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Introduction

Global warming is an important factor in today's era. Elements like environmental pollution, leakage of hazardous gases in nuclear and chemical industries etc. adds up to global warming. Thus, real-time monitoring of causes of global warming is vital for domestic sector as well as medical field so as to uphold human health and safety. Since few years, gas sensor has been one of the emerging application in nano fabrication for environmental well-being due to its essential requirement in automotive industry, space application, environment monitoring. Its extensive use in fire alarm systems for domestic segment and to detect explosive and hazardous gases in defence establishments is also a significant factor that supports fabrication of such type of sensors. High sensitivity and selectivity towards hazardous gases along with fast response and recovery time are the key challenge for fabricating efficient gas sensors. Miniaturization of gas sensors and making it power efficient, consequently becomes most demanding conditions for real time environmental monitoring to prevent causalities. To incorporate with increasing demands of gas sensors, metal oxide based nano sensors play an imperative role due to its high sensors response, fast response/recovery time, low power consumption, low operating temperature along with its nano scale fabrication and low manufacturing cost. All these properties provide most favourable platform for nano sensors fabrication industries in comparison to conventional gas sensors.

This chapter is focused on gas sensors, their types and their sensing phenomenon. In addition, advantages of metal oxide based nanosenors for hazardous gases and nanostructures enhanced sensors response over thin film technology is also discussed. Hydrogen as a hazardous gas and its gas sensing mechanism is discoursed in next section followed by various post deposition methods for nanorods based sensors and schottky contacted gas sensors such as swift heavy ion irradiation and gamma irradiation enhanced sensor's performance. Formerly, literature review with work motivation, research objective and structure of thesis is conferred.

1.1 IMPORTANCE OF HYDROGEN GAS SENSOR

Hydrogen is an evolving energy source which has an extensive area of application that includes thermal power plants, hydrogen engines, fuel cells [Saad and Prakash, 2013; White *et al.*, 2006; Dodds *et al.*, 2015]. It is also highly used in chemical (for environmental safty) and aerospace applications. Due to highly combustible nature with low flash point, hydrogen is highly ignitable even at 4% hydrogen concentration in air. Hydrogen is light and has smallest molecules having strong tendency to get leakage which demands early detection of leak to avoid any causality. Hydrogen being highly inflammable in nature, it is indispensable to monitor hydrogen gas levels promptly in radioactive ecosystems like nuclear power plants, nuclear reactors, nuclear waste storage tanks [Chino *et al.*, 2011; Hubert *et al.*, 2014].

As hydrogen gas can get diffused into metal and make metal internally corrosive and weaken metal strength, it is very difficult to store hydrogen [Eberle *et al.*, 2009; Gratez, 2009]. Consequently, seepage of hydrogen gas during hydrogen production, nuclear processing, storing and transporting may result in inevitable circumstances. Henceforth, simultaneous supervision and prediction of critical levels of hydrogen gas leak is obligatory to lower the threat of outburst. Therefore, for optimum surveillance of hydrogen gas, gas sensors with energy efficient, low operating temperature, high selectivity and sensitivity, made of long lasting material, compact size and radioactive environment stability are desired. Figure 1.1 depicts commercial hydrogen applications.

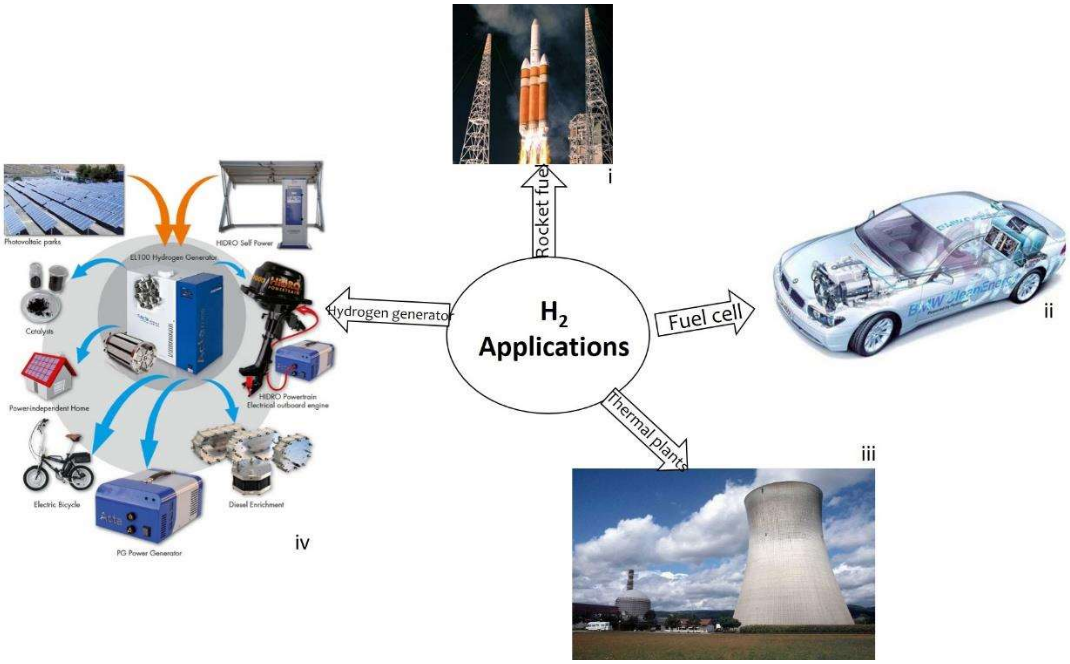


Figure 1.1: Commercial hydrogen applications (*Source*: i Popular Mechanics, 2016 ; ii BMW, 2016; iii Picture Newsletter, 2016; iv Fuel Cell Markets, 2016)

1.2 GAS SENSOR

Gas sensor is basically known as chemical sensor. Chemical sensor is a transducer device which transforms chemical information into electrical signals. When target gas is exposed to gas sensor, it changes physical properties of sensing layer such as mass, electrical conductivity, capacitance which can be measured in form of analytical signals [Bochenkov and Sergeev, 2010]. Traditionally, gas sensor has two main section viz. sensing layer and transducer. Initially, target gas reacts with sensing layer and changes its physical, electrical, optical, magnetic, thermal, calorimetric or piezoelectric properties. Transducer transforms chemical information into a form of energy which gives information about chemical reactions.

From past few decades, gas sensors have been classified according to their operating principle and sensing materials. Classification of gas sensors, gas sensing principles and fabrication techniques are some major areas of gas sensors in which enormous research have been carried out. In addition, it has been observed that the sensing results can be changed to a large extent by changing sensing material's morphology, nature of sensor's contact and using post deposition techniques.

1.2.1. Classification of Gas Sensor

Essentially, there are large number of sensing methods by which target gas can be analysed in the form of quantitative and qualitative analysis. Among these methods, gas sensor with high sensor response, fast response with selectivity, low operating temperature and compact size is desirable in practicality. Gas sensors are classified on the basis of their sensing mechanisms that comprises of two principal methods of variation in properties namely electrical properties variation such as polymer, semiconductor metal oxide and carbon nanotube; and other kinds of variation in properties like electrical, mass, optical, piezoelectric, calorimetric properties. Figure 1.2 shows gas sensor classification based on sensing mechanism.

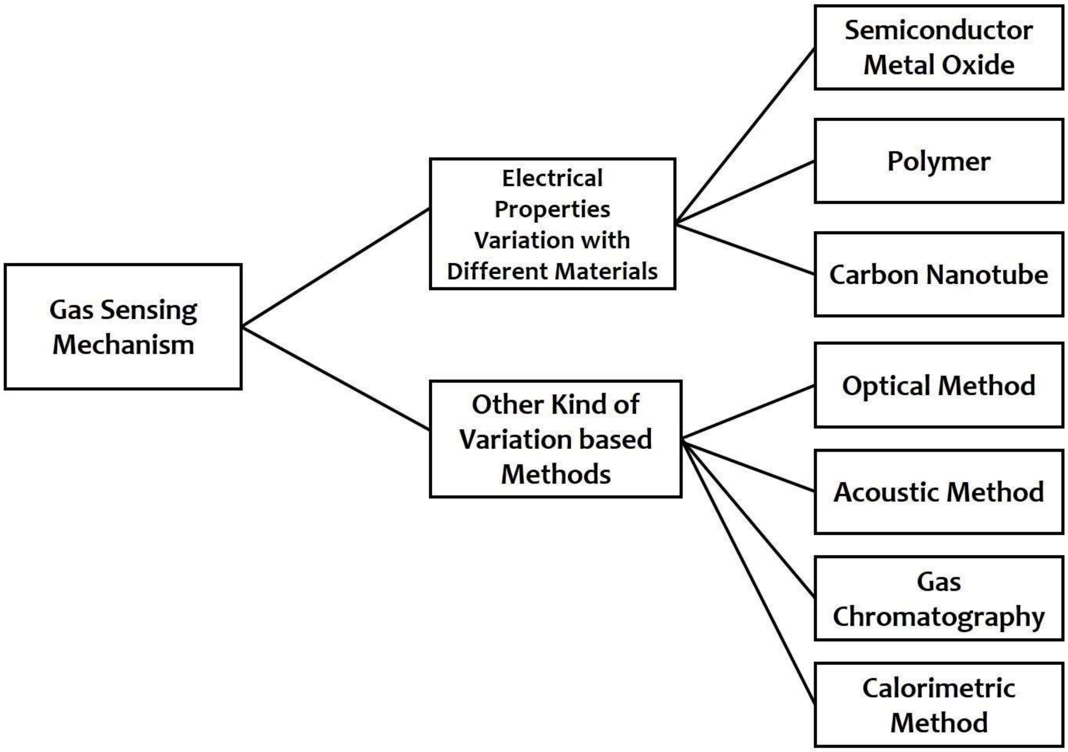


Figure 1.2: Gas sensor classification based on sensing mechanism (*Source*: Liu *et al.*, 2012)

1.2.1.1 Optical Gas Sensor

Optical principle based gas sensor are infrequently used in commercial applications. Basically, optical gas sensors are based on spectroscopic analysis which includes absorption or emission spectroscopy approach. For specific gases, absorption or emission of photons are concentration dependent. By using spectroscopy, target gas and its concentration can be optimized. In addition to optical gas sensors, fiber optic sensors are also used [Ghetia *et al.,* 2013]. Such gas sensors require more complex system for achieving high sensitivity with low limit of detection and selectivity [Rubio *et al.*, 2007]. Although these kind of gas sensors gives high selectivity and fastest response but are very costly and their miniaturization is not possible.

1.2.1.2 Gas Chromatograph

Gas chromatography is chiefly used in laboratory gas sensors. This approach ensures excellent gas sensor sensitivity, selectivity and long-time detection. Such gas sensors also have excellent gas separation quality. Even small amount of gas concentration from various gases mixers can be detected [Hobbs *et al.*, 1995]. Gas chromatographer is very bulky in size which is major drawback towards miniaturized energy efficient gas sensors. These sensors also require ample cost for fabrication.

1.2.1.3 Calorimetric Gas Sensor

Calorimetric gas sensors are solid state sensors which can detect all combustible gases and gases having thermal conductivity difference with respect to air. In these type of gas sensors, small ceramic pellets are used as sensing elements in which resistance varies when target gas reacts with it. Calorimetric gas sensor sensing mechanism can be apportioned into catalytic and thermal conductivity approach [Zanini *et al.,* 1995; Vereshchagina *et al.,* 2015]. In catalytic sensor, when target gas reacts with sensing element, it generates heat on the sensing elements which can be measured. In addition to these, thermal conductivity of sensing element also changes as operating temperature and the gas flow changes. These sensors are simple, durable and cost effective in nature. Main drawbacks of these sensors are low sensitivity and selectivity where improvement is required.

1.2.1.4 Acoustic Method based Gas Sensor

These type of Sensors are basically used in wireless sensor network by ultrasonic methods. Using ultrasonic methods, these sensors can avoid environmental disturbance as compared to chemical sensors. The ultrasonic method basically depends on the speed of light, acoustic impedance measurement and attenuation measurement [Hallewell *et al.*, 1988]. These methods have high precision in gas detection and for such sensors, building wireless nodes requires high power and cost. These sensors also have low sensitivity and the sensor response changes with change in environmental conditions.

1.2.1.5 Polymers based Gas Sensor

Generally, volatile organic compounds like alcohol and formaldehyde easily evaporate at room temperature and small concentration of these can have adverse effects on human health. Polymer based gas sensors are most commonly used for volatile organic gases or solvent vapour in gas phase detection at low temperature [Bai and Shi, 2007]. When solvent vapours react with polymers and get adsorbed by polymers, physical properties such as mass or dielectric properties in polymer changes. There are conducting and non-conduction polymer based sensors available for organic and inorganic gases [Lakard *et al.,* 2015]. In conduction polymer, as name describes, when interacted with vapour or gases, the conductivity changes. Doping can improve conducting properties of these polymers which may support in enhancing sensing response. Non-conducting polymers are widely using as coating layer for various sensing materials. Sensor with such coating have enhanced sensitivity. These polymers are coated on surface acoustic wave sensor, bulk acoustic wave sensor or capacitive sensor. Surface acoustic wave sensor performance can get enhanced even with thin coating of polymer layer that results in change in overall electrical performance in comparison to surface acoustic wave sensors [Avramov *et al.*, 2000]. Along with these advantages, polymer based gas sensors also have certain disadvantages such as long term instability, poor selectivity and irreversibility.

1.2.1.6 Carbon Nanotube based Gas Sensor

Due to their unique properties and large surface to volume ratio, carbon nanotube based gas sensors have been used for various gases even at lower gas concentrations [Rigoni *et al.,* 2013]. These carbon nanotubes have great adsorptive capacity and has large reaction area which changes electrical properties such as capacitance and resistance. To further improve sensitivity and selectivity at low operating temperature, carbon nanotubes can be incorporated with catalysts that enhances sensing. Although there are many advantages of carbon nanotube based gas sensors, fabrication of these nanotubes is very difficult. Repeatability is also very low which makes it highly expensive process.

1.2.1.7 Semiconductor Metal Oxide based Gas Sensors

Semiconductor metal oxide based sensor is a highly capable gas sensors approach in solid state gas sensors due to its advantages of low cost, miniaturization capabilities, high performance and easy integration with microelectronic systems [Comini *et al.*, 2002]. Generally, there are subsequent transition metal oxide and non-transition metal oxide available which changes their electric properties when reacts with target gases: Cr_2O_3, ZnO, TiO_2, WO_3, SnO_2, V_2O_3, NiO, CuO, Fe_2O_3, MoO_3, In_2O_3, Al_2O_3, CeO_2 [Wang *et al.*, 2010]. Most commonly used metal oxide based semiconductors are n-type such as ZnO and SnO_2. These gas sensors are highly sensible for both reducing gases like H_2, H_2S, CO, ethanol etc. and oxidizing gases such as O_2, NO_2 and that makes it an excellent sensor for domestic, environmental, automobile and industrial applications [Arafat *et al*., 2012]. With 1-dimentional nanostructure based sensors, fast response with high sensitivity at low operating temperature and cost effective fabrication is possible [Huang and Wan, 2009]. Furthermore, enhancement of sensitivity to a large extent at low operating temperature can be achieved using doping of metal oxide, Schottky contacted gas sensors and post deposition techniques. Hence, these aspects like high response, selectivity and low power consumption are key issues for researchers to overcome.

1.2.2 Comparison of Gas Sensors

So far, various type of gas sensors has been studied with different gas sensing mechanism. Table 1.1 depicts relative comparisons of advantages and disadvantages associated with various sensing mechanism based gas sensors.

Table 1.1: Relative comparisons of advantages and disadvantages of various gas sensors (*Source*: Liu *et al*., 2012)

Type of Gas sensors	***Advantages***	***Disadvantages***
Semiconductor Metal Oxide based Gas Sensor	➢ Low cost ➢ Shortest response time ➢ Wide range of target Gas ➢ Long life time ➢ Moderate sensitivity	➢ Relatively low selectivity and sensitivity ➢ Sensitive to environmental factors ➢ High power Consumption
Polymer based Gas Sensor	➢ Highly Sensitive ➢ Fast response time ➢ Low cost of fabrication ➢ Simple and portable structure	➢ Long-time instability ➢ Irreversibility ➢ Poor selectivity
Carbon Nanotubes based Gas Sensor	➢ Ultra-sensitive ➢ Low weight ➢ Fast response ➢ Large surface to volume ratio	➢ Difficult to fabricate and lacks repeatability ➢ High cost
Optical Gas sensor	➢ Long life span ➢ Insensitive to environmental change	➢ Difficult to miniaturize ➢ High power consumption ➢ High cost
Calorimetric Gas Sensor	➢ Stable at ambient temperature ➢ Low cost ➢ Low limit of detection is possible	➢ Risk of catalyst poisoning and explosion ➢ Poor selectivity
Gas Chromatography	➢ Excellent separation performance ➢ High sensitivity and selectivity	➢ High cost ➢ Difficult to miniaturize for portable devices
Acoustic Gas Sensor	➢ Long life span	➢ Low sensitive ➢ Sensitive to environmental change

As from above comparison between pros and cons of each type of gas sensors, metal oxide semiconductor based gas sensors become most suitable and demanding gas sensing approach for our research work due to its fastest response capabilities with moderate sensitivity. It is highly cost effective, gives long term stability and has wide range of gases detection. According to demand of current nano-sensors, high sensitivity, low power consumption and low concentration detection can be achieved using nanostructures modification and post deposition approaches.

In this thesis work, ZnO nanostructures and nanorods have been used as metal oxide semiconductor for hydrogen nanosensors. ZnO with larger band gap (~3.3 eV) and large exciton binding energy (~60 meV) engrossed many researchers interest due to its remarkable performance in electronics and photonic devices [Ozgur *et al.*, 2005]. In recent years, nanostructure materials have magnetized ample attention due to their unique electronic, optoelectronic, piezoelectric and mechanical properties. These properties make it most desirable metal oxide semiconductor material for gas sensing application [Choi and Jang, 2010]. The performance of such nano devices are expected to be superior as the quantum confinement of charge carriers in small dimension gives rise to spectacular variation in properties [Lin *et al.*, 2006; Gu *et al.*, 2004]. ZnO nanostructures of various types such as nanowires (NWs), nanotubes (NTs) and nanorods (NRs) have been widely studied due to their unique material properties and are used in various applications such as gas sensors [Arafat *et al.*, 2012], UV lasers [Luo *et al.*, 2006], solar cells [Anta *et al.*, 2012], photo-detectors, bio-sensors [Willander *et al.*, 2009] and light emitted diode [Yang *et al.*, 2008]. Due to the presence of native defects and zinc interstitial vacancies, ZnO always behaves as n-type semiconductor [Look *et al.*, 2003].

1.2.3 Characteristics of Gas Sensor

Gas sensing is chiefly a surface phenomenon. As discussed earlier, interaction between target gas and sensing layer causes change in electric or other properties such as mass, piezoelectric, optical properties can be defined in form of gas sensor's performance parameters. Thus, gas sensor's key sensing parameters comprises of sensors response/sensitivity, response and recovery time, selectivity, detection limit, operating temperature and stability. Ideally, gas sensor should have high sensitivity, high selectivity, fast response and recovery time, minimum power consumption, low working temperature and characteristics with lowest limit of detection [Bochenkov and Sergeev, 2010].

1.2.3.1 Sensor Response/ Selectivity

Sensors response/sensitivity is defined as relative change in resistance/voltage/current with respect to air resistance/voltage/current while introducing target gas for n-type semiconductor with reducing gas. There are many other forms in terms of relative change in voltage/current with respect to base voltage/current which can define gas sensor response. It is defined by following equation [Kumar *et al.*, 2015]

$$S = \left(\frac{R_a - R_g}{R_a} = \frac{\Delta R}{R_a} \right) \text{or} \left(\frac{\Delta I}{I_a} \right) \text{or} \left(\frac{\Delta V}{V_a} \right) \tag{1.1}$$

where R_a, I_a and V_a are the resistance, current and voltage in presence of air, respectively. Relative change in electrical properties in presence of target gas can be defined as $\Delta R/\Delta V/\Delta I$ where $R_g/I_g/V_g$ are resistance/current/voltage in presence of target gas, respectively.

1.2.3.2 Response and Recovery Time

Sensor's response time is the time taken by gas senor output signal to reach 90% of its saturation value when target gas is introduced to sensor. Whereas, recovery time is the time taken by gas sensor to return to its 90 % value of base resistance when target gas is removed and dry air is introduced to sensor [Hung *et al.*, 2009; Tamaekong *et al.*, 2009].

1.2.3.3 Selectivity and Limit of Detection

Gas sensor's selectivity is defined as ratio of sensitivity in presence of interference gas with respect to sensitivity in presence of target gas. Thus, desirable sensor should have high selectivity and it should detect lowest concentration of target gas (as ppm level).

1.2.3.4 Operating Temperature

Sensor's operating temperature is temperature at which sensor is highly stable and gives maximum sensitivity even in the presence of lowest concentration of target gas. For present scenario, operating temperature for gas sensors should be minimum which will make these gas sensors more energy efficient [Choi and Jang, 2010].

1.3 GAS SENSING MECHANISM

Metal oxide based gas sensors such as ZnO, SnO_2 and TiO_2 have been widely studied and investigated in past [Arafat *et al.*, 2012; Gopal and Schierbum, 1995; Barsan and Weimar, 2003]. Gas sensing mechanism is a surface phenomenon which strongly depends on nature of surface reaction with adsorb and desorb reactive species. Thus, complete sensing mechanism can be explained in terms of adsorption-desorption mechanism. When metal oxide surface comes in contact with oxygen, chemisorption of oxygen on the metal oxide surface takes place. Initially, when metal oxide is exposed to oxygen, oxygen molecules gets adsorbed on metal oxide surface. These adsorbed oxygen molecule extracts electron from conduction band of metal oxide grains and creates O_2^-, O^- and O^{2-} ions on the surface. Adsorption of oxygen ions on the metal oxide grains are highly temperature dependent [Watchakun *et al.*, 2011; Chen *et al.*, 2011]. Adsorption of oxygen molecules on metal oxide surface and its chemisorption reactions can be explained by following equation [Lupan *et al.*, 2010]

$$O_2(gas) \Leftrightarrow O_2(adsorb); O_2(adsorb) + e^- \rightarrow O_2^-(adsorb); \frac{1}{2}O_2 + e^- \rightarrow O^-(adsorb) \qquad (1.2)$$

In above equation, when metal oxide grains are exposed to environmental oxygen, oxygen molecules get adsorbed on surface and extract electrons from conduction region. Extraction of electrons create depletion region in grains due to which, net carrier concentration in metal oxide decreases and as a result, resistance of metal oxide gets increased. Such mechanism is essentially supported by n type of metal oxide semiconductors such as ZnO, SnO_2 etc. whereas contrary behaviour has been observed in p type metal oxide semiconductor (CuO, NiO etc.). The chemisorbed oxygen ions (O_2^-, O^- and O^{2-}) reactions strongly depends on operating temperature [Hsu *et al.*, 2014]. At low operating temperature (T<150 °C), adsorption of O_2^- are more dominant than other ions. And as operating temperature increases towards higher limit ((T>150 °C), adsorption of O^- and O^{2-} ions on metal surface gets more dominating and O_2^- disappears swiftly.

Figure 1.3 depicts energy band model for metal oxide semiconductor compressed power. It shows adsorption of oxygen molecules on grains and creation of depletion region also known as space charge layer. At the contact of two grain boundaries, it forms a barrier for electron flow which causes increase in resistance value in comparison to ideal condition.

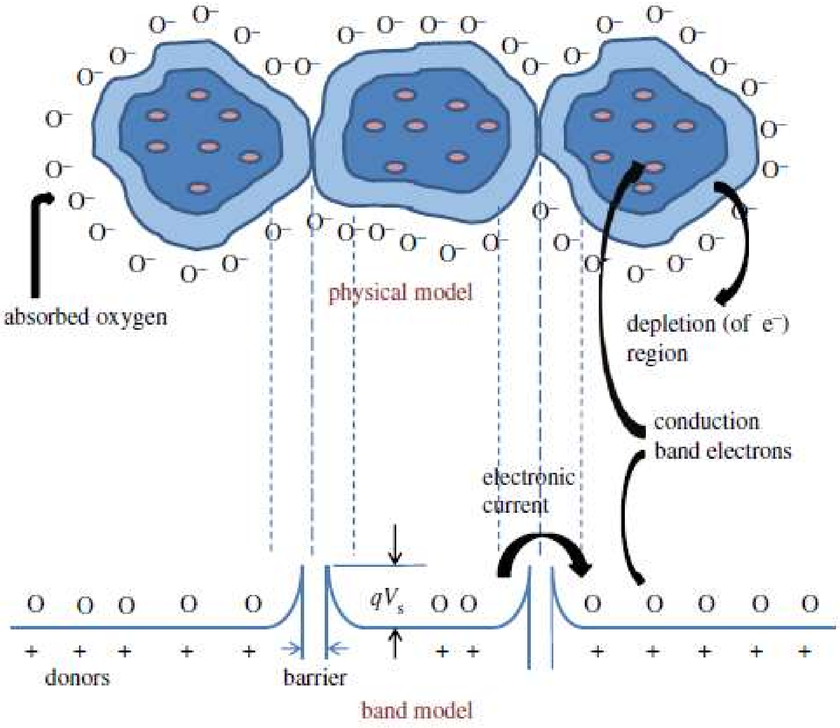


Figure 1.3: Energy band model for metal oxide semiconductor grains of compressed power where qV_s is barrier height between two grains (*Source*: Sharma and Madou, 2012)

Environmentally hazardous gases are mainly divided into two categories namely oxidizing and reducing gases which primarily resembles their reaction mechanism when they get exposed to metal oxide surface. Gases like H_2, H_2S, CO, CH_4, NH_3 etc. belong to reducing gas category whilst NO, NO_2, CO_2 etc. belongs to oxidizing gas category [Wetchakun *et al.*, 2011]. For example, when the senor is exposed to hydrogen gas, hydrogen molecules react with adsorbed oxygen ions and the reaction releases electron in the conduction band of metal oxide which decreases depletion width and increases electron concentration. For n-type metal oxide, overall resistance decreases as hydrogen molecules reacts with adsorbed oxygen. H_2O is also produced as a by-product of redox reaction. In [Gu *et al.*, 2012], brief introduction of hydrogen sensing mechanism by metal oxide semiconductor is given. Figure 1.4 shows hydrogen sensing mechanism of metal oxide semiconductor based sensor.

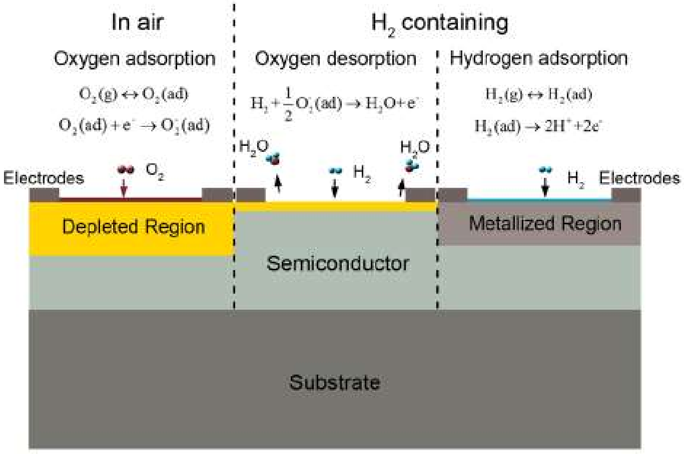


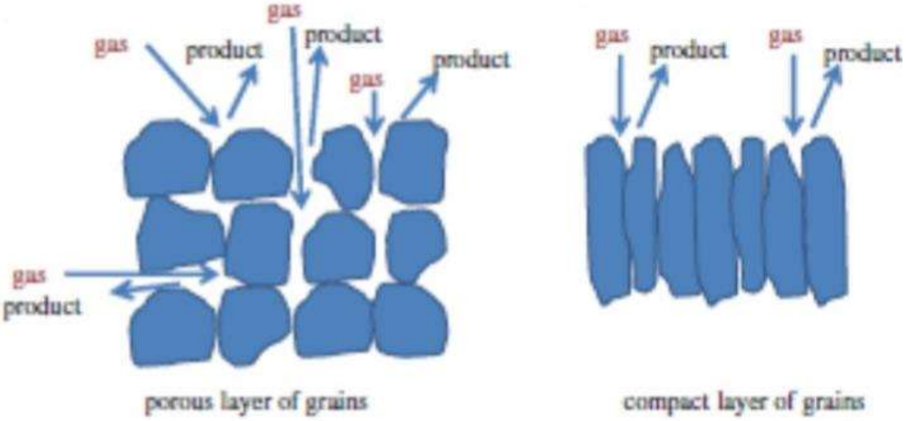
Figure 1.4: Hydrogen sensing mechanism for metal oxide semiconductor sensor (*Source*: Gu *et al.*, 2012)

1.4 ENHANCEMENT FACTOR OF SENSITIVITY

Gas sensing in metal oxide semiconductor based sensors is a surface phenomenon. Gas sensitivity of target gases can be enhanced by changing crystallinity, surface morphology, grain size and increasing surface to volume ratio. In addition to enhancement of sensors response, Schottky contacted gas sensors can also enhance sensors sensitivity to a large extent. As discussed in previous section, gas sensor response can be modulated by post deposition techniques such as gamma irradiation and swift heavy ion irradiation. Thus, it is necessary to understand 1-D nano structured gas sensor's superiority in comparison to conventional thin film based sensors.

1.4.1 1-D Nanostructured based Gas Sensors

As stated earlier, efficient gas sensors are those sensors which shows key qualities such as fast response or recovery time and high sensitivity even at low operating temperature and has low limit of detection. In metal oxide semiconductor based gas sensors, sensors response is highly dependent on surface of metal oxide semiconductor. Traditional thin film based gas sensor gives poor sensor response as gas molecules only react with surface grains [Adaman *et al.*, 2009]. Authors in [Sharma and Madou, 2012] explains relative comparison between compact thin film and porous thin film gas sensing mechanism. Compact thin film shows low sensors response in comparison to porous thin films because gas adsorption/desorption reactions only taken place at surface grains in compact thin films. But in porous thin films, gas diffuses into sensing layer and provides large surface reaction area. And due to larger surface reaction area, gas sensor's sensitivity increases. Figure 1.5 depicts pictorial representation of gas sensing in (a) compact layer and (b) porous layer.



(a) **(b)**

Figure 1.5: Pictorial representation of gas sensing: (a) Compact layer and (b) Porous layer (*Source*: Sharma and Madou, 2012)

In addition to achieving enhanced sensor response and response/recovery time, researchers have shown their inclination towards 1-D semiconductor metal oxides. 1-D nanostructure (nanorods, nanotubes, nanowires etc.) based gas sensor is the most promising technology over thin film based gas sensor technology due to its high surface to volume ratio and miniaturization capability that helps in achieving gas sensing at low temperature with enhanced sensitivity and stability. Also, large surface to volume ratio of nanorods enhances surface adsorption/desorption of hydrogen molecules and results in massive change in electronic properties and enables lower limit of detection at low operating temperature [Ahn *et al.*, 2009; Chen *et al.*, 2011; Pan *et al.*, 2015; Zhang *et al.*, 2011; Barsan *et al.*, 2007]. As mentioned earlier, adsorption/desorption of oxygen on metal oxide grains increases/decreases the width of depletion region. Consequently, 1-D nanostructures used in gas sensors such as nanorods, nanowires, nanobelts etc. already have dimensions similar to the depletion width. Due to similar dimensions, oxygen adsorptions causes large change in depletion region width as most of the conduction band electrons are involved in adsorption process. Thus, nanostructure's size, its morphology and crystallinity have been leading factors for gas sensitivity. Authors in [Liao *et al.*, 2007], demonstrated ZnO nanorods based H_2S and C_2H_5OH gas sensor sensitivity as a function of nanorod's size. As nanorod's diameter varies from 800nm to 100 nm, sensitivity for both gases increases.

For this thesis work, ZnO nanorods/n-Si based nanosensors were fabricated for low temperature hydrogen gas sensor response.

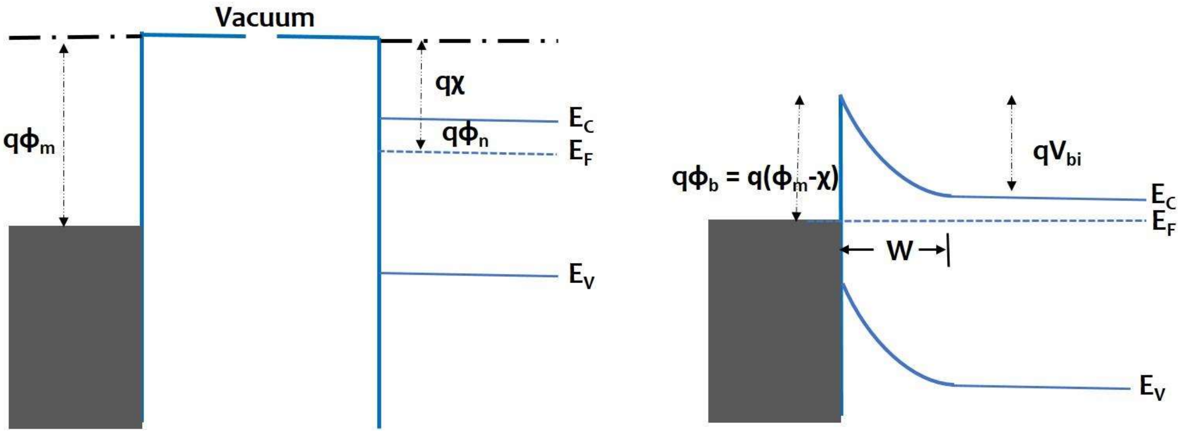
1.4.2 Schottky Contacted Nanostructured based Gas Sensors

In this section, initially, significance of metal semiconductor Schottky junction have been studied. Concurrently, semiconductor-semiconductor heterojunction electrical characterization is also studied. And finally, role of Schottky contact in semiconductor metal oxide based gas sensors is emphasized.

1.4.2.1 Metal- Semiconductor Contacts

Semiconductor technology has always been a fascinating area for research since few decades. The nature of metal semiconductor junction always plays an important role in device characterization and its application. In [Mott, 1938], author has proposed very first concept about barrier formation in semiconductors. The presence of stable space charge region in semiconductor forms potential barrier. These rectifying metal semiconductors contacts can explain precisely about the electrical behavior of the junction. Formation of metal semiconductor junction can control electrical properties such as current conduction and capacitive behavior which strongly depends on barrier formation.

When metal semiconductor makes a junction, their fermi level aligns to achieve a steady state condition. Due to this fermi level alignment, band bending takes place which further causes electron flow from semiconductor to metal [Sze and Ng, 2007]. Figure 1.6 depicts energy band diagram of metal and n-type semiconductor contact in vacuum and in equilibrium state.



(a) (b)

Figure 1.6: Energy band diagram of metal and n-type semiconductor contact: (a) Before equilibrium and (b) After equilibrium (Sze and Ng, 2007)

Where ϕ_m and χ are metal work function and electron affinity of semiconductor, respectively. The potential difference $q\phi_n$ represents energy difference between conduction band and fermi level of semiconductor and W is depletion region width. And, due to junction formation between metal and semiconductor, depletion region is formed in semiconductor as flow of majority charge carrier (n-type semiconductor) generates excess negative charge on metal and positive charge in semiconductor. Hence, induced contact potential acts as barrier height which is equal to the difference between metal work function and electron affinity of semiconductor ($q\phi_{b=}$ $q(\phi_m-\chi)$). This barrier height represents perfect contact formation between metal semiconductor junctions without any interface states at junction. However, metal work function is highly influenced by surface contamination. The barrier height modification can be done by either using interface states or unwanted interface layers. Due to these interface states, tunnelling occurs through barrier which reduces barrier height [Potje-Kamloth, 2008]. And as a result, metal semiconductor contact may behave as ohmic or Schottky junction which highly depends on difference of work function of metal and electron affinity of semiconductor. However, small difference between metal work function and semiconductor electron affinity forms ohmic junction which illustrates linear behaviour of current conduction with very low junction resistance. The current conduction strongly depends on applied voltage with minimal resistance across the junction.

For Schottky contact, current conduction shows rectifying behaviour with larger junction resistance due to huge barrier height with larger metal work function and semiconductor electron affinity. According to thermionic emission theory, barrier height of junction should be greater than kT where k is Boltzmann constant and T is operating temperature. This theory postulates about rectifying current conduction mechanism where even at low operating temperature, electron with higher energy is able to surmount energy barrier. In succeeding chapter, broad discussion about current conduction mechanism at Schottky heterojunctions has been proposed and barrier height with ideality factor for various heterojunctions has been calculated.

We have learnt about metal semiconductor junction and its role in electrical characterization of devices. In addition, semiconductor-semiconductor heterojunction also plays a significant role in electrical transport studies. Current conduction mechanism, its optical and electrical properties has always been highly influenced by nature of heterojunction. These heterojunctions based semiconductor devices have vast and versatile real life applications. When two semiconductors with different band gap, different work function and electron affinities forms a heterojunction, it causes band bending and introduces conduction band off set with valence band offset at junction. Due to such large band offsets, only majority carrier takes part in current conduction and current shows rectifying behaviour.

1.4.2.2 Schottky Contacted Gas Sensing Enhancement

Schottky diodes have been extensively attracting researcher's interest as nano-device fabrication becomes a very simple task with easy availability of transition metal Pt, Pd, Au or Ni. These transition metals with large work function (>5 eV) are excellent sources for high quality metal contact formation so as to reduce losses in device. As conferred previously, gas sensing is surface phenomenon and adsorption/desorption of target gas causes larger change in depletion region in nanostructure. When schottky contact is fabricated on these nanostructures, both schottky contact and nanostructure contributes to hydrogen sensing. This combined contribution enhances sensor performance and enables low operating temperature sensing [Irokawa, 2011; Yadav *et al.*, 2013].

When these transition metals come in contact with hydrogen, hydrogen molecule gets adsorbed and dissociates into metal surface. Subsequently, these adsorbed hydrogen atoms get infused in metal towards metal semiconductor interfaces, get polarized at interface and creates dipoles at junction. These dipoles act as interface states which enhances current conduction through tunnelling mechanism and reduces Schottky barrier to great extent. Dipoles at junctions also creates electric field at interface which declines degree of band bending and reduces barrier height to large extent. Many researchers have observed enhanced sensor preformation due to Schottky junction [Dilonardo *et al.*, 2016; Basu *et al.*, 2009; Ramgir *et al.*, 2013]. Authors in [Zhang *et al.*, 2008; Lee *et al.*, 2014] have proposed double Schottky barrier for metal semiconductor oxides and enhanced sensors preformation with hydrogen gas. Surface treatment of these Schottky contacts also enhances sensor performance [Pearton *et al.*, 2004]. Figure 1.7 depicts lowering Schottky barrier due to hydrogen in energy band diagram for metal semiconductor.

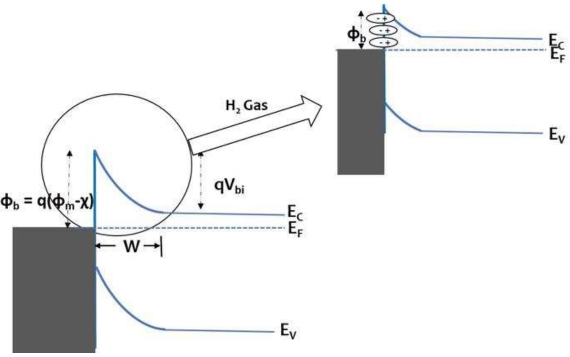


Figure 1.7: Lowering Schottky barrier due to hydrogen in energy band diagram for metal semiconductors

1.4.3 Post Deposition Techniques (Swift Heavy Ion and Gamma Irradiation)

Swift heavy ions irradiation and gamma irradiations have been studied as they modify structural, optical, magnetic properties along with material crystallinity. By changing key properties such as crystallinity and surface morphology, gas sensing performance can be enhanced.

In material science, heavy energy ion interaction with materials have been mainly studied. The interaction of ion beam with solids mainly depends on key properties like ion energy, ion fluence and ion species. There are two kinds of irradiation techniques viz. low energy ions and swift heavy ions. In low energy ions (up to keV), ions get implanted into the material and modifies the surface properties of the material. Whereas, in swift heavy ions (MeV to GeV), ion beams pass through the material and generates displacement damage effect. In swift heavy ion irradiation, these ions losses energy into material via either elastic collision (displacements of atoms) or inelastic collision where excitation in electronic system occurs. When these heavy ions pass through material, they transfer energy either by coulomb explosion or by thermal spike model [Aumayr *et al.*, 2011]. Because of ionization of atoms in solids, a repulsive force is generated along ion path which act as coulomb explosion. When these heavy ions pass through matter in narrow cylindrical path, it changes material properties by inducing local heating along its trajectory. This local heating represents thermal spike model. In [Srivastava *et al.*, 2006], author has demonstrated increased gas sensitivity of conductive polymer with increase in ion fluences. Rawat and Chandra in [Rawat and Chandra, 2011] shows modified I-V behavior of transition metal oxide nanoparticles with swift heavy ion irradiation. Structural and optical properties modification of ZnO-CuO nano-composite material with swift heavy ion fluences is shown by the authors of [Kuriakose *et al.*, 2015].

In addition to irradiation effects on semiconductor, gamma irradiation also changes electronic system of material and other properties as well. Gamma rays transfer energy to material via ionization or excitation process when the material is exposed to gamma irradiation. As irradiation fluences energy increases, an ionization process takes place with displacement damage effects. The ionizing effect is usually generated by various irradiations such as gamma irradiation, x-ray irradiation, ultraviolet ray irradiation etc. [Messenger and Ash, 1986]. These ionization effects enhance conductivity of material by increasing excess charge carrier concentration. Gamma irradiation strongly influences optical and structural properties of the material. At high irradiation doses, displacement damage effects are more dominant, due to which the material gets heated locally, which further causes change in structural, optical properties and surface morphologies. These irradiation changes properties of the material and also causes defects which can highly influence gas sensor's relative response and response/recovery time.

1.5 LITERATURE REVIEW

Review of ZnO nanostructure based hydrogen sensors have been given in this section. In addition, the effect of Schottky contacted ZnO nanostructure on hydrogen gas sensing have been studied and sensor's performance related to such alterations is observed.

1.5.1 ZnO Nanostructure based Hydrogen Senor

As gained from the learnings above, 1-Dimnetional nanostructure based gas sensors show fast sensor response, fast response/ recovery time, has low limit of detection and work at low operating temperature in comparison to conventional thin film based gas sensors. In these gas sensor devices, ohmic contact is fabricated [Al-Hardan *et al.*, 2010]. Conventional thin film based sensors require high operating temperature to achieve good sensitivity. As hydrogen sensing is a surface phenomenon, some researchers have suggested that changing surface morphology from thin film to wire like structure, high sensitivity can be achieved at high operating temperature [Hung *et al.*, 2009]. As we have observed that due to shortage of surface reaction area availability, thin film based hydrogen sensors are no longer required. 1-D nanostructure based hydrogen sensors are capable to give high sensitivity with fast response towards hydrogen gas even at low operating temperature due to large surface to volume ratio and larger reaction areas. Operating temperature and hydrogen concentration always act as key factors in gas sensor sensitivity. As operating temperature increases with increase in hydrogen concentration, more gases reacts with nanostructure which increases sensitivity [Hsu *et al.*, 2014]. Author in [Wang *et al.*, 2006] proposed hydrogen gas sensor using vertically aligned ZnO nanorods arrays which was synthesized on ZnO thin films. It gave maximum sensitivity (R_{air}/R_{gas}) of ~11 at 250 °C for 1000 ppm. Room temperature sensing is also proposed with least detection limit of 20 ppm. In [Qurashi *et al.*, 2009], author has also proposed ZnO nanowires dynamic response for hydrogen sensor. It gives sensors dynamic response ranging ($\Delta R/R_{air}$) from 0.5 - 0.95 for 150 - 250 °C operating temperature and hydrogen concentration varying from 500-1500 ppm. Author [Quarashi *et al.*, 2011] in his subsequent study, analyzed that ZnO nanorods based hydrogen sensors show reversible response with maximum sensitivity ($\Delta R/R_{air}$) of ~2.1 for 200 °C and 1000ppm hydrogen concentration. Author's findings include sensor's response time of ~300 sec and that the sensor's response is a function of temperature. Li *et al.* in [Li *et al.*, 2007] proposed surface depleted controlled gas sensing of ZnO NRs (15 nm diameter) achieving maximum sensitivity (R_{air}/R_{gas}) of 13 for 1000 ppm hydrogen at 300 °C operating temperature. When hydrogen concentration was increased from 50 ppm to 1000 ppm, increase in sensitivity at given operating temperature was perceived. In [Rout *et al.*, 2006], ZnO nanorods and nanowire with or without Pt doped hydrogen sensing were proposed with gas sensitivity ($S=R_{air}/R_{gas}$) varying from 12-23 for operating temperature ranging from 150-200 °C for 1000 ppm hydrogen concentration. Aligned nanorods were synthesized on Al_2O_3 substrate by [Bie *et al.*, 2007] giving sensor response ($S=R_{air}/R_{gas}$) of 10.41 for 100 ppm hydrogen at 350 °C operating temperature. Effect of surface morphology and crystallinity on gas sensing was proposed by Zhang *et a.l* in [Zhang *et al.*, 2014] where annealing treatment was given and gas sensitivity ($\Delta R/R_{air}$) was increased from 2.22 to 3.56 for 2.5×10^{-6} at

425 °C operating temperature. For flexible electronics, ZnO nanorods were grown over flexible kapton tape by [Hassan *et al.*, 2013], where relative sensitivities $(\Delta I/I_{air})$ were realized from 0.42-1.75 for operating temperature varying from RT- 200 °C at 2% hydrogen concentration.

However, further enhancement in sensitivity and response time with low operating temperature can be achieved by using single 1-D nanostructure based hydrogen sensor fabricated using lithography or focused ion beam approach. Researcher Lupan *et al.* proposed sensing mechanism for single ZnO NRs based hydrogen sensor. These sensors showed fast response even at low operating temperature. In [Lupan *et al.*, 2008], individual ZnO nanorods revealed 4% sensitivity $((\Delta R/R_{air})x100)$ at 20 ppm hydrogen concentration at room temperature. ZnO nanowire based hydrogen senor also demonstrated fast response and with increase in nanowire diameter from 100nm to 600nm, eventually decreasing hydrogen gas response. Single ZnO nanowire based hydrogen sensor with capability of sensing low hydrogen concentration has been proposed in [Cardoza-Contreras *et al.*, 2015]. It demonstrated sensors response $((\Delta R/R_{air})x100)$ of 14 % at 100 °C for 121 ppm hydrogen concentration.

Although single nanowire or nanorods based hydrogen gas sensor shows high response and gives low limit of hydrogen detection at low operating temperature in comparison to ZnO nanorods/nanowires based hydrogen sensor. However, fabrication of single nanowire based hydrogen sensor using microscopic lithography approach and ion beam approach is very pricey and high precision and dedication is required to handle it.

Thus, in this proposition, our main focus will be towards fabrication of ohmic contacted and Schottky contacted ZnO NRs based hydrogen sensor with high sensitivity at low operating temperature.

1.5.2 Schottky Contacted ZnO Nanostructure based Hydrogen Senor

As studied in previous sections, gas sensor's sensitivity and low limit of detection ability can be enhanced by using Schottky contact in hydrogen nano sensors. Schottky contact formation even in conventional ZnO thin film based devices results in enhanced senor preformation with fast hydrogen gas response at 330 °C and large shift in reverse bias voltage of up to 751.14 mV for 0.06 to 1% hydrogen [Yu *et al.*, 2009]. Rout et al. in [Rout *et al.*, 2007] demonstrated hydrogen sensing for Au contacted ZnO nanowire and exhibited sensitivity (R_{air}/R_{gas}) of ~3-10 for 100 to 1000 ppm hydrogen at room temperature. In [Das *et al.*, 2010], Pt/ZnO single ZnO nanorod based hydrogen sensor was fabricated that had maximum sensitivity $((\Delta I/I_{air})x100)$ of around 90% even at 2500 ppm hydrogen concentration. Pt contacted ZnO nanorods arrays showed 24.8 % hydrogen sensitivity $(((\Delta R/R_{air})x100)$ at 250 °C for 70 ppm hydrogen concentration in [Lee *et al.*, 2011]. [Ozturak *et al.*, 2014] studied lateral Au contacted Pd doped ZnO nanorods and demonstrated higher sensor response $(\Delta I/I_{air})$ in comparison to Pd contacted ZnO nanorods in operating temperature ranging between RT to 200 °C due to two factors, firstly, Schottky junction and secondly, metal catalyst's enhanced performance. Table 1.2 shows literature survey on ZnO nano-structures and Schottky contacted ZnO nanosensors for hydrogen sensing.

Table 1.2: Survey on ZnO nano-structures and Schottky contacted ZnO nano-sensors for hydrogen sensing

Nano-Sensor	Sensitivity/ Sensor's Response	Response Time	Operating Temperature	H_2 Concentration	Publication
ZnO NRs	11 (5)	Few sec	250 °C	1000 ppm	Wang *et al.*, 2006
ZnO NRs	2.1 (4)	300 sec	200 °C	1000 ppm	Qurashi *et al.*, 2011

ZnO NRs(set 1)	18-32 (5)	-	150 °C- 200 °C	1000ppm	Rout *et al.*, 2006
ZnO NRs(set 2)	50-80 (5)	-	150 °C- 200 °C	1000ppm	Rout *et al.*, 2006
ZnO NRs	13 (5)	-	300 °C	1000ppm	Li *et al.*, 2007
ZnO NR	0.6 (3)	50-80 sec	RT	150 ppm	Lupan *et al.*, 2007
ZnO NRs	0.42-1.75 (2)	-	RT-200 °C	2 %	Hassan *et al.*, 2013
ZnO NRs	1.95-3.56 (4)	15-19 sec	425 °C	2.5-25 ppm	Zhang *et al.*, 2014
ZnO NRs	98% (3)	-	250 °C	100 ppm	Sinha *et al.*, 2016
ZnO NW	34% (3)	-	RT	100 ppm	Lupan *et al.*, 2010
ZnO NW	4% (3)	-	RT	200 ppm	Lupan *et al.*, 2008
ZnO Nanobelts	15.32 (5)	-	385 °C	1%	Sadak *et al.*, 2005
ZnO Nanowire	2.5 (5)	-	200 °C	100ppm	Khan *et al.*, 2010
ZnO nanowire	8%-14 % (3)	29 sec	RT-100 °C	121 ppm	Cardoza-Contreras *et al.*, 2015
ZnO wire like film	2.83 (4)	1.5 min	200 °C		Hung *et al.*, 2009
ZnO nanowires	0.5-0.95 (4)	65 sec	150- 250 °C	500-1500 ppm	Qurashi *et al.*, 2009
ZnO Nanorods	10.41 (5)	-	350 °C	100 ppm	Bie *et al.*, 2007
Schottky Contacted ZnO based Hydrogen Nanosensor					
Au/ZnO Nanowire	3-10 (5)	-	RT	100-1000 ppm	Rout *et al.*, 2007
Pt/ZnO	90% (1)	55 sec	RT	2500 ppm	Das *et al.*, 2010
Pd/ZnO/ITO	0.9 (2)	-	100 °C	500 ppm	Ozturk *et al.*, 2014
Au/Zno/Au	0.5-0.6 (2)	-	RT	200-300 ppm	Ozturk *et al.*, 2014
Pt/ZnO NRs array	24.8 % (3)	-	250 °C	70 ppm	Lee *et al.*, 2011
Pt/ZnO nanostructure	325 mV RB voltage shift	-	625 °C	1%	Shafiei *et al.*, 2010

Pd/ZnO nanostructure	24.8-99.5 % (3)	-	RT- 200 °C	100-1000 ppm	Al-salman and Abdullah, 2013
Pt/ nanostructed ZnO film	Maximum 751.14 mV RB voltage shift	102-93 sec	330 °C	0.06-1%	Yu *et al.*, 2009

$^{1}(\Delta I/I_{air}x100)$, $^{2}(\Delta I/I_{air})$, $^{3}((\Delta R/R_{air})x100)$, $^{4}(\Delta R/R_{air})$, $^{5}(R_{air}/R_{gas})$

1.6 MOTIVATION

Gas sensor is one of the emerging application in nano fabrication since last decade due to its extreme prominence in automotive and space application, environment monitoring, domestic sector to detect explosive and hazards gases. Among all other hazards gases, hydrogen is most desirable gas for detection because of its highly flammable nature at high temperature and not easy-handling nature. Hydrogen is widely used in fuel cells, hydrogen engines etc. which provides strong motivations to develop high selectively, compact and energy efficient hydrogen gas sensor operating at low temperature and direct electronic interface with existing silicon technology.

Over a decade, varies kind of gas sensors have been developed with different sensing materials and sensing mechanisms. However, metal semiconductor oxide based gas sensors are potential candidates for sensing platform due to their fast response, low cost, high sensitivity, easy to use, ability to detect large number of gases with miniaturization capabilities. Among these metal oxides based semiconductors, ZnO is widely used semiconductor material as it possesses high electron mobility, intrinsically n type behavior, and high chemical and thermal stability under sensor operating conditions. As gas sensors response strongly depends on surface morphologies, 1-D nanostructure (nanorods, nanotubes, nanowires etc.) based gas sensor is most promising technology because of its high surface to volume ratio and miniaturization capability that helps in achieving low temperature gas sensing, enhanced sensitivity and stability. ZnO nanorods based hydrogen sensors could achieve better relative response with fast response. Recovery time makes it attractive approach for sensors fabrications. The relative response and response/recovery time can be tuned by operating temperature and hydrogen concentrations.

To further enhance the sensor response, Schottky barrier plays an important role by varying the barrier height with adsorption and desorption of gases that causes large change in sensors response even for low hydrogen concentration (ppm level) and low operating temperature.

In addition to further sensors relative response enhancement, post deposition technique such as swift heavy ion irradiation and gamma irradiation is used which causes surface modulation due to irradiation and ZnO based nanosensors response can be modified.

1.7 RESEARCH OBJECTIVE

The prime objective of this thesis work is to present low temperature hydrogen sensor based on ZnO NRs/Si heterojunction followed by Schottky contacted ZnO NRs based hydrogen sensor for low hydrogen concentration (5 ppm to 1%, 5%) that operates at low operating temperature (≤150 °C). Author aims to study gas sensing performance for these nanosensor and show how sensors performance and sensing mechanism can be correlated with morphology, crystallinity and by variation in Schottky contacts. In addition to sensor performance enhancement, effect of surface modulation techniques such as swift heavy ion irradiation and gamma irradiation have been investigated.

In this thesis, the author aims for:

- Optimization and characterization of nano-crystalline ZnO thin films followed by deposition of vertically aligned ZnO nanorods over various substrate.
- Study of temperature dependent electrical characterization with current conduction mechanism for ZnO NRs/Si heterojunction and determine the effect of barrier inhomogeneities on Schottky barrier's basic parameters.
- Fabricate defect free ZnO NRs based nanosensors that can be used for low temperature hydrogen sensing application.
- Enhancement of sensor's relative response using Schottky Au-contacted ZnO nanorods based hydrogen sensors for 1% and 5% hydrogen concentration with low operating temperature (≤ 150 °C). For further enhancement of hydrogen sensing even for ppm level detection (5 ppm to 1%), Pd contacted ZnO NRs based hydrogen sensors are fabricated and characterized.
- Study the surface modulation technique using gamma and swift heavy ion irradiation for ZnO nanostructure based hydrogen sensor to modify sensors response.

1.8 ORGANIZATION OF THESIS

This thesis is organized as follows

Chapter 1: This chapter presents brief introduction about existing gas sensing mechanism based sensors, their relative comparison and superiority of metal oxide semiconductor based gas sensor using ZnO. In addition to this, gas sensor performance characterization, gas sensing mechanism along with sensors performance influencing key factors explained. Then brief literature review on ZnO nanostructure based hydrogen sensor given followed by motivation, objective and organization of thesis mentioned.

Chapter 2: This chapter basically devoted towards understanding of deposition, irradiation and structural, optical, surface morphology and electrical characterization techniques with gas sensing characterization have been explained.

Chapter 3: This chapter explains deposition and characterization of nanocrystalline ZnO thin films over silicon substrate. This includes growth mechanism of thin films, deposition of ZnO thin films using RF sputtering technique and effects of deposition parameters on structural characterization with stress analysis and surface morphology variation studied.

Chapter 4: This chapter focused on deposition and optimization of well aligned ZnO nanorods over various substrate. In addition to this, initially growth mechanism of nano rods has been discussed. For conformation of deposition of high quality and crystalline ZnO nanorods and effect deposition parameter as well as substrate variation have been explained by structural, optical and surface morphology characterization.

Chapter 5: In this chapter, firstly ZnO NRs/ Si heterojunction fabricated and characterized. Then temperature dependent electrical characterization with current conduction mechanism have been studied. Effect of barrier inhomogeneities on Schottky heterojunction has been calculated. In following section, fabrication and characterization of defect free ZnO nanorods and its ZnO NRs/Si/ZnO junction application for low temperature hydrogen sensing has been studied and proposed gas sensing mechanism.

Chapter 6: This chapter focused on fabrication and optimization of Schottky contacted ZnO NRs based hydrogen sensor. Then hydrogen sensor response with rise/recovery time for various hydrogen concentration (1% and 5 %) with various operating temperature (50 °C to 150 °C) have been studied. The gas sensing mechanism also proposed nano-sensor. In last section gives effect of changing Schottky contact metal from Au to Pd, nanosensors shows high response even for very low hydrogen concentration (5 to 1000 ppm) at moderate operating temperature (up to 150 °C).

Chapter 7: In this chapter, effect of gamma irradiation on Schottky contacted ZnO nanorods has been studied which includes structural, optical characterization and surface morphology variation with gamma irradiation and influenced gas sensors response and response/recovery time with various operating temperature and hydrogen concentration have been proposed. Then gas sensing mechanism also proposed to explains effect of gamma irradiation on gas sensing.

Chapter 8: This chapter explains effect of swift heavy ion irradiation on structural, optical and surface morphology of nanocrystaline ZnO thin films. The gas sensors response with response and recovery time for various operating temperature and 5% hydrogen concentration have been studied.

Chapter 9: In last chapter, thesis work summery with scope of future has been given.

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