CHAPTER - 1

INTRODUCTION

In current industrialization time zone, desired electricity and power generation depends on the utilization of coal mines and natural gas resources. Thus the importance of monitoring of harmful gases such as methane, ammonia, carbon monoxide etc is need of the hour. In these gases, methane is inflammable and explosive in the presence of air. So, main concern of the thesis is to fabricate the thin film based gas sensor for detection of methane, So that the life of the people who are working as main support for our industries can be made safer. Thus we need a high sensitive gas sensor specifically for the sensing of methane gas.

1.1 Need for gas sensors

The Latin word *"sentire"* resemble to *"sensor"*. Present day, modern society depends on the industries and faces numerous problems such as exhaust of toxic gases and air pollution and these problems have been introduced into the society due to rapid industrialization. The monitoring of the exits gases needs for better gas sensors for detection and control. Many types of gas sensors with a wide range of industrial applications are available; for monitoring of air pollution, chemical processes and exhaust from combustion factories. Thus applications of sensors are in wide range such as laboratories, factories, fuel cells and power stations [Capone *et al.* (2003)].

The current needs are divided in three main categories for gases monitoring sensors [Moseley, (1997)]:

1. Monitoring for breathable atmospheres and investigation of combustion conditions.
2. Flammable gases in air, to measure the order of lower explosive limit (LEL) and upper explosive limit (UEL).
3. Inspections of toxic gases in air.

Therefore, needs of gas sensors for effectively detection these gases is to prevent the most of the above dangers situations. The following requirements are listed gives for an ideal Sensor [Moseley *et al.* (1991)]:

1. High Response
2. Low Response time
3. Better Selectivity
4. Non poisonous
5. Non contamination
6. Easy fabrication
7. Easy operation
8. Small size

The above listed characteristics have been the dominant field of extensive research for developing a gas sensor for different gases.

1.2 Necessity of a gas sensor for methane gas

Methane is a saturated hydrocarbon with colorless, tasteless and odorless characteristics. It is not toxic but is an explosive gas. The availability of methane is 40% in the gas mixture in the coal mines and approximately 45 to 85 % in the 'Natural gases'. It is also found in low concentration in oil wells and at marshy places, paddy farm, plant's wastes and carbonic material wastes. It becomes combustible when LEL and UEL (lower and upper explosive limit) are 5%, to 15 % respectively, in the air environment [Air Product USA (1999), Basu *et al.* 2009 Mosahebfard *et al.* (2017), United Nations Publications (2010)]. The chemical reaction for combustion of the methane with the air [Sharma, (1998)] is given below:-

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + HEAT\ (\Delta = 213\ Kcal / mol)$$

Though methane is explosive gas but it's used in the chemical industries [Sharma, (1998)] as :-

1. Fuels.
2. 'Gas carbon' made by methane is used in the making of 'Carbon rod' which is used as a 'Plate' for electric furnace and batteries.
3. 'Carbon black' made by methane, is used in the making of printing ink, paints and motor tyers.
4. Methylalchohol and formaldihyde are also made by methane.
5. It is a good source of hydrogen.
6. It is used for obtaining syenthesis gas ($CO + 3H_2$).

1.3 Gas Sensors

Gas sensors are classified based on their operating principles [Hulanicki *et al.* (1991), Mandelis *et al.* (1993)]. In this section sensor types are briefly explained.

1.3.1 Semiconductor Gas Sensor

It was the innovation of Barttain and Bardeen that there occurs a variation in the electrical properties as conductivity due to the gas adsorption on a semiconductor surface. Since then many efforts have been done to prepare devices for the reliable detection of toxic and flammable gases in domestic environments [Jardine, (2000)].

The electrical conductivity will depend on the composition of the materials and atmosphere surrounding with temperature. Most oxides will change its conductivity depending on the ambient O_2 concentration and the initial reaction of atmospheric O_2 with lattice vacancies in the oxides and reduction in electron concentration. This results in various O_2 species at different temperatures and O_2 pressures. T. Seiyama *et. al.*, reported to metal oxide semiconductor utilized in gas sensing.

The applications of semi-conducting gas sensors range from environmental monitoring to industrial and domestic applications [Barsan *et al.* (2001)]. A simple MOS gas sensor layout is shown in Fig. 1.1

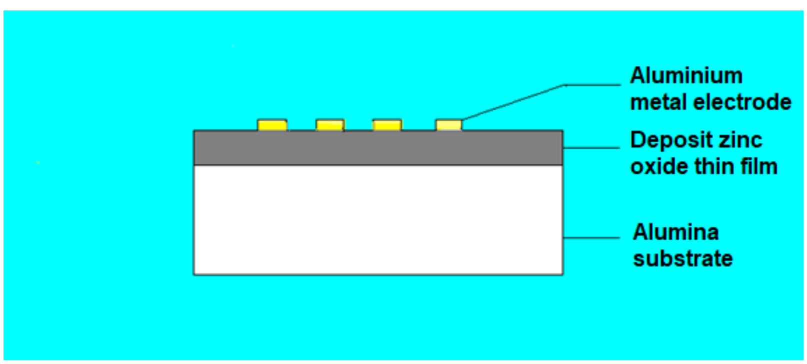

Fig.1.1. A simple layout of a metal oxide semiconductor based sensor.

1.3.2 Schottky Barrier Sensor

Schottky barrier sensor is based on “Schottky barrier theory”. When metal contacts with semiconductor then Fermi level of metal and semiconductor aligned itself due to work function difference between them. Presence of any dielectric between metal and semiconductor results in shift of Fermi level. A Simple layout of this type sensor shown in Fig. 1.2. The fabrication of ohmic contact is formed followed by the deposition of catalytic metal deposition on topside of semiconductor. If this contact interact with gas molecules at surface then changes electrical properties by adsorption theory and lowers to schottky barrier [Mandelis *et al.* (1993)].

Here, ψ_{MA}, φ_{BA}, E_C, E_V in the air.

Ψ_{MG}, φ_{BA}, E_{CG}, E_{VG} in the gas.

M is metal as Pt, Pd etc.

Fig.1.2. A simple layout of a Schottky barrier sensor.

1.3.3 MOSFET Sensor

MOSFET is known as "Metal oxide semiconductor field effect transistor". A basic structure of a MOSFET is shown in Fig. 1.3. The fabrication includes source and drain, growth of a thin gate oxide, deposition of catalytic gate metal and contacts of source and drain. Threshold voltage of the MOSFET sensor changes on interaction of the gate material, mostly a catalytic metal, with the intendented gas molecules due to corresponding changes in the work functions of the oxide layers and metal. The sensitivity and selectivity of the sensor depend upon operated temperature and catalytic metal [Mandelis *et al.* (1993)].

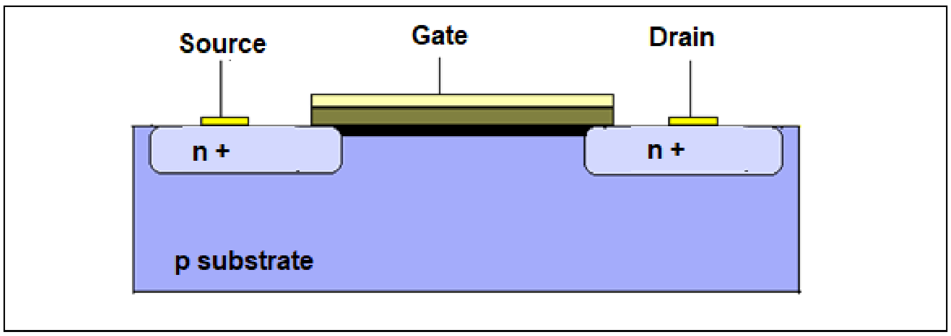

Fig.1.3. A simple layout of a MOSFET gas sensor.

1.3.4 Surface Acoustic Wave Sensor

Surface acoustic waves are sensitive to the state of a substrate surface along which the wave is propagating. The adsorption of molecules from the gas states on the substrate surface produces in particular mass loading of this surface and modifies the SAW propagation parameters, which is shown as changes in the output signal. This principle is employed in the SAW gas sensors of the mass-sensitive type (Fig. 1.4).

There are different types of surface acoustic wave sensors (SAW) like, acoustic plate mode (APM), thickness shear mode (TSM) and flexural plate wave (FPW). The SAW devices are fabricated using photolithography.The acoustic waves launched by these transducer ranges from few to hundreds of megahertz [Drafts, (2001)].

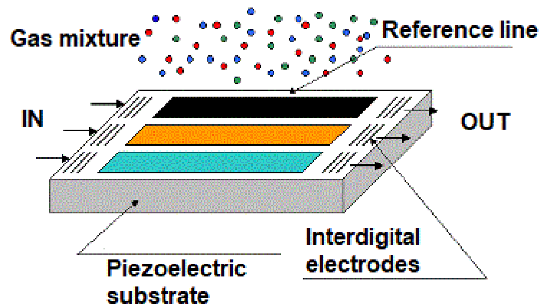

Fig.1.4. A simple layout of a surface acoustic wave sensor.

1.3.5 Fiber Optic Sensor

Fiber optic sensor based on variation in the optical properties. In these types of sensor some of the length of optical wave guide is coated as sensing layer. When gas molecules interact to sensing layer then electron exhanges occur on the surface of transparent semiconductor, cause of that refractive index changed. Refractive index of core is greater than cladding. The transmitted monochromatic polarized light is detected by light detector and variation in reflection angle is observed [Capone *et al.* (2003)] (Fig. 1.5).

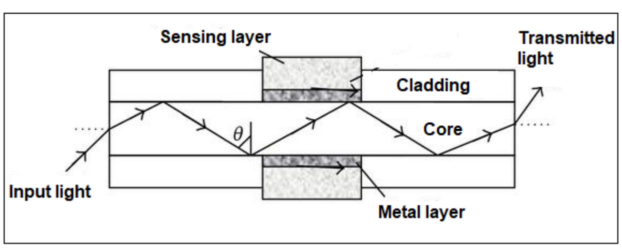

Fig.1.5. Simple diagram of fiber optic sensor

1.4 Properties of Zinc Oxide

Zinc oxide is a periodic group of II –VI compound semiconductor material and having large band gap such as 3.7 eV at room temperature. It is a most used material for various applications such as gas sensors, transparent conductive oxide electrodes, piezoelectric devices, surface acoustic wave devices. Recently ZnO have also attracted attention of its possible application in light emitting diode (LED) because optical properties of ZnO are similar to those of GaN.

Zinc oxide is insoluble in water and soluble in alkalis. It is also known as zinc white calamine. The composition of zinc oxide crystals are alternately arranged in a layer of zinc and oxygen atoms forms a hexagonal structure. In this crystal structure of ZnO, both zinc and oxygen ions are coordinated, having four positive ions and four negative ions respectively, and form strong ionic bond between them (Fig. 1.6) [Gupta *et al.* (1990), Hur *et al.* (2003) Jagadish *et al.* (2011), Norton *et al.* (2004)]. The properties of zinc oxide are presented in Table 1.1

Table 1.1. Properties of Zinc Oxide

Crystal structure	Hexagonal , Wurtzite
Molecular weight	81.38
Lattice constant	In ZnO hexagonal unit cell, a=3.246Å, c=5.207 Å, c/a=1.601, u=0.375

Density	5.67 g/cm^3
Melting point	2250°K
Boiling point	2635°K
Thermal expansion coefficient	4.3×10^{-6}/°K at 20°C 7.7×10^{-6}/°K at 600°C
Band gap at room temperature	3.37eV
Electron and hole effective mass	m_e^*=0.28, m^*_h=0.59
Refractive index	2.008
Static dielectric constant	8.656

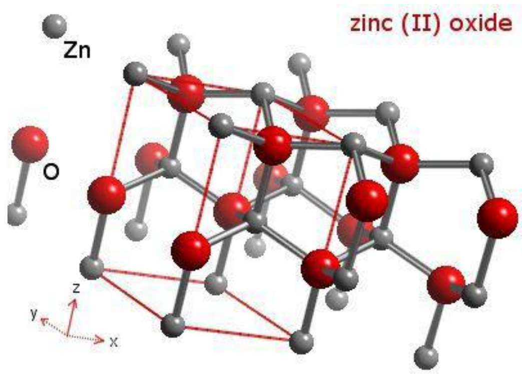

Fig.1.6 The basic structure of zinc oxide [www.webelements.com]

1.4.1 Electrical Properties of Zinc Oxide

Zinc oxide is used in gas sensor material because its electrical properties changes in the presence of gas molecules. The electrical properties of zinc oxide changes due to combined effect of surface and bulk properties. Both of them are discussed in following section.

1.4.1.1 Surface Effects

Surface conductivity of the sensor material changes due to the adsorption of gas species on its surface. Initially oxygen species adsorbed on the surface of the sensor, due to this change in the surface conductivity occurred. When surface is exposed by the intended gas then the gas molecule adsorbs on the surface and remove the adsorbed oxygen species, due to this charge carrier of the conduction band becomes free electrons, hence conductivity of the sensor surface changes. The changes in surface conductivity of ZnO also depend upon the grain size, operational temperature and gas concentration [Wilson *et al.* (2001)].

1.4.1.2 Bulk Effects

Total conductivity of a semiconductor can be written as the sum of the electron (σ_n) and hole (σ_p) conductivities. If both the conduction processes are assumed independently then

$$\sigma_{tot} = \sigma_n + \sigma_p + \sum \sigma_{ions} \qquad (1)$$

$$\approx \sigma_n + \sigma_p$$

$$R_{bulk} = 1 / [\sigma_{tot} A]$$

Where, A is Cross section area.

Non-stoichiometry properties of semiconductor and diffused oxygen vacancies is given as a result of partial pressure of oxygen and function of conductivity of sensing layer as

$$\sigma = A \exp (- E_a / kT) P^m \qquad (2)$$

σ = Conductivity

E_a = Conduction activation energy

P = Partial Pressure

m is constant and its value depends upon dominant type bulk defects involved in the equilibrium between oxygen and sensor [Moseley (1992), Moseley *et al.* (1996), Moseley (1997)] .

1.5 Basic theory for methane sensing using thin film Zinc oxide

In 1959, heiland *et al.*, reported to effect of the gas sensitive on electrical conductivity of ZnO. The conductivity of thin layers of films of Zinc oxide, increased with orders of magnitude in vacuum and decreased in atmosphere at 500°K, the detection of H_2, O_2 and hydrocarbans by expedient of conductivity of surface changes in Zinc oxide crystals and thin film have been introduced and demonstrated. The sensing mechanism is based on W.H. Barttian and J. Bardeen adsorption theory. The oxidation or reduction process of zinc oxide semicounductor depends upon surrounding atmospheric gases such as oxygen, target gas [Morrison, (1981)].

In air environment, oxygen molecules adsorb on the surface and at the grain boundaries and trap the electrons from conduction band to form O_2^-, O^- and O^{2-} ions depending on the operational temperatures; O_2^- forms below 100 °C, O^- form between 100 °C and 300 °C, O^{2-} form above 300 °C [Takata *et al.* (1976)]. When methane interact with oxygen species, electrons trap into conduction band react with CH_4 and species removed along with the production of CO_2 and H_2O as depicted in Reaction (5) [Basu *et al.* (2008), Motaung *et al.* (2013)].

$$O_{2(gas)} \rightleftharpoons O_{2(ads)} \quad (3)$$

$$O_{2(ads)} + e^- \rightleftharpoons O_2^-{}_{(ads)} \quad (4)$$

$$O_{2(ads)} + 2e^- \rightleftharpoons 2O^-{}_{(ads)} \quad (5)$$

$$O^-{}_{(ads)} + e^- \rightleftharpoons O^{2-}{}_{(ads)} \quad (6)$$

Here, ads denotes to adsorption.

At the surface following reaction take place :

$$O_2 + 2e \rightarrow 2O^- \quad \text{(Oxidation of surface material)} \qquad (7)$$

Thus, oxygen species created depletion layer on the surface of ZnO. The result is decreases in electrical conductivity of active material.

In the presence of methane gas (reducing gas), It reacts at the boundaries of gains with chemisorbed oxygen species as follows (Eq. 8) :

$$CH_4 + 4O^-_{(ads)} \rightarrow CO_2 + 2H_2O + 4e^-_{(bulk)} \quad \text{(Reduction of surface material)} \qquad (8)$$

Therefore, negative charge carriers added to the bulk which increases the conductivity of metal oxide. By measuring this differnce in the conductivity, we can detect to the presence of methane gas as shown in Fig. 1.7 [Sze, (1994)].

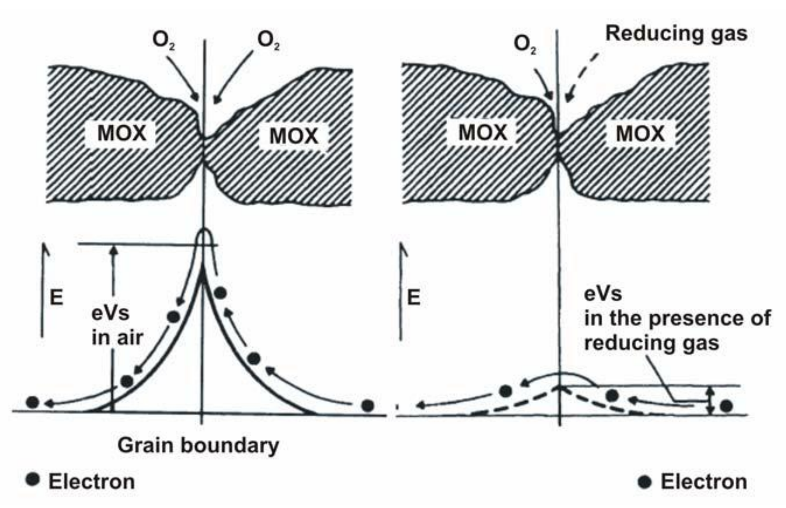

Fig.1.7. Reaction at the grain boundaries

At high temperature (above 150 °C) oxygen vacencies diffuses from interior grains to the surface or surface to interior grains due to **'non-stoichmetric'** properties of oxide material.

The reaction of oxygen gas molecules and oxygen vacencies is shown below as :-

O (oxygen molecules) $\longleftrightarrow$ Vo (oxygen vacencies) + 2e + ½ O_2 (gas phase oxygen) (9)

The relationship between the oxygen (O_2) partial pressure and the eletrical conductivity (σ) of a valance oxide is given by Equation (2) [Moseley *et al.* (1996), Xu, Y *et al.* (2000)].

Equalibrium constant, $K = (V_o)\ n^2\ (P)^{1/2}$ (10)

n is electrons concentration

Electrons concentration balance with oxygen vacencies concentration as -

$$V_o = n/2$$

Hence, $K = [n^3/2]\ P^{1/2}$ (11)

Thus, relationship between conduction band electron concentration and oxygen partial pressure is given by,

$$n \ \alpha \ P^{1/6} \quad (12)$$

Sensor sensitivity is high, If |n| is high.

1.5.1 Moisture Effects

Atmospheric moisture can be adsorb on the surface of zinc oxide as:

a) H_2O molecular water by physisorption

b) OH^- hydroxides by chemisorption

Both of the above cases, there is increase in the electrical conductivity of zinc oxide , because OH^- bound with Zn atoms and rest H ions reduce by the oxygens which increases the negative charge carriers [Damico *et al.* (1995), Sears *et al.* (2000)].

1.5.2 Grain size Effects

The sensitivity of gas sensor depends upon average grain size D of the ZnO, Rothschild and Komen showed that charge density is proportional to 1/D. If grain size are smaller than L (depth of space charge region), then more O^- ions are reduced which increase the conductivity in the presence of reducing gas. Therefore smaller grain size gives more sensitivity. In nanocrystalline metal oxides the particle size is small hence it has more sensitivity and increase the bulk atoms potential energy. Effect of different condition of grain size with respect to space charge region length is shown in Fig. 1.8 [Basu *et al.* (2009), Bochenkov *et al.* (2005), Ogawa *et al.* (1982)].

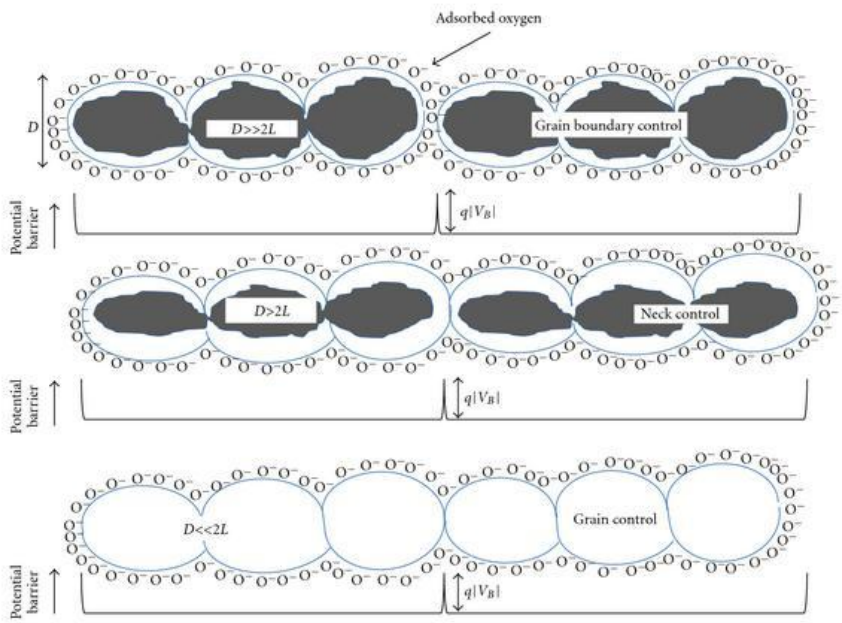

Fig.1.8. Effect of grain size

1.5.3 Porosity Effects

Porous metal oxide give good response compare to compact or dense metal oxide, beacause in the compact layer gas can not pentrate into the surface layer, While in the porous condition gas can pentrate into entire volume and activate sensing reaction, therefore porous layer is more suitable than compact layers. If the thickness is less than depth of depletion layer then surface is compact otherwise porous (Fig. 1.9 a, b) [Barsan *et al.* (2001), Basu *et al.* (2009), Holland *et al.* (1999)].

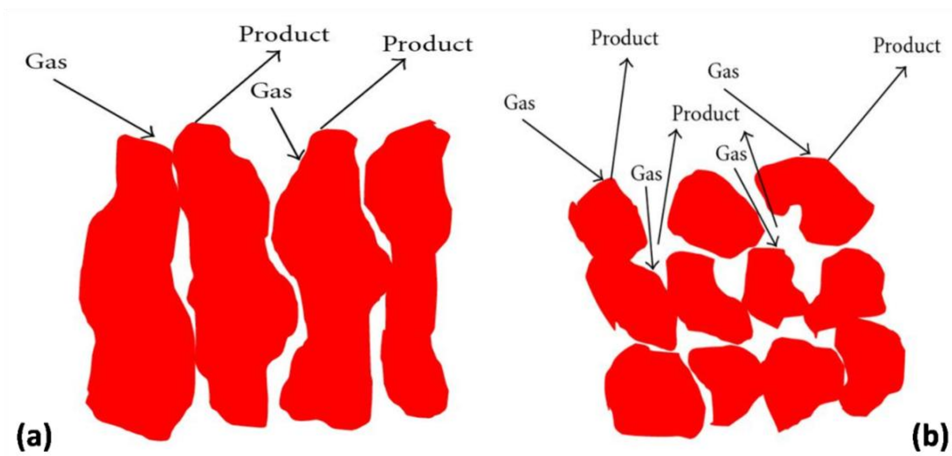

Fig.1.9. Simple diagram (a) Compact layer and (b) Porous layer

1.6 Role of Nano-Structure in Gas Sensing

Recent literatures reported to improved gas sensing properties for ethanol, ammonia and carbon dioxide by the changing in the nanostructured in the ZnO thin film, For example, ZnO hollow 1D nanofibers used in the sensing of ethanol (C_2H_6O), ZnO nanoparticles/ reduced graphene oxide bilayer thin film showed improved sensitivity for ammonia (NH_3), Sodium doped ZnO thin film showed enhance sensitivity for carbon dioxide (CO_2). As, Zinc Oxide is the promising material for the sensing of methane (CH_4), carbon monoxide (CO) and hydrogen sulphide (H_2S) and Fe doped ZnO thin films are shown to have superior sensing activity than pure ZnO due to enhanced formation the oxygen species on surface at the ambient oxygen partial pressures [Sharma *et al.* (2012)].

Nano structuring of thin film have high porosity than flat film and the increased porosity of the materials increases the diffusion rate of gases in thin film resulting into faster adsorption process. Recent literatures reported that different ZnO based nano structures such as nanorods, nanofiberes, nanorod-arrayn, nano-belts based sensors show enhance sensitivity and better responses. M. Yin *et al.* reported the ZnO nanorods based ethanol sensor in operating range of 5 to 500 ppm alcohol vapor at 370°C. 2-D nanostructures of ZnO are employed in gas sensing and their sensitivity properties enhance due to the large specific area and high surface to volume ratio present in nanostructures. ZnO based flat thin film methane sensor were developed in large extent implying various kind of nano-structuring [Chow *et al.* (2013), Kumar *et al.* (2015), Zhu *et al.* (2017)]. Doping effect of Na, Fe, Cu, Co etc. in zinc oxide based thin films also improved for gas detection [Basyooni *et al.* (2017), Rambu *et al.* (2013), Baranowska-Korczyc *et al.* (2012), Gong *et al.* (2006), Malik *et al.* (2015), Misra *et al.* (2016), Hu *et al.* (2016), Rambu *et al.* (2015)].

1.7 Preparation and Characterizations Technique

Preparation of samples as undoped zinc oxide flat thin film, 8 % Fe doped nano-wrinkled, 8 % Cu, Co, Ni doped zinc oxide thin films, undoped ZnO nano-wired, 8 % Cu doped ZnO nano-strips and 8 % Fe doped ZnO nano-net thin films included in thesis on the basis of literature survey and experimental researches up to 8 % doping effect of Fe, Cu, Co, Ni in zinc oxide based nano-structured thin films was better response for methane sensing. The deposition of films was using technique of spin coating and drop casting on glass substrates.

1.7.1 Glass Substrate

Glass substrate was used for the fabrication of thin film sensor [Hill *et al.* (2016), Morey (1931), Morey (1938)]. Glasses are cheap and easily avialabe in laboratory. In this thesis ordinary glass was used in experiments. It is necessary to clean the glass substrate before the ZnO based thin film depositions. Substrate (2.5 × 2.5 cm) is cleaned ultrasonically in acetone, trichloroethylene, methanol and high purified water for 5 min, finally etched with HF solution and keep in oven at 150 ^{o}C for dry.

1.7.2 Deposition Techniques

The deposition of thin film on the glass substrate, mostly carried out using techniques such as drop casting, dip coating, spray pyrolysis, and spin coating and sputtering [Gao *et al* (2013), Lmai *et al.* (2016), Ohya *et al.* (1996), Rambu *et al* (2013),]. There are techniques useful on the basis of thickness controlling and the cost effectiveness. The drop, dip and spray coating are inexpensive while thickness is not controlled in the accuracy. Spin and sputter depositions technique is thickness controlled but sputter are more expensive and power consumption technique than spin. So spin coating are utilized in this thesis work. These methods of coating are briefly explained in the sections.

1.7.2.1 Drop casting

Drop casting is very simple technique casting of drop on the substrate and heat at required temperature generate the film depending upon the more substrate. This technique used for depositions of thick films.

1.7.2.2 Dip coating

Dip coating is based on dip process. In this process, substrate dips in the solution with desirable time and thickness controlled by concentrations and dip angle.

1.7.2.3 Spray pyrolysis

This coating technique is based on the spray by the aerosol, which is colloid suspension and liquid droplets in gas and atomizer nozzle. The thickness controlled by the spray timing. Spray could be on normal substrate or hot substrate.

1.7.2.4 Spin coating

This technique is based on substrate spining at constant rpm and drop by drop casting. Further heating 100 ^{o}C to 250 ^{o}C. In this way, we deposited the zinc oxide film on the glass substrate by the electro-spin rpm pattern from 500 to 3000 rpm. We used spin coating because film adhesion on substrate is good, uniform film deposition and thickness of film can be controlled by this method. Thickness controlled by solution concentration or spin rpm. Dropped solution speared by the resultant of circular and concentric force. In this thesis, deposition of thin film was carried out work using by utilizing the spin system "DELTA SCIENTIFIC EQUIPMENT, SPIN COATER MODEL DELTA SPIN-1" and heating was done at hot plate.

1.7.2.5 Sputtering

This technique is used for deposition of material by using physical removal of atoms from target material on the substrate. Sputtering system includes chamber, fix target, substrate table, where target is cathode while substrate is anode. High electric field is applied at high vacuum followed by argon gas flow then argon atoms are ionized which creates the plasma inside the chamber. The charge particles of plasma (Ar ions) accelerated through electric field towards the cathode (target), and collide (these collisions may be elastic or inelastic or series) to target and sputter target atoms are deposited on substrate. Sputtering is mainly of two types DC sputtering and RF sputtering. [Gao F *et al.* (2013), Singh K *et al.* (2015)].

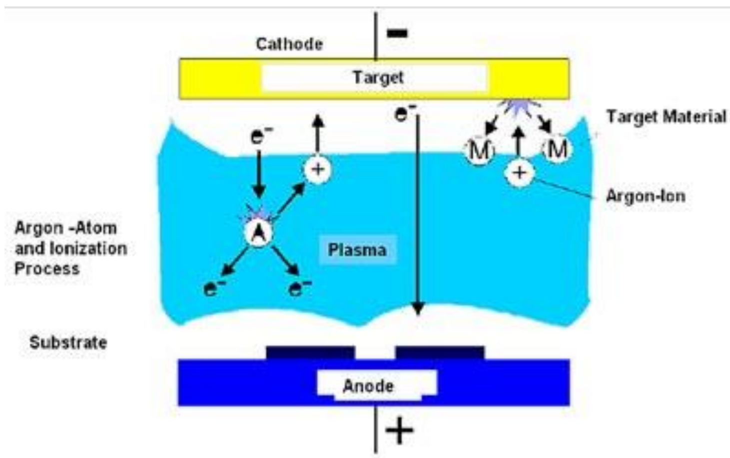

Fig.1.10 A simple Sputtering setup

1.7.3 Characterizations

XRD (X-ray diffraction) was carried out using RIGAKU DIFFRACTOMETER (Smart Lab 9KW, Target: Cu Kα, λ=1.54Å) for the analysis of nano crystalline structures and grains of the thin film. SEM (Scanning electron microscope) and EDX (Energy Dispersive X-Ray Spectrometry) was carried out using EVO-18 Research ZEISS for the analysis of surface morphology, grains structure and compositions. Field Emission Scanning Electron Microscope (FE-SEM) or High Resolution Scanning Electron Microscope (HR-SEM) using NOVA NANO SEM 450 was utilized for analysis of nano morphologies. Roughness of thin film surface was studied by 2D and 3D AFM (Atomic Force Microscope) by using NT-MDT- NTEGRA, the scan mode is semi contact and mounting rate is 0.5 Hz.

1.7.4 Thickness Measurement

For measuring the thickness of the deposited thin films profilometer is used. The thickness of the films varies according to the spin rpm and time. The profilometer is used for measuring the thickness and roughness of the film samples. In the profilometer, diamond stylus, which moves vertically for the contact force on the sample and horizontally for the thickness measurement. We can measure the minimum and maximum thickness using the 'Stylus Profilometer' up to 10 nm and 1mm respectively. The radius of the diamond stylus can vary from 20 nm to 25 µm.

1.7.5 Metallization

Metallization is the last step of sensor fabrication to make electrodes to the measure the resistance. Here, aluminum metal mask (8 cm × 8 cm × 2 mm) was used to make the contact of 1 mm, 2 mm, 3 mm and 4 mm diameter in groups of four at a distance of 3 mm. Each group is separated by 2 to 2.5 mm distance. Ag is used for making of electrode because Ag is cheap compared to Au and is a good conductive material. The desirable sized of electrode fabrication using metal mask. Silver contacts were made by the paste method using dotted aluminum metal mask and kept in oven at 250 °C for one and half hour for drying. Metal shown in Fig. 1.11.

Fig.1.11. Photograph of aluminum sheet metal mask

1.7.6 Sensing Study

It methane was exposed on sensor, then we measured the resistance of film and decrease in the resistance was observed and change was stable. When gas flow was closed and gas was removed from testing chamber, then resistance increases again and recovers to the original resistance. In ambient atmosphere, formation of chemisorbed oxygen species at different levels of temperatures. The species created to depletion layer at film surfaces and nano-micro grains boundaries. When reducing gas such as methane was present and gas molecules react with depletion layers, then electrons trap into the conduction band and resistance decreases.

It is the measure of sensor response. It is indicates the disturbance or flotation or variation in the physical or chemical or electrical properties of sensing or active material in the presence of detecting or testing gas. It also depends upon temperature, gas concentration and surface morphology. Sensitivity is determined by the percentage of changed resistance of the film in the gas. High sensitivity is required for a smart sensor. The percentage sensitivity (%) of the sensor of calculated using the formula given below [Choudhary *et al.* (2013), Ghosh *et al.* (2014)].

$$\text{Response or Sensitivity of sensor (\%)} = [(R_a - R_g) / R_a] \times 100 \qquad (13)$$

Where, R_a is resistance of thin film in the air and R_g in presence of reducing gas.

The gas testing set-up included methane and nitrogen cylinders (for target gas and carrier gas), MFC's (for gases flow control), testing gas chamber, heater supply and FLUKE-107 600V multimeter (for resistance measurement). Schematic diagram of gas testing setup is shown in Fig.1.12 and photograph is shown in Fig.1.13. In testing procedure first step sensor was placed in testing chamber and all electrical connections were made, further set the heater voltage for required temperature and MFCs were set for the required gas concentration. In second step, gas was flow in the testing chamber, and then finally measurement was recorded using FLUKE-107 600V and repeated steps for different operating temperatures.

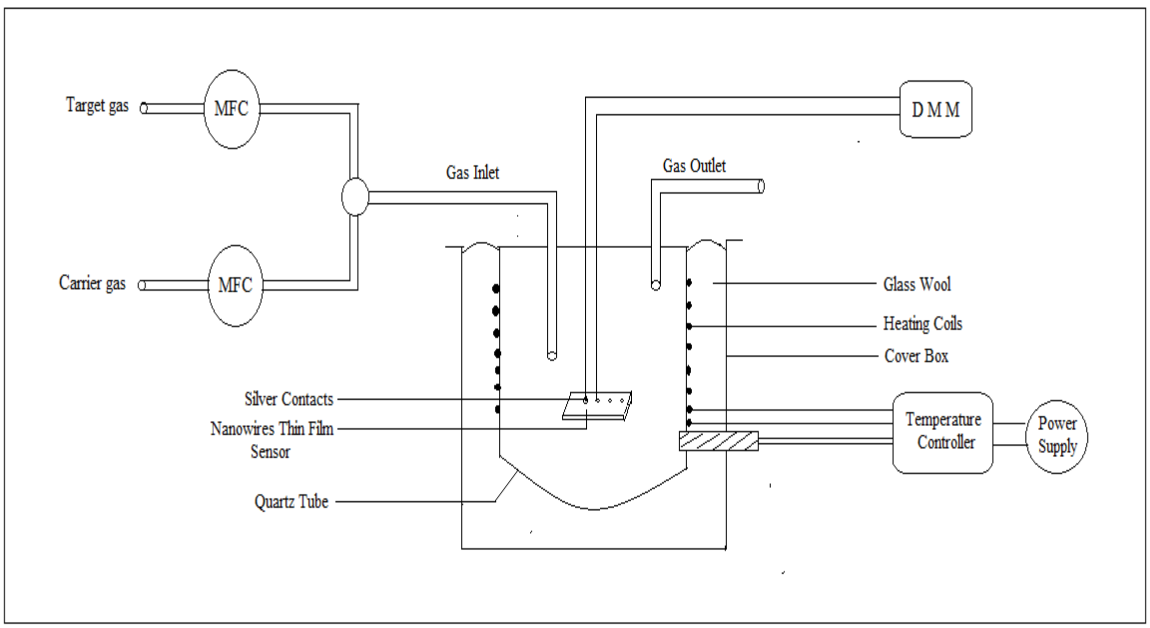

Fig.1.12. Schematic diagram of the testing setup.

Fig.1.13. Photograph of the testing setup (In circle).

1.8 Goals

Aim of the thesis is fabrication of undoped, iron, copper, cobalt and nickel doped ZnO based nano-structured thin film gas sensors and methane sensing and detection activities of develped thin films with different concentrations of methane gas at different operating temperatures to make superior methane sensors.

1.9 Organization

The chapters of the thesis are organized as follow :-

1. Chapter 1, Inroduction.
2. Chapter 2, Preparation and characterization of thin film sensors
3. Chapter 3, Methane sensing and detaction activity of undopped ZnO thin films
4. Chapter 4, Nano-wrinkled Fe doped ZnO thin film for application in methane detection

5. Chapter 5, Study of Cu doped ZnO thin film in methane sensing
6. Chapter 6, Application of Co doped ZnO thin film in methane sensing
7. Chapter 7, Methane detection using Ni doped ZnO thin film
8. Chapter 8, Study of undoped nano-wired ZnO, Cu doped ZnO Nano-strips and Fe doped ZnO Nano-net thin films for application in methane sensing
9. Chapter 9, Summary and scope