas sensor plays very important role in detection many of such gases like ZnO and WO_3 based sensors promising material for sensing hydrogen and methane gas at very low concentration [5.22-5.26]. The wide band gap energy of these materials i.e. 3.37eV for ZnO and ~2.6 – 3.6 eV for WO_3 at room temperature respectively make them very

sensitive metal oxide for gas sensing application. These are n type compound having electron its majority.

Thus in this chapter fabrication of the MEMS based gas sensor on p-Si wafer and an efficient interfacing timing circuit have been studied for detection of hydrogen and methane gas. The circuit comprises of a bridge network with sensing element as one of its arm, amplifier, and time conversion circuit. Bridge circuit produces incremental change in resistance because of variation of the gas percentage which in turn creates incremental voltage. This incremental voltage is amplified to a desired level so that adequate voltage can be provided to a timing circuit. Finally timing circuit generates variable time signals which are almost linearly related to the gas percentage variation.

5.2 Recent Work

According to Moore's Law, in semiconductor industries, the device size is reducing day by day. The reducing in device size has been shown by many researchers [5.27-5.35]. The sensor devices follow the same rule. As a hydrogen detecting device, the hydrogen sensor is essentially a transducer that transforms the variation of physical or chemical properties into an electrical signal for practical applications. According to the variation of electrical and optical properties of SMOs under a hydrogen-containing atmosphere, the SMO hydrogen sensors can be divided into four types: resistance based, work function based, optical and acoustic sensors.

In 1950, Wagner *et al*. reported the variation of electrical properties when ZnO is exposed to reducing gases [5.36]. Work function based hydrogen sensors are operated based on the variation of work function induced by hydrogen. These sensors generally formed by the metal/oxide/semiconductor (MOS) layers. According to the difference in structure, the work function based hydrogen sensors can be divided into three major types: the Schottky diode type, MOS capacitor type and the MOS field effect transistor (MOSFET) type. In Schottky diode type sensor, the top electrode is the gas sensitive metal layer, which forms a Schottky contact at

the interface between the metal and semiconductor (or a thin oxide layer deposited on the semiconductor), while the bottom electrode is a metal layer that form Ohmic contact with the semiconductor film, or sometimes a gas sensitive metal layer as well to form the back-to-back Schottky junction structure (mostly used for semiconductor thin film or NW based hydrogen sensors). Hydrogen molecules can get adsorbed and dissociated into hydrogen atoms in the gas sensitive metal layer (generally Pd, Pt, Au, Ag and Cu, *etc*.). The diffusion of hydrogen atoms may lead to the formation of dipole layer at the interface between metal and oxide, which changes the work function of the metal and results in the variation of Schottky barrier height at the interface. Consequently, the measured voltage in *I-V* curve will be shifted corresponding to the adsorbed hydrogen atoms, which can be used for detecting concentrations. Several SMOs were employed to form the Schottky diode sensors, including SnO_2, TiO_2, ZnO and Nb_2O_5, *etc*. [5.37-5.41]. The MOS capacitor hydrogen sensors are similar in structure to Schottky diode type sensors. However, a thick insulator layer is deposited between the catalytic sensitive metal layer and the semiconductor layer to prevent the current conduction and build up a charge-accumulation layer on both sides. When the sensor is exposed to a hydrogen-containing atmosphere, the dissociated hydrogen atoms can diffuse into the metal/insulator interface and lead to a lateral shift in the *C-V* plots corresponding to the hydrogen concentration [5.42]. MOSFET or metal-insulator-semiconductor field effect transistor (MISFET) hydrogen sensor also based on the variation of work function of the catalytic hydrogen sensitive metal (gate electrode) under exposure to hydrogen gas. Typically, the MOSFET device consists of a metal-SiO_2-Si structure, in which two Si regions were ion-implanted to form the source and drain. Moreover, the Schottky barrier between metal and semiconductor can also be used for building the source and drain junction. After the source is grounded, the conductivity between source and drain can be modified by adjusting the gate voltage (V_{GS}). When this sensor is exposed to a hydrogen-containing atmosphere, the hydrogen atoms diffused to the interface between metal and insulator can form a dipole layer and

thus change the gate voltage, which finally results in the variation of measured voltage signal corresponding to the hydrogen concentration.

After that, a series of research works about the sensing behavior of SMO to reducing gases were reported by Seiyama, et al. since the 1960s [5.40]. Up to present, many kinds of SMO were investigated as hydrogen sensing materials, including SnO_2, ZnO, TiO_2, Nb_2O_5, In_2O_3, FeO, Fe_2O_3, NiO, Ga_2O_3, Sb_2O_5, MoO_3, V_2O_5 and WO_3, [5.30-5.42] which exhibit large variations in resistance after exposure to hydrogen gas. Among them, SnO_2 and ZnO are the mostly used SMOs in the resistance type hydrogen sensors. The resistance-based sensing mechanism of SMO is complicated, and has been investigated by many researchers. The commonly accepted mechanism is based on the variation of the surface electron depletion region due to the reaction between hydrogen and the chemisorbed oxygen on the surface. The typical structure of a resistance based SMO hydrogen sensor consists of a SMO layer on an insulating substrate and two electrodes, as well as a heater under the sensitive layer. During operation the sensitive layer will be heated to a certain temperature for enhancement of the sensing performance. This temperature, which depends on the sensitive oxide materials used, is typically several hundred degrees Celsius. The resistance (R) of the sensitive layer will change due to the exposure to hydrogen gas. The variation depends on the hydrogen concentration and exhibits an approximately linear relationship with the hydrogen concentration within a certain range. Besides at present, some other types of the commercially available hydrogen sensors include electrochemical, thermoelectric, metallic, optical and acoustic ones, *etc*. This type of hydrogen sensors still suffers however from high operation temperatures, which results in high power consumption and potential safety hazards. Moreover, the cross selectivity to other combustible or reducing gases is another critical issue, which should be restricted to enhance the sensing accuracy.

From the view of current research trend a proper WO_3 and ZnO MOS based gas sensor with interfacing circuit is proposed for detection of hydrogen and methane gases. The solgel based techniques is used for fabrication purpose. A timing circuit is

proposed which converts the signal output to proper timing form so that it can be sent to desired location without degradation in quality and quantity.

5.3 Theory and Fabrication

The thin films of WO_3 and ZnO have been studied by sol-gel method using Tungsten hexa-choloride in [5.39], and Zinc acetate dihydrates in [5.40] as a precursor. The phase transformation, defects and morphological study has been carried out in [5.41-5.42]. The sol–gel method has emerged as one of the most promising processing route being particularly efficient in producing thin, transparent, homogeneous, multi component oxide films of many compositions on various substrates at low cost. In addition, it also allows the tuning of the thickness of the film by varying synthesis parameters [5.41]. The p-Si wafer is taken as substrate and the lithography method being used for the backside etching of silicon wafer. A layer of SiO_2 has been deposited on Si wafer to use as a dielectric membrane. By using E-beam evaporation technique DilverP1 heater plate is also deposited on thermally grown SiO_2 layer. Then a layer of SiO_2 is deposited on heater plate which acts as an isolation layer between sensing and heating layer. The active layers of ZnO and WO_3 are placed on SiO2 layer using spin coating method for ZnO and WO_3 based sensors as shown in figure 1. To produce ZnO sol a starting material zinc acetate dehydrate ($Zn(CH_3COO)_2.2H_2O$) is dissolved in a mixture of ethanol and mono-ethanolamine (M.E.A.) solution with a concentration of 0.75 mol L-1. MEA acts at the same time as a base and a complexing agent and the M.E.A. to zinc acetate molar ratio is fixed at 2. Using heat treatment on the dried films at 500°C for 2 hours, the crystalline films are obtained. Care has been taken to select proper annealing temperature to get proper crystalline structure for active layers (ZnO and WO_3). The precursor solution is deposited on Si substrates by spin-coating (3000 rpm, 30 sec) method.

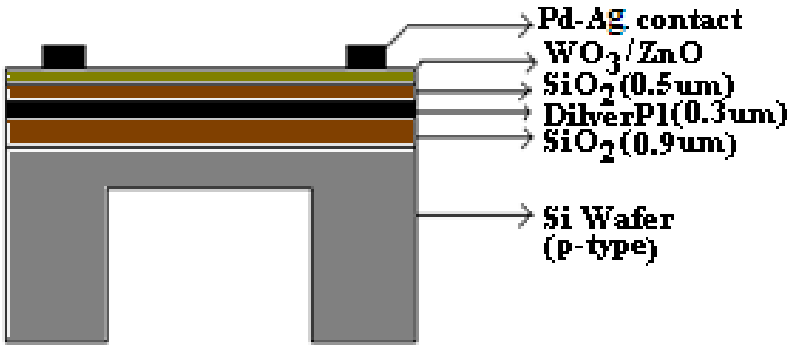

Fig. 5.1 Layer Structure of the proposed Sensor

Similarly, a starting material WCl_6 is used as a precursor to prepare WO_3 sol. WCl_6 is dissolved in isopropanol at a ratio of 10g/150ml and stayed in dry air for 3 days. Then the sol is deposited by spin coating method (3000rpm, 30sec) and the substrate is dried in air at 150°C for 30 minutes. Post deposition heat treatment (annealing) at 600°C for 2 hours is carried out to improve microstructure and crystalline properties of the deposited thin film. Then Palladium Silver (Pd-Ag) (70%-30%) is deposited for metallic contact formation. Four samples have been fabricated i.e., two WO_3 based sensor samples and two ZnO based sensor samples each for H_2 and CH_4.

Table 5.1: Description of the fabricated samples.

Sample Number	Description		
	Substrate	Sensing Layer	Top Contact and Bottom Contact
S1	p-Si <100>	WO_3	Pd-Ag (70%)
S2	p-Si <100>	ZnO	Pd-Ag (70%)

The Scanning Electron Microscopy (SEM) method is used to analyze the surface of WO_3 and ZnO films as shown in the figure 5.2(a-b). Then the surface morphology and the grain size are studied from the fig. 5.2.

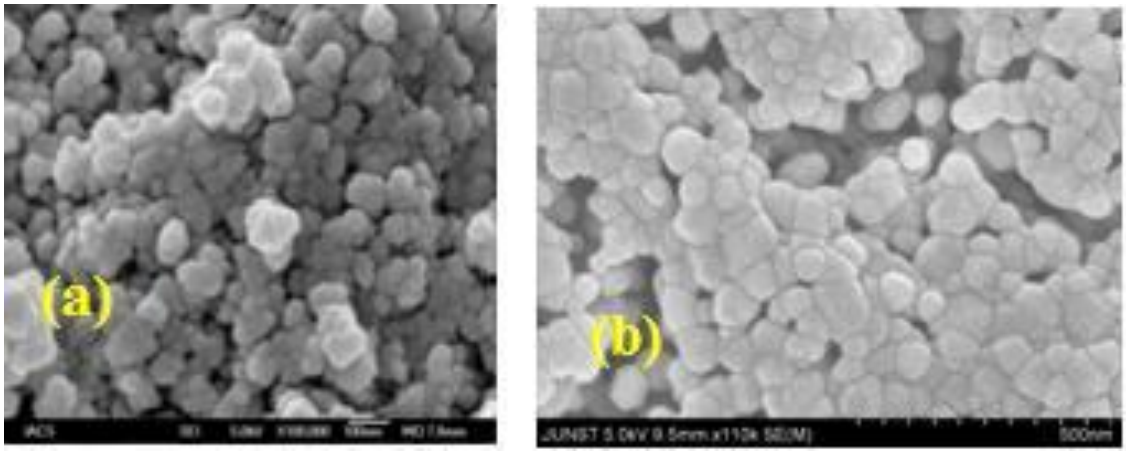

Figure 5.2 (a-b) SEM image of WO_3 and ZnO sensor

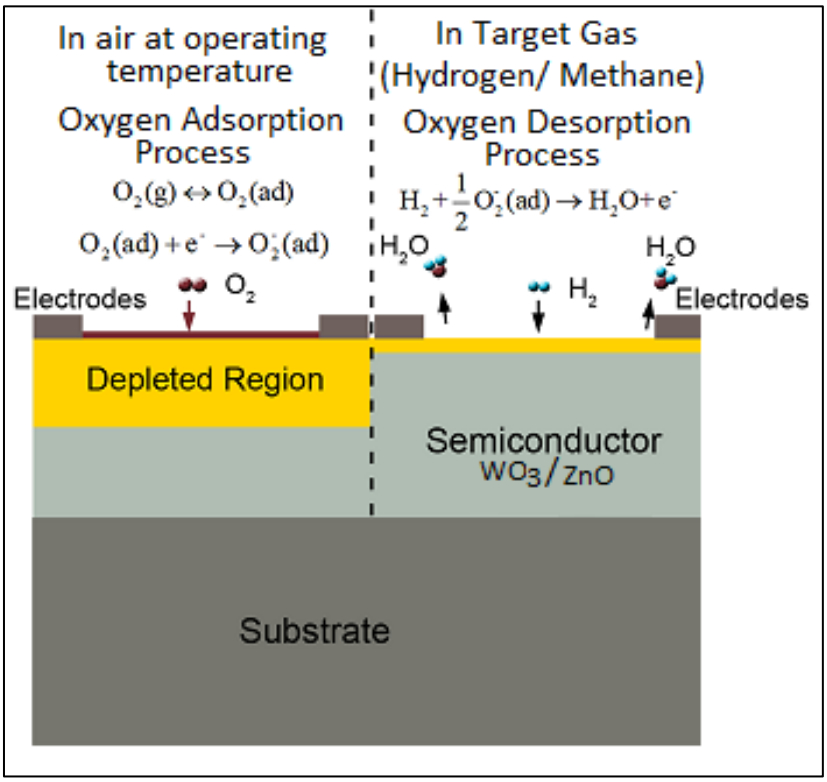

Figure 5.3 Sensing mechanism of the gas sensors

Figure 5.3 shows basic sensing mechanism of the sensor. At operating temperature the air oxygen molecules are chemically adsorbed at the surface of sensing layer producing depletion region (lack of charge carrier). Hence the resistance of the sensor increases. During presence of target gas (H_2/ CH_4) oxygen desorption process starts where hydrogen molecules directly react with adsorbed oxygen molecules. As a result free charge carriers are created and resistance decreases

A setup consisting of a cylindrical testing chamber made of corning glass tube (10 cm × 4 cm) for the purpose of testing the response of the sensor is used as shown in figure 5.4. Using a copper constantan thermocouple, the temperature of testing chamber is maintained within ±1°C. The sensor samples are connected with fine copper wires and inserted in the setup. For ultra-high purity hydrogen gas, IOLAR grade N_2 is used as the carrier gas. Hydrogen gas is mixed in proportionate ratio in a mixing chamber followed by a mixing coil. The gas flow is controlled by mass flow controller (MFC) (Alicat scientific, M-50SCCM-D) for hydrogen gas and mass flow meter (MFM) (Alicat scientific, M-1000SCCM-D) for N_2 gas. At the time of testing the gas pressure on the sensor has been kept at 1 atm. The electrodes are connected to an Agilent U1252A Multimeter with Agilent GUI Data logging software (ver. 2.0) for sensor resistance measurement.

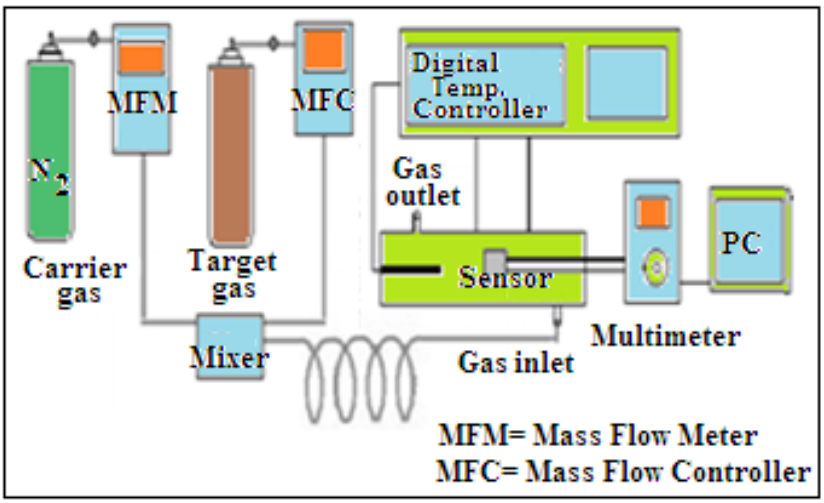

Figure 5.4 The gas sensor testing setup

The sensitivity of the sensors is being studied for Hydrogen (H_2) and Methane (CH_4) gases for ZnO and WO_3 based sensors. The concentration of the gases varies from 0.1% to 1%. The response magnitude (sensitivity, S) of the sensor is defined as:

$$S\% = \frac{R_A - R_G}{R_A} * 100$$

where R_A is the sample resistance in N_2 (i.e. at 0% hydrogen/methane concentration) and R_G is the sample resistance at a given concentration of the target gas (H_2/CH_4).

The sensitivity is measured in presence of H_2 and CH_4 gas at different concentrations (from 0.1% to 1%). The operating temperature, response-recovery times and the sensitivity are the most important parameters of any gas sensor. The operating temperature of sensor samples is experimentally determined by keeping the respective gas concentrations at 0.5% and varying the temperature from 100°C to 350°C and calculating the sensitivity. The fig.5 shows the variation of sensitivity of the sensors with respect to temperature. The operating temperature of WO_3 and ZnO based sensors for CH_4 and H_2 are 220˚C, 200˚C (for WO_3) and 255˚C, 230˚C (for ZnO) respectively.

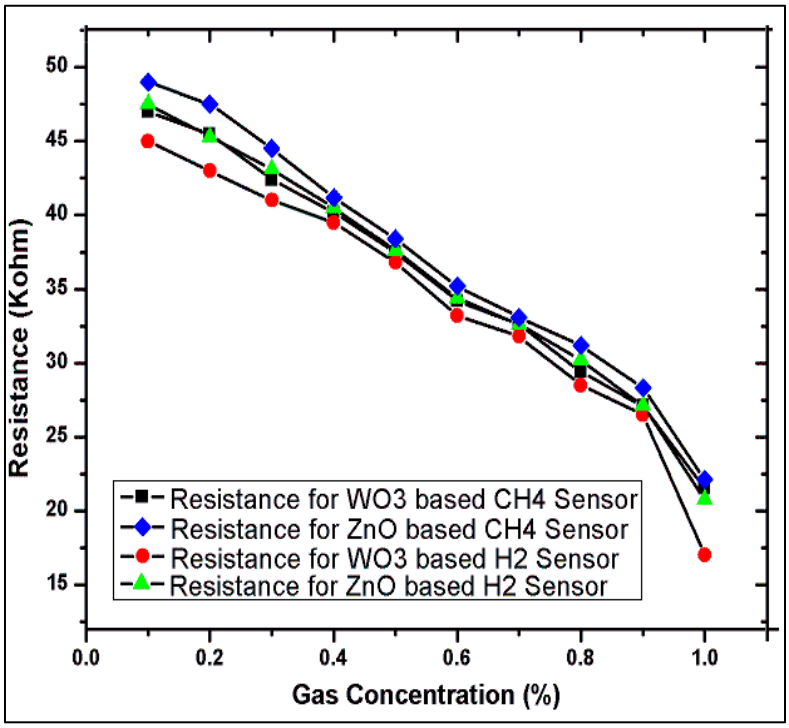

Fig. 5.5 Resistance vs. gas concentration for WO_3 and ZnO sensors

Figure 5.5 shows the change in sensor resistance with hydrogen & methane gas concentration. A linear relationship exists between the gas concentration and the sensor resistance as depicted in figure 5.5. All the samples behave as 'n' type Metal Oxide Semiconductor (MOS) sensors that are the conductivity of the sensors increases in presence of target reducing gases. The sensitivity of the gas sensors is plotted in figure 5.6 where the gas sensor sensitivity increases with the increase of hydrogen/methane concentration as a linear function. The maximum sensitivity of

the sensors are 62.31% for WO3 based H2 sensor, 56.21% for ZnO based H2 senor, 54.25% for WO3 based CH4 sensor and 54.89% for ZnO based CH4 senor with 1% of hydrogen and methane gas respectively

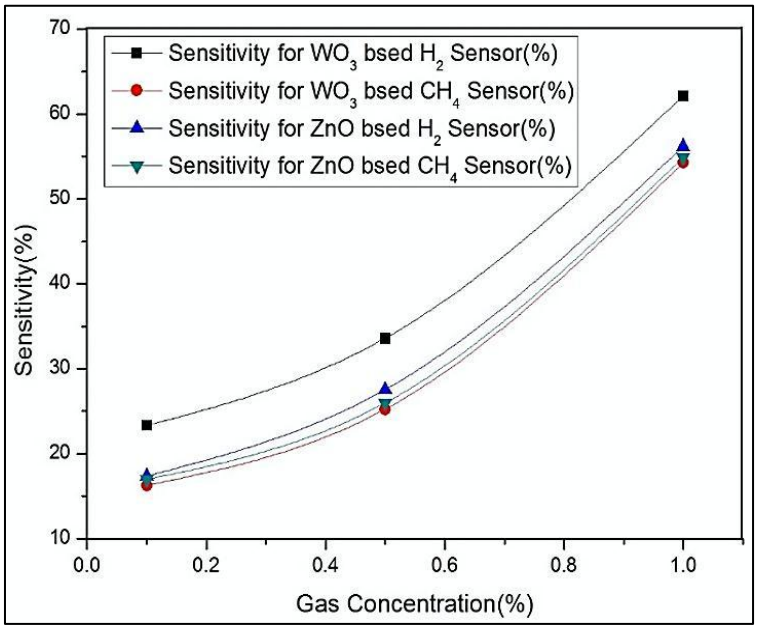

Fig. 5.6 Sensitivity vs. gas concentration for WO_3 and ZnO samples

5.4 V-T conversion circuit

The block diagram of voltage to time (V-T) conversion system for the proposed gas sensor and the complete circuit diagram of the proposed system are shown in figure 5.7 and figure 5.8 respectively. Basic elements of transmission system are bridge circuit (for accurate detection of very small change in resistance), instrumentation amplifier (for amplifying the small voltage), and a timer circuit (for converting voltage change to equivalent time change). The following sections discuss the design and implementation of different components of the proposed system.

The schematic diagram of the circuit is shown in figure 5.8. Section A of the figure enclosed by dotted block is the bridge circuit used in this work which is a simple Wheatstone bridge circuit. Here $R_3$is the sensor resistor. With a small change of $R_3$the output voltage V_{AB} will change. The voltage difference between node A and B is applied to section B (Instrumentation Amplifier).

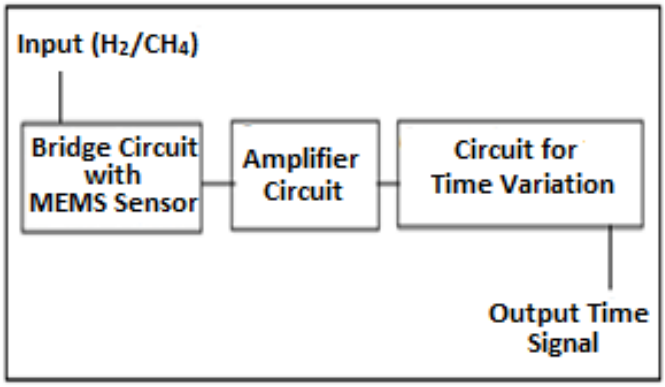

Figure 5.7 Block diagram of the proposed signal conditioning circuit.

At the balance condition of active bridge

$$\frac{R_3}{R_4} = \frac{R_1}{R_2}$$

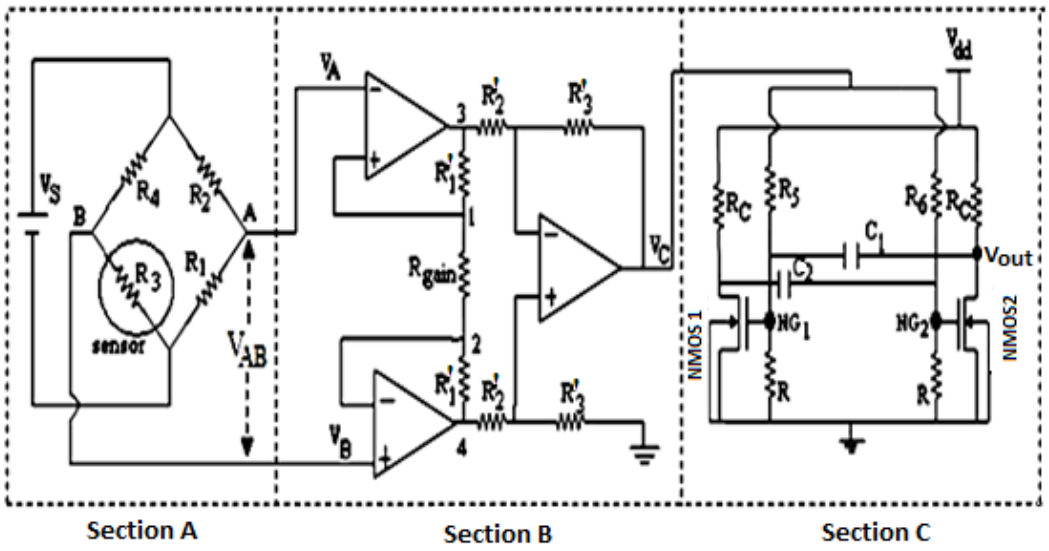

Figure 5.8 Complete circuit diagram of proposed signal conditioning circuit

With small change in R_3 the bridge circuit will become unbalanced.

Now the voltage $V_{AB}=(\frac{R_3}{R_4+R_3}-\frac{R_1}{R_2+R_1})V_s$ (1)

where V_s is the supply voltage.

Let the small change in R_3 be ΔR_3 , due to change in H_2/CH_4 concentration. Now

the modified equation is $V'_{AB}=(\frac{R_3+\Delta R_3}{R_4+R_3+\Delta R_3}-\frac{R_1}{R_2+R_1})V_s$ (2)

Change in voltage,

$$\Delta V_{AB}=V'_{AB}\sim V_{AB}=\frac{R_4\Delta R_3}{(R_4+R_3+\Delta R_3)(R_4+R_3)}V_s \quad (3)$$

HereΔR_3 is very small so $(R_4+R_3)\gg\Delta R_3$

$$\therefore \Delta V_{AB}=\frac{R_4\Delta R_3}{(R_4+R_3)^2}V_s$$

This show $\Delta V_{AB}\propto \Delta R_3$(where other terms are constant, K=$\frac{R_4}{(R_4+R_3)^2}V_s$), the small change in resistance will change the output voltage. The variation of output voltage (V_{AB}) with change in sensor resistance is plotted in figure 5.9.

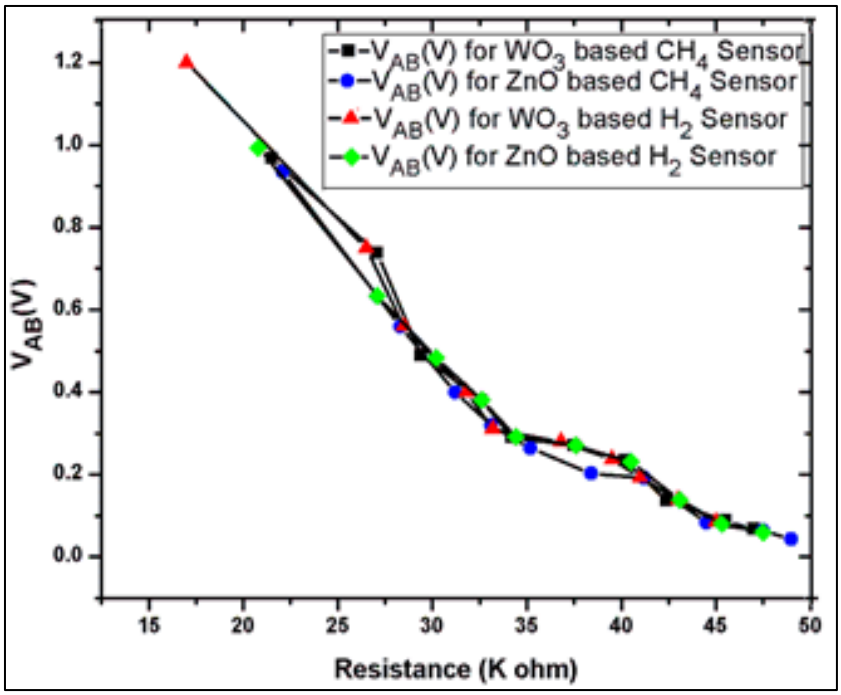

Figure 5.9 Output of the Bridge Circuit (V_{AB}) vs Sensor Resistance

In section B, the instrumentation amplifier circuit is constructed from a buffer differential amplifier stage. The upper left op-amp is used as a negative feedback amplifier. The voltage at node 1 is $V_A$and similarly the voltage at node 2 is V_B. Now the voltage across the resistor R_{gain} is the difference between the voltage $V_A$and V_B. This voltage drops across R_{gain}causes a currentflow through it.

$$I=\frac{V_A-V_B}{Rgain} \quad (4)$$

This current will flow through $R'_1$and can be written as

$$I=\frac{V_3-V_4}{2R'_1+R_{gain}} \quad (5)$$

As a result voltage drop between node 3 and 4 is equal to

$V_{34} = V_{AB}\left(1+\frac{2R'_1}{R_{gain}}\right)$ using (1), V_{34} can be rewritten as

$$V_{34} = \left(\frac{R_3}{R_4+R_3}-\frac{R_1}{R_2+R_1}\right)\left(1+\frac{2R'_1}{R_{gain}}\right)V_s \quad (6)$$

The right most amplifier is a standard differential amplifier with gain=$\frac{R'_3}{R'_2}$. The buffer gain is increased by putting R_{gain} between the two inverting inputs.

Now the gain of the differential amplifier is

$$\text{Gain}=\frac{V_c}{V_{AB}} = \left(1+\frac{2R'_1}{R_{gain}}\right)\frac{R'_3}{R'_2} \quad (7)$$

Now V_c can be written as using (1)

$$V_c = \left(\frac{R_3}{R_4+R_3}-\frac{R_1}{R_2+R_1}\right)\left(1+\frac{2R'_1}{R_{gain}}\right)\frac{R'_3}{R'_2}V_s \quad (8)$$

With change in sensor resistance the voltage at node 'c' will change as follows:

$$V'_c = \left(\frac{R_3+\Delta R_3}{R_4+R_3+\Delta R_3}-\frac{R_1}{R_2+R_1}\right)\left(1+\frac{2R'_1}{R_{gain}}\right)\frac{R'_3}{R'_2}V_s$$

The difference in voltage is

$$\Delta V_c = V'_c \sim V_c = \left(1+\frac{2R'_1}{R_{gain}}\right)\frac{R'_3}{R'_2}\frac{R_4\Delta R_3}{(R_4+R_3)^2}V_s \quad (9)$$

Now the change in voltage $\Delta V_C \propto \Delta R_3$ (keeping all other parameters constant).The variation of output voltage of instrumentation amplifier with change in input voltage from bridge circuit is plotted in figure 5.10.

Section C, the last part of the proposed sensing system is a MOSFET based timing circuit. The output of the instrumentation amplifier (section B) is applied to the input of section C. The change in node voltage (V_C) is directly fed to resistance R_5 and R_6. Consider no current flow through the gate pin of a MOSFET. There will be no

discharge of capacitor through the gate of the n-channel MOSFETs. The circuit shown here can operate even with high or low resistors R_5 and R_6, hence small capacitors can be used to get low or high time signal. Thus the variation of voltage V_C can control the time change over a wide range with the change of H_2 or CH_4 concentration.

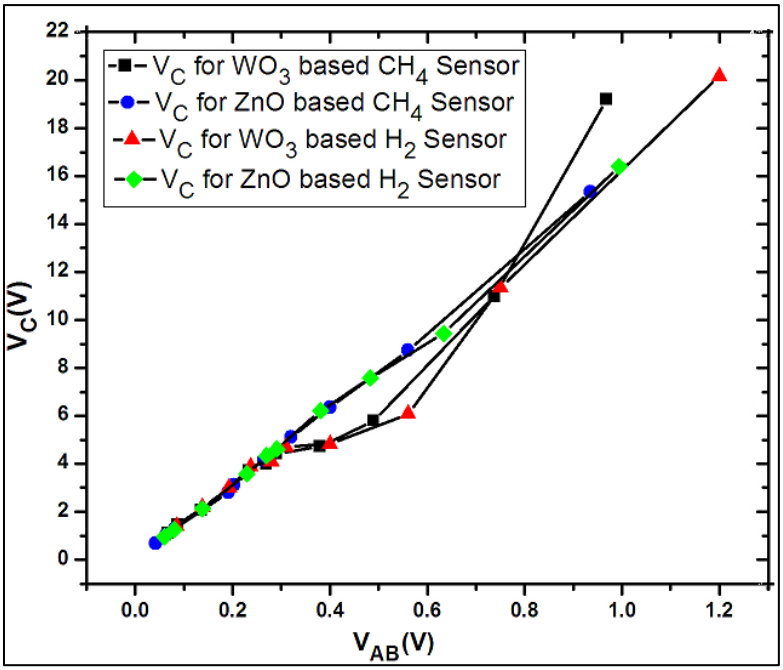

Figure 5.10 Input voltage (V_{AB}) from bridge circuit vs output (V_c) voltage of instrumentation amplifier

The timing circuit output may be varied by adjusting R_5, R_6, C_1, and C_2. The time period is varied by connecting R_5 and R_6 to an auxiliary voltageV_C which is directly related with

$$V_{NG1} = (V_{ON} - V_{dd}) + (V_{dd} + V_C - V_{ON})(1 - e^{-t/R_5C_1}) \qquad (10)$$

where V_{NG1}, V_{ON} are the gate voltage and On voltage of MOSFET 1 respectively. This finally gives

$$V_{NG1} = V_C - (V_{dd} + V_C)e^{-t/R_5C_1} \qquad (11)$$

(V_{ON} ignored as V_{ON}<<V_{dd})

Now at the time t=T/2 the gate voltage (V_{NG1}) will be equal to V_{ON} that finally leads to $V_{ON} = V_C - (V_{dd} + V_C)e^{-(T/2)/R_5C_1}$

By ignoring the voltage V_{ON} and putting the value of V_C, Time period (T) can be written as

$$T = 2R_5C_1(\ln(1 + \frac{V_{dd}}{(\frac{R_3}{R4+R3} - \frac{R_1}{R2+R1})(1+\frac{2R'_1}{Rgain})\frac{R'_3}{R'_2}\text{Vs}})) \quad (12)$$

Now with change of V_C due to change of H_2 /CH_4 concentration, the time period of the output signal changes to:

$$T' = 2R_5C_1(\ln(1 + \frac{V_{dd}}{(\frac{R_3+\Delta R_3}{R_4+R_3+\Delta R_3} - \frac{R_1}{R2+R1})(1+\frac{2R'_1}{Rgain})\frac{R'_3}{R'_2}\text{Vs}})) \quad (13)$$

Thus change in time period from T to T′

$$\Delta T = 2R_5C_1(\ln(1 + \frac{V_{dd}}{(1+\frac{2R'_1}{Rgain})\frac{R'_3}{R'_2}\frac{R_4\Delta R_3}{(R_4+R_3)^2}\text{Vs}})) \quad (14)$$

Equation (14) shows the change of output signal time period is proportionally related to change in resistance across the sensor (R_3). The figures 12(i-ii) show the calibration graph of the proposed signal conditioning system at different concentration of H_2 and CH_4.The time period of the output signal as shown fig. 5.11 reduces with increasing gas concentration. The resistance of the sensor samples reduces with increasing gas concentration with increase of free charge carrier (conductivity). That directly reflects to the output time signal. Figure 5.12 also shows the calibrated graph for sensor resistance with output time signal. The increase in resistance with decrease in gas concentration directly reflects to the output time signal.

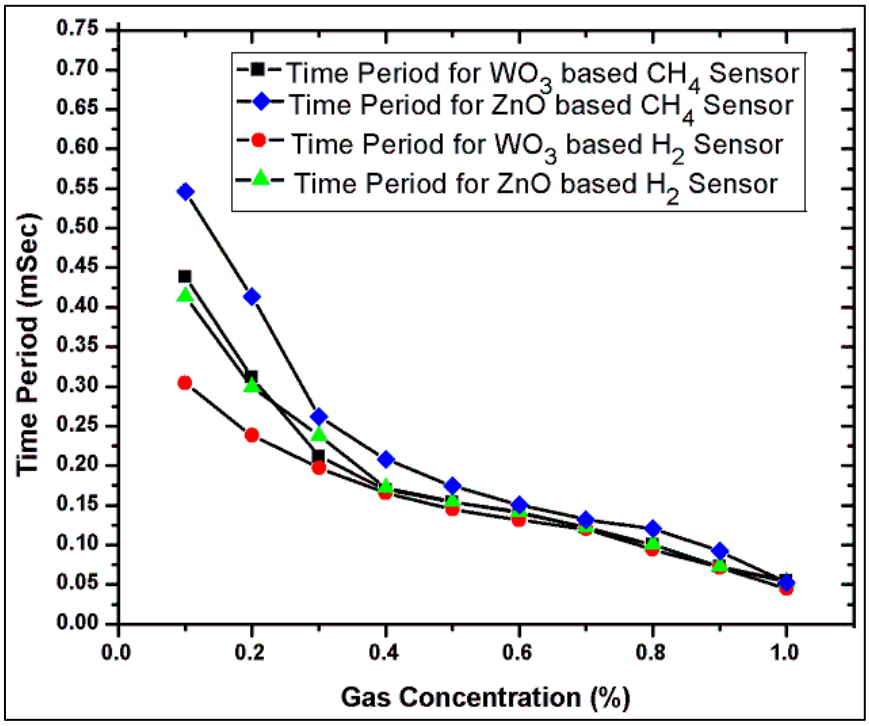

Figure 5.11 Calibration graph of the proposed system with respect to gas concentration.

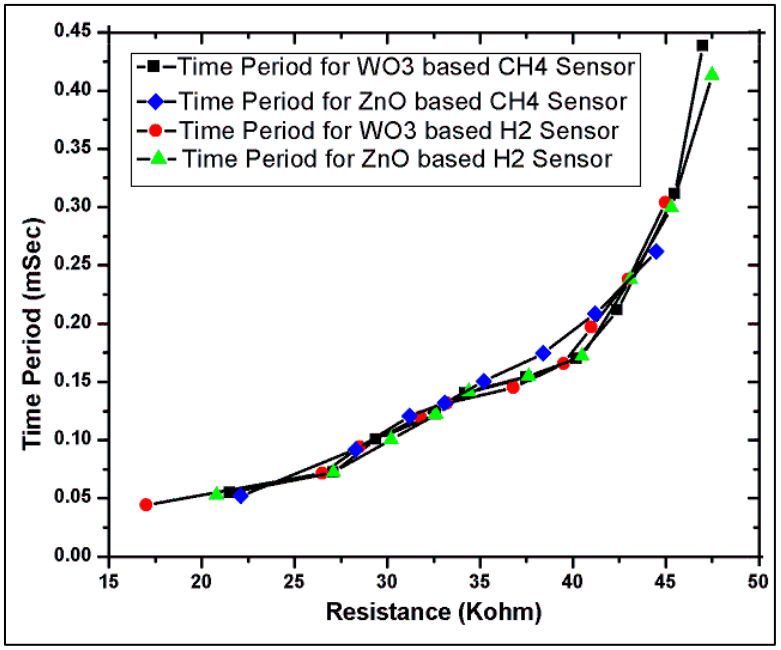

Figure 5.12 Calibration graph of the proposed system with respect to sensor resistance.

5.5 Results Analysis

The complete circuit is implemented on bread board using op-amp and discrete values of resistances and capacitances. Care has been taken to minimize the time errors and response delay of op-amps. Figure 5.8 has been implemented using highly precise Op-Amp with high input impedance (1012Ω) and slew rate of 13 V/μs like LF-353. The effectiveness is tested of the circuit by taking discrete precision variable resistance for R3, then taking the resistive sensor. The variation of experimental result with respect to calibrated result is shown in fig. 5.13 (i-iv). The time period change with hydrogen and methane concentration is very much significant with little nonlinearity with respect to calibrated graphs as show in fig. 5.12 Polycrystalline semiconductors have large number of grains and grain boundaries to interact with gaseous molecule in its vicinity. The local potential barrier rise in polycrystalline semiconductor like ZnO or WO_3 materials plays significant role in sensing H_2 and CH_4 gases. The electrical properties of the surface of the thin film sensor and surface boundaries between the grains are affected by adsorption and desorption process of the gaseous molecule. Thus the resistance is measured from the two contacts taken from the top of the sensing film and it shows 'n' type conductivity for both the Nanomaterial thin film sensor. The increase in conductivity at the elevated temperature in presence of reducing gas (H_2 or CH_4) is directly mapped to our proposed electronic signal processing circuit. With increase of gas concentration the output signal's time period is reduced. The change of H_2 concentration from 0.1% to 1% results change of time signal from 0.05msec to 0.45msec for both the sensors. Similar result is also observed for CH_4 sensor. This form of timing signals can be directly used for further decision making system located at a long distance.

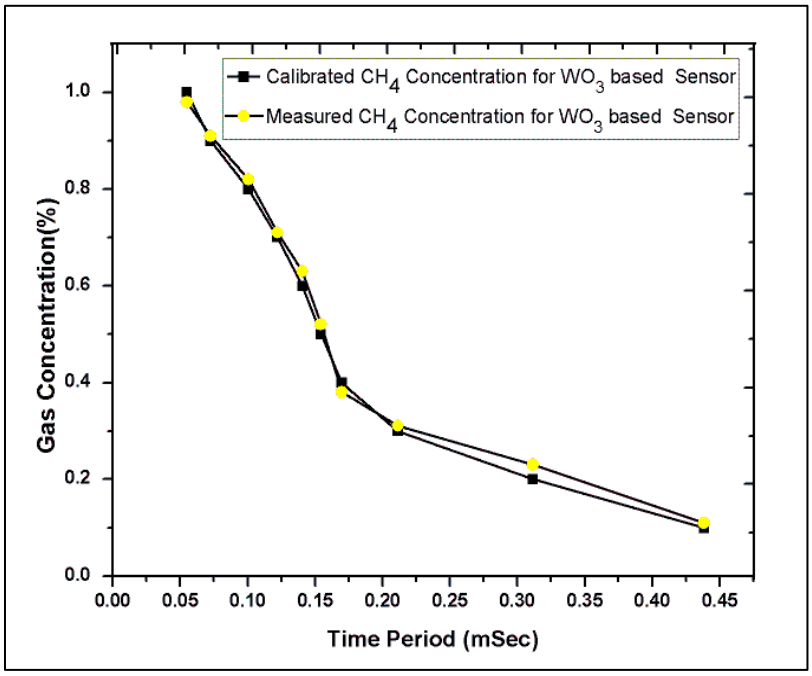

Figure 5.13(i) Response curve of the WO_3 Methane Sensor

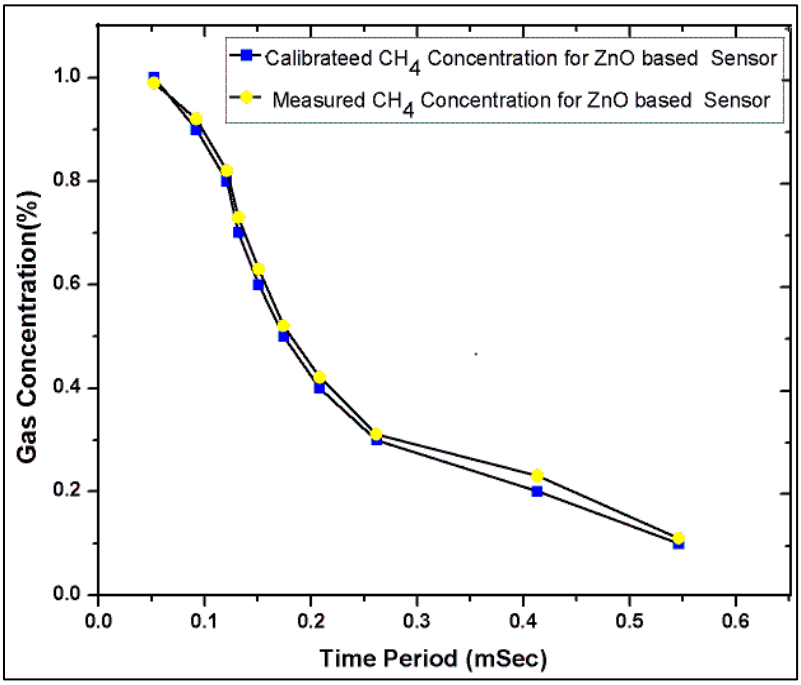

Figure 5.13 (ii) Response curve of the ZnO Methane Sensor

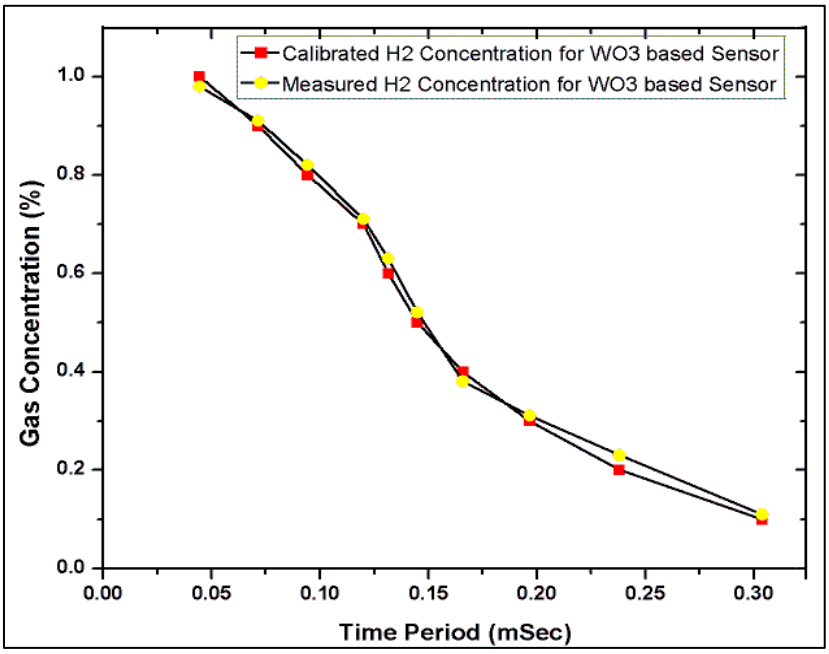

Figure 5.13 (iii) Response curve of the WO_3 Hydrogen Sensor

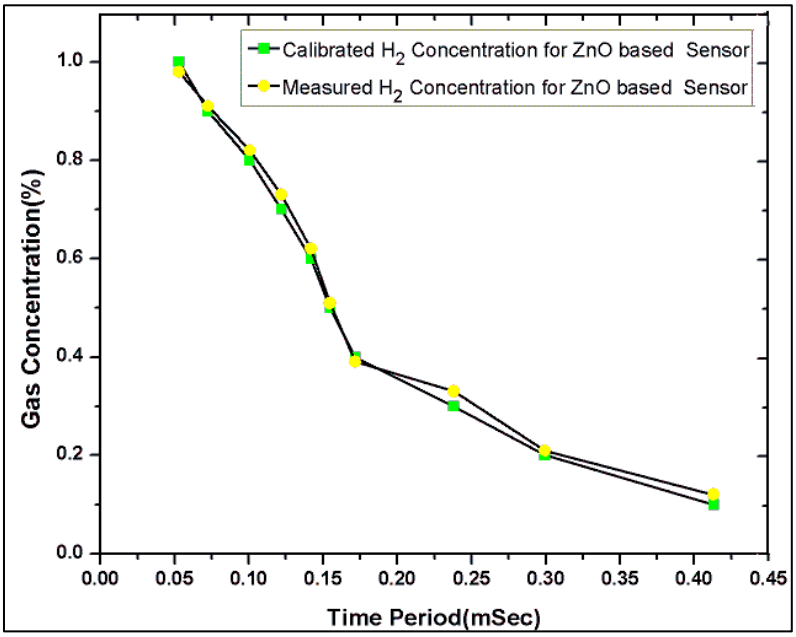

Figure 5.13 (iv) Response curve of the ZnO Hydrogen Sensor

The table1 shows the result of our proposed system. The target gas's concentration has been varied from 0.1%- 1% and corresponding the output signal time period is noted. The result shows good agreement between our calibrated and measured value.

The cost effective, highly sensitive and lower power dissipated sensor node to sense H_2 and CH_4 leakage by a proper electronic circuit which can be easily implemented

with highly sensitive electronic circuit is proposed. It can easily convert the change in resistance of the sensor to time period. The selected sensing materials WO_3 & ZnO show very promising and highly sensitive characteristics in presence of H_2 & CH_4 gas. The proposed interfacing circuit is very simple, cheap and requires only few components to implement. The experimental result confirms predicted theoretical value. The effectiveness of the circuit is tested for both types of material WO_3 & ZnO and the results show satisfactory agreement between theoretical prediction and practical values with respect to sensitivity, linearity & cost.

Table5.2 Result of our proposed system

Sensor type	**Target Gas**	**Concentration variation (%)**	**Time period variation (mSec)**
WO_3	Methane (CH_4)	0.1% to 1%	0.05 to 0.45
ZnO	Methane (CH_4)	0.1% to 1%	0.05 to 0.55
WO_3	Hydrogen (H_2)	0.1% to 1%	0.05 to 0.31
ZnO	Hydrogen (H_2)	0.1% to 1%	0.06 to 0.43

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Chapter 6

Development of a RFID based system for detection of leakage of Ethanol vapour with tags as sensors

6.1 Introduction

The trend in the automated industry is to move towards fast and real time identification, further improving the high level of accuracy needed to enable continuous identification and monitoring. Such a level of real time knowledge is often called ambient intelligence. In the recent years the process of automatic identification (Auto-ID) have become very popular in many service industries, purchasing and distribution logistics, industry and manufacturing companies [6.1-6.5]. Radio Frequency Identification (RFID) is the most reliable way to electronically identify, data capture, control, track and inventory items using RF communication [6.6-6.10]. The basic component of RFID technology is RFID reader, tag and server. Initially reader reads the tag data and sends it directly to server connected with reader. All types of tag data are then stored at server from where the administrator makes decisions according to the needs of application. The RFID technology provides vast area of application because of its operation mode in different frequency zone. It can be used in small distance application by using passive tags or long distance applications by using semi passive-active tags. The RFID technology does not require any line of sight communication. This enables the user to use RFID technology more efficiently than existing bar code technology. One such area where it can provide significant advantages is in detection of different hazardous gases and the restriction of spreading in environment directly [6.11-6.17]. There are different hazardous gases like toxic gases which are the gases that are harmful to humans like ammonia, chlorine, sulfur, and many others. These gases are also flammable, capable of burning in certain concentrations at presence of oxygen which make them more dangerous to use in public place. Like flammable gases, combustible gas requires the presence of oxygen. Now a day these types of gases are regularly produced in different industries like coal, mine, cement, beverages etc. So it is required to sense the leakage of these gases timely and effectively. In this scenario the researchers are continuously finding different kind of sensors like thick film sensor, thin film sensor,

carbon nanotube based sensor, fiber optic based sensor, reduced graphin oxide based sensors and many more. Different sensors have different pros and cons. The thick film sensor operates at high temperature that makes its life time shorter whereas thin film sensors are having lower operating temperature. But the selectivity and operating temperature of graphin based sensors are far better than thin film sensors. However the fabrication process of graphin based sensors is lengthy and costly whereas thin film sensors can be fabricated easily by sol gel process. Besides designing of sensor, the researchers are also working to design more efficient sensor based system so that the sensor data can be send properly [6.18-6.21]. Different new technologies like RFID are getting attention as sensing device to make efficient sensor based system.

Hence many researchers are working in the area of detection these kinds of gases using different materials; different fabrication techniques and showing improvement day by day towards more enhanced gas detection sensor and system. In this research work an effort has been made to design and investigate Radio Frequency Identification (RFID) based system to detect hazardous gas like ethanol, hydrogen. The main component of RFID system is RFID tags which has been used as sensor device for monitoring and detection purpose.

6.2 Literature Review

The miniaturization of device size is the trend of VLSI technology. Day by day the feature size of the CMOS device is reduced drastically. Hence researchers from around the globe are working towards different new efficient device structures [6.22-6.29]. Similar evolution is also occurring in the field of sensing device. Different new materials, different new fabrication techniques, different new technologies are coming as sensor and sensor based system. One of them is RFID technology. The abbreviation of RFID is Radio Frequency Identification. It is used for product identification and gathering information of products automatically. RFID does not

required line of sight communication. This feature makes RFID a better technology with respect to present bar code technology. A RFID system is made up of different components like RFID tag (having an antenna for communication, a chip for unique identification using EPC and data storage) RFID Reader or interrogator (for data emission and reception directly from tag) and a host computer connected to RFID reader (for data saving and analysis). The RFID antenna is made up of a metal pattern which imposes the emission frequency. The designed antenna should have a low cost substrate, easy fabrication process, environmental friendly and have proper impedance matching circuit. The next is the chip which is made up of bits for encoding information about the product. The Electronic Product Code (EPC) is unique to each tag and is recorded at the time of production. The chip can be classified in terms of data access in 2 ways i.e. Read only chips and Read-Write chips. The EPC protocols are developed by EPC Global Cooperation. The EPC code contains 64 bits or 96 bits with different functionalities like a header, an EPC manager, a serial number and an object class [6.30-6.31]. The next part of RFID system is a reader which is an electronic apparatus for electromagnetic wave emission and reception. It recognizes the identification of the tag through the tag ID (pro-vided by the chip manufacturer). The reader has also the capability to decode the information carried by the incident wave by using internal decoder [6.30]. The next is RFID tags which can be categorized in three types: Active tags, passive tags and semi passive tags.

6.2.1 Active tags

The tags are having own power source battery which is used for powering the chip and wave transmission. The reading range of the active tags is wider than other tags like 30 m or more. The rate of transmission is fast and simultaneously reading of tags is high with respect to other tags. They are mostly used rewriteable chips. However, the major disadvantages are cost and the size. The life time of the tag depends on the battery life.

6.2.2 Passive tags

These tags do not contain onboard battery sources and completely depends on the wave emitted by the reader for powering their chip. The tags send backscatter electromagnetic wave to communicate with the reader. This type of tag has a lower reading range with respect to active tags. The transmission rate depends on the operating frequency of the tag. The passive tag chip is write once and multiple readings type. The main advantages of the passive tags are low cost, long operational life, small size and light weight which make them potential candidates for developing low cost devices.

6.2.3 Semi-passive tags

Semi-passive tags are also self-battery powered only for the chip. Most of the times the battery of the tags remains off. Hence the life span of the tags increases. The power source of these tags increases the working range compared to passive tags or acts as a power supply to interfacing sensor circuit with the chip. These tags still rely on the reader for electromagnetic wave emission. Their reading range is greater than passive one but lesser than active RFID tags.

Passive tags can be used for three different types of frequencies: Ultra High Frequency (UHF) 860-960 MHz, High Frequency (HF) 13.56 MHz and Low Frequency (LF) 125-134 KHz. The range of UHF passive tag is typically 20–30 ft. They are faster but required more power. On the other hand HF tags have ranges less than 3 ft. The LF tags require less power and can be used with non-metal objects but have low reading range about a foot only. RFID technology finds different sectors for its applications like food industries supply chain management companies, animal husbandries and many more.

An ethanol refinery had a series of outdoor storage tanks containing ethanol. The facility wanted a gas detection and emergency alarm system to monitor for leaks around the storage tanks. Besides ethanol is a key element in many industrial activities. It is a good source to enhance the economic condition. Thus production and maintenance process are the key parameters in those industries. Ethanol is also

volatile, flammable, colorless element (in vapour form). When ethanol vapor combines with air in the presence of ignition sources, fires and explosions can result. The lower and upper explosive limits of ethanol are 3.3 percent and 19 percent, respectively and a blend of 85 percent ethanol and 15 percent gasoline has lower and upper explosive limits of 1.4 percent and 19 percent, respectively. There are many ethanol based sensors available in the literature starting from FET based to schottky diode based, metal oxide based to nanoparticle (NP) based and OD,1D,2D sensors[6.30-6.40]. Among different materials (like TiO_2, ZnO, SnO_2, CuO etc.) WO_3 is much promised and widely used material due to its high sensitivity, fast response time, low band gap, high mobility towards different gases (H_2, CO_2, NO_2 etc.)[6.41-6.50]. In our present work we have made some modification to increase the sensitivity and response time of the WO_3 based sensor. We have studied the catalytic effects of Pd, Pt, after mixing with WO_3 material. We also have taken the most cost effective but accurate technique sol gel method to prepare those sensing materials. Bijoy Kantha et al. [6.31] have shown the effect of Pd modified WO_3 sensor in the presence of H_2 gas. The operating temperatures of unmodified 'n' type WO_3 and Pd modified WO_3 are 300°C and 200°C with sensitivity 58% and 62.3% respectively. In another work [6.41] 'p' type CuO based ethanol sensor has been fabricated using oxidation technique having optimum temperature 240°C with response recovery time 110sec and 120sec respectively. Hence continuous observation is necessary to control any leakage of ethanol at an early stage. The RFID technology may be used as sensing device in this application area. In literature many researchers are working with this technology as sensing devices in various areas. Like the author Puma, M. C. et al. [6.9] measured the feed intake behavior of flocks of birds using RFID tag as sensor where individual IDs were not available. Thus for describing group feeding behavior the study was good, reliable and less costly. Even researchers are using the RFID technology with wireless sensor network for more robust system. Mobile Wireless Sensor Network allows continuous monitoring of livestock with cost effective way and greater robustness with respect to human observation technique.

Hiroaki et al. [6.10] have worked with Global Positioning System (GPS) technology to continuous monitor the gazing behavior of cattle which enable the farmers to utilize gazing field effectively and preferred habitats of livestock. Mayer et al. [6.11] proposed a real time Global System for Mobile (GSM) based system for data retrieval from animal for improvement of behavior tracking process. Wireless Sensor Network based system to monitor avian influenza in poultry farms has been demonstrated by Hironao Okada et al. [6.13]. However the researchers have faced several challenges to implement GSM or GPS based livestock monitoring system like battery lifetime, cost, robustness in architecture and many more. Hence in this present work low cost, highly robust RFID passive tag based monitoring system is designed to detect hazardous gas ethanol.

6.3 Fabrication of the thin film sensor

The thin film of ZnO has been fabricated by sol-gel method using Zinc acetate dehydrate as a precursor. As a starting material, zinc acetate dehydrate ($Zn(CH_3COO)_2.2H_2O$) was dissolved in a mixture of ethanol and mono-ethanolamine (MEA) solution with a concentration of 0.75 mol L^{-1}. MEA acts at the same time as a base and a complex agent and the MEA to zinc acetate molar ratio was fixed at 2. Using heat treatment on the dried films at 500˚C for 2 hours, we obtain the crystalline films. The backside of the Si wafer was etched by lithography method. The dielectric membrane of 0.6 μm SiO_2 was deposited on Si wafer. DilverP1 heater plate (0.2 μm) was deposited on SiO_2 membrane using e-beam evaporation technique. A layer of 0.3 μm SiO_2 then deposited on heater element for isolation purpose between heating plate and sensing layer. Next the prepared sol gel of ZnO was placed on the SiO_2 layer by spin coating method at 3000 rpm for 30s. Three combinations of sol gel have been prepared to form three different sensors-unmodified ZnO sensor, Pd modified ZnO sensor and Pt modified ZnO sensor. Simultaneously the sol gel of modifier Platinum (Pt) has been prepared. A solution

of poly vinyl pyrrolidone (PVP) 40mM and Sodium nitrate ($NaNO_3$) was prepared. Then solution of 90mM of chloroplatinic acid hydrate (H_2PtCl_6) and ethylene glycol was also prepared. Two solutions are mixed rapidly at 180°C. The nanoparticles of Pt were dispersed in ethanol giving a 40mM sol. Then sol of ZnO and Pt are mixed and in order to get nominal noble metal concentration. Next to make Pd modified ZnO sensor, an aqueous solu-tion of 0.1 (M) $PdCl_2$ was prepared. Sensor sample was dipped in the solution for 20 seconds three times and was calcined at 130°C for 20 minutes. Figure 6.1 shows the basic sensor structure where the sensing layer may be only ZnO or ZnO with Pt or ZnO with Pd.

Figure 6.2 shows the experimental set up of ethanol vapour sensor measurement. The sensor chamber is made of glass(Length 30cm and diameter 4cm).The sensor is inserted into the chamber (by contact connection). The temperature controller (TC)

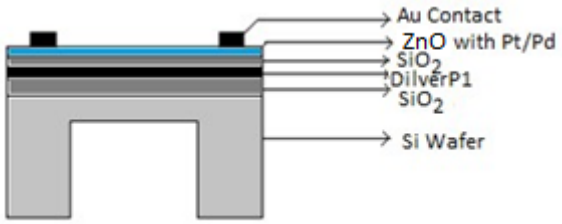

Fig.6.1 Structure of WO3 modified by Pt/Pd thin film sensor (not to scale)

was used to attain the operating temperature of the sensor. Resistive heating coil (≈ 8cm of constant heating zone, with temperature accuracy ±10 ^{0}C) was used internally in Temperature controller for heating purpose. The gas flow and mixing ratio were precisely monitored and controlled with the help of mass flow controller (MFC) (Alicat scientific, M-50SCCM-D). The homogeneous mixture carrying the desired percentage of the target vapour was fed into the chamber with a flexible PVC pipe. During the testing the gas pressure on the sensor was 1atm was maintained. An automated volt-amperometric data acquisition system (Agilent U1252A) was used to measure the changes in resistance under various operating temperature and vapour concentration.

1) Crystalline size of grown particles: The grown nanocrystalline's average size is achieved by XRD results. It is calculated by the Scherer's equation as follows [6.42]

$$D = \frac{k\lambda}{\beta cos\theta} \qquad \text{eq. (6.1)}$$

Where the space factor k is 0.9 and λ,θ, β are X-ray wavelength, the Bragg angle and full width of the diffraction line at the half of the maximum intensity respectively. Based on the equation the average crystalline size of only ZnO Pd modified ZnO, Pt modified ZnO are 20nm, 14nm and 11nm respectively calcined at 600°C.

2) Sensitivity: The sensitivity of the fabricated sensor is calculated by following equation:

$$S\% = \frac{R_a - R_y}{R_a} \qquad \text{eq. (6.2)}$$

Where R_a and R_v are the resistances in presence of N_2 and in presence of ethanol vapour respectively.

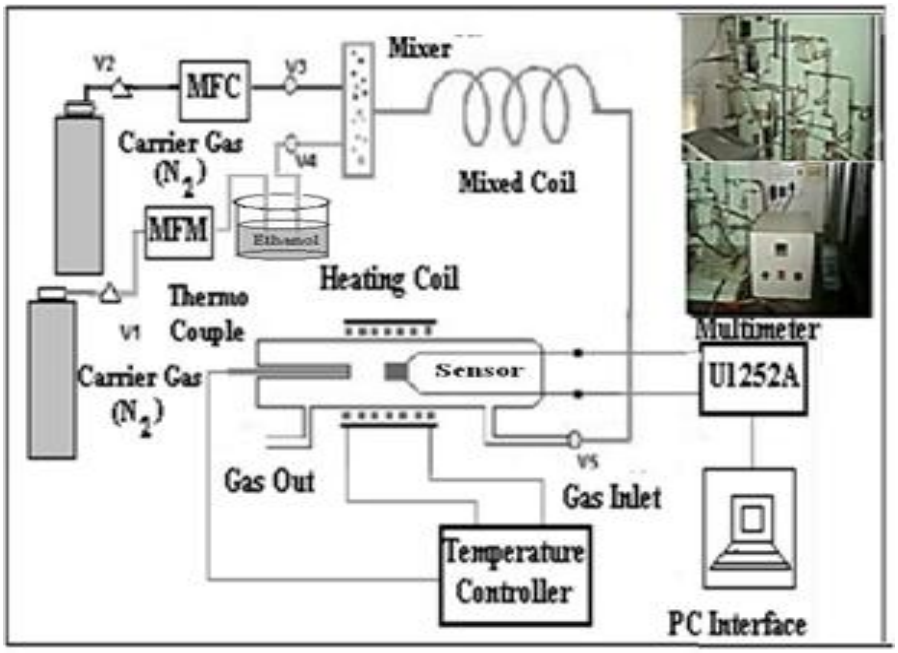

Figure 6.2 Experimental set up

The XRD pattern of ZnO samples have shown in the fig. 6.3. The nanoparticle size of fabricated sensors plays very important role for sensing ethanol vapour. The diameter of the particle must be as low as possible so that the surface to volume ratio increases. That means more surface nanoparticles can react with target ethanol

vapour and the sensitivity of the sensor increases accordingly. In this work the Pt modified ZnO based sensor having the lowest diameter with respect to other samples. Hence the sensing features and other sensing parameters like operating temperature enhanced for Pt modified ZnO sensor. The operating temperature plays important role for senor as it determines the life time and reliability of the sensor. The operating temperature is measured for different sensors at fixed concentration of ethanol vapour with varying temperature and sensitivity. As temperature increases the sensitivity of the sensor increases initially and after a certain level sensitivity starts to decrease. This indicates the operating temperature of the sensor. The scanning electron microscope (SEM) structure of the sensor is shown in fig. 6.4 (a-c). The fig.6.4 shows distribution of the nanoparticles at sensor's surface in nanoscale region. It clearly shows that the surface to volume ratio for Pt modified sensor is greater than other structures.

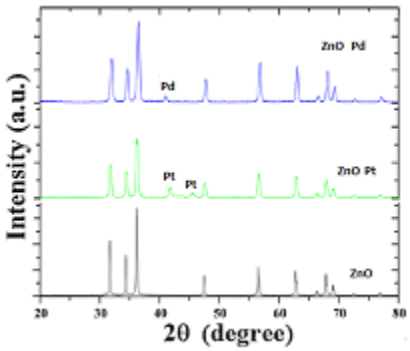

Figure6.3 XRD pattern of the bare ZnO sample

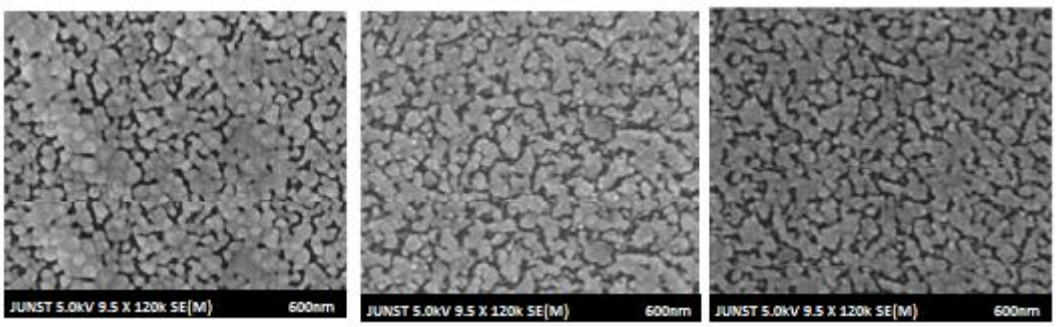

Figure6.4 (a-c) SEM of bare ZnO, Pd modified ZnO and Pt modified ZnO

The operating temperatures of the sensors are 320˚C, 230˚C and 200˚C for unmodified ZnO, Pd modified ZnO and Pt modified ZnO respectively as shown fig 6.5.

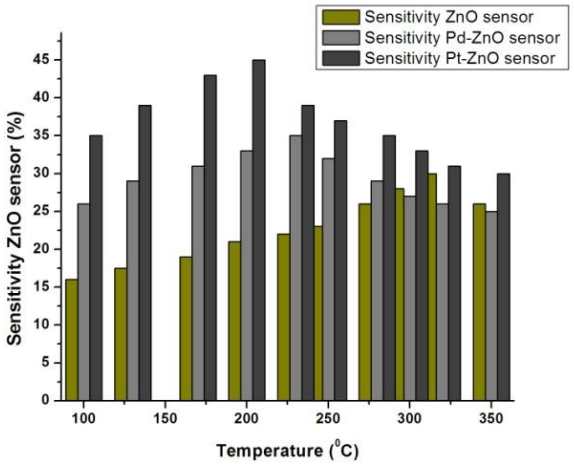

Figure 6.5 Sensitivity of ZnO sensor vs. temperature

By varying the concentration of the ethanol vapor from 1500ppm to 5000ppm the change in conductivity was measured at fixed operating temperature for the three samples (shown in fig.6.6). The reducing gas ethanol reacted with oxygen adsorbed on the surface of the sensor rather lattice oxygen. The adsorption of the C_2H_5OH vapour on ZnO surface can take place by the following route:

$$C_2H_5OH\ (vap) + O\text{-}(ads) \rightarrow CH_3CHO(ads) + H_2O(vap) + e^- \qquad \text{eq. (6.3)}$$

$$CH_3CHO(ads) + O(lattice) \rightarrow CH_3CHO(vap) + VO \qquad \text{eq. (6.4)}$$

The current voltage characteristic of fabricated sensor is shown in fig. 6.7. At reverse bias condition there is no sign of currents. However in forward bias condition, the current in Pt modified sensor is greater than the current of ZnO based other sensors which show that modified sensor is better than unmodified one to detect ethanol leakage.

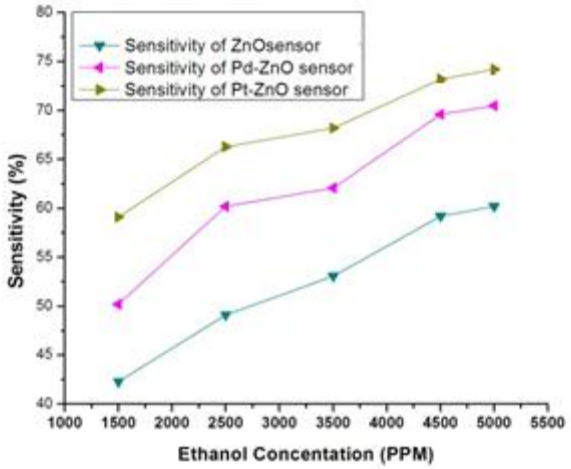

Figure 6.6 The sensitivity vs. concentration variation graph

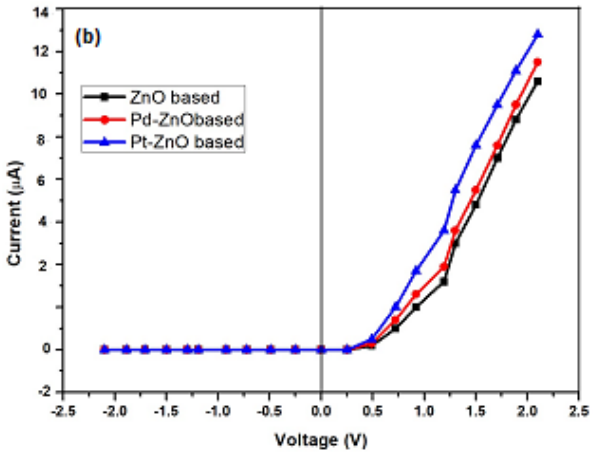

Figure 6.7 I-V characteristics of fabricated sensor

The cross sensitivity is an important feature of any gas sensor. The cross sensitivity of the fabricated sensors are measured with respect to hydrogen and methane gas(as shown fig. 6.8). It is observed that only for ethanol sensor the sensitivity of the fabricated sensor is better than other two gases. This feature suggests that the fabricated sensors can be used precisely for sensing ethanol leakage.

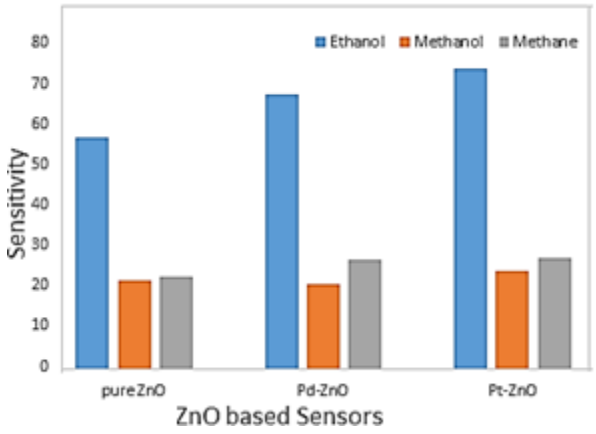

Figure 6.8 Selectivity of fabricated sensor

The experimental study is carried out to calculate response time (T_{RES} in seconds) and recovery time (T_{REC} in seconds) of the fabricated sensors samples at their respective operating temperature. Figure 6.9 depicts the graphical representation of the response and recovery time for all the samples. It directly proves that addition of noble metals enhances these properties of the sensors.

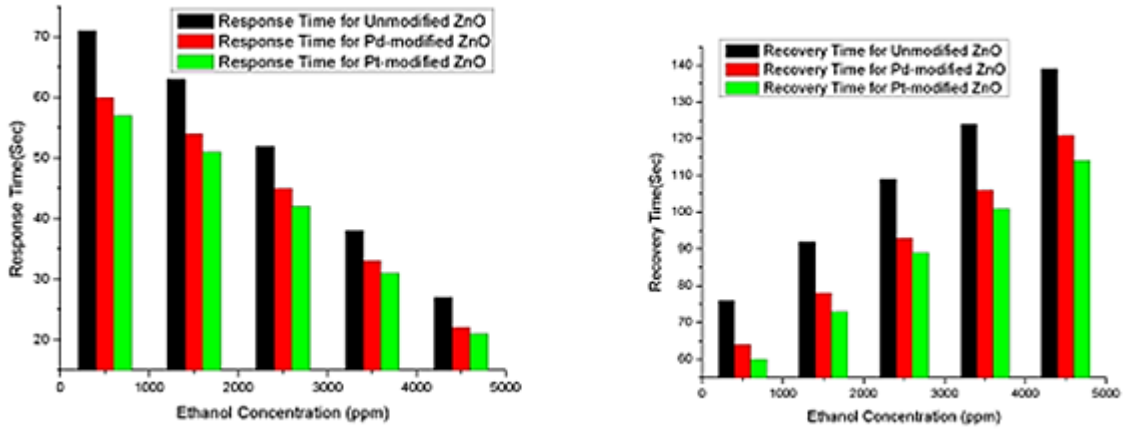

Figure 6.9 Response time and Recovery time vs. ethanol concentration for ZnO sensors

6.4 Design of RFID based system

The implementation of the proposed system has been carried out in laboratory with the help of passive RFID reader, passive RFID tag with WO_3 based sensor, basic Stamp processor, and a monitoring computer.

- RFID Reader: The passive RFID reader interrogates with passive RFID tag sensor and the passive tag sensor is powered up & send back (backscatter) the stored information of tag to the reader. The stamp processor connected with the reader extracts the information of chicken (ID) from the received packet string. Then the processor merges the tag ID with Cage ID and sends it to the monitoring station. Then this information directly store into the data base of our design program. Figure 6.10 shows the front and back view of the reader.

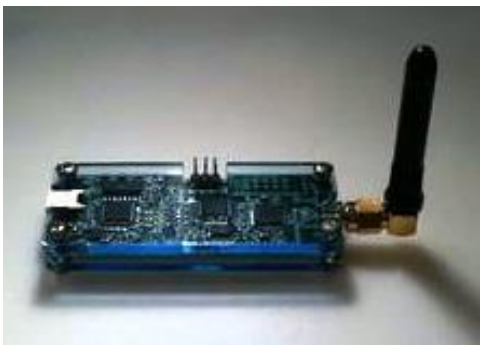

Figure 6.10 RFID Reader Front and Back View

- RFID Tag: Passive RFID ring type tags are used in this work which is very compatible to fit with chicken's leg. Thus our system can easily extract all the information about any single unit precisely which is very important to detect the bird flu. So that not only we can separate the affected chicken from the farm but also we can restrict the spreading of the disease. The RFID ring type passive tag and tag attached chicken is shown in the fig. 6.11.

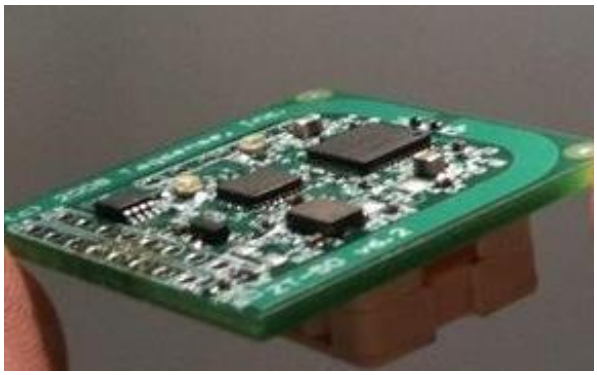

Figure 6.11 RFID Tag

- Basic Stamp processor: The low cost basic stamp processor (as shown in fig 6.12) has been used to implement the system. The RFID readers are connected to the stamp processor to extract data from each reader and send them directly to the monitoring system.
- Monitoring PC: The data from sensors enter to the monitoring PC through the basic stamp processor. Then the designed program in monitoring PC controls all actions according to the design algorithm and generate alarm signal when ethanol leakage is detected.

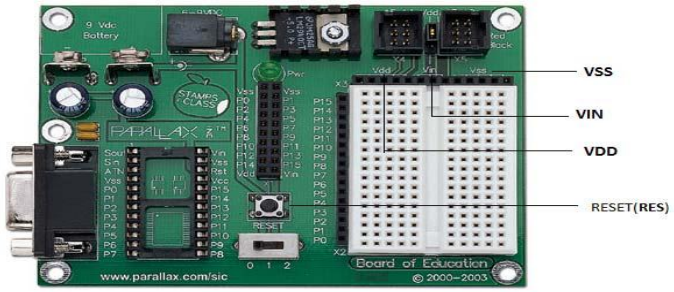

Figure 6.12 Basic stamp processor used in our system

Along with the leakage detection process, the proposed system can be used to improve the management process of the ethanol manufacturing industries. The other main features of the proposed system are cost effective tracking, reusability of the used RFID passive tags. Thus the design system offers very cost effective utilization of resources.

The main fact that our system heavily rely on is the both active RFID tags and readers are capable of bidirectional communication with each other. After receiving the data from the sensor the tag sends the data directly to the reader. Sensing voltage from the sensor may vary from 0.2-1.8V corresponding to the concentration of ethanol 0.05% to 0.5%. In the monitoring area many RFID active tags are attached at different areas. The ethanol sensor is directly connected with the tag at its analog input terminal. With the leakage of the ethanol vapour the voltage at the input terminal changes and this change will reflect on tag beacon packet. Then the tag sends beacon packet to reader. In our design module most of the time, the tags are in

sleep mode so that the power consumption of active tags are reduced and life time of the tags increased. Tags can be programmed accordingly with input voltage range. Thus we can control the status of these active tags (sleep mode/wake up mode). The reader then extracts all the necessary information from the beacon packet (Tag ID, Signal Strength, input voltage) and sends the all information to base station. Then the final decision and necessary actions will be taken by the proposed designed program and alarming system will be turned on automatically. The designed system can be programmed such a way that it can detects the position of the tag with respect to its signal strength level and also properly detect the particular tag with highest signal strength level depending on the voltage level the leakage of ethanol vapour. Our proposed system can easily detect the ethanol vapour leakage at a very low concentration and also can set alarm very fast and cost effective manner to reduce loss in terms of money and life. The flow chart of the proposed system is shown fig. 6.13.

When a reader received multiple command packets (tag beacon packets) from different tags, it reads the information contained in the packet (that is the tag ID, input voltage level and signal strength) and sends directly to the base station. The design program after receiving the data, stores them in a look up table as shown below (Table 6.1). It then applies selection sort to sort the look up table in ascending order with respect to the signal strength as shown below Table 6.2.

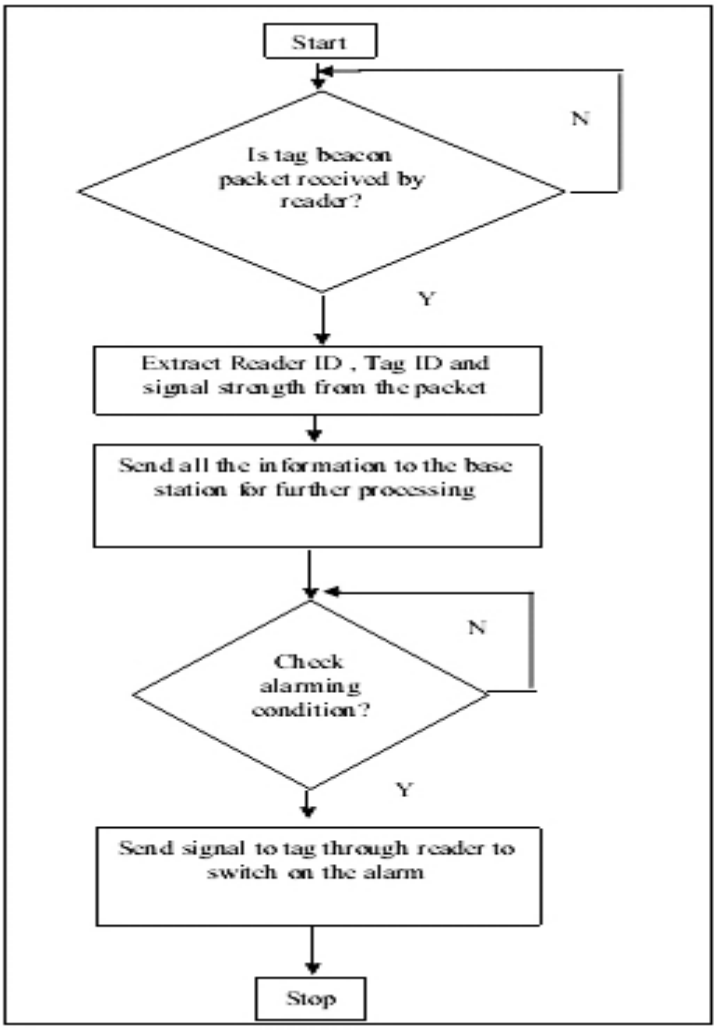

Figure 6.13 Flowchart of our proposed system

TABLE 6.1 LOOK UP TABLE AS MAINTAINED BY THE PROCESSOR

Serial No.	Tag_ID	Voltage Level	Signal Strength
1	FAFA	1.4	B5
2	FCCF	0.8	FB
3	EFAB	1.1	AE
-	-		-

TABLE 6.2 SORTED LOOK UP TABLE AS MAINTAINED BY THE PROCESSOR

Serial No.	Tag_ID	Voltage Level	Signal Strength
1	FCCF	0.8	FB
2	EFAB	1.1	AE
3	FAFA	1.4	B5
-	-	-	-

The tag ID corresponding to the last row in the look up table is our desired tag ID. This is because it corresponds to the tag position where leakage is the maximum. Our system is designed such a way that it can detect multiple leakage point at a time so that loss can be minimized. A brief comparison of proposed system with available work in literature is shown in table 6.3.

TABLE 6.3 COMPARISION TABLE WITH OTHER WORKS

Factors	**Ref[18]**	**Ref[15]**	**Ref[10]**	**Our work**
Cost	Medium	Medium	High	Low
Hardware components requirement	More	Less	More	Less
Individual/ Group Detection	Group	Individual	Group	Group
Reusability of Components	Not Possible	Possible	Not Possible	Possible
Surveillance region width	Small	Small	Wide	Wide

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Chapter 7

Conclusion and Future Work

7.1 Concluding Remarks

7.2 Future Work

7.1 Conluding Remarks

In the present work a comprehensive theoretical and experimental study of the characteristics of metal oxide semiconductor sensors and their applications are investigated. The details of the research work are summarized in below.

Metal oxide gas sensors plays a vital role in gas sensing applications in domestic and industrial applications. Detection and monitoring of flammable, odorless and toxic gases is important. Hence low dimensional thin film metal oxide sensors which can identify different hazardous gases quickly are essential so that they will be compact, portable and less power consuming.

Semiconductor metal oxides are found to be an excellent gas sensing material. Usually, the operating temperatures of the thin film metal oxides are 150^0C to 300^0C. Hence in chapter 3 an effort has been made to improve the sensing characteristics of WO_3 based ethanol sensor using noble metals like Pt, Pd by using sol gel fabrication technique. The noble metal is used as a catalyst for the modification of the surface reactions of thin film in the presence of sensing gases. The operating temperature of the gas sensor has been improved after using Pt (170^0C) which is lower than both normal WO_3 based sensor (300^0C) and Pd modified WO_3 sensor (210^0C) as shown in table 3.1. The most important characteristics of gas sensor that is sensitivity also enhances from 62% to 77.2% for normal WO_3 and Pt modified WO_3 based sensor. The characteristics of sensing layers are examined by XRD and SEM methods that shows the presence of Pt, Tungsten, and Oxygen particles as evident from fig. 3.2(d). The result also reveals that sensing layer's surface morphology and nanoparticle diameter enhanced with addition to Palladium (Pd) and Platinum (Pt) for the gas sensor [vide fig. 3.2(a-c)]. Similar effect also revels during measurement of selectivity, response time and recovery time of the fabricated sensors [vide fig. 3.5-3.6, 3.8-3.9].

Gas senosrs' characteristics also depends on different parameters like grain size, annealing temperature, different device structures like schottkey, homo junction, hetero junction etc. Hence in the chapter 4 an effort has ben made to enhance the sensor characteristics by incorporating two important factor i.e.

annealing temperature, and hetero structure device. It is observed that the post fabrication annealing process has greater influence on the important parameters of thin film sensor like particle size and lattice constants. The study has been made for three different temperatures 350˚C, 500˚C, 600˚C. The minimum value for average crystalline size of the ZnO thin film is obtained at 350˚C annealing temperature [vide fig. 4.3 and table 4.1] and highest sensititvity is achieved for this structure for hydrogen sensing application as revealed from the fig. 4.10. However with increasing the annealing temperature the particles try to agglomerate so the average particle size increases for higher temperature thus sensitivity decreases [vide fig. 4.11]. Then, the gas sensing characteristics of ZnO-WO_3 hetero-junction device is investigated for an application of detecting hydrogen and methane gases. The comparative study also carried out with normal WO_3, ZnO type structures. The performance of the hetero structure further enhances by adding noble metals Pd into the surface of the metal oxide as evident from fig. 4.12. Nanocrystalline thin film is deposited on p-Si<100> substrate using a sol-gel deposition spin coating method for the formation of hetero-junction device. Pd-Ag alloy is needed to make the electrical contact on the both sides of two different devices. XRD and SEM are employed to characterize the structure of the hetero-junction device [vide fig.4.5-4.7]. The Pd modified composite sensor provides the lowest operating temperature 160˚C with highest sensitivity 83.1 % at 1000ppm H_2 gas where the operating temperature of ZnO based sensor is 230˚C with low sensitivity 69% at same concentration of H_2 gas as revealed from fig. 4.12. Similar effect can also be seen for response time of the sensor. The response time of Pd modified WO_3-ZnO sensor is 38sec whereas for ZnO based sensor is 64 sec [vide fig. 4.13-4.14]. This clearly shows improvement in heterostructure devices as compared to other sensor devices. The cross selectivity of the sensors is measured with respect to other potentially hazardous gas like methane, methanol and ethanol [vide fig. 4.15]. Therefore, Pd surface sensitized sol gel grown ZnO-WO_3 thin film can act as a very good hydrogen sensor at the optimum working temperature of 160˚C as revealed from fig. 4.12-4.15.

Gas sensors are generally used to detect the harmful and flammable gases in the industry and the environment. So, gas sensor with proper signal conditioning

unit is required to detect the flammable gases in the environment. In recent times, tungsten oxide (WO_3) and zinc oxide (ZnO) are extensively used as a gas sensing materials due to its various advantages such as good thermal stability, compatibility with Si technology, easy fabrication, high sensitivity and low cost. The performance of the semiconductor metal oxide based gas sensor with signal conditioning unit is improved through the reduction of operating temperature and the minimization of power consumption. Hence in this thesis work initially different methods are taken to improve the sensitivity of gas senor then a low cost, highly reliable conditioning circuit is proposed in chapter 5 based on simple netwroks like bridge circuit, amplifier, and voltage to time conversion circuit fig.5.7. Bridge circuit produces incremental change in resistance because of variation of the gas percentage which in turn creates incremental voltage. This incremental voltage is amplified to a desired level so that adequate voltage can be provided to a timing circuit. Finally timing circuit generates variable time signals which are almost linearly related to the gas percentage variation as evident from fig.5.8-5.10(ii). The change of output signal time period is proportionally related to change in resistance across the sensor. The complete circuit is implemented on bread board using op-amp and discrete values of resistances and capacitances [vide fig. 5.7]. The effectiveness of the circuit is tested by taking discrete precision variable sensor resistance, then taking the resistive sensor. The comparison between the experimental result and calibrated result shows little nonlinearity with respect to calibrated graphs [vide fig. 5.11(i) - 5.11(iv)]. This result confirms the reliability of our proposed system.

Finally in chapter 6 a RFID tag based sensor system has been proposed to detect leakage of ethanol vapour. Ethanol has been used for many domestic applications. Besides, there are huge number of brevarge industries for producing ethanol based products. Thus leakage of loss of ethanol could create huge economic loss as well as therat to human kind. Due to odourless nad colurless features the ethanol leakage detection is very challenging. Hence RFID based a ethanol sensing device is fabricated in this chapter using low cost hardware resources like RFID tag, reader, basic stamp processor, solgel fabrication method. Dependign upon the concentration leakage % RFID tag sensor generate a signal voltage to RFID reader. Then designed

program model will collect all the data and generate alarm signal accrding to our design algorithm [vide fig. 6.12]. The design sensor can detect the ethanol with efficiency 78.5% for 5000PPM concentration as evident from fig. 6.6. The SEM and XRD of the fabricated sensor reveals the formation of nano structure [vide fig. 6.3 and 6.4(a-c)]. The cross selsctivity and I-V characteristics of the fabricated sensors are experimentally checked [vide fig. 6.6 and 6.7]. A brief comparison of our proposed system has been made with existing work in table 6.3 which shows our proposed system is better with respect to cost, hardware component, indivisual detection, reusability of components and surveilliance region width.

7.2 Future Work

Temperature is an important factor for the metal oxide gas sensors. Typical curves of gas response vs. temperature were shown in fig. 5.11. The response is improved and reach to maximum at a operating temperature, and then degraded rapidly with increasing the temperature. The researchers concluded that the shape of nano particles increase after the operating temperature which results lowering the sensitivity and unstability in gas sensor's response. Thus effect of temperature need more attention during future work. Another important factor is environmental humidity which influences the performance of metal oxide gas sensors. The mechanism of sensing water vapor and other pollutant gas such as ethanol, hydrogen etc. is different. Water adsorbing on the metal oxide surface will not donate electrons to sensing layers. Moreover, it will lower the sensitivity of metal oxide sensors due to the reaction between the surface oxygen and the water molecules. Finally this will lead to a decrease in sensitivity of the sensor. Besides the adsorption of water molecules leads to less chemisorption of oxygen species on the surface of sensor, that causes decrease of the surface area which finally leads to lowering the sensor response. Hence in future work effect of humidity must be taken as a consideration for fabricating any type of gas sensor.