Fabrication and Design of Thin Film Sensor and IoT Based Sensor System

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By

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CERTIFICATE OF EXAMINATION

This is to certify that the thesis entitled "**Fabrication and Design of Thin Film Sensor and IoT Based Sensor System**" has been carried out by **Bikram Biswas (Roll No: 001610703014, Examination Roll No: M6VLS19004 and Registration No: 137286 of 2016-17)** under my guidance and supervision and can be accepted in partial fulfilment for the degree of Master of Technology in VLSI Design and Microelectronics Technology. In my opinion the work fulfils the requirement for which it is submitted. To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other organization.

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CERTIFICATE OF APPROVAL*

The foregoing thesis is hereby approved as a credible study of an engineering subject and presented in a manner satisfactory to authorization acceptance as pre-requisite to the degree for which it has been submitted.it is understood that by this approve any statement made, opinion or conclusion drawn there in but approve the thesis only for which it is submitted.

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DECLARATION OF ORIGINALITY AND COMPLIANCE OF ACADEMIC ETHICS

I hereby declare that the thesis contains literature survey and original research work done by the undersigned candidate, as a part of her Master of Technology in VLSI Design and Microelectronics Technology.

All information in this document has been obtained and presented in accordance with the academic rules and ethical conduct.

I also declare that as required by the code of conduct, I have fully cited and referenced all material and results that are not original to this work.

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ABSTRACT

The devices that can produce responses with the change in physical conditions such as pressure, temperature, humidity, gas concentration etc are known as sensors. Now-a-days Sensors are becoming part of our daily lives. Gas sensing materials are utilized for the detection of toxic gases as well as gases like acetylene, ammonia, hydrogen, propane, propylene, methane and ethanol etc. Semiconductor gas sensors play a major role in this field with good stability, high sensitivity and longer life time. During last few decades the features of semiconductor gas sensors are enhanced drastically. The application of different types of sensors in agricultural field along with Internet of Things (IOT) have been gradually increased in the recent years. To meet the growing demands and to feed the masses, more agricultural land is required. The land requirement can be mitigated by using vertical farming. This technique involves growing crops in a vertically stacked manner in an indoor controlled environment. Vertical farming is environment friendly and pesticide free.

In the present study highly responsive Pd, Pt modified WO_3 and Pd modified TiO_2-CuO thin film ethanol and hydrogen sensors, respectively, by using sol-gel process. Prepared thin film was characterized by scanning electron microscope (SEM), field emission scanning electron microscope (FESEM) and x-ray diffraction (XRD). Sensitivity of Pd modified TiO_2-CuO hydrogen sensors was investigated at operating temperature 50^0C-250^0C and different gas concentrations (3000 ppm). An economic but accurate ethanol detection system has been realized along with a signal conditioning circuit where a timing resistance of a 555 timer is formed by a WO_3 based thin film sensor. The incremental resistance change due to the variation of gas concentration results in the change in frequency of the astable multivibrator. Finally, by measuring the frequency, the ethanol percentage can be estimated. The whole system is simple and can be realized with only a few hardware components. It has been observed that Pd-doped and Pt-doped thin film sensors have better responsivity in comparison with the undoped thin film sensors.

Vertical farming is an unconventional farming technique that has gained relevance in recent years, as existing agricultural lands fail to meet the needs of the growing population. Smart monitoring of the ambient parameters in vertical farming can improve the productivity and quality of the crops. A system has been proposed to develop sensor arrays that can measure the ambient parameters and upload the data onto the ThinkSpeak Cloud, using the Intel Edison wireless module. The web-based application can be used to analyze and monitor the light, temperature, humidity and soil moisture of the vertical farming stacks. Using the Virtuino app, SMS can be sent if the parameters fall below a threshold value.

CHAPTER I

INTRODUCTION

1.1 Introduction:

Over the years, the fabrications of low size devices and reliable gas sensors with reduced power consumption have attracted considerable attention [1.1-1.3]. In this substance, several studies have been discussed on hydrogen and ethanol detection due to safety reasons as an illustration, gas detection in industries, gas detection in food industries, environmental gas detection, gas detection in biomedical and space applications. Hydrogen is an odorless, colorless, non-toxic, non-metallic, highly combustible diatomic and explosive gas. So, it is a major challenge to detect gas efficiently. Over the last few decades, the concentration measurement and detection of hydrogen gas leakage has been done and various approaches proposed to realize hydrogen sensor with effective performance [1.4-1.6]. However, the presently used H_2 sensors have some drawbacks like low response time, recovery time and poor longevity. So there is a requirement of high performance H_2 sensor for different industries as well as ethanol also.

Different metal oxides have been used for sensing material like ZnO, WO_3, CuO, TiO_2, Cr_2O_3, Mn_2O_3, Co_3O_4, NiO, Ta_2O_5, La_2O_3, CeO_2, Nd_2O_3 ,SrO, In_2O_3, V_2O_3, Fe_2O_3, GeO_2, Nb_2O_5, MoO_3, [1.7]. Now-a-days, mixed metal oxides are used for better sensing application. Some nobel metal are used like (Pd, Pt, Au, Ag) to modified the surface of the metal oxides for better sensitivity[1.8-1.10].These metal oxides are useful for the detection of toxic gases like H_2, CO, NO_2, CO_2 etc. Mixed metal oxide based sensor have been widely used for gas detection. Various processes are available for deposition of TiO_2 -CuO mixed metal thin film, such as sol gel process, RF sputtering, pulse laser deposition (PLD), molecular beam epitaxy (MBE), metal organic chemical vapor deposition (MOCVD) etc. Sol gel process is very efficient by virtue of being low cost, room temperature operation and simplicity. The next challenge is to design the most efficient sensor based systems. In literature different technologies are available to design such system like RFID [1.11-1.14], Internet of things (IOT) [1.15-1.18] and many more.

Increase in the worldwide population combined with the rise in per capita consumption of modern man has led to increased demand for food. To meet the growing demands and to feed the masses, more agricultural land is required. This has led to increased pressure on existing farmlands (which are being harvested multiple times in a year) as well as necessitated the acquisition of more land for agriculture. But an increased understanding of the adverse effects of deforestation has led man to think of alternative ways to optimize land use in agriculture. One such solution is vertical farming. This technique involves growing crops in a vertically stacked manner in an indoor controlled environment. Vertical farming is environment friendly and pesticide free. But this technique is highly critical as it requires constant monitoring of the ambient parameters. Vertical farming is usually practiced in large warehouses which can be several storey's tall. The sunlight is replaced by LED lights. The controlling parameters for vertical farming are mainly ambient light, ambient temperature, soil moisture and humidity. Several automation techniques have been previously suggested for optimizing resource use, such as accommodation of actuation by automated irrigation systems [1.16] [1.19] but wireless monitoring using IoT in the field of vertical agriculture has not been previously suggested. The ambient parameters must be monitored for each stack along the vertical columns. This requires a set of sensors for each vertical stack. The large amounts of data generated by these sensors need an efficient data management system. Using the Internet of Things (IoT), we can efficiently manage the sensor data, identify redundant sensor readings and visualize it with the help of web based applications [1.15][1.20]. Thus, a convenient IoT based system may be developed for vertical farming.

1.2 Objective:

The objective of the research are to develop heterojunction tungsten oxide (WO_3), mixed metal oxide TiO_2-CuO conductometric gas sensor using sol gel method and study its sensing characteristics such as sensitivity, selectivity, response time & recovery time in presence of ethanol vapour and hydrogen gas respectively. And also application of the sensor with IOT technology in agriculture. Characterization of the deposited film was also carried out. A detail study of sol gel process gives basic concepts of material processing and its features as sensor. Then material preparation by sol gel process and fabrication of thin film sensor on Si wafer has been carried out. Then characterization parameters (sensitivity, selectivity, response time, recovery time, stability) of the senor are determined from experimental result.

For smart monitoring of the ambient parameters in vertical farming can improve the productivity and quality of the crops. A system has been proposed to develop sensor arrays that can measure the ambient parameters and upload the data onto the ThinkSpeak Cloud, using the Intel Edison wireless module. The web-based application can be used to analyze and monitor the light, temperature, humidity and soil moisture of the vertical farming stacks. Using the Virtuino app, SMS can be sent if the parameters fall below a threshold value.

1.3 Thesis Organization

The thesis consists of six chapters & is presented as follows

Chapter: I

Chapter 1 Gives basic introduction about metaloxide gas sensor and its parameters & author motivation for performing this work. And also the application of different sensors with IoT in the field of vertical farming agricultural area.

Chapter: II

In this chapter it describes the literature review on various aspect of gas sensing. It describes different types of metal oxide gas sensor available in literature (resistive, homojunction, heterojunction, schottky and mixed metal oxide type gas sensors), their construction principle (receptor function and transducer function), limitations (high operational temperature, low selectivity, low sensitivity) & basic characteristics (response sensitivity, response time, recovery time, selectivity, stability). Then it describes different process used to fabricate these types of metal oxide semiconductor mainly focuses on thin film technique and their pros and cons. Next it presented the different volatile organic compound (as ethanol is one of volatile compound) sensors, a study of different material based sensor with their performance (sensitivity).

Chapter : III

In this chapter, It have been proposed and experimentally evaluated the feasibility of incremental frequency change due to change in contact gas percentage, as a sensing parameter for WO_3 based thin film ethanol detector. In the present work, an economic but accurate ethanol detection system has been realized along with a signal conditioning circuit where a timing resistance of a 555 timer is constituted by a WO_3 based thin film sensor. The incremental resistance change due to the variation of gas concentration results in the change in frequency of the astable multivibrator. Finally, by measuring the frequency using an oscillator, the ethanol percentage can be estimated. The whole system is simple and can be realized with only a few hardware components. Further, accuracy has been enhanced using the Pd and Pt modified WO_3 based thin film sensor.

Chapter: IV

In this chapter, it have been shown that high response Pd modified TiO_2-CuO thin film hydrogen sensors have been prepared by using sol-gel process. Prepared thin film was characterized by field emission scanning electron microscope (FESEM). Sensitivity of hydrogen sensors was observed at operating temperature 50^0C-250^0C and different gas concentrations (3000 ppm). It has been observed that Pd-doped thin film sensors have better responsivity in comparison with the undoped thin film sensors.

Chapter:V

In this chapter a system has been proposed to develop sensor arrays that can measure the ambient parameters and upload the data onto the ThinkSpeak Cloud, using the Intel Edison wireless module. Vertical farming is an unconventional farming technique that has gained relevance in recent years, as existing agricultural lands fail to meet the needs of the growing population. Smart monitoring of the ambient parameters in vertical farming can improve the productivity and quality of the crops. The web-based application can be used to analyze and monitor the light, temperature, humidity and soil moisture of the vertical farming stacks. Using the Virtuino app, SMS can be sent if the parameters fall below a threshold value.

Chapter: VI

Presents conclusion of this thesis & suggest future work. In the conclusion it focuses on the performance of ethanol and hydrogen sensor in terms of its characteristics like response time, recovery time. Then improvement techniques of the performance of sensor are described. Mixed metal oxides and deposition of different metals (Pd, Pt, Fe etc) are two best way to improve the performance of the gas sensor. And also application of the sensor with IOT technology in agriculture.

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CHAPTER II

BASIC OF MOS GAS SENSORS AND IOT BASED SYSTEMS

2.1 Introduction

Different types of metaloxide gas sensors, their fundamental characteristics, operational principle & limitations have been described in this chapter. The size of devices reduced drastically and different types of devices have been manufactured with technological advancement. Different kinds of process have been introduced in designing gas sensors. Different types of conduction process for different modes of gas sensors have been resulted. These all points are described in the following section along with advantages and disadvantages of metal oxide gas sensors. Then an overview of processes available to prepare sensor material has been described. Deposition techniques are also modernized with technological advancement. So advanced deposition techniques are presented mainly focusing on sol gel process. Hydrogen is a flammable gas. So a brief study of different metal oxide gas sensor focusing on hydrogen sensor with metal oxide semiconductor material and their sensitivity , selectivity, response time, effect of doping etc.

2.2 Different metal oxide gas sensor

From the last few decades different types of metal oxide gas sensors have been designed. Metal oxide gas sensors are solid state gas sensor. A wide overview of these types of gas sensors are described in this section. Basic characterization parameter of metal oxide gas sensors are presented. The sensor conductivity change with the interaction between gaseous molecule and the sensor. Hence this construction principle and limitations of metal oxide semiconductor gas sensors are also described in this section.

2.2.1 Types of MOS gas sensor

There are various structures of metal oxide gas sensors available. Few important structures are described below:

Resistive Type: At a fixed temperature charge transfer occurs during chemisorptions & catalytic reaction at the surface and at grain boundaries of sensor material by the interaction with target gas. Advantage is ease of fabrication & direct measurement capability. Resistance is measured between two contacts place on the top of sensing material which is deposited on a non-conducting material like glass, alumina, SiO_2 etc.

Schottky Type: Schottky junction made by catalytic noble metals with semiconducting metal oxides. Catalytic metal electrode using contacts like Pd, Pt, Rh etc a schottky type metal oxide gas sensor can be formed ,it shows improvement in response magnitude, response time. Reducing gas like hydrogen or ethanol are present which containing molecules after chemisorption on metal electrode atomic H_2 produced. This will diffuses through metal/metal oxide junction and reduces the catalytic metal work function which change schottky energy barrier. Thus change in I-V/C-V characteristics can be observed [2.1].

Homo-junction Type: There are various types of metal oxide semiconductors showing 'n' type or 'p' type conductivity. Chance to be Available of 'n' type conductive metal oxide semiconductors (like SnO_2, TiO_2, WO_3) are more than metal oxide semiconductors with 'p' type conductivity like CuO, NiO. Hence the fabrication of semiconducting p-n homo-junction can be formed. A p-n ZnO homojunction metal oxide gas sensor can be formed to sense the H_2 gas [2.2][2.19][2.20[2.28].

Heterojunction Type: Using two different material like ZnO(n)/CuO(p) a heterojunction metal oxide gas sensor can be formed. It has been used for CO detection[2.3][2.20], H_2S & ethanol detection [2.4][2.27].Besides ZnO(n)/Si(p) heterojunction sensor has been implemented as H_2 sensor and methane gas sensor[2.5].

Mixed Metal Oxide Type: Electronic structure of both mixing material modifies by mixed metal oxide. Accordingly bulk and surface properties changes. Transport properties will change, bulk properties like a band gap, Fermi level position and at the surface grain size, grain boundary also change. Hence overall gas sensing properties enhances. Some example in literature TiO_2-CuO, SnO_2 – TiO_2, SnO_2– WO_3, TiO_2 – WO_3 [2.7-2.10][2.25].

2.2.2 Construction principle of MOS gas sensor

According to the principle of Conductometric metal oxide gas sensors are constructed by two key functions:

- Receptor Function
- Transducer Function

Simultaneously the grain size, porosity & thickness of metal oxide films, incorporation noble metal as electrode contact on metal oxide or dispersion of metal oxide surface plays very important role. In general conductometric chemical gas sensor first recognizes a chemical substance (receptor function) then transduces chemical signal into aout put electrical signal (transducer function).

Transducer Function : It is related to the ability to transport electrons through grain boundaries. In metal oxide gas sensor, the gas sensing reaction takes place at the surface of the individual particles and at grain boundaries. Electron (charge particle) conducts through different grains. The deposited film microstructure (i.e. particle size and film porosity) [2.10], charge transport hence magnitude of conductivity change depend on the ratio between particle size and Debye Length(Distance over which charge separation occur in semiconductor). If grain size>Debye Length then depletion of the space charge region between grain boundaries control the conductivity variation. On the other hand if grain sizeis less than Debye Length then depletion of the entire particle occur and band bending not arises. This situation results in high conductivity change when exposed to target gas. Thus nano-material particle (<10nm) results large surface area and high sensitivity.

Receptor Function: Various interactions depends between the surface and target gas such as adsorption, ion exchange or electrochemical reaction. Oxygen from air directly adsorbed on the oxide grains and produces negatively charge ions. Hence producing surface space charge layer depleted of electrons (space charge layer thickness 'L') which causes band bending and thickness of the space charge layer also decreases because reducing gas inject electrons to the conduction band of the sensing material [2.8].On the other side for oxidizing gases the conductivity decreases as oxidizing gases extract electrons .The mobility of the carrier plays an important role because it provides the proportionality constant of the change of electrical conductivity when number of main carrier count changes as a result of gas solid interactions. WO_3 and TiO_2 film have very small electron mobility (high resistivity) which ranges from .03 to .2 cm2v-1s-1 [2.9].

The Metal Oxide gas Sensor follows some basic mechanism during gas sensing like (a) surface reaction with adsorbed gases, (b) Ion exchange, (c) Direct gas adsorption. The sensor characteristics will vary depending on whether the sensor material is 'n' or 'p' type and whether the interfering gases are reducing / oxidizing. As for case ZnO ('n' type) sensor material and reducing gas (hydrogen gas) the gas will react with oxygen ions to form neutral molecules leading to electron transfer to sensor material and consequently decrease the resistance.

Oxygen molecules from air adsorb onto the surface of metal oxide layer to form O_2 -, O- and O_2- ions by extracting electrons from conduction band depending on temperature& type of metal oxide ['n'/'p' type]. The oxygen adsorbates play a vital role to detect gaseous/vapour species. It has been proved [2.11] by TRD,FTIR and ESR techniques that dominant oxygen species are

Molecular (O_2-) below 150^0C

Atomic (O-) between 150 to 300^0C

Atomic (O_2-) above 300^0C

The oxygen adsorption can be described by the following rate equation:

O_2 (g) ⟶ O_2(ads) (2.1)

$e^- + O_2\ (ads) \longrightarrow O_2^-\ (ads)$ (2.2)

$2e^- + O_2\ (ads) \longrightarrow 2O^-\ (ads)$ (2.3)

$e^- + O^-\ (ads) \longrightarrow O2^-\ (ads)$ (2.4)

All these reactions are controlled by different reactive constants. After application of target gas the following reactions will take place.

$X + O_2^-\ (ads) \longrightarrow XO_2(g) + e^-$ (2.5)

$X + O^-\ (ads) \longrightarrow XO\ (g) + e$ (2.6)

$X + O_2^-\ (ads) \longrightarrow XO_2\ (gas) + 2e^-$ (2.7)

Thus electrons are transferred to the surface of n type semiconductor and then ionize the oxygen adsorbates to form oxygen ions. As a result a –ve charge is developed at the surface, the surface layer depleted of electrons and depletion layer created [2.12]. Now width of the depletion layer decreases as reducing gas transferred electron to conduction band, hence the conductivity changes accordingly.

In case of single crystalline structure, the surface belongs to an idle bulk material without grain boundaries; the influence of depletion layer plays very little importance in conduction process through surface. But in case of polycrystalline film, each interface between grains gives rise to a band bending. At inter-granular contact, the conduction is restricted by the schottky potential barrier due to depletion layer and electrons are required to overcome the energy barrier eVs. Now change in barrier height causes change in the electrical resistance of the material in presence of gaseous atmosphere [2.13].

Importance of dimension in gas sensing: Nanomaterials are having at least one of their dimensions less than 100nm. Besides reducing further dimension in other side of a bulk material, we get 2D nanolayer, 1D nanowire, 0D nano cluster [2.14]. Most of atoms are now surface atom thus increasing effective number of sites available for reaction. Increase surface area to volume ratio with decrease in grain size plays key role in gas sensing mechanism. As the grain size decreases it becomes comparable with depletion layer depth (Debye Length). The grain diameter is normally same as Debye length. When grain size is large enough with respect to Debye length then surface reaction does not affect the bulk region. The surface charge carrier density

$n_s = n_b \exp(- q^*Vs/KT)$. (2.8)

Where n_b = concentration of free charge carrier

qVs = Activation energy

T = temperature in K

K= Boltzman constant

Now when grain size is comparable to the depth of bulk region then activation energy

$$\Delta E \approx KT\left(\frac{D}{4\lambda}\right) \qquad (2.9)$$

Where D = grain diameter

λ = depth of depletion width

If ΔE is comparable to the thermal energy then electron concentration will occur in the grain & leads to flat band case. For grain size lower than 10nm complete depletion of charge carrier occurs inside the grain & a flat band occur in a wide range of temperature. Moreover the adsorption process occurs in metal oxide semiconductor gas sensor. Higher surface to volume ratio favors gas adsorption (change in conductivity), decrease response time & increase sensitivity.

2.2.3 Basic characteristics of metal oxide semiconductor gas sensor

The nature of sensor material ('n' or 'p' type semiconductor metal oxide) and the target gas (oxidizing or reducing) governs the increase or decrease in the electrical resistance. Generally the electrical resistance of a conductometric metal oxide gas sensor changes upon exposure to the molecules of the target gas. For an 'n' type semiconductor material exposed to reducing gases, the resistance decreases alternatively exposure to the oxidizing gas results increase in resistance. The variation of resistance of a sensor with time on exposure and withdrawal of the target gas is depicted following curve shown in Figure 2.1.

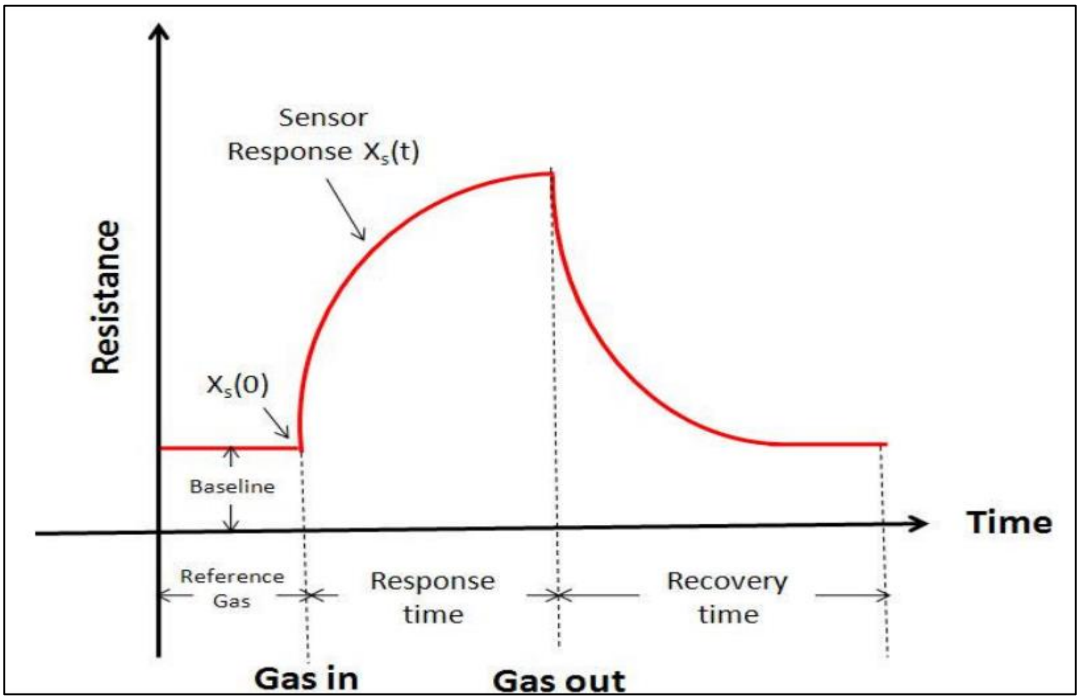

Fig. 2.1 Response Curve(Source : www.shodhganga.inflibnet.ac.in)

The figure shows initially the sensor is in reference gas. The resistance across the sensor contact is fixed Xs(O). Then odorant is applied and resistance across the sensor performance of a gas sensor is characterized by the following five parameters:

- Sensitivity or response amplitude
- Response Time
- Recovery Time
- Selectivity
- Stability

Brief descriptions of these parameters are as follows:

- **Sensitivity:** The ratio of the change in the electrical resistance in the air and test gas Δ R= Ra – Rg , to its resistance in the dry air Ra gives sensitivity for 'n' type metal oxide semiconductor. In case of 'p' type metal oxide semiconductor the sensitivity is defined as the ratio of the change in the electrical resistance in the test gar and air, Δ R= Rg –Ra to its resistance in the dry air (Ra).

$$S = \frac{\Delta R}{Ra} \tag{2.10}$$

Sensitivity is often used to indicate the response magnitude. However, in true sense the sensitivity of a gas sensor is defined as the derivative of the response to the gas concentration.

- **Response Time:** This is the time interval over which resistance of the sensor material attains a fixed percentage (usually 90%) of the final value when the sensor is exposed to the full scale concentration of the gas. It is usually expressed as T90, T80 etc. A T80 of 50s means that the sensor exhibits 80% of saturation value of resistance in 50s.
- **Recovery Time:** It is time interval over which sensor resistance reduces to 10% of the saturation value when the sensor is exposed to the full scale concentration of the gas then placed in the clean air. A sensor should have small recovery time so that it can be used over and over again.
- **Selectivity:** Most of the chemiresistive sensors show high value of sensitivity to many gases under similar operating conditions. Thus selectivity of a sensor towards target gas is expressed in terms of dimension that compares the concentration of the corresponding interfering gas that produces same sensor signal. It is expressed as

Selectivity=(Sensitivity of the sensor for interfacing gas/Sensitivity towards desired gas).

- **Stability:** The ability of a sensor to maintain its properties when operated continuously for long durations is called its stability. Good sensors have long term stability that last up to several years without showing a drift in sensor performance.

2.2.4 Recent Development in the Sensor Field

In literature many types of gas sensors are developed using different types sensing materials and methods. These gas sensors can be classified as solid electrolyte, infrared absorption, electrochemical, catalytic combustion, thermal conductive and semiconductor metal oxide type sensors [2.44]. Among these gas sensors semiconductor metal oxide sensors are smaller size, cheap, repeatable and low power-consuming. The 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 [2.45]. The electrochemical reactions between the target gas and the surface of the semiconductor metal oxide 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 [2.41-2.43]. The response magnitude of the sensing device is changed largely due to these additives. High crystalline structure, doping of different noble materials and easy production rate increase the demand of research to develop different nanoparticle based semiconductor metal oxide gas sensors 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 [2.26]. So different sensors are produced which are commercially available like electrochemical, semiconductor, thermoelectric, metallic, optical and acoustic etc. In literature the mostly studied ethanol sensors are based on TiO_2 , ZnO, WO_3 based semiconductor metal oxide structures. These structures are different types like thin film, nanorod, nanotube, nanofiber and many more. 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., [2.44] 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. [2.45]. 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 semiconductor metal oxide 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 [2.25]. 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 $BaTiO_3/CuO/La_2O_3$ [2.18]. 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, nano rod, nano flower, 1D, 2D, heterostructures and many more. Thin film WO_3 for LPG detection is carried out in, flower like WO_3 by CVD process fabricated in [2.26] for detection of butaol. Further WO_3

nanoplates and WO_3 spheres are also fabricated and investigated for detection ethaylacetate, methanol and ethanol [2.46]. In literature many processes have been used to synthesize WO_3 like thermal evaporation [2.47], chemical vapor deposition [2.48], and template assisted growth [2.49], hydrothermal method 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 [2.50], PH value, reaction time can be modulated. The WO_3 material has some inherent advantage over other materials like CuO, Fe_2O_3, In_2O_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 [2.40].

2.3 Study of Different Existing Process to Prepare Sensor Material

The sensor material 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 2.2.2, 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. Deposition techniques are broadly divided according Figure 2.2.

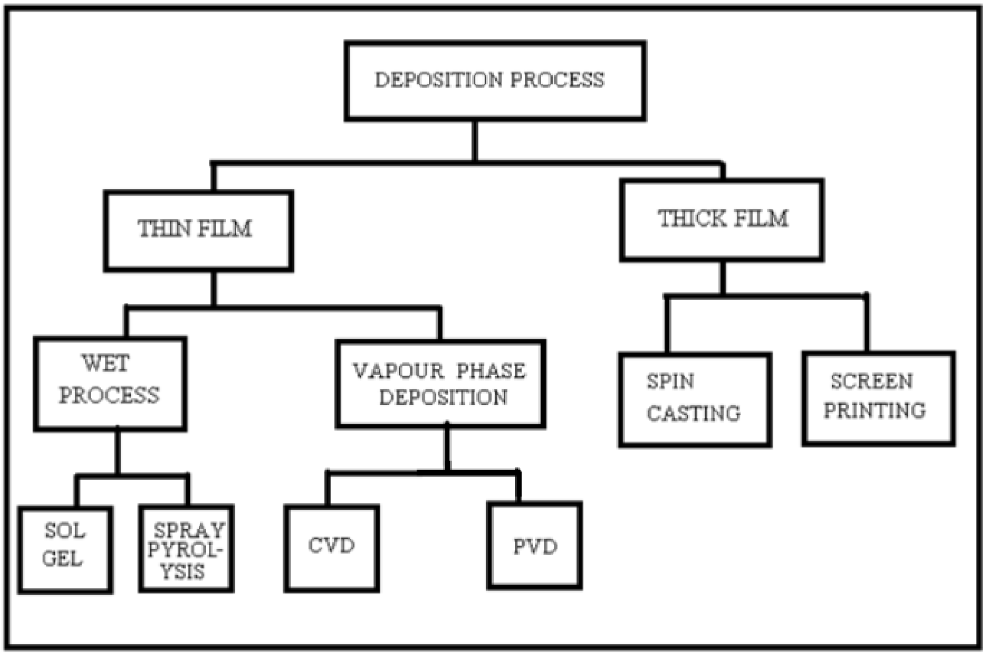

Fig. 2.2 Different types of deposition

Different deposition processes are described below (according the figure): •**Thin Film process:** It is carried out in two different modes wet process and vapour phase deposition.

Sol Gel : 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 oxideinvolves connecting the metal centers with oxo (M-O-M) or hydroxo(M-OHM) bridges therefore generating metal oxo/ metal hydroxo polymers insolution. 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. 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 pictorial view of overall sol gel process is shown in below Figure 2.3

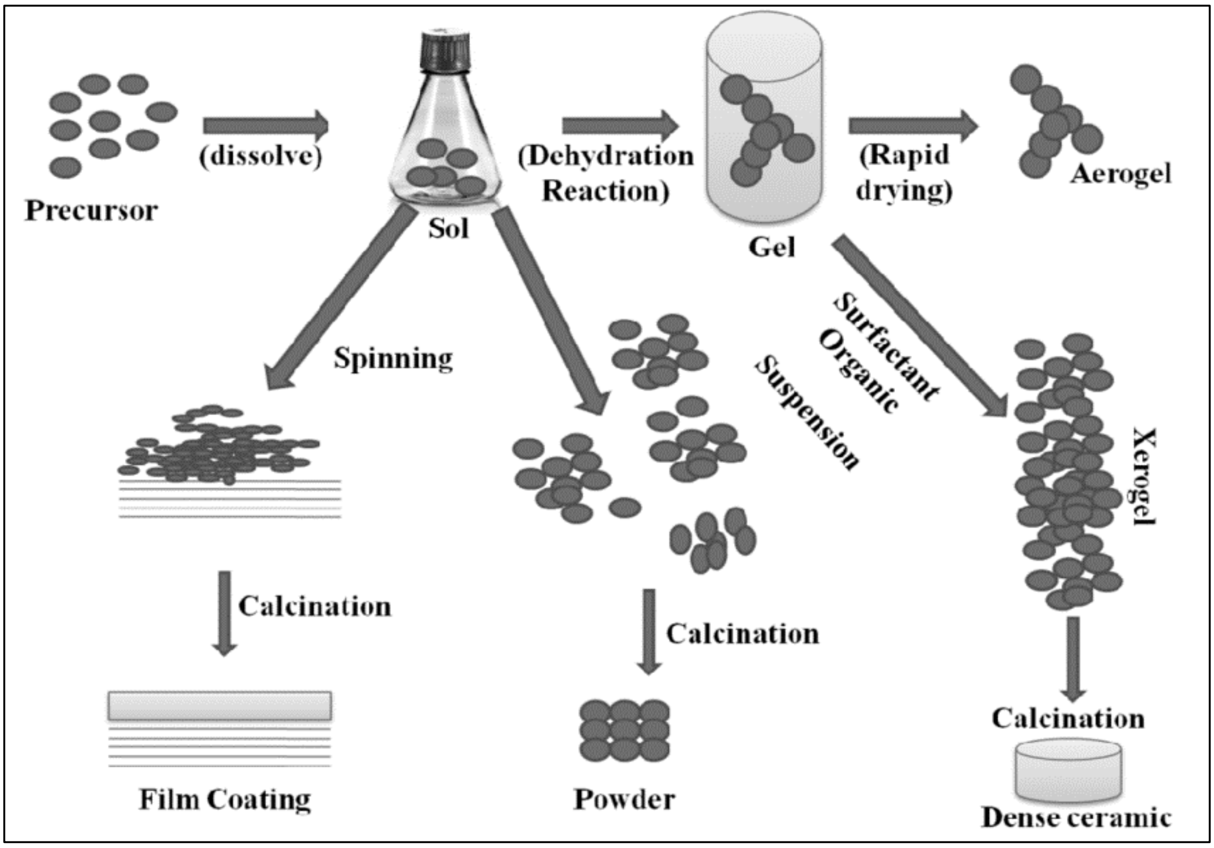

Fig. 2.3. Sol Gel Process

Thin film coating, Aerogel, Xerogel can be formed by sol gel method. In essence; the sol gel process usually consists of four steps:

1. The desired colloidal particles once dispersed in a liquid to form a sol.
2. The deposition of sol solution produces the coatings on the substrates by spraying, dipping or spinning.
3. The particles in sol are polymerized through the removal of the stabilizing components and produce a gel in a state of a continuous network.
4. The final heat treatments pyrolyze the remaining organic or inorganic components and form an amorphous or crystalline coating.

The main advantages of sol gel method are as follows:

1. Cheap and low temperature technique that allows fine control on the product's chemical composition.
2. Can easily shape materials into complex geometries in a gel state.
3. 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.
4. Can produce thin bond coating to provide excellent adhesion between the metallic substrate and the top coat.
5. Can produce thick coating to provide corrosion protection performance.
6. Can have low temperature sintering capability, usually 20^0-600^0C.

The main application areas of sol gel process are as follows:

1. Sol gel derived materials have diverse application in optics, electronics, energy, spaces, bio-sensor, and medicine technology.
2. Other elements (metal, metal oxides) can be easily incorporated into the final product and silica lite sol formed by this method is very stable.
3. It can be used in ceramic manufacturing process, as an investment casting material or as a means of producing very thin films of metal oxides for various processes.

Keeping in mind all the advantages and application area of sol gel technique, it is adopted for deposition of sensor material in this research work. Now the other deposition techniques are briefly described as follows:

Spray Pyrolysis: It involves atomization of a liquid precursor through a series of reactors, where the aerosol droplets undergo evaporation, solution condensation with the droplet, drying, thermolysis of the precipitate particle at higher temperature to form a microporous particle which then sintered to give a dense film.

Chemical Vapour Deposition(CVD): It involves exposing a substrate of choice to a mixture of volatile precursor that react or decompose on the substrate to give the desired product. A wide variety of CVD technique involve Atmospheric pressure CVD, Low Pressure CVD, Plasma Enhanced CVD etc.

Physical Vapour Deposition (PVD): It uses physical means as opposed to chemical vapour deposition techniques. Different PVD techniques are evaporation, sputtering, pulsed laser deposition.

- **Thick Film Process:** With advancements of technology and lowering size of the devices the thick film deposition techniques are mostly replaced by thin film technology.

2.4 Limitation of metal oxide gas sensor

The limitations of existing metal oxide gas sensors are as follows:

Operating Temperature: Almost all sensors that have been investigated till now show response to the target gas at operating temperature 2000C to 5000C. This causes high power consumption, low long term stability. Thus many research works are focused towards improving sensitivity of metal oxide gas sensor at lower temperature. The solutions are like mixed metal oxide semiconductor gas sensor such as SnO_2-ZnO, TiO_2-CuO, Fe_2O_3-ZnO, ZnO-CuO [16-18].

Low Sensitivity: Enhanced to increase sensitivity receptor function can be doped with noble metals such as Platinum (Pt), Gold (Au), Palladium (Pd), Silver (Ag) etc. So these noble metals chemically sensitize the metal oxide surface. Thus chemical reaction at the surface increased enhancing the overall sensitivity of gas sensor. By adding metal additives to the surface the sensitivity can be improved. In this case oxygen molecules from the ambient temperature can be easily dissociated and migrate to the surface of metal oxide.

Low Selectivity: Metal oxide gas sensors are sensitive simultaneously to a wide range of gases. Selectivity can be improved by the influence of operating temperature on the sensitivity of sensor as surface reaction (chemisorptions) is function of temperature. Then the solution is neural network. The idea is inspired from the biological olfactory system. In this system an array of sensors with different functionality is employed and their data are proceed by neural networks to determine the gas concentration.

Hence the researchers are working to overcome these limitations by using different methods like:

1. Mixed Metal Oxide structure
2. Using different noble catalytic metal modifier
3. Using 2D,1D structures of different metals
4. Reduced Graphin Oxide (RGO) based structures.

Thus in this work the first and second methods have been chosen for enhancing purpose of the gas sensor.

2.5 Basic of IOT based sensor system

Internet of Things can be defined as communication between things with each other with the help of internet. The term internet is defined as networks of networks which connect millions of users with internet protocols. Several devices like computer, mobile, watch, personal systems and business organizations are connected to Internet. The meaning of the term Thing is the devices which turn into intelligent objects. It is also a part of all devices of this real world. The Internet of Things can be defined as simply an interaction between the physical and digital worlds. The physical world interacts with digital world using a panel of sensors and actuators.

IoT can also be defined as “An open and comprehensive network of intelligent objects that have the capacity toauto-organize, share information, data and resources, reacting and acting in face of situations and changes in the environment”[2.30][2.38].

Recent advancements in the field of sensors and nanotechnology combined with the advent of Internet of Things (IoT), cloud computing, data mining and improved machine learning algorithms, have resulted in the development of smart systems that can continuously process and analyze sensory data [2.31-2.32]. These smart systems are bringing about a revolution in the areas of communication, transport, healthcare, security, smart cities, agriculture, etc [2.33][2.35-2.37]. A particular area where smart monitoring systems have found wide application is the field of agriculture [2.34][2.39].

2.6 HISTORY OF IOT:

The IoT leads the world to a new era where Things can communicate, transform and compute the information as per the requirements. The term Internet of Things was coined by Kevin Auston, the Executive Director of Auto-ID Labs in MIT in 1999.

TABLE:2.1 Literature Survey of IoT

Year	**Industrial Participation & Involvement**
1999	• The term Internet of Things is coined by Kevin Ashton, Executive Director of the Auto-ID Center in Massachute Institute of Technology (MIT) • Neil Gershenfeld first time spoken about IoT principles in his book titled " When Things Start to Think" • MIT Auto -ID Lab, originally founded by Kevin Ashton, David Brock and Sanjay Sarma in this year. They helped to develop the Electronic Product Code
2000	LG announced its first Internet of refrigeratorplans
2003	RFID is deployed in US Dept of Defence
2005	UN's International Telecommunications Union (ITU) published its first report on the Internet of Things
2008	Recognition by the EU and the First European IoT conference is held. A group of companies launched the IPSO Alliance to promote the use of IP in networks of "Smart Objects" and to enable the Internet of Things. The FCC voted5-0 to approve opening the use of the 'white space' spectrum
2009	The IoT was born according to Cisco's Business Solutions Group
2010	Chinese Premier Wen Jiabao calls the IoT akey industry for China and has plans to make major investments in Internet of Things
2011	IPv6 public launch-The new protocol allows for 340, 282, 366, 920, 938, 463, 463, 374,607, 431,768,211, 456 (2128) addresses

Thus the advancement of IOT based framework increases the scope of the application of this technology in the domain of making different smart systems like sensor based systems for industries, farmers, common man and many more.

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CHAPTER III

WO_3 THIN FILM SENSOR BASED SYSTEM FOR ETHANOL DETECTION

3.1 Introduction:

Gas sensing materials are utilized for the detection of toxic gases as well as volatile organic gases like ethanol, methanol etc. in the industries [3.1-3.3]. WO_3 metal oxide has various advantages such as wide band gap and better optical properties. For this reason, WO_3 metal oxide has recently emerged as the most used material in gas sensing applications [3.4-3.5]. So, the WO_3 metal oxide is an optimal sensing material in the field of gas sensing. To develop the thin film, different methods are used such as RF sputtering, screen printed, CVD (chemical vapor deposition), sol–gel and thermal evaporation [3.6-3.9]. The response magnitude of the sensor may be increased by the introduction of the noble metals like Pd, Nb, Pt, Zn [3.10-3.15][3.23].

Recently, scientists have developed nanomaterial for fabricating nano sensors with high sensitivity and low response time [3.6][3.24]. Now, the aim is to design a sensor with signal conditioning circuits that facilitate calibration, data storing and transmission. Sometimes it is necessary to transmit a signal from measuring environment to a desired location. For long distance transmission, if the signal is in analog form then the accuracy of the transmitted signal may be reduced due to noise. So, we use an on-board analog to digital converter to convert the signal into digital form before transmission, as digital signals have high accuracy, high noise immunity, low output signal power, facility of interfacing, integration and coding.[3.16-3.18]

In this paper, a signal conditioning circuit comprising of a 555 timer based astable multivibrator has been presented for a resistive sensor. The change in frequency is directly proportional to the change in resistance. The duty cycle of the output wave also varies with the change in sensor resistance. Primarily, we have used discrete metallic resistance to convert incremental resistance change into frequency. Experiments have also been conducted to convert the resistive value of the resistive ethanol sensor into frequency. The proposed ethanol sensor is based on WO_3 thin film [3.19].

3.2 Sensor Fabrication

For depositing the WO_3 thin film on the silicon substrate (P-Si), sol–gel process is used because it is a simple and low-cost technique for deposition [3.20][3.22][3.25]. There are different precursors available for depositing the WO_3 thin film, such astungsten hexachloride, tungsten alkoxides, colloidal tungsten acid solution, choro alkoxide solution and perox-poly metallic acid. In this research work, WCl_6 (Tungsten hexachloride) has been used as a precursor to prepare the WO_3 thin film. At first, five gram WCl_6 is dipped in 100 ml isopropanol. Then the mixture is placed in dry air (at room temperature) for 45 hours. After that, the obtained sol is deposited on the front side surface of p-Si substrate by spin coating and dissociated at 100 °C for 10 min. The deposited thin film has a nanostructure as observed in Fig 3.1

Now, our aim is to increase the surface to volume ratio, response magnitude & adsorption rate of the target gas and decrease the operating temperature. We have achieved these characteristics by modifying the surface using noble metals like Palladium (Pd), Platinum (Pt), etc. $PdCl_2$ solution is used to modify the surface of the WO_3 thin film [3.21]. For the preparation of Pd modified WO_3 thin film, WCl_6 chemical compound and $PdCl_2$ aqueous solution of 0.01(M) are prepared. The sensor sample is dipped in the solution for 15 seconds three times and is subjected to calcination at 125^0C for 15 minutes. Initially, $PdCl_2$ easily dissociates into Pd^{++} and Cl^- ions. Then Pd^{++} ion takes two surface electrons from the WO_3 thin film and is converted to Pd. E-beam vacuum evaporation technique is used to deposit Pd-Ag contact on the top of the surface.

The gas sensing property of the fabricated sensor is observed within a gas chamber having inlet and outlet for gases. The sensor behavior has been studied by mixing the ethanol (C_2H_5OH) and nitrogen (N_2) gas in a certain ratio in a mixing chamber which is followed by a mixing coil. The mixing ratio and gas flow are precisely monitored by controlling the mass flow meter (MFM, Alicat Scientifc, M-50SCCM-D) and mass flow controller (MFC, Alicat Scientifc, M-1000SCCM-D).

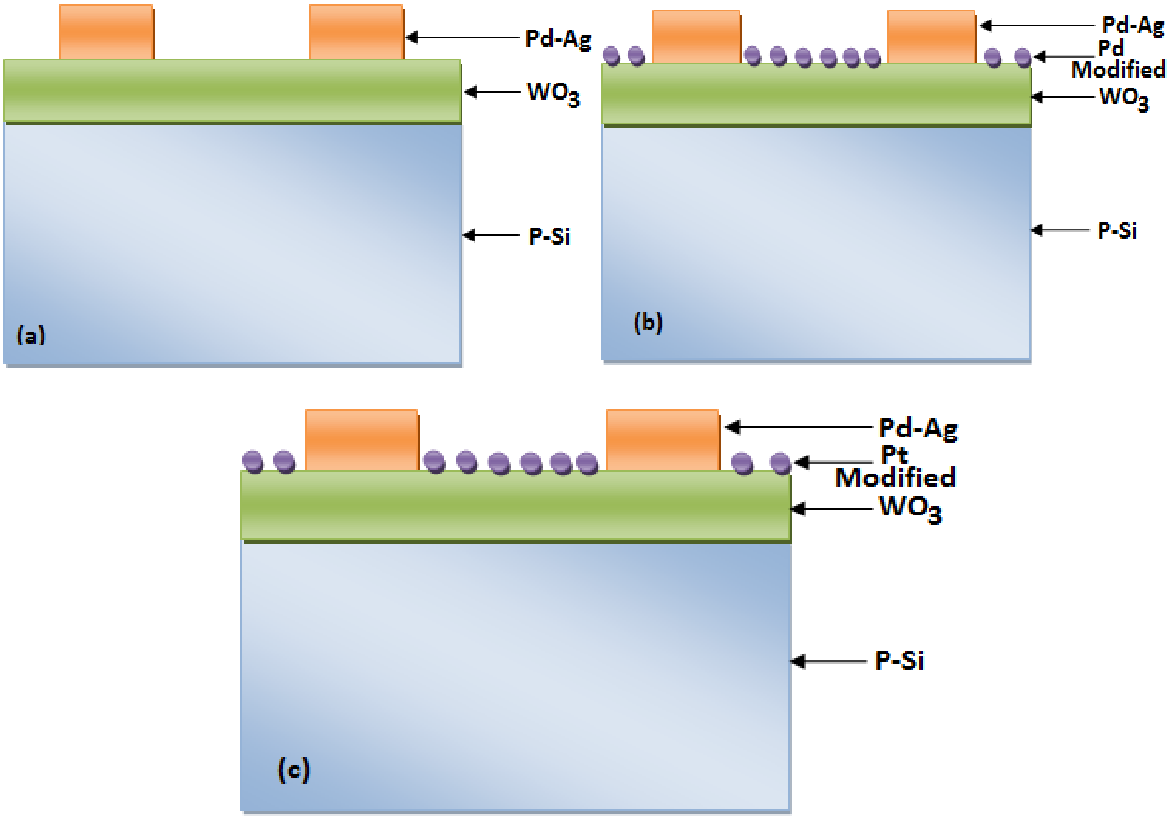


Fig 3.1. (a) WO_3 based Sensor Structure. (b) WO_3 based Pd modified Sensor Structure. (c) WO_3 based Pt modified Sensor Structure.

3.3 Experimental Setup

Figure 3.2 shows the experimental set up for the ethanol vapor sensor. 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) is used to attain the operating temperature of the sensor. Resistive heating coil (≈ 8cm of the constant heating zone, with temperature accuracy ±10C) is used internally in temperature controller for heating purpose. The gas flow and mixing ratio are precisely monitored and controlled with the help of mass flow controller (MFC). The homogeneous mixture carrying the desired percentage of the target vapor is fed into the chamber with a flexible PVC pipe. During testing, the gas pressure on the sensor is maintained at 1atm. An automated data acquisition system is used to measure the change in resistance under various operating temperatures and vapor concentrations. The sensor is connected to a signal conditioning circuit which is a 555 timer based astable multivibrator. The output of the bread board circuit is measured by an oscilloscope.

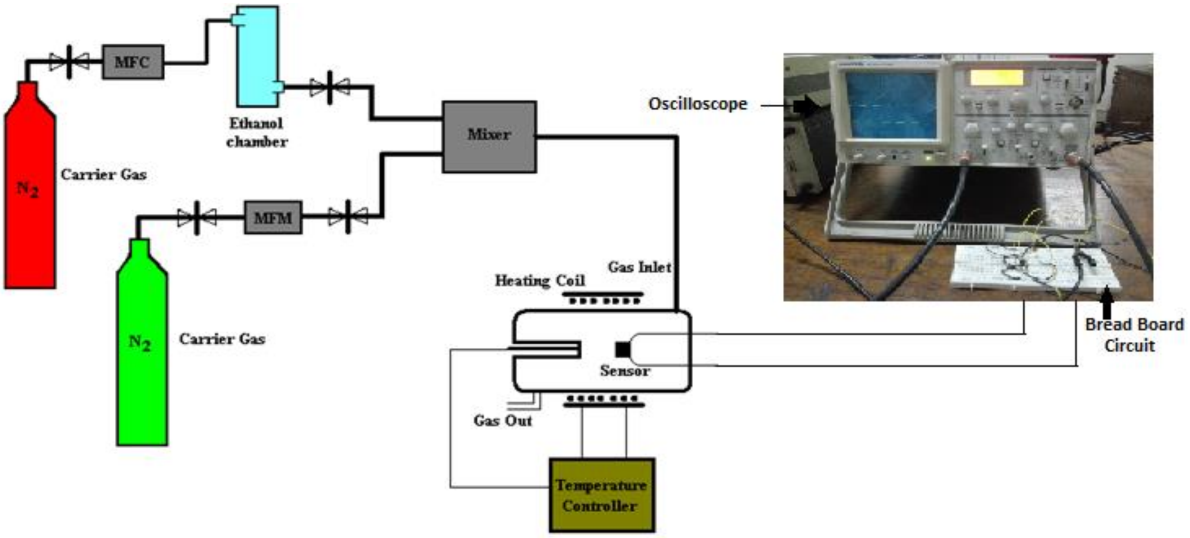


Fig 3.2. Experimental set up of ethanol vapor sensor.

3.4 Design of Signal Conditioning Circuit

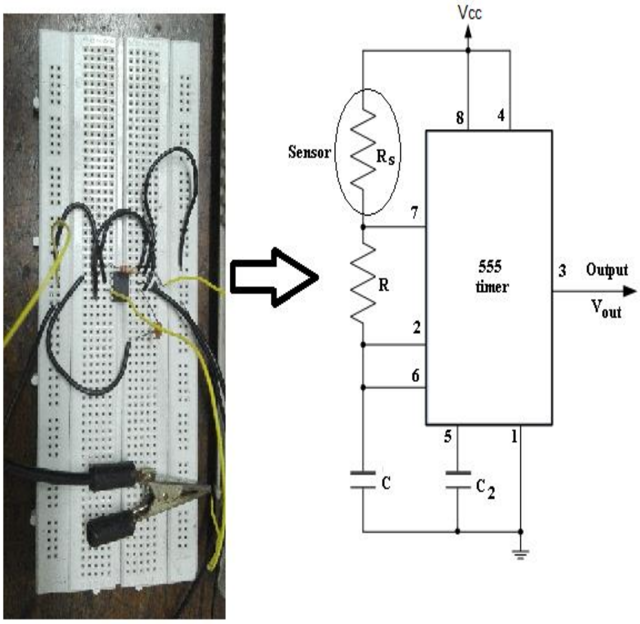


Fig 3.3. 555 timer based multivibrator

Fig. 3.3 shows the signal conditioning circuit (555 timer based astable multivibrator circuit). Pin 5 is the control voltage pin which is not used. So to avoid high frequency noise it is connected to a capacitor C$_2$ whose other end is connected to ground. Here R_S is the resistive ethanol sensor which changes its value with the change of concentration of ethanol. Due to the change in resistance, the frequency of the output signal will change following the designated equation:

$$\Delta f = \frac{\Delta R_S}{0.693C\left(R_S - \Delta R_S + 2R\right)\left(R_S + 2R\right)}$$

$T1$ is the high time of the output wave, $T_1 = 0.693C(R_S + R)$ (3.1)

And $T2$ is the low time,

$$T_2 = 0.693RC \tag{3.2}$$

Time period,

$$T = T_1 + T_2 = 0.693C(R_S + 2R) \tag{3.3}$$

Now with the change in ethanol concentration, the sensor resistance changed to $R'S$

∴ The time period changes to

$$T' = 0.693C(R'_S + 2R) \tag{3.4}$$

The change in time period,

$$\Delta T = \left(T' \sim T\right) = 0.693(R'_S \sim R)C = 0.693\Delta R_S C \tag{3.5}$$

Frequency, $f = \frac{1}{T} = \frac{1}{0.693(R_S + 2R)C}$ (3.6)

Or, $(R_S + 2R) = \frac{1}{0.693Cf}$ (3.7)

Or, $R_S = \frac{1}{0.693Cf} - 2R$ (3.8)

Due to change in resistance, the frequency changes to

$$f' = \frac{1}{T'} = \frac{1}{0.693(R'_S + 2R)C} \tag{3.9}$$

Or, $R'_S = \frac{1}{0.693Cf'} - 2R$ (3.10)

$\therefore$ The change in frequency,

$$\Delta f = (f' \sim f) = \frac{\Delta R_S}{0.693C(R_S - \Delta R_S + 2R)(R_S + 2R)} \qquad (3.11)$$

Here ΔR_S is very small compare to $(R_S + 2R)$. So, we can write

$$(R_S - \Delta R_S + 2R) \approx (R_S + 2R)$$

Now $\Delta f = \Delta R_S \times K$ (3.12)

Where, K is a constant.

We can say from Eq. [13] that change in frequency is directly proportional to the change in sensor resistance.

$$\therefore\ \Delta R_S = (R - R'_S) = \frac{1}{0.693C}\left(\frac{1}{f} - \frac{1}{f'}\right) = \frac{\Delta f}{0.693Cff'} \qquad (3.13)$$

Now we can find the change in resistance with the change in frequency from the oscilloscope.

3.5 Results and Discussion

The sensor morphology have been observed by Scanning Electron Microscopy (SEM) and XRD (X-ray diffraction). Then the relation between the sensor response and response of the signal conditioning circuit have been observed as shown below.

3.5.1 Microstructure Characteristics

The average size of the grown nano crystal was achieved by XRD (X-ray diffraction pattern as shown in Fig. 3.5) results. It is calculated by the Scherer's equation as follows

$$D = \frac{k\lambda}{\beta \cos\theta} \qquad (3.14)$$

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 WO_3, Pd modified WO_3, Pt modified WO_3 are 11.8nm, 6nm and 5.4nm respectively, calcined under 600°C.

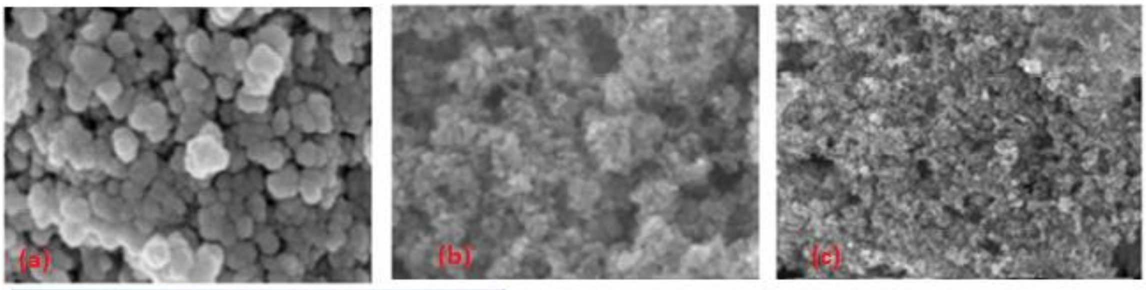


Fig 3.4. (a) SEM of WO_3 (b) SEM of Pd modified WO_3 (c) SEM of Pt modified WO_3

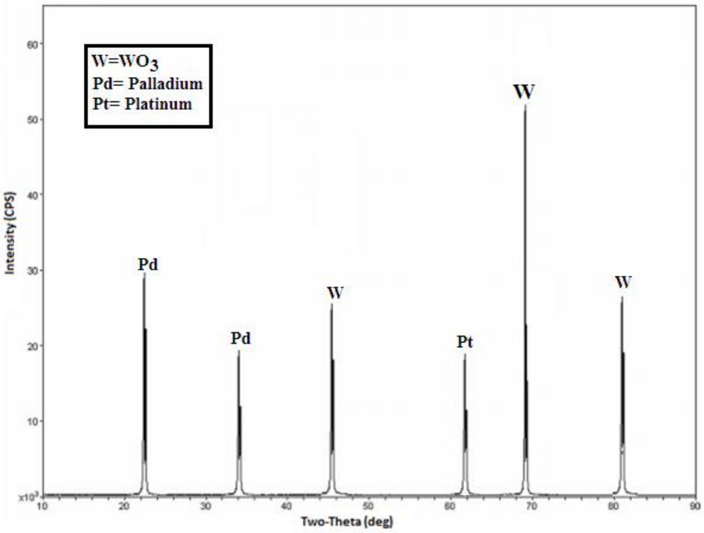


Fig 3.5 XRD pattern of WO3 thin film sensor after modification of Pd

The SEM surface of unmodified WO_3, Pd modified WO_3 and Pt modified WO_3 film is shown in the Fig.3.4. The surface morphology and the grain size were studied from the figure. The average grain size of WO_3 nanoparticle is 70-95 nm.

3.5.2 Sensor Response with different parameter

The sensitivity (S) is defined as the percentage of the resistance deviation at gas exposure from the resistance in N_2.

$$\text{Sensitivity, } S(\%) = \frac{R_a - R_g}{R_a} \times 100\% \qquad (3.15)$$

Where Ra is the sample resistance in N_2 (i.e. at 0% ethanol concentration) and Rg is the sample resistance at a given concentration of the target gas (ethanol). The reducing gas ethanol reacts with oxygen adsorbed on the surface of the sensor rather than the lattice oxygen. The adsorption of the C_2H_5OH vapor on WO_3 surface can take place by the following route:

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

By varying the concentration of the ethanol vapor from 192 ppm to 3117 ppm (0.0192-0.3%), the change in conductivity is measured at fixed operating temperature (300^{0}C for unmodified WO_3, 210^{0}C for Pd modified WO_3 and 170^{0}C for Pt modified WO_3 based sensor) as shown in Fig. 3.7. The conductivity of the sensors increases at presence of target gases as shown in fig. 3.6(a). The sensitivity of the gas sensors is plotted in figure 3.6(b) where the sensitivity increases with the increase of ethanol concentration. To calculate the sensor resistance the frequency values is taken from the oscilloscope directly. Response time and recovery time of the sensor is very important parameters to observe. Response time is the time interval over which resistance of the sensor material attains 90 percentage of the final value when the target gas is on. On the other hand recovery time is the time interval over which sensor resistance reduces to 10 percent of the saturation value when target gas is removed. A small value in response time and recovery time is most desirable in a real-time application.

Table 3.1: Comparison of the Current work with previously reported work.

Tested Samples	**Operating Temperature (^{0}C)**	**Ethanol Concentration Ranges (ppm)**	**Response Time (T_{RES})**			**Recovery Time (T_{REC})**			**Frequency (kHZ)**	**Ref.**
Pt-WO_3	170	500	48	54	68	51	57	72	No resistance to frequency converter circuit used	[3.21]
Pd-WO_3	210	1500	41	48	59	62	68	86		
WO_3	300	2500	32	37	46	71	82	102		
		3500	25	27	33	82	92	115		
		4500	19	21	26	91	102	128		

Pt-WO_3	150	0.05%	45	52	65	47	55	70	0.90-1.20	**This work**
Pd-WO_3	200	0.1%	40	47	50	55	62	78		
WO_3	300	0.15%	35	43	45	60	69	85		
		0.2%	30	37	42	70	75	93		
		0.25%	27	32	37	75	84	102		
		0.3%	22	27	32	82	90	110		

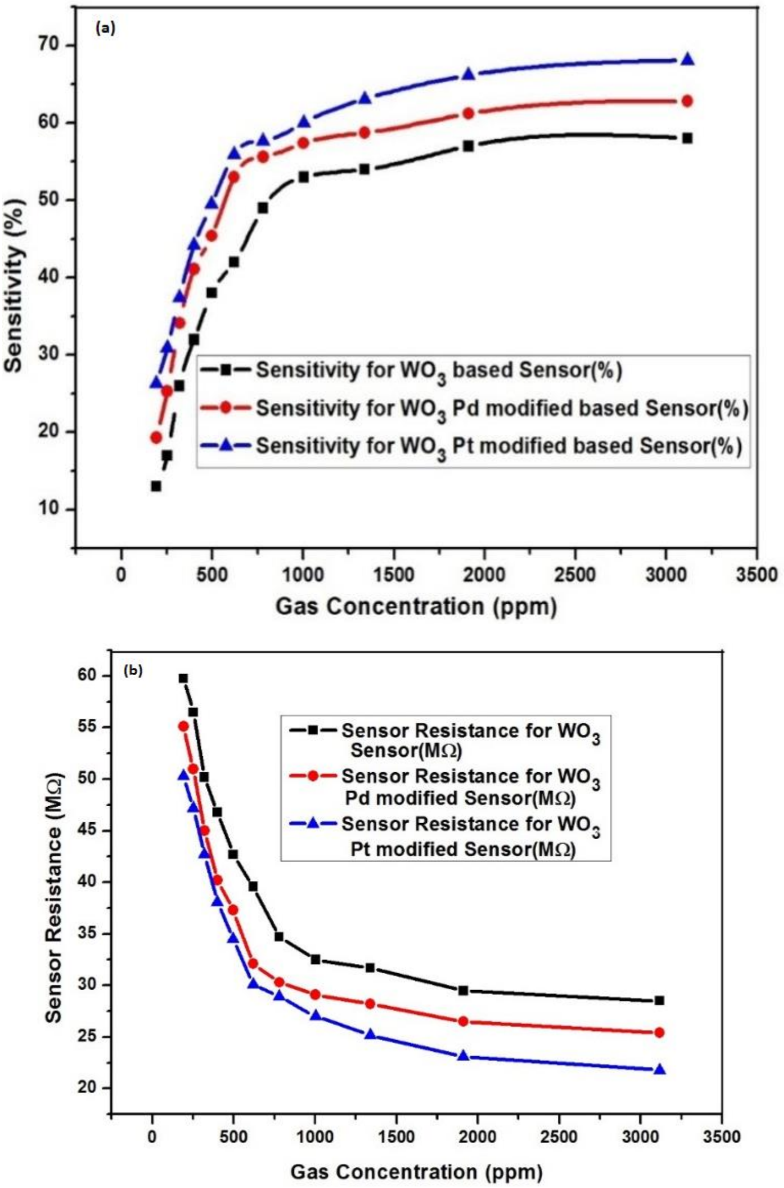


Fig 3.6. (a)-(b) Sensor resistance and Sensitivity as a function of gas concentration.

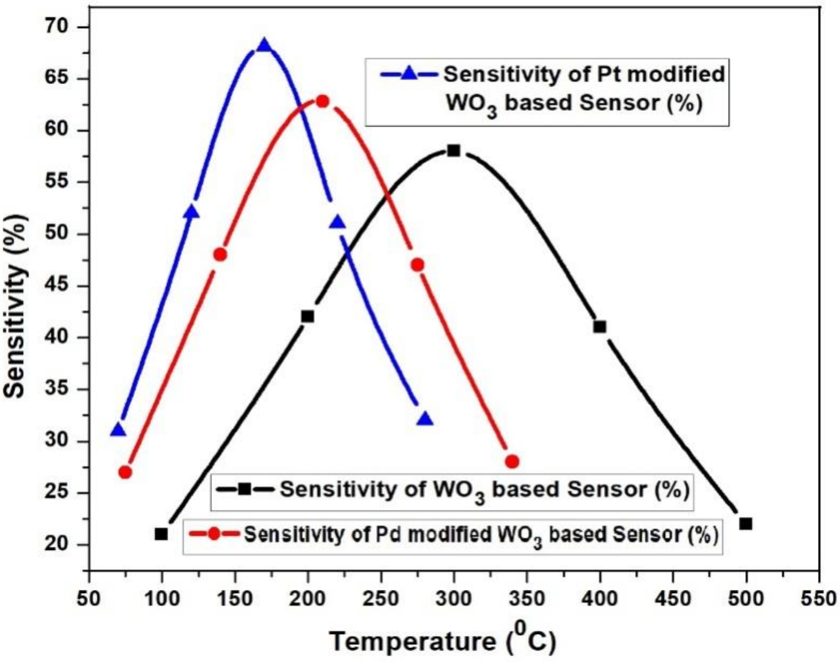
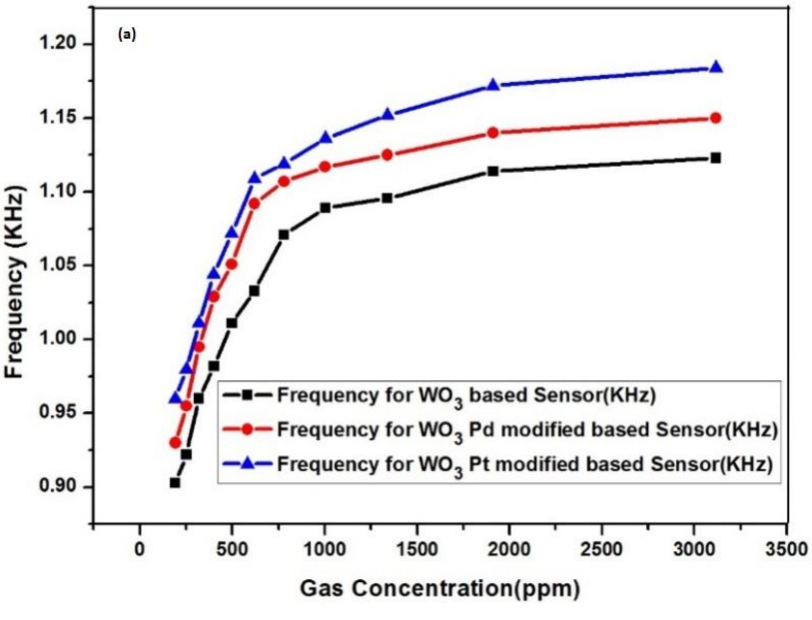


Fig 3.7. Temperature vs Sensitivity curve

The required test circuit for signal conditioning unit has been realized using bread board along with a 555 timer based astable multivibrtator circuit, where the sensor element is designated as a timing resistance as shown in the Fig. 3.3. The sensor is calibrated with a known percentage of the test gas. Finally, the sensor is tested with certain gas percentages, the corresponding resistance values of the sensor are measured and frequency of the astable multivibrator is calculated. The calculated frequencies and the corresponding gas percentages are then plotted on a curve along with the calibration curve. The calibrated curve of the proposed signal conditioning system at different concentrations (ppm) of Ethanol is shown in Fig. 3.8.



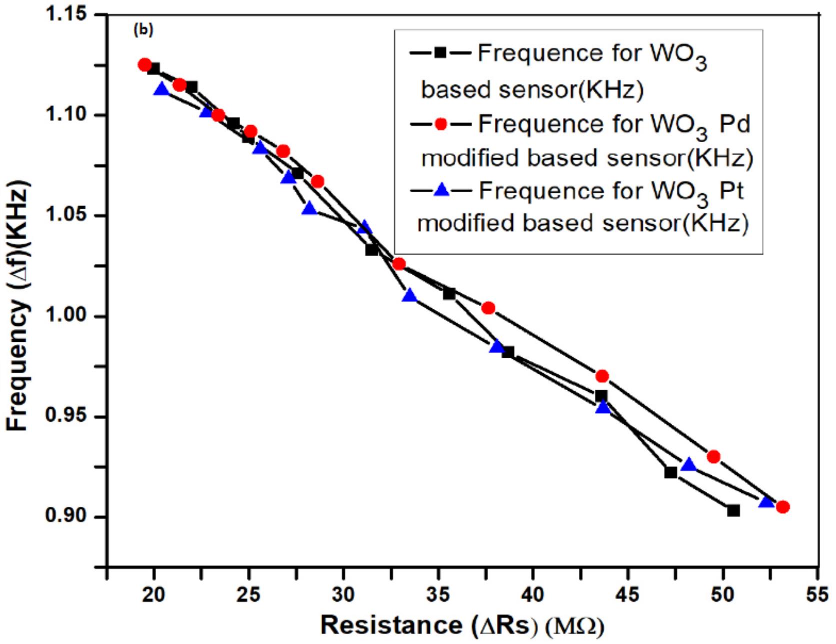


Fig 3.8. (a) Frequency vs gas concentration (b) change in frequency vs change in resistance.

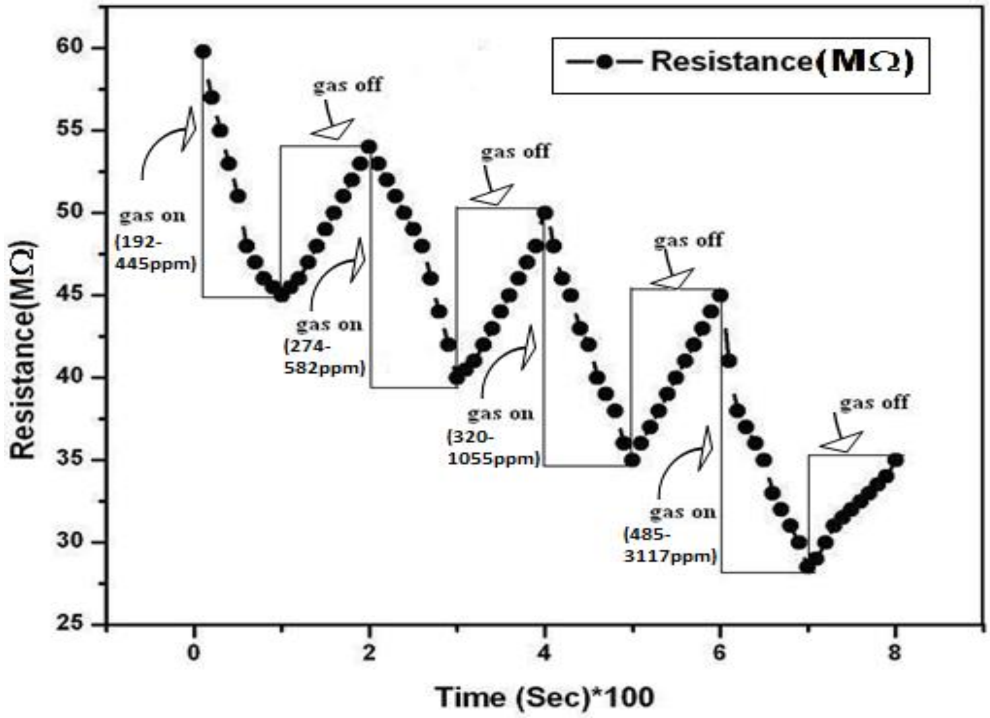


Fig 3.9. The repeatability of WO_3 thin film in presence of ethanol.

It is observed that in the presence of ethanol the sensor resistance decreases. Conversely, if the ethanol supply is cut off, the sensor resistance increases (shown in Fig. 3.9).

The MOX based gas sensors were mainly based on the apparent change of the electrical conductivity resulting from adsorption and desorption of gas molecules on the of gas-sensing materials surface. When n-type metal oxides were exposed to air, oxygen molecules, absorbed on its surface, would generate chemisorbed oxygen species (O_2^{-}, O^{-} , and O_2-) by capturing electrons from its surface and lead to the formation of hole-accumulation layers (HALs) on the surface of materials. The hole- conduction occurred mainly along the near surface HALs, which resulted in the increase of the conductivity. When the gas percentages (%) increases, the reducing gases' molecules preferred to react with the chemisorbed oxygen species and the hole concentration and hole-accumulation layers decreased, principal to the changing of the conductivity.

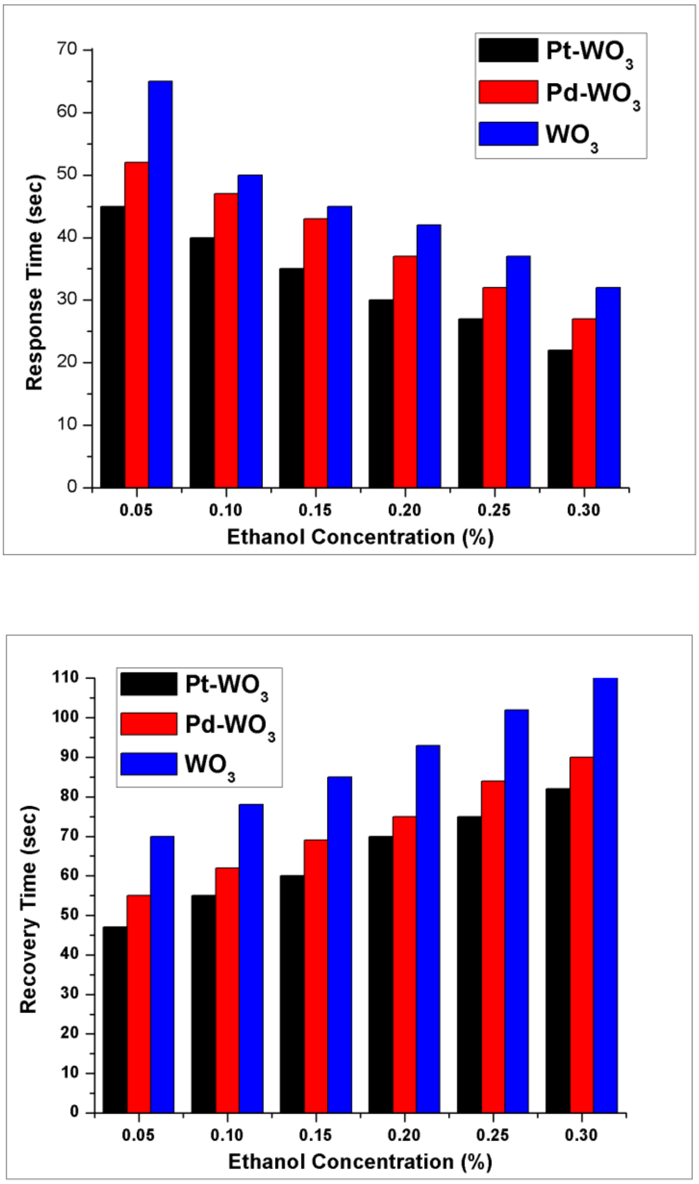


Fig 3.10(a-b). Response time and Recovery time vs ethanol concentration (%).

Fig. 3.10 shows a comparative study of the response and recovery time of Pt, Pd modified and unmodified WO_3 based sensor.

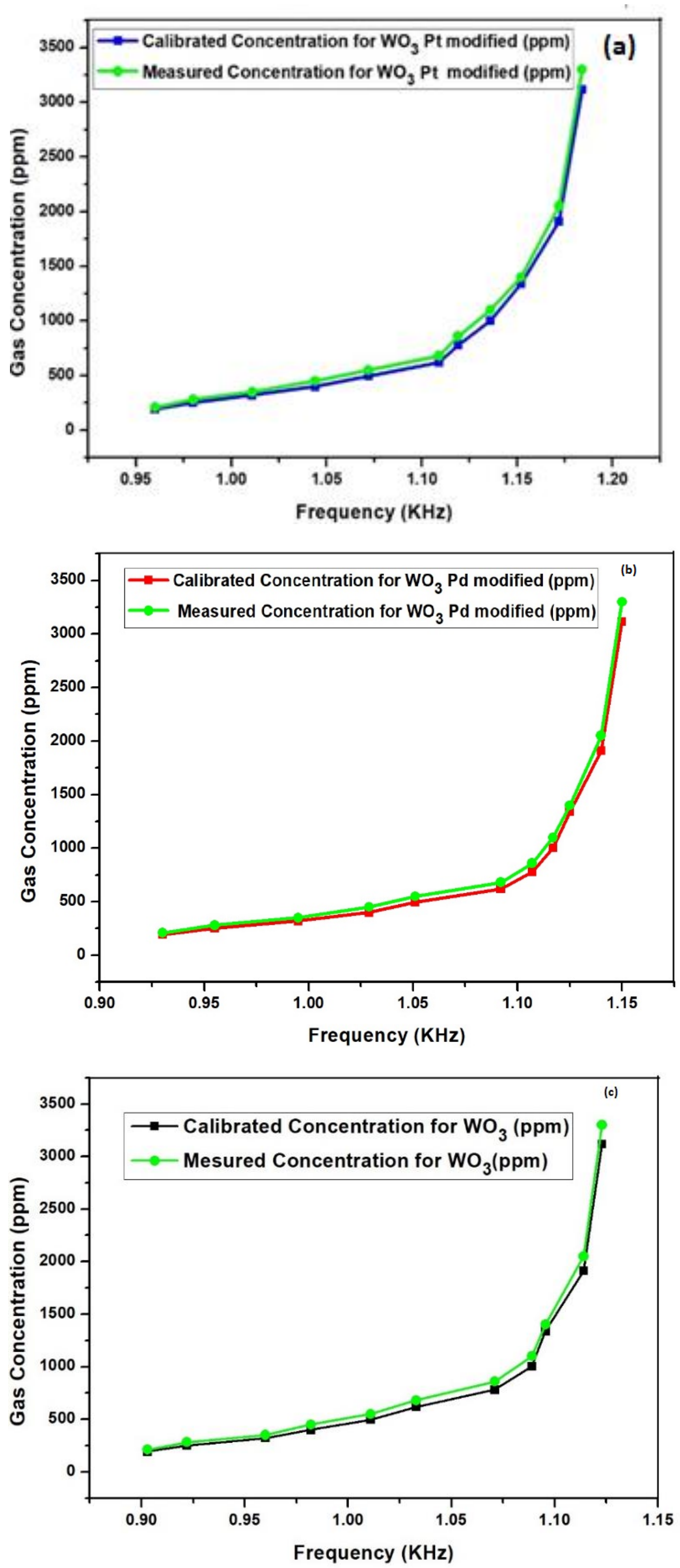


Fig 3.11(a-c). Response curve of the system, comparison of measured values with calibration curve value.

Now we can write

$$\Delta\text{Concentration}=K'\frac{1}{\Delta R_S}=K'\frac{\Delta f}{0.693Cff'} \qquad (3.16)$$

Where K' is constant to be found from calibration curve and then use it in the measurement. It has been observed that the calculated and calibrated results agree with each other as evident from the Fig. 3.11(a-c), justifying the accuracy of the proposed sensor based system. It is evident from the Fig. 8 that Pd modified WO_3 based sensor system is better as compared to unmodified WO_3 based sensor system. Also, Pt modified WO_3 based sensor is better as compared to Pd modified WO_3 based sensor in terms of sensitivity.

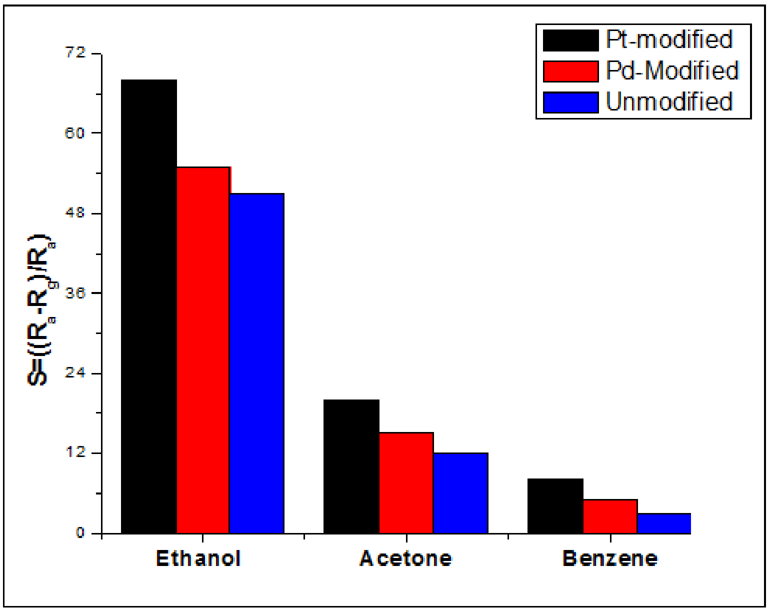


Fig 3.12. Selectivity curve of Pt, Pd and unmodified WO_3 sensor towards 1000 ppm ethanol, acetone and benzene at optimal operating temperature.

Selectivity curve of the different gases with the concentration of 1000 ppm at optimal operating temperature are shown in the Fig.3.12. The figure shows that Pt modified WO_3 thin film based gas sensor have highest selectivity range as compared to the Pd modified and unmodified WO_3 thin film gas sensors, which was helpful for the effective detection of ethanol in multifarious atmosphere.

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CHAPTER IV

FABRICATION PROCESS OF MIXED METAL OXIDES THIN FILM GAS SENSOR FOR DETECTION OF HYDROGEN

4.1 Introduction:

In this chapter work, high response Pd modified TiO_2-CuO thin film hydrogen sensors have been prepared by using sol-gel process. Prepared thin film was characterized by field emission scanning electron microscope (FESEM). Sensitivity of hydrogen sensors was observed at operating temperature 50^0C-250^0C and different gas concentrations (3000 ppm). It has been observed that Pd-doped thin film sensors have better responsivity in comparison with the undoped thin film sensors.

Over the years, the fabrications of low size devices and reliable gas sensors with reduced power consumption have attracted considerable attention [4.1-4.3]. In this substance, several studies have been discussed on hydrogen detection due to safety reasons as an illustration, gas detection in industries, gas detection in food industries, environmental gas detection, gas detection in biomedical and space applications. Hydrogen is an odorless, colorless, non-toxic, non-metallic, highly combustible diatomic and explosive gas. So, it is a major challenge to detect gas efficiently. Over the last few decades, the concentration measurement and detection of hydrogen gas leakage has been done and various approaches proposed to realize hydrogen sensor with effective performance [4.4-4.6]. However, the presently used H_2 sensors have some drawbacks like low response time, recovery time and poor longevity. So there is a requirement of high performance H_2 sensor for different industries. Different metal oxides have been used for sensing material like ZnO, WO_3, CuO, TiO_2, Cr_2O_3, Mn_2O_3, Co_3O_4, NiO, Ta_2O_5, La_2O_3, CeO_2, Nd_2O_3 ,SrO, In_2O_3, V_2O_3, Fe_2O_3, GeO_2, Nb_2O_5, MoO_3, [4.7]. Now-a-days, mixed metal oxides are used for better sensing application. Some nobel metal are used like (Pd, Pt, Au, Ag) to modified the surface of the metal oxides for better sensitivity[4.8-4.10].These metal oxides are useful for the detection of toxic gases like H_2, CO, NO_2, CO_2 etc. Mixed metal oxide based sensor have been widely used for gas detection. Various processes are available for deposition of TiO_2 -CuO mixed metal thin film, such as sol gel process, RF sputtering, pulse laser deposition (PLD), molecular beam epitaxy (MBE), metal organic chemical vapor deposition (MOCVD) etc. Sol gel process is very efficient by virtue of being low cost, room temperature operation and simplicity. In this proposed work, TiO_2-CuO mixed metal oxide thin film has been prepared by the use of sol-gel technique. To enhance the sensitivity of mixed metal oxides we incorporated $PdCl_2$ solution on the top of thin film sensors. We found that, Pd/ TiO_2-CuO thin film sensors obtained better sensitivity in comparison with the undoped thin film sensors. At operating temperature 150^0C, proposed Pd-doped thin film sensors gets high sensitivity as compared to the undoped prepared samples. Now researchers are trying to use different technology like RFID as sensing device to overcome the limitations [4.11-4.17]. RFID provides no line of sight communication, different frequency of applications, cost effective way of implementation of work. However further performance improvement is essential.

4.2. Sensor Fabrication

The gas sensor material is prepared by sol-gel process. The substrate on which the sensor material is placed also plays very important role during sensing behavior. Hence the substrate is prepared before sensor fabrication and it requires the following important steps:

4.2.1 Substrate Preparation

During fabrication of metal oxide semiconductor gas sensor a Silicon wafer has been taken as a substrate. Semiconductor metal oxides powders were coated onto the substrates for gas sensing measurements, which formed thick films of the material on the substrates. In this work, the substrate used was of outer diameter 2 mm, length 4 mm, and thickness 0.5 mm. The unshaped wafer orsubstrate is cut into the desired size according to the lab measurement setup. The shaped substrate was then washed with dilute HCl to dissolve out the surface contaminants. After that the substrates went under a comprehensive ultrasonic cleaning process. This cleaning part (detailed describe in part.4.4) is very important as the semiconducting oxides are sensitive to contaminants, which can affect sensors stability and sensitivity. Then aluminum wire attached by silver paste at the ends of the substrates. The substrates were then annealed at temperature range of 350-650^{0}C.

4.2.2 Substrate verification

Testing of the Silicon wafer (substrate) is very important to determine whether thewafer is ‘n’ type or ‘p’ type. The following instruments are used to carry out the hot probe method. Hot probe method is the simplest process to determine the type of impurity of Si wafer.

1. Heating Probe

2. Voltmeter

In voltmeter positive probe (+ve) is heated and both prove (+ve & -ve) are touched on the substrate (n. b. maintaining a minimum gap between them).

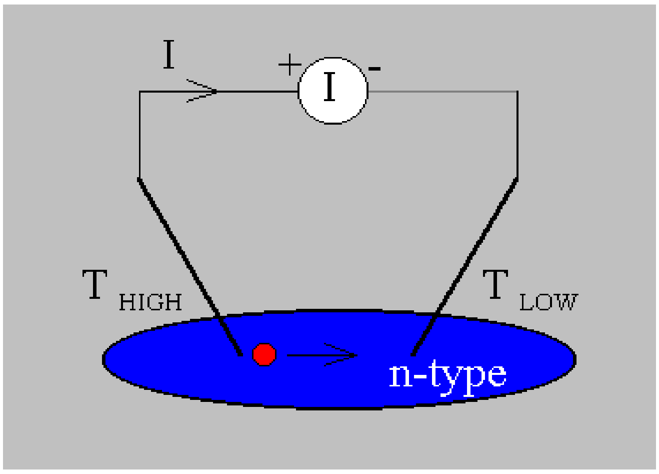


Fig.4.1. Hot probe setup.

It is required to determine the type of the semiconductor whether it is P-type or N-type. This can be done with the help of HOT PROBE METHOD.

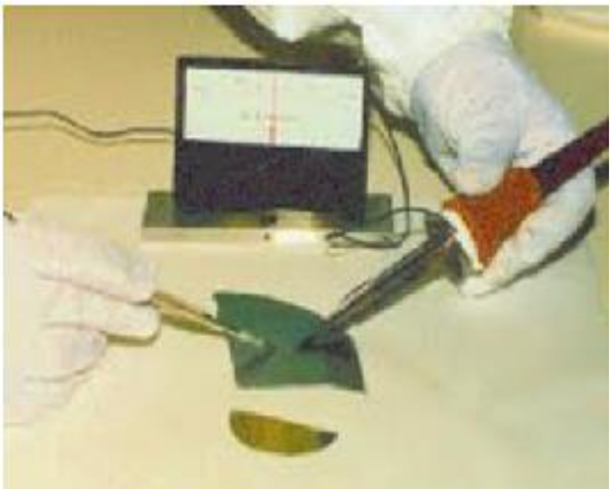


Fig.4.2. Hot probe Method.

A hot probe is a method of determining quickly whether a semiconductor sample is n (negative) type or p (positive) type. A voltmeter is attached to the sample, and a heat source, such as a soldering iron, is placed on one of the leads. The heat source will cause charge carriers (electrons in an n-type, electron holes in a p-type) to move away from the lead. This will cause a voltage difference. For example, if the heat source is placed on the positive lead of a voltmeter attached to an n-type semiconductor, a positive voltage reading will result as the area around the heat source/positive lead becomes positively charged and a negative voltage reading will result in p-type semiconductor.

4.2.3 Substrate Cleaning:

Types of impurities are:

i. Dust
ii. Oil and grease
iii. Inorganic compound
iv. Organic compound
    a) Acidic organic compound
    b) Alkaline organic compound
v. Oxide

Processes of removing impurities:

I. Acid process
II. Dry plasma process

Acid Process:

This process is cheaper and hence used in industries to remove impurities on silicon wafer surface.

Dry Plasma Process:

An electron is directed from cathode to anode and meanwhile a gas is introduced to etch a layer of silicon wafer. This method is costlier.

After removal of impurities the pure silicon wafer becomes hydrophobic in nature.

Cleaning process for different types of impurities is as follows:

For Dust Particles:

Take the sample and trichloroethylene (TCE), boil for 5 minutes and then 3 minutes in ultrasonic cleaner.

For Oil and Grease:

Take sample and acetone, boil for 5 minutes and then 3 minutes in ultrasonic cleaner.

For Inorganic Compound :

Take H_2SO_4 and H_2O_2 with the ratio of 1:1 then wait till the reaction stops and then clean in de-ionized water. This reaction is exothermic in nature.

For Acidic Organic Compounds :

Take H_2O, H_2O_2, NH_4OH with the ratio of 5:1:1 and heat at 70^0C for 10 minutes and then pass it into cold water.

For Alkaline Organic Compounds :

Take H_2O, H_2O_2 and HCL with the ratio of 6:1:1 and heat at 70^0C for 10 minutes and then clean in de-ionized water.

For Oxide :

The sample is dipped in 10% HF for 3 to 4 minutes.

4.2.4 TiO_2 and CuO thin film Preparation

Sol-gel method is a simple and low cost method to prepare TiO_2 thin film by using Tin (IV) tert-butoxide as a precursor. Tin (IV) tert-butoxide was mixed to ethanol and HCl at certain percentage and placed in dry air for 48 hours. After that spin coating technique is used to drop the obtained sol onto the p-si substrate. Initially, the substrate was cleaned and dried at 100oC. The gel film was dehydrated in air at 150^0C for 20 minutes. To get the crystalline film, the dried film was annealed at 500^0C–750^0C for 3 hours.

CuO thin film was prepared by simple and low cost deposition sol-gel process by using copper. The aqueous solution of $CuCl_2.6H_2O$(0.2M) is prepared in cleaned round bottom flask.1ml glacial acetic acid is added to above aqueous solution and heated to 100^0 C with constant stirring. 0.4gm of NaOH above heated solution till pH reaches to 7.the color of the solution turned from light blue to dark blue immediately. The obtained precipitate was dried in air 24 hour; the powder is further used for characterization of CuO nano particles. After that prepared sol was transferred on oxidized Si substrate by spin coating meathod (1200 rpm, duration 10s) and dried at 150^0C for 30 minute. To get the CuO nanocrystalline thin film, the film was again annealed at 350^0C for 1 hour.

4.3 Fabrication Process of the proposed sensor

Fabrication steps of Pd modified thin film sensor for detection of hydrogen is shown in the Fig. 4.3 In step (1), p-Si substrate is taken and cleaned. After cleaning in step (2), by using dip-coating method, prepared TiO_2-CuO thin film is deposited on the p-Si substrate. In step (3), $PdCl_2$ solutions prepared and deposited on the top of TiO_2-CuO layer by spin coating method (1200 rpm and 25 sec). Al metal electrodes is formed in the step (4). In step (5), copper wire is taken for connectivity of the prepared thin film devices.

The device structure is shown in the figure 4.4. In the figure 4.4(a), it has been shown that the unmodified TiO_2-CuO hydrogen sensor structure and in figure 4.4(b), the Pd modified TiO2-CuO hydrogen sensor structure.

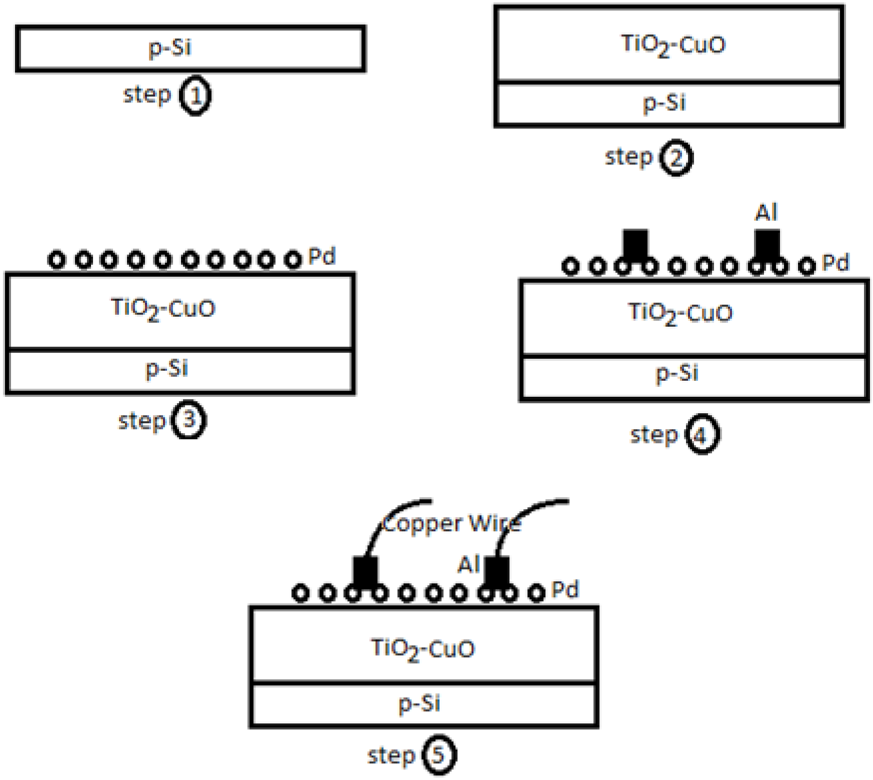


Fig. 4.3 Fabrication steps of prepared thin film sensor.

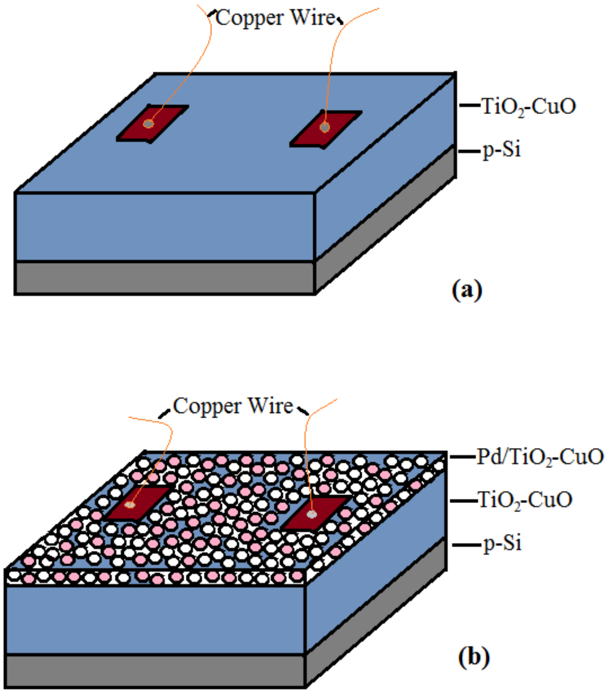


Fig.4.4. (a) TiO_2-CuO/p-Si (b)Pd/TiO_2-CuO/p-Si

4.4 Experimental Details

The experimental setup is shown in Fig. 4.5. and the device structure is shown in Fig. 4.4 Nitrogen has been used as a carrier gas with a mass flow controller (MFC) which controls the gas flow and hydrogen as the target gas with a mass flow meter (MFM) which controls the gas flow. Hydrogen and nitrogen are mixed in the mixing chamber. The electrical behaviour of the thin film sensors in presence of H_2 and absence of H_2 are measured by using agilent multimeter (U1252A). Temperature of the measurement chamber is controlled by the temperature controller.

Sensitivity of the thin film sensor has been measured by the equation 5.1.

$$S(\%) = \frac{R_n - R_g}{R_n} \times 100 \qquad (5.1)$$

Where, Rn is the resistance of the sensor in carrier gas (N2) and Rg is the resistance in the presence of hydrogen gas.

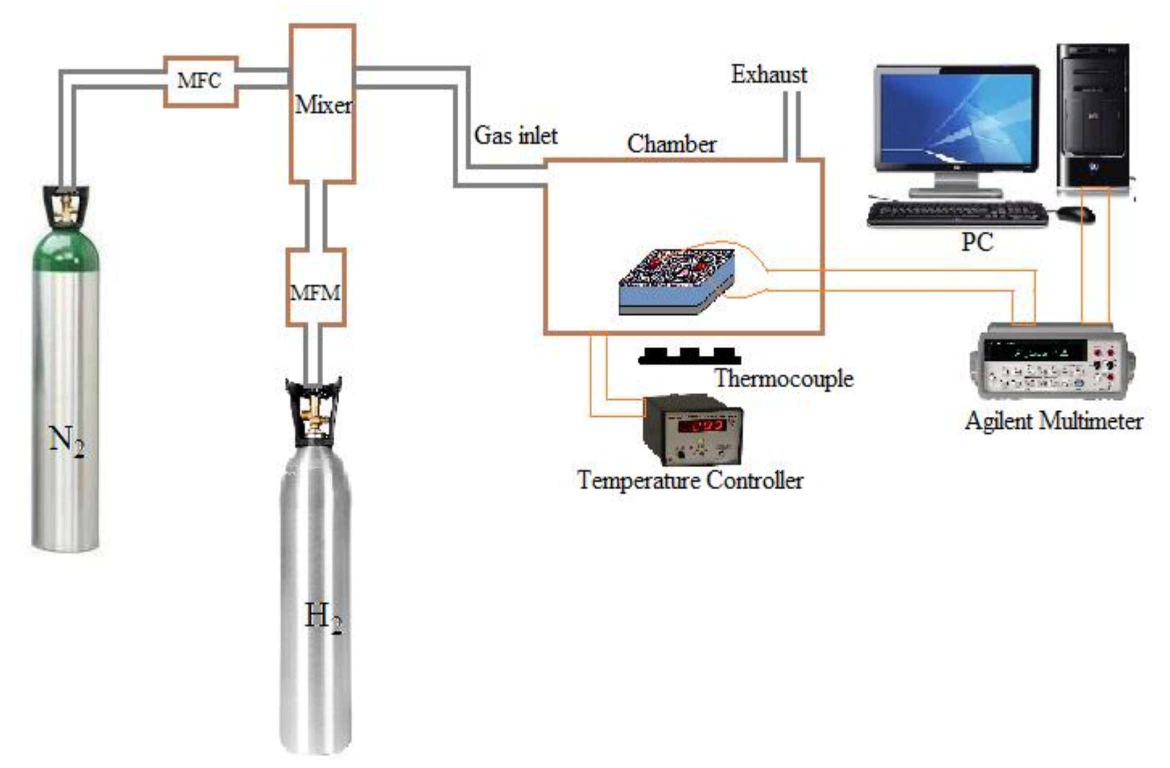


Fig. 4.5. Experimental Setup.

Fig. 4.6. Experimental Setup for TiO_2-CuO Hydrogen gas sensor.

Effect of Operating Temperature

- Temperature has an effect on the physical properties of the semiconductor sensor material (charge-carrier concentration, Debye length, and work function).
- Higher temperature the charge-carrier concentration (and the conductivity) increases and the Debye length decreases. This is one possible reason for the decreasing sensitivity of sensors at higher temperatures.
- Dynamic properties of the sensors (response and recovery times) depend exponentially on the operating temperature.
- The surface coverage, co-adsorption, chemical decomposition, or other reactions are also temperature dependent, resulting in different static characteristics at different temperature.

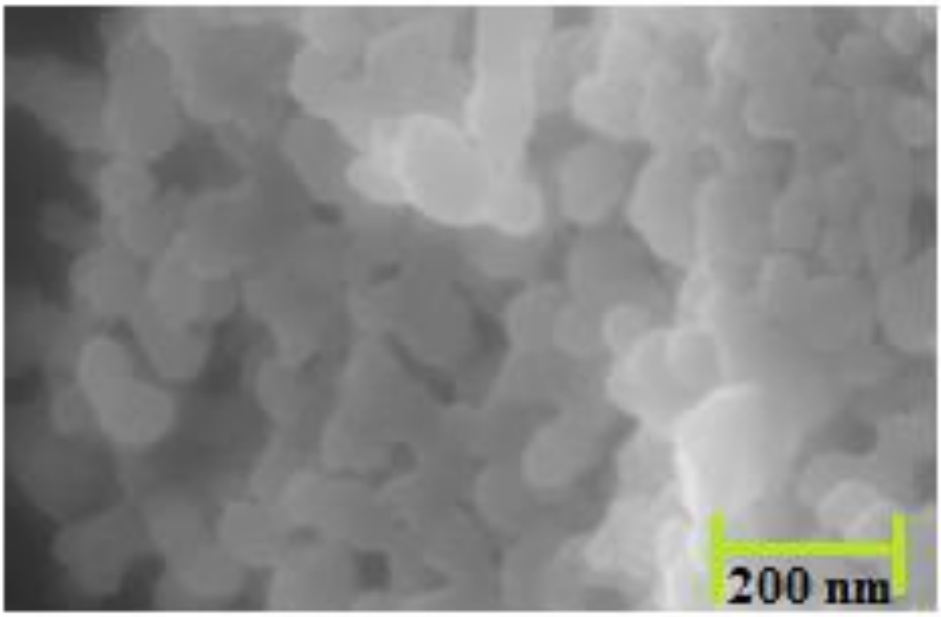
Mechanism of gas detection

In the gas sensing mechanism the most important processes are surface interactions. These may change surface properties and thus affect the measured resistance. If the current that flows through the sample takes a path far away from the interface between the sensing layer and the atmosphere, the measured resistance cannot be used to detect gas concentration variations. Therefore in the following discussion it is supposed that the current flowing through the sensing layer is significantly disturbed by surface interactions. This section describes some of the most common interactions taking place on a solid-gas interface and how they are related to some common thermodynamic variables, such as, temperature and pressure. In order to affect the current flowing through the sensing layer, gas molecules have to interact with the layer surface. This usually starts through adsorption and desorption processes. These interactions have characteristic lifetimes and energies, that will control adsorption rate, desorption rate and coverage of each atmospheric compound.

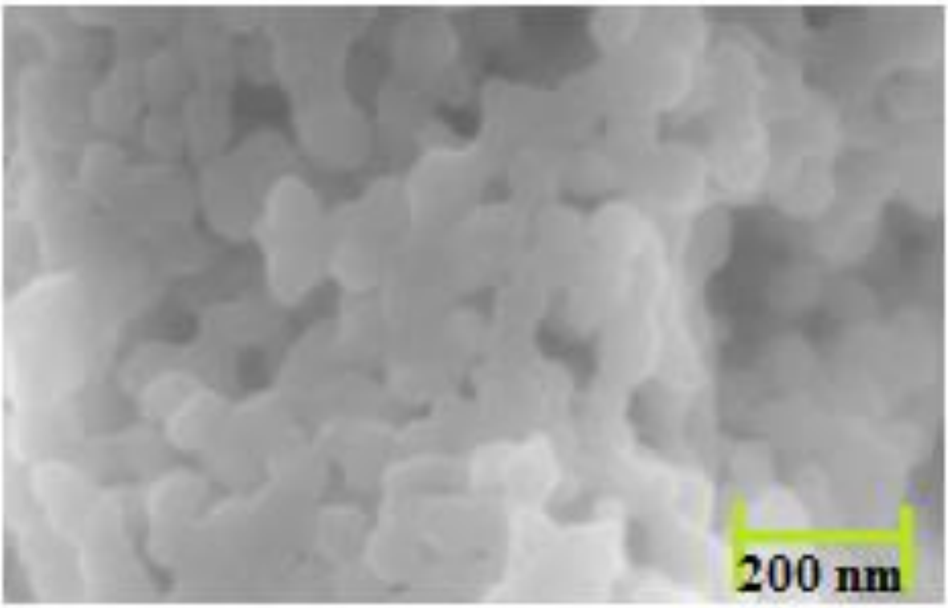
4.5 Result and Discussion

4.5.1 Surface morphology

Surface morphology (Field Emission Scanning Electron Microscopy) of prepared thin film sensors are shown in the Fig. 4.7 FESEM suggests that sol-gel grown metal oxides have different polycrystalline size (78 nm-92nm). FESEM characteristics also found that deposited Pd-doped TiO_2-CuO thin have sharper grain size in comparison with the unmodified TiO_2-CuO thin film allowing better adsorption H_2 in the letter case.



(a)



(b)

Fig. 4.7. FESEM image of (a) undoped and (b) Pd-doped TiO_2-CuO thin film sensor.

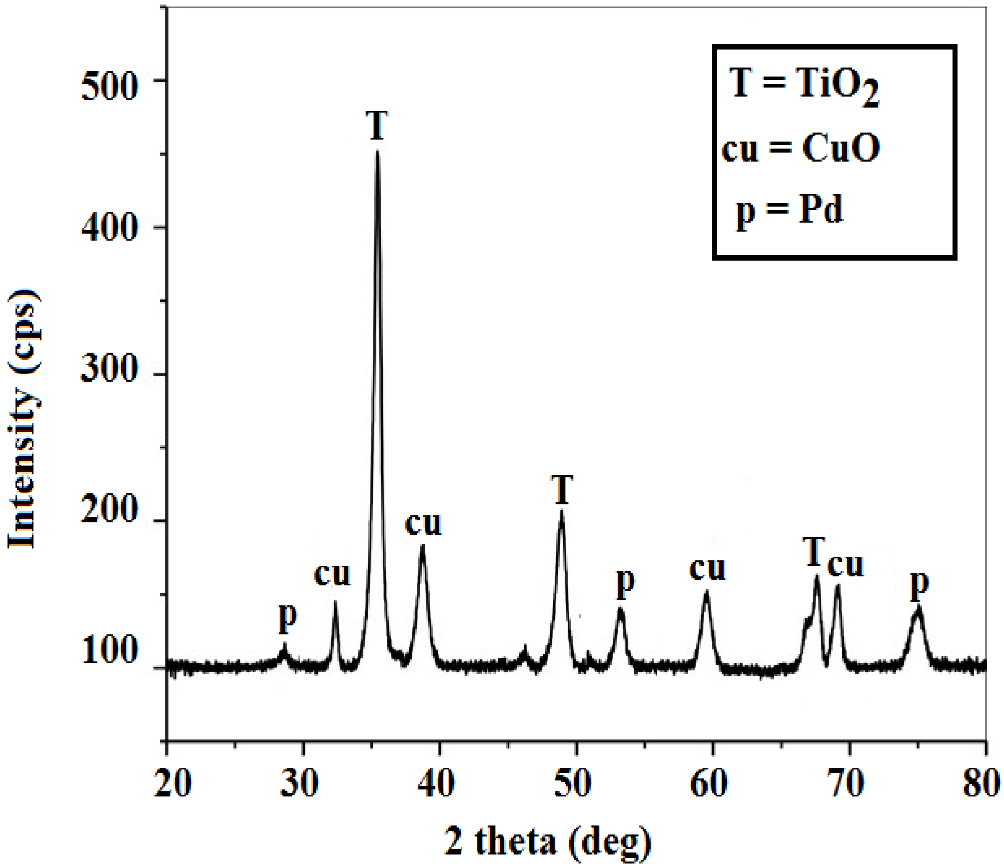


Fig. 4.8 XRD pattern of Pd modified TiO_2-CuO thin film sensor.

Fig. 4.8 shows the XRD peaks of Pd modified TiO_2-CuO thin film sensors at operating temperature 150^0C. Prepared sample clearly indicates that deposited nano film is available in the sample which different peaks obtained at different angles (2θ= 29.20-75.10).

4.5.2 Sensitivity as a function of gas concentration and temperature

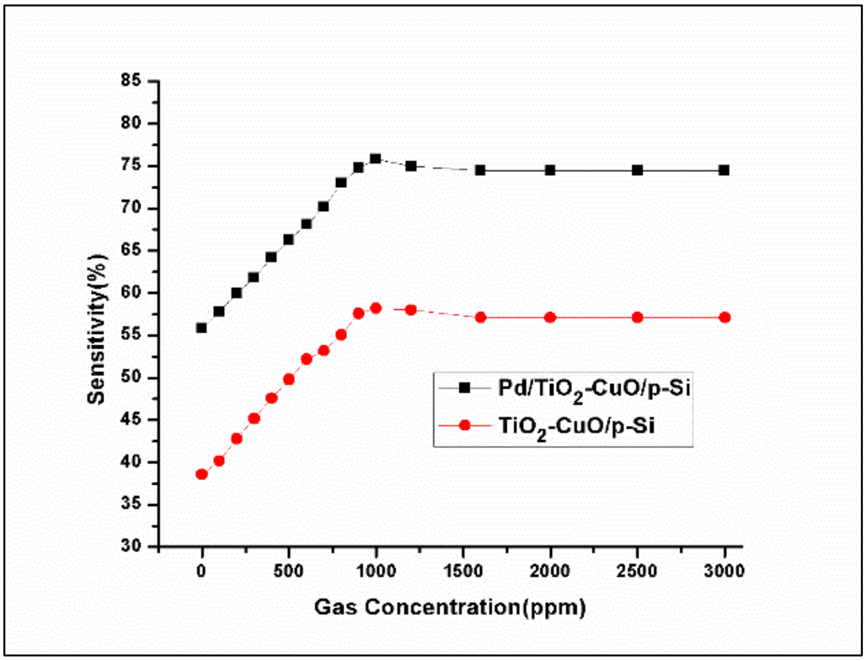


Fig. 4.9. Sensitivity vs gas concentration for both Pd modified and unmodified

Table: 4.1 Sensitivity vs gas concentration for both Pd modified and unmodified

Hydrogen Concentration (ppm)	**Sensitivity (%) for Pd Modified**	**Sensitivity (%) for Unmodified**
0	55.8	38.6
100	57.8	40.2
200	60	42.8
300	61.8	45.2
400	64.2	47.6
500	66.3	49.8
600	68.1	52.2

700	70.2	53.2
800	73	55.1
900	74.8	57.6
1000	75.8	58.2
1200	75	58
1600	74.5	57.1
2000	74.5	57.1
3000	74.5	57.1

The variation of sensitivity w.r.t gas concentration changes is shown in Fig. 4.9 With the increase in gas concentration the sensitivity also increases and after 1100 ppm of concentration the sensor shows highest sensitivity. After that the sensitivity saturate because hydrogen gas molecules are desorbed by the high conductive Pd/TiO_2-CuO surface.

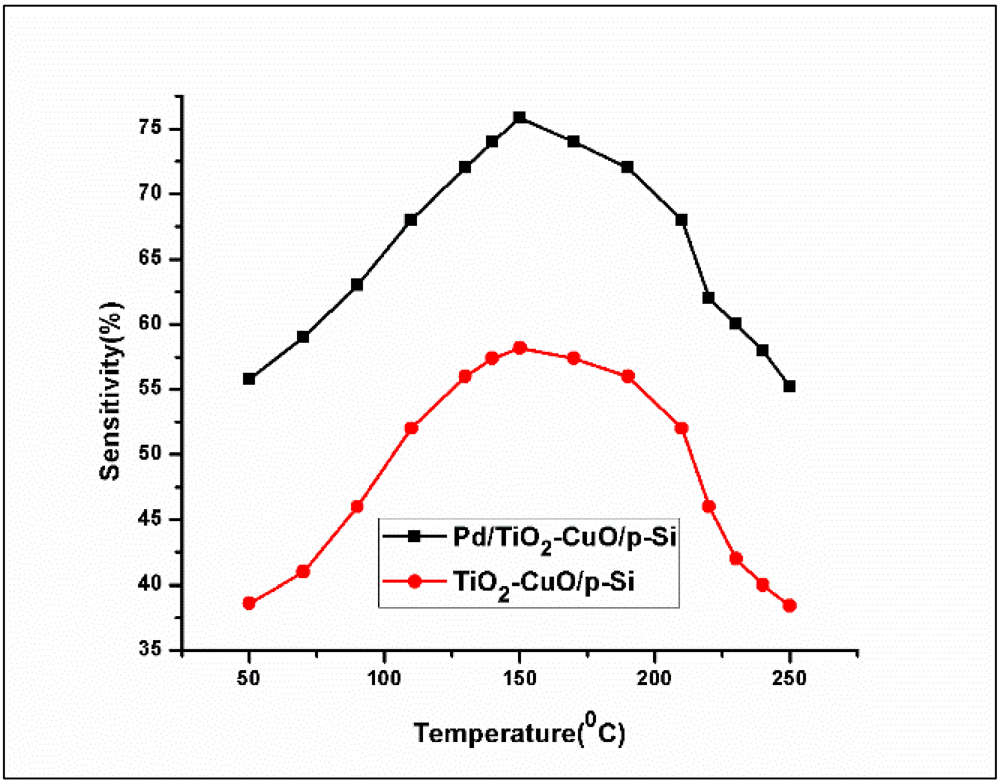


Fig. 4.10. Sensitivity vs temperature.

Table: 4.2 Sensitivity vs Operating Temperature for both Pd modified and unmodified

Operating Temperature(^{O}C)	**Sensitivity (%) for Pd Modified**	**Sensitivity (%) for Unmodified**
140	74	57.4
150	75.8	58.2
170	74.1	57.4
190	72.3	56.1
210	68.2	52.2
220	62.5	46.4
230	60.1	42.3
240	58.2	40
250	55.2	38.4

How sensitivity has changed with operating temperature of the sensor is shown in the Fig. 4.10 It has been observed that the sensor has shown the highest sensitivity at the temperature of 150^0C. Pd modified TiO_2-CuO sensor has given the highest sensitivity compared to unmodified TiO_2-CuO sensor.

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CHAPTER V

IOT BASED SYSTEM FOR VERTICALFARMING

5.1 Introduction:

Increase in the worldwide population combined with the rise in per capita consumption of modern man has led to increased demand for food. To meet the growing demands and to feed the masses, more agricultural land is required. This has led to increased pressure on existing farmlands (which are being harvested multiple times in a year) as well as necessitated the acquisition of more land for agriculture. But an increased understanding of the adverse effects of deforestation has led man to think of alternative ways to optimize land use in agriculture. One such solution is vertical farming. This technique involves growing crops in a vertically stacked manner in an indoor controlled environment. Vertical farming is environment friendly and pesticide free. But this technique is highly critical as it requires constant monitoring of the ambient parameters. Vertical farming is usually practiced in large warehouses which can be several storey's tall. The sunlight is replaced by LED lights. The controlling parameters for vertical farming are mainly ambient light, ambient temperature, soil moisture and humidity. Several automation techniques have been previously suggested for optimizing resource use, such as accommodation of actuation by automated irrigation systems [5.1]-[5.2],[5.12]-[5.19] but wireless monitoring using IoT in the field of vertical agriculture has not been previously suggested.

The ambient parameters must be monitored for each stack along the vertical columns. This requires a set of sensors for each vertical stack. The large amounts of data generated by these sensors need an efficient data management system. Using the Internet of Things (IoT), we can efficiently manage the sensor data, identify redundant sensor readings and visualize it with the help of web based applications [5.3]. Thus, a convenient IoT based system may be developed for vertical farming.

5.2 IOT System Architecture:

Implementation of IoT concept is basically depends on its architecture. It have 5 layer architecture are the perception,Transport, Processing, application and Business layers.

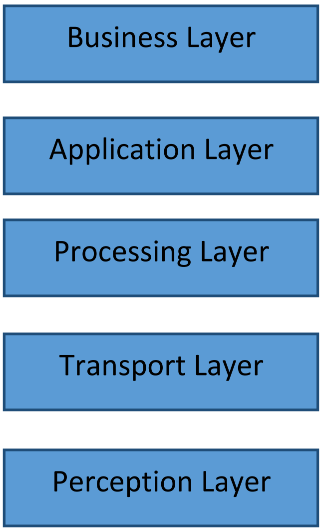
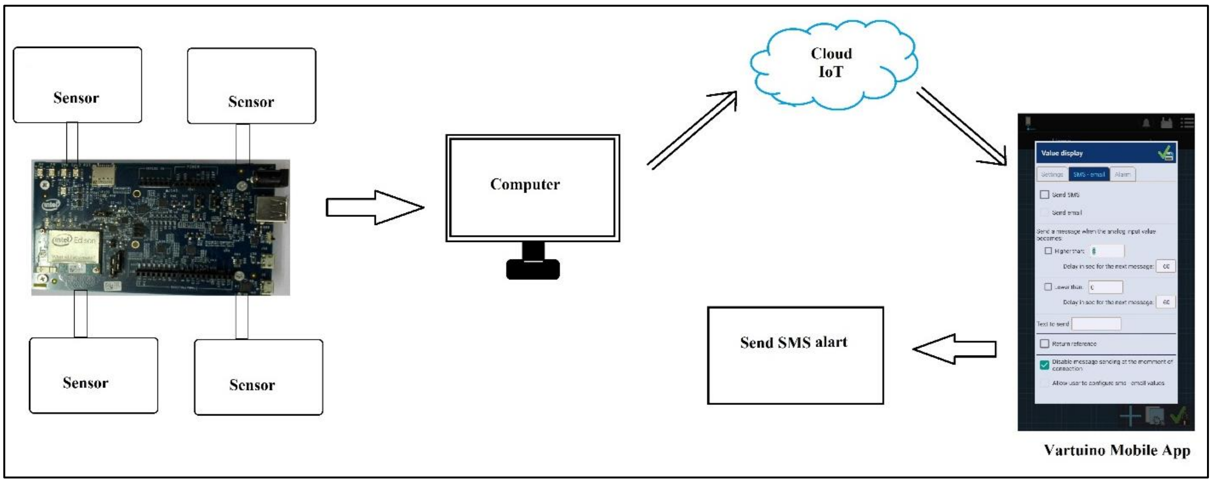


Fig. 5.1. Layer of the architecture

IoT (Internet of Things) is an emerging concept and a paradigm that seeks toconnect a variety of things or objects that are able to interact and coordinate witheach other with the help of wireless and wired connections [5.6]-[5.7][5.11]. Aided by theInternet and the advances in cloud computing technology, IoT has extensive scopeof application in multiple areas such as transport, healthcare, security, communication, infotainment and smart cities.The system architecture as shown in figure 5.2 consists of microcontroller, different sensors, computer, the cloud and the end devices. From a functional point of view,the IoT needs a set of basic components or modules to facilitate the connection of‘things’:

- A module for interaction with local IoT devices (smart sensors). Thismodule acquires observations from sensors and forwards it to remoteservers for analysis and storage.
- A module for interaction with remote IoT devices.
- Module for application specific data analysis and processing.
- User interface module (web or mobile).



☐ Send SMS
Send email
Send a message when the analog input value becomes:
☐ Higher than: 0
Delay in sec for the next message: 60
☐ Lower than: 0
Delay in sec for the next message: 60
Text to send
☐ Return reference
☑ Disable message sending at the momment of connection
Allow user to configure sms - email values

Fig. 5.2. System Structure

From the data flow point of view the IoT comprises of the following:

- **End Devices-** These are the sensors or actuators which directly interact with the surrounding environment to acquire some information (sensors) or perform some changes on the surroundings (actuators). These devices must light-weight and power efficient. They are not O.S based and are often referred to as dumb devices as they have no decision-makingcapabilities.
- **Propagation Node-** The propagation node gathers and stores data. These are based on operating system. The nodes check the efficacy of the incoming sensor data and prunes redundant data. Data from the propagation node is periodically bundled and sent to the cloud via ipV6 or ipV4.
- **Filter Gateway and Machine Learning-** Once the data is uploaded through the internet onto the cloud, it is sent for analysis and storage.

The proposed system comprises of- (1) the set of sensors that facilitate the monitoring of the ambient conditions; namely, ambient light sensor, soil moisture sensor, humidity sensor and ambient temperature sensor, (2) a data transmission pathway through which the sensor data can be communicated wirelessly using a microcontroller and a wireless module, (3) a web based application to visualize the sensor data.

5.3 Proposed IOT based System for Vertical Farming

The concept of verticalfarming has been shown in the Fig.2.3. where the levels represent the verticalfarming stacks.

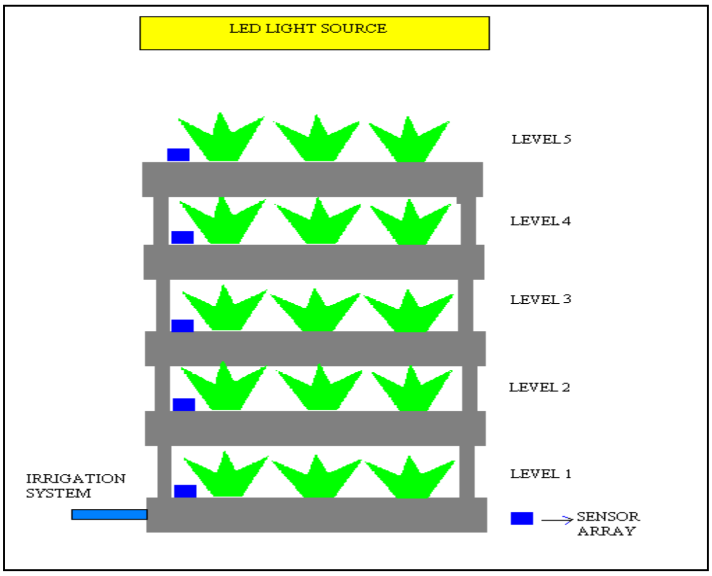


Fig.5.3. Diagrammatic representation of vertical farming aided by ambient sensor arrays

The propose system for the IoT based vertical farming has been shown in the figure 5.4. Vertical farming is mostly practiced indoors and hence, there is no sunlight. The sunlight is simulated with the use of LED lights that enable the plants to carry out photosynthesis. Thus, monitoring the ambient light is necessary to provide optimum photonic energy for proper photosynthesis. Hence, our system uses an ambient light sensor. Temperature and moisture are also critical for the health of the plants in an indoor environment [5.8]-[5.9]. This creates the need for using temperature and humidity sensors. Finally, monitoring the soil moisture constantly and generating an alarm if the moisture level falls below a set threshold, is required. For this we have used soil moisture sensor [5.10]. The four sensors together form a sensor array.

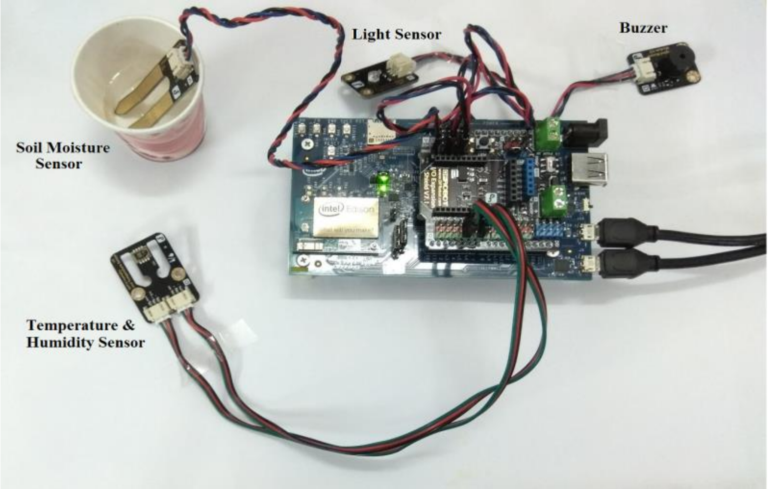


Fig.5.4. Prototype of the proposed system

The data from the sensors must be constantly monitored in real time in order to initiate necessary actions that will ensure the health of the growing crops. The proposed system uses Intel Edison wireless module that is mounted on an Arduino prototype. The Intel Edison is a computer-on-module that has found extensive use as a development system for wearable devices and IoT based applications. Computer-on-modules (COMs) are complete embedded computers built on a single circuit board. The board runs on Linux OS with developmental support for Ardunio IDE, Eclipse and Intel XDK. In our system the board has been programmed to receive the readings from the aforementioned sensors, generate an alarm when soil moisture falls below optimum threshold and upload the sensor readings onto the cloud. The program is pushed through the serial port of the Arduino prototype and is available in the application section. The backend service calls the .exe of this application. Since, it is Linux based, the PuTTY tool is used to configure the Edison Board with the Wireless Local Area Network (WLAN) to facilitate communication with the Internet.

5.4 Result and Discussions

To facilitate the monitoring of the sensor data remotely, a web-based user interface has been made with the help of ThingSpeak. ThingSpeak is an open source IoT application that allows for the storage and retrieval of data from ‘things’ using the HTTP protocol over the internet or a local area network. A channel was created on ThingSpeak platform and was named ‘Farm’. The API Keys of the channel were used on the programming end so that the sensor data could be viewed in the channel. Four fields were created for the purpose of visualizing the data from the four sensors. Hence, with the help of ThingsSpeak remote monitoring of sensor value is possible. For the mobile based monitoring interface, Virtuino was used. Virtuino is an Android app which shows the sensor data graphically and also allows sending of SMS when the sensor reading crosses a threshold (which can be programmed).

The components of the sensor array are as follows:

- Ambient Light Sensor V2 (SKU: DFR0026) - this analog sensor is used to measure the light intensity. The illumination range varies from 1 Lux to 6000 Lux.
- SHT1x Humidity and Temperature sensor (SKU: DFR0066) – the humidity sensor is pre-calibrated in a precision humidity chamber. The sensor output is in

%humidity or relative humidity. The temperature sensor provides the room temperature value in degree Celsius.

- Soil Moisture sensor (SKU: SEN0114) – the soil moisture has two probes to pass current through the soil. The resistance value obtained reflects the moisture content of the soil. Presence of water improves the soil conductivity and vice-versa.

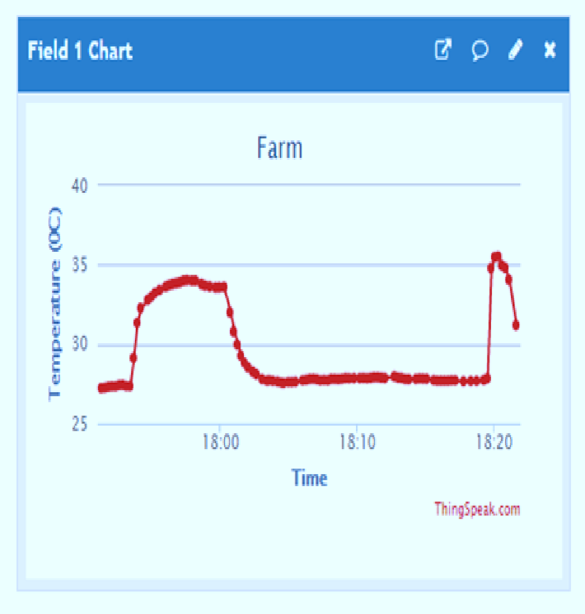


Fig.5.5. Results for the temperature sensor obtained from ThinkSpeak

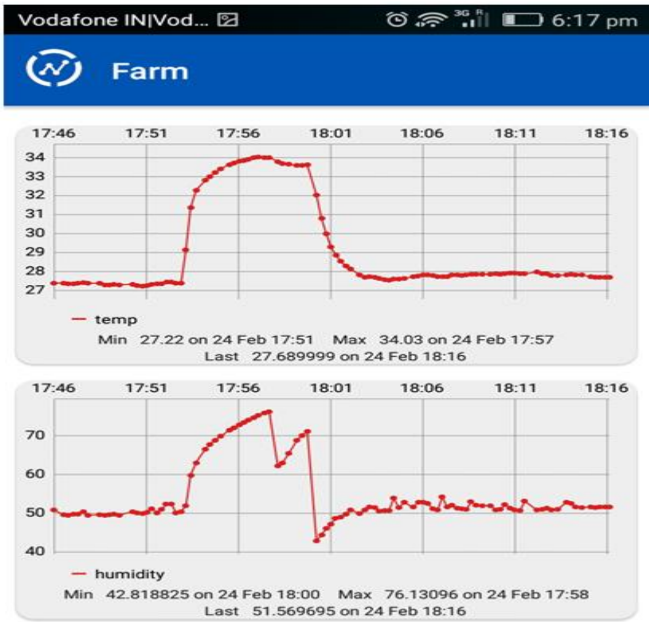


Fig.5.6. Results for the temperature and humidity sensor obtained from Virtuino

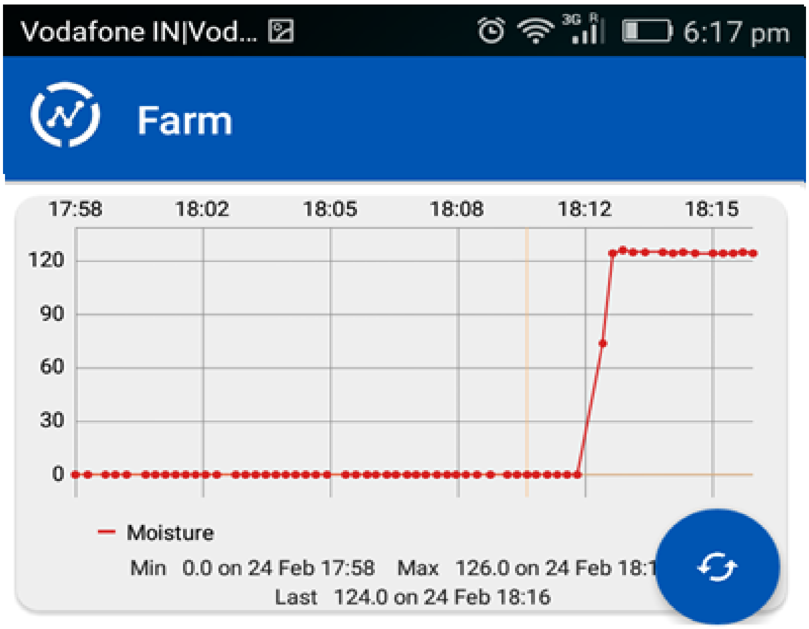


Fig.5.7. Results from the soil moisture sensor obtained from Virtuino

Fig 5.5. shows the graphical reading of the ambient temperature sensor in degree Celsius. Fig 5.6. shows the Virtuino graphs for temperature and humidity sensors. The Virtuino can be programmed to send SMS when the temperature and humidity values fall above or below predetermined thresholds. The threshold values depend upon several factors, like the type of crop grown, etc. Fig. 5.7 and 5.8 show the Virtuino and the ThingSpeak graphs for the soil moisture sensor, respectively. The soil moisture sensor is calibrated in terms of moisture levels. If the soil moisture falls below a certain predefined level, the buzzer rings an alarm that can notify the farmers to switch on the irrigation system for the concerned vertical stack.

Fig.5.8. Results from the soil moisture sensor obtained from ThingSpeak

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CHAPTER VI

CONCLUSION AND FUTURE WORK

6.1 Conclusion
6.2 Future work

6.1 Conclusion

In the present work a comprehensive theoretical and experimental study of the characteristics of low dimensional semiconductor (metal oxide) sensor and application of some sensor with IOT technology in agriculture have been investigated. The details of the research work are concluded here.

The gas sensing characteristics of WO_3-Si hetero-junction device has been investigated for as application of the low dimensional device in gas detection. The performance of gas sensing metal oxide has been enhanced by adding noble metals into the surface of the metal oxide. The noble metal like Pt, Pd are employed to improve the sensitivity of gas sensor towards ethanol vapour. The noble metal has been used as a catalyst for the modification of the surface reactions of thin film in the presence of sensing gas. In chapter 3, the electrical response of WO_3-Si hetero-junction device towards ethanol gas is studied. The effect of noble metal such as Pd, Pt on the working temperature has been also investigated. Nano crystalline WO_3 thin film has been deposited on p-Si<100> substrate using a sol-gel deposition method for the formation of hetero-junction device. Three types of sensing devices (Pd, Pt surface sensitized WO_3 surface and un-sensitized WO_3 surface) have been taken to study the gas sensing characteristics (Figure 3.6). XRD and SEM are employed to characterize the structure of the hetero-junction device (Figure 3.4 and Figure 3.5). The heterojunction devices have been tested at different working temperatures (50^0C- 500^0C) to get their maximum response magnitudes (max sensitivity 68% Figure 3.7). The response magnitude of the WO_3 thin film sensor has been investigated at different concentrations (192ppm to 3117ppm) of ethanol gas (Figure 3.6). The readout circuit for the sensor is described (Figure 3.3). The Pd, Pt noble metal plays an important role in lowering the working temperature of sensor. It is observed that the working temperature of WO_3 thin film is reduced from 300^0C (un-modified) to 210^0C (Pd surface modified) to 170^0C (Pt surface modified). Therefore, Pd, Pt surface modified sol gel grown WO_3 thin film can act as a very good ethanol sensor at the optimum working temperature of 210^0C and 170^0C respectively.

Similarly the study of thin film TiO_2-CuO mixed metal oxide sensor fabricated by sol gel process has been investigated in chapter 4. To increase the response of the sensor, the surface has been modified by Pd. Three types of sensing devices (Pd modified WO_3 surface and un-modified WO_3 surface (Figure 4.4)) have been taken to study the gas sensing characteristics (Table 4.1 and 4.2). By varying the temperature from 50^0C to 250^0C, it has been found that the operating temperature is 150^0C. The response magnitude of the WO_3 thin film sensor has been investigated at different concentrations of hydrogen gas (Figure 4.9). Pd modified sensor hs shown better response compare to unmodified towards hydrogen.

The proposed system (Figure 5.4) for vertical farming can measure the ambient parameters and upload the data onto the ThinkSpeak Cloud (Figure 5.5 and 5.8), using the Intel Edison wireless module. The web-based application can be used to analyze and monitor the light, temperature, humidity and soil moisture of the vertical farming stacks. Using the Virtuino app, SMS can be sent if the parameters fall below a threshold value (Figure 5.6 and 5.7). Future work includes integration of the system with RFID technology such that each vertical stack can be uniquely identified. The system can be further improved by accommodating actuation such as automated irrigation system and temperature control. Incorporation of pH sensors and gas sensors into the existing system can further address the criticality of the vertical farming technique.

6.2 Future work

Temperature is an important factor for the metal oxide gas sensors. 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.

Research Publications of Bikram Biswas Relevant to the Current Thesis

Journal

1. **Bikram Biswas**, Subhashis Roy, Anup Dey and Subir Kumar Sarkar **“Fabrication of a WO_3 conductometric activated thin film sensor for resistance-to-frequency conversion based sensing application”**, IETE Journal of Research. Taylor & Francis, https://doi.org/10.1080/03772063.2019.1615387

Conference

2. **Bikram Biswas**, Sutanni Bhowmick, Mandira Biswas, Anup Dey, Subhashis Roy and Subir Kumar Sarkar **“Simulation of Capacitive Multilayered Bio-Sensor for Sensing Biomolecules”**, IEEE-EECCMC Jan 2018.
3. **Bikram Biswas**, Sutanni Bhowmick, Mandira Biswas, Subhashis Roy, Anup Dey and Subir Kumar Sarkar **“IoT-Based Smart Heart-Health Monitoring System”**, IEEE-ICNTET Sept 2018.
4. Sutanni Bhowmick, **Bikram Biswas**, Mandira Biswas, Anup Dey, Subhashis Roy and Subir Kumar Sarkar **“Application of IoT Enabled Smart Agriculture in Vertical Farming”**, Advances in Communication, Devices and Networking,DOI: 10.1007/978-981-13-3450-4_56, vol.537, pp 521-528, 2019.
5. **Bikram Biswas**, Anup Dey, Subhashis Roy, Sudhabindu Ray and Subir Kumar Sarkar, “ **Pd Doped TiO_2 – CuO Mixed Metal Oxide Thin Film Sensor for H_2 Sensing Application** ” 2019 Devices for Integrated Circuit (DevIC), Kalyani, India. March 23-24, 2019.