Fabrication of Metal Chalcogenide One Dimensional Nanostructures for Toxic Gas Sensing Application.

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Supervisor: Dr. Muhammad Aftab Akram

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Certificate

This is to certify that work in this thesis has been carried out by Mr. Hamza ul Haq, Mr. Muhammad Adil Sandhu and completed under my supervision in Nano-synthesis laboratory, school of chemical and materials engineering, National University of Sciences and Technology, H-12, Islamabad, Pakistan.

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Dedication

This work is dedicated to all those who carve a path for themselves despite sheer hardships and opposition. This work is symbol of courage and commitment for those who feel exhausted and loose hope. This work is dedicated to loving parents and honest friends who believe in you.

Acknowledgment

Praise be to Allah, the Cherisher and Sustainer of the worlds; (Surah Al-Fatiha, 1)

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Last, but not the least, this achievement would not have been possible without the support and prayers of our parents. They are the ultimate source of inspiration and courage for us who stood by us through thick and thin.

Abstract

Zinc Oxide (ZnO) is a wide-band- gap (3.37 eV) semiconductor of II-VI semiconductor group. The native doping of the semiconductor due to oxygen vacancies or zinc interstitial is n-type. Synthesis of (One- Dimension) 1D structure of ZnO is a potential candidate for Gas Sensing, UV sensing and Immuno-sensors for Viruses, in LEDs and in Solar Cell application as an electron transporting layer. The realization of high aspect ratio of Sodium doped ZnO nanorods is critical to the development of high-quality nanostructure based optoelectronic and electronic devices. In this project, we aim a solution-based synthesis method to grow vertically aligned high aspect ratio nanorod on transparent conducting oxide (TCO) substrate for UV light and Gas sensing applications (for sensing CH_4, CO and CO_2) at room temperature. It will be investigated whether the diameter and aspect ratio of the nanorods are affected by the addition of polyethyleneimine (PEI) to precursor solution used as well as by variations in the growth temperature and the concentration of the precursor solution. Graphene and other 2D materials also may be utilize for making ZnO based nanocomposites. The structural, morphological, optical and gas sensing properties of synthesized ZnO and Doped ZnO arrays shall also be examined.

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CHAPTER 1: INTRODUCTION

1.0) GAS SENSING AN INTRODUCTION:

With the advancement in the chemical, automotive and aerospace industries, emission of some serious hazardous gases also arise. To deal with this problem engineers and researchers gets busy in designing a set of materials and their structural configuration such that they can be used as Gas Sensor or a Transducer. Usually a sensor is an electronic device which is designed in such a way that in certain conditions it will changes its properties set according to its calibration. In case of metal oxide gas sensors, they change their conductivity to the exposure of certain gas for which they are designed for. Gas sensors are usually used in those areas where there is a chance of exposure to dangerous gases is present. To avoid this gas sensors are used they detect the presence of dangerous gases and gives a signal and in case of fatal amount of gas they just provoke the safety system.

Gas sensors are evaluated based on their sensitivity and selectivity and in accordance to these parameters they are used in different applications for different environment. When better selectivity is required with low cost then metal oxide semiconductor are best to opt for. [1]

In the mid of 20th century for the first time in history chemo-resistive gas sensors were introduced. A scientist named Seyama design a gas sensing layer by depositing a thin film of ZnO. Before him two scientist Brattian and Bardeen demonstrated the effect of atmosphere on some semiconductors such as Ga in 1950s at Bell Laboratories. After getting influenced by the work of seyama another scientist Shaver in 1967 explain the changes in properties of oxides semiconductor by the addition of some noble metals (e.g., Pt, Pd, Ir, Rh). After the fabrication of SnO_2 in 1970s by Tugachi a whole new world of gas sensing material opens, and new technologies and mechanism introduced for the application of gas sensing. [2]

1.1) ADVANCEMENT IN TECHNOLOGY

Sensor technology has been widely investigated and utilized for gas detection. A classification of sensing technologies is given, based on the variation of electrical and other properties. There are different sensing materials that are present now days, including metal oxide semiconductors, polymers, carbon nanotubes, and moisture absorbing materials. Other methods such as optical, calorimetric, acoustic and gas chromatographic and their selectivity and sensitivity are taken in focus for performance measures and to compare different sensing technologies and to analyze their factors and indicators on different conditions. [3]

Gas sensing technology has become more significant because of its widespread and common applications in following areas: [4]

1. Industrial production
2. Automotive industry
3. Indoor air quality and supervision
4. Medical applications
5. Environmental studies

1.1.1) CLASSIFICATION

There are different gas sensing methods based on sensing principles and classifies into two groups:

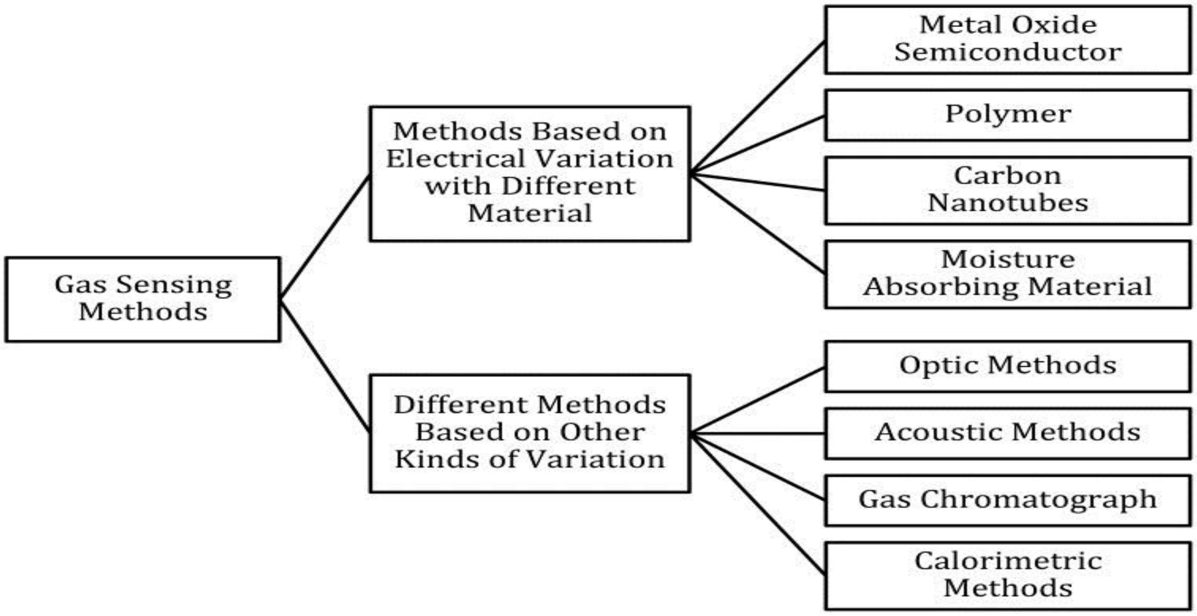


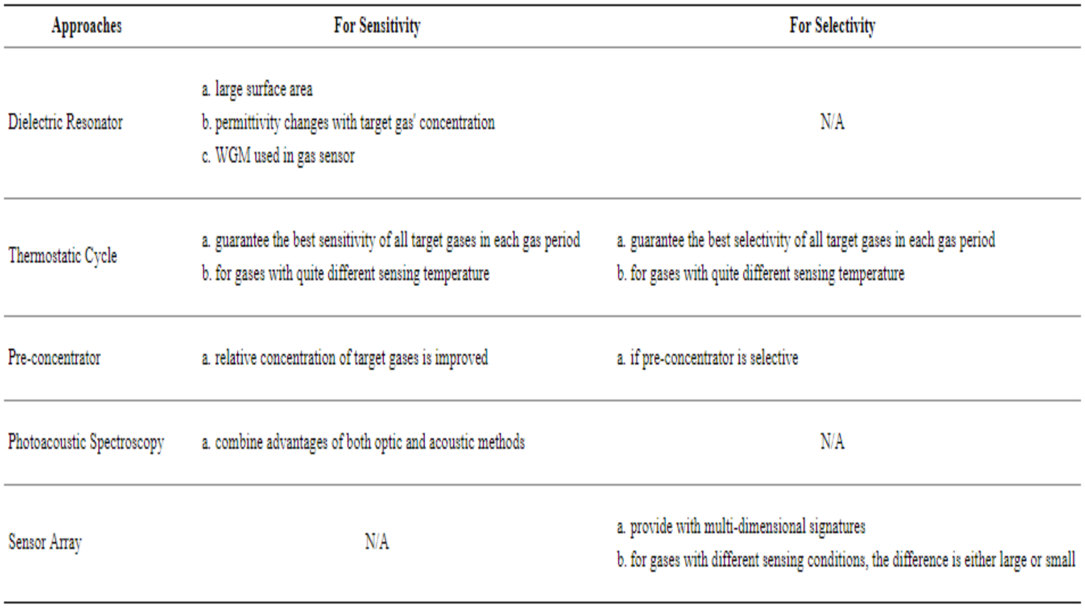
Fig 1; Classification of Gas Sensors

1.1.2) PERFORMANCE INDICATORS

1. Sensitivity
2. Selectivity
3. Response time
4. Energy consumption
5. Reversibility

6. Adsorptive capacity
7. Fabrication cost

In many cases sensitivity and selectivity are both vital indicators in designing and applying sensors. A sensor should have a sufficient sensitivity to give people a signal before concentration reaches a maximum dangerous value. The selectivity of gas sensors which determines whether they could detect the target gases without being interfered by other gases. Selectivity is the ability of gas sensors to verify specific type of gas among mixture of gases as gas sensors have a drawback for poor selectivity so generally approaches that improve selectivity fall in two categories: 1)Exploiting different properties of target gases to give multidimensional signatures and selectivity on some properties may be poor when mixed with specific gases, the cross sensitivity with one specific interfering gas does not exist on all properties, and thus the overall sensing result could distinguish target gases with a far more precise performance. 2)Utilizing the difference between optimal conditions for sensing target gases and corresponding conditions for other gases. [5]



Approaches	For Sensitivity	For Selectivity
Dielectric Resonator	a. large surface area b. permittivity changes with target gas' concentration c. WGM used in gas sensor	N/A
Thermostatic Cycle	a. guarantee the best sensitivity of all target gases in each gas period b. for gases with quite different sensing temperature	a. guarantee the best selectivity of all target gases in each gas period b. for gases with quite different sensing temperature
Pre-concentrator	a. relative concentration of target gases is improved	a. if pre-concentrator is selective
Photoacoustic Spectroscopy	a. combine advantages of both optic and acoustic methods	N/A
Sensor Array	N/A	a. provide with multi-dimensional signatures b. for gases with different sensing conditions, the difference is either large or small

Figure 2 Summary of approaches improving sensitivity and selectivity

1.2) TYPES OF GAS SENSING MATERIALS

Gas sensors based on semiconducting metal oxides are being widely used for sensing gases and vapors. The merits of these materials include their reliability, low cost and easy implementation. Nanostructures of metal oxides are most effective as gas sensing materials. Some of the sensing materials are metal oxide semiconductors such as ZnO, SnO_2, TiO_2 and WO_3.

1.2.1) TIN OXIDE

Law et.al, analyzed room temperature sensing properties of a single crystalline tin oxide nanowire sensor towards nitrogen dioxide. NO2 chemisorb strongly on SnO2 surface and at room temperature desorption is not complete when the NO2 is removed. UV light was used to activate both the adsorption and desorption process. In the dark, oxygen adsorbs on the surface capturing electrons from the semiconductor and creates a depletion layer. When exposed to UV, photo-generated holes migrate to the surface and recombine with electrons releasing oxygen ions, with an increase in conductance. The detection limit was 2 - 10 ppm of nitrogen dioxide.

1.2.2) INDIUM DIOXIDE

Indium oxide nanowires have been tested towards ethanol by Xiangfeng et.al. A mixture of In2O3 nanowire and polyvinyl alcohol solution was coated on alumina tubes with two gold contacts at the end; a heating wire was inserted in the tube to operate in the temperature range 100 - 500 ◦ C. The resistance of the nanowires was monitored in presence of air, ethanol and other gases. The highest response was obtained with ethanol, the detection limit was estimated to be equal to 100 ppm.

1.2.3) MOLYBDENUM OXIDE

Molybdenum oxide nanorods based gas sensing was reported. The MoO3 nanorods were characterized by high response to ethanol and CO at temperatures in the range of 100 ◦ C. The response of thin films with the same structure was comparatively studied and nanorods based sensor resulted in one order of magnitude more sensitive due to the high surface to volume ratio and reduced lateral dimensions of the nanorods.

1.2.4) OTHER METAL OXIDES

Sawicka et.al. presented the nitrogen sensing properties of tungsten oxide nanowires prepared with electrospinning. The effect of processing parameter variations was studied and a comparison with thin films prepared by sol-gel was also presented. WO3 nanowires showed better NO2 sensing performances compared to sol-gel processed films due to increase in surface area of nanowires.

A large amount of literature is available on the gas sensing properties of carbon nanotubes. Only little attention is put in the studies of gas sensing properties of metal oxide based tubular structures. Varghese et.al. studied the hydrogen sensing properties of titania nano-tubes. The tests were performed in nitrogen atmosphere and 1% H2. The response time increased with temperature and the response time was 2-3 min. [6]

1.3) ZINC OXIDE

ZnO is wide bandgap i.e. 3.4 eV II – VI compound semiconductor which has a non-centrosymmetric wurtzite structure with polar surfaces and lattice parameters a = 0.3296 and c = 0.52065 nm. The lack of center of symmetry results in strong piezoelectric effect and pyroelectric properties also used in mechanical actuators and piezoelectric sensors. ZnO is transparent to visible light and can be made highly conductive by doping. The structure consists of number of alternating planes composed of tetrahedrally coordinated O^{2-} and Zn^{2+} ions, stacked alternately along the c-axis. ZnO has a polar surface and the most common polar surface is the basal plane. Dipole moments are created which results in spontaneous polarization which are produced by the oppositely charged ions. Structure of ZnO is atomically flat, stable and without reconstruction. [7]

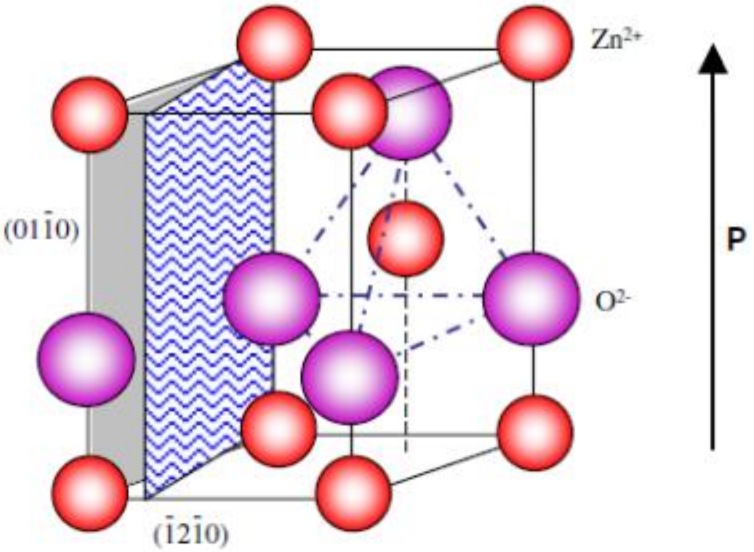


Figure 3 The Wurtzite structure model of ZnO. The tetrahedral coordination of Zn-O is shown

ZnO is a versatile functional material that has a diverse group of growth morphologies, such as nanocombs, nanorings, nanohelixs, nanobelts, nanowires and nanocage.

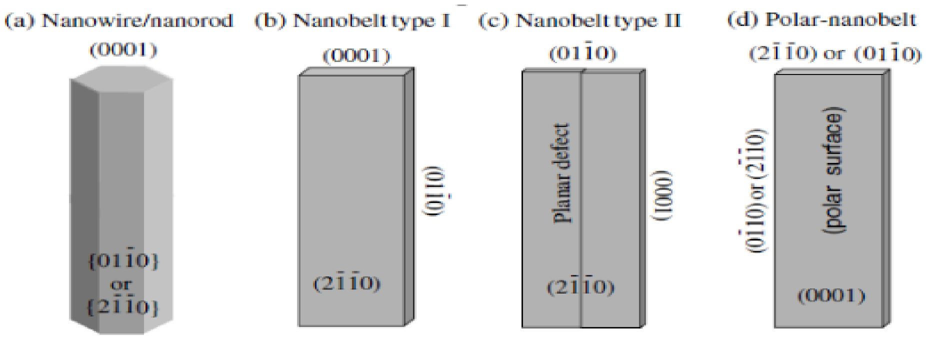


Figure4 Typical growth morphologies of one dimensional ZnO nanostructures and the corresponding facets.

1.4) EFFECT OF DOPING

Doping of semiconductor materials is an important concept to modify the properties of the semiconductor to make them more efficient. So, doping can also be used in modifying the gas sensing properties of metal oxide semiconductors gas sensors. Generally doping can be defined as the addition of some foreign impurities in trace amount at the lattice position of the base materials.

Using n-type ZnO as a base semiconductor for the fabrication of gas sensors, we can improve its properties by the addition of some impurities at the lattice points of hexagonal wurtzite crystal structure. There are lot of noble metals present for this job but some of them gives wonderful results both in gas sensing and in ultraviolet light detections. Doping also improve the parameters like sensitivity and selectivity of the gas sensor. Some of the best dopants used for this purpose are described below.

1.4.1) DOPING WITH ALUMINUM (Al)

Al is considered as the 2nd most abundant element on this planet. It is the most economical metal that can be used in variety of applications. It has highly reflected surface and a good conductor of electricity. Its crystal structure is face centered cubic. [8] Due to its huge set of applications it can also be used in ZnO based gas sensors as dopant material. Doping the ZnO with Al provides better sensitivity of Carbon monoxide hence improving the selectivity of the gas sensors. Doping with Al decreases the sensing temperature and assists in UV irradiation. Al belongs to III group of the periodic table and when doped into the crystal lattice of ZnO, great number of electrons are introduced into the system and hence band gap decreases as the defect concentration increases. So, sensors become more sensitive to the presence of gases. Fig below describes the effect of Al doped samples on the sensing temperature of the gas sensor. [9]

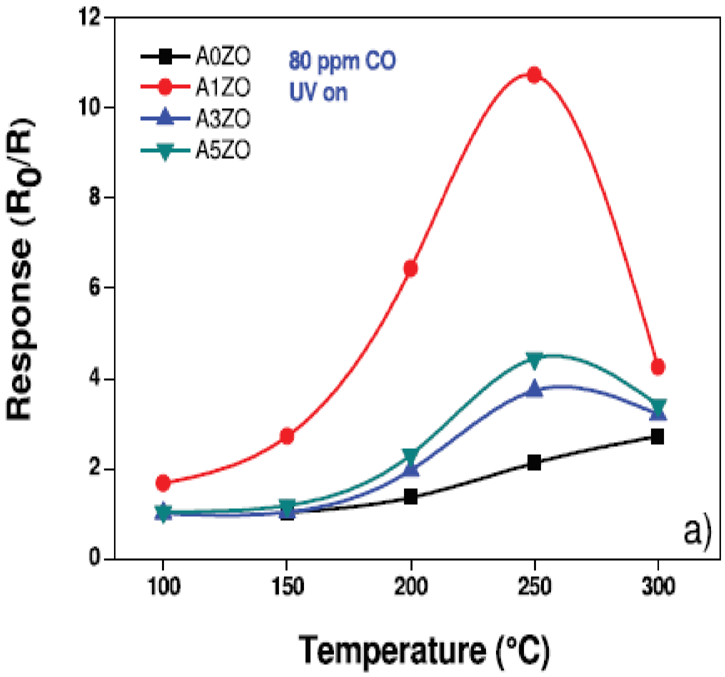


Figure 5 Response to 80 ppm CO of the AZO based sensor as a function of the temperature under UV light

1.4.2) DOPING WITH CALCIUM (Ca)

Ca is one of the most important metal found in periodic table. Having a molecular mass of 40.07µ it is found in many inorganic compounds present in earth. It belongs to II group of the periodic table and that is the reason for its high reactivity towards other elements of the periodic table. With melting temperature of 842 °C it is a good conductor of heat and electricity having a shiny silver-white color.

Doping a ZnO gas senor with Ca results in better selectivity towards CO_2. As CO_2 is a fuel gas to produce CO which is extremely fatal if inhaled so detecting the CO_2 in air is more beneficial to detect CO. Moreover, CO_2 is major source of global warming so detecting it and reducing its amount by some chemical reactions can reduce its effect towards global warming. When can Ca is doped into the lattice of ZnO it creates alkaline regions. CO_2 is being acidic react with these regions and for carbonates and bicarbonates. These precipitates on sensing temperature release electrons in the conductions band hence produce variation in the

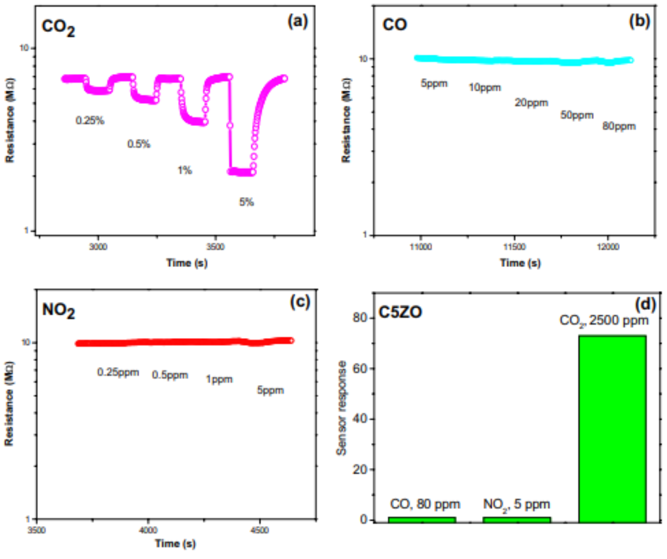


Figure 6 Response of C5ZO sensor to different concentration of $C0_2$ CO NO_2

conductivity of the sensor through which we can detect the presence of CO_2 in the environment. [10]

1.4.3) DOPING WITH GRAPENE

Graphene is the two-dimensional (2D) layer of graphite. It is considered as wonder material of the modern world because of its very high strength and high conductivity. It will be the potential component of modern super capacitors.

Doping of graphene with in the lattice of ZnO leads towards the selectivity of NO_2 gas. Nitrogen dioxide is a very toxic and colorful gas. It produced in many industries as a byproduct of many chemical reactions. Introduction of graphene in ZnO makes the sensor more sensitive to NO_2 and decreases the response time for the detection of gases. [11]

1.4.4) DOPING WITH SODIUM (Na)

Na is one of the most reactive metal present in the periodic table. Due to its high reactivity, it is stored in kerosene oil. Na belongs to IA group of periodic-table and with an atomic mass of 22.98977µ. It is silvery white in color and is very soft that it can be cut with a knife.

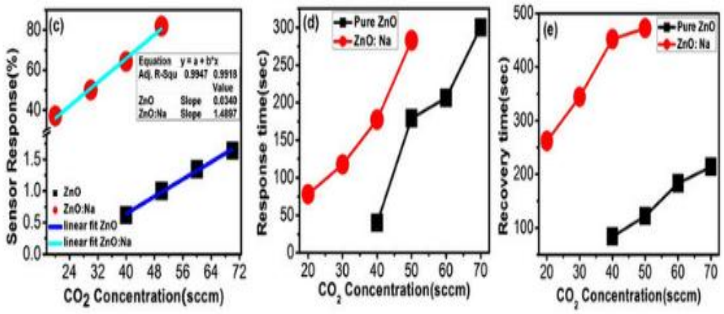


Figure 7 The sensor response% as a function of CO_2 concentration in sccm unit, response time (t_{res}) and recovery time (t_{recov})of pure and 2.5 % Na doped ZnO vs CO_2 concentration inn sccm unit

A ZnO sensor doped with Na is more selective towards CO_2. So, they can be used for the detection of CO_2. When Na is introduced into the lattice of ZnO resistance of sensor increases 30 times on the exposure of CO_2 and hence provides better results as compared to simple ZnO gas sensor. [12]

1.5) ENVIRONMENTAL IMPORTANCE

The world is growing at a rapid pace and along with it industrial evolution is also taking place. This boom in the industrialization bring more economical products for daily use but this is not all. It also the cause of global warming and emission of very toxic gases in the environment. Due to this a lot of fatal respiratory diseases also spreading whole across the world. So, detection of these gases is very important to make a life healthier and less vulnerable.

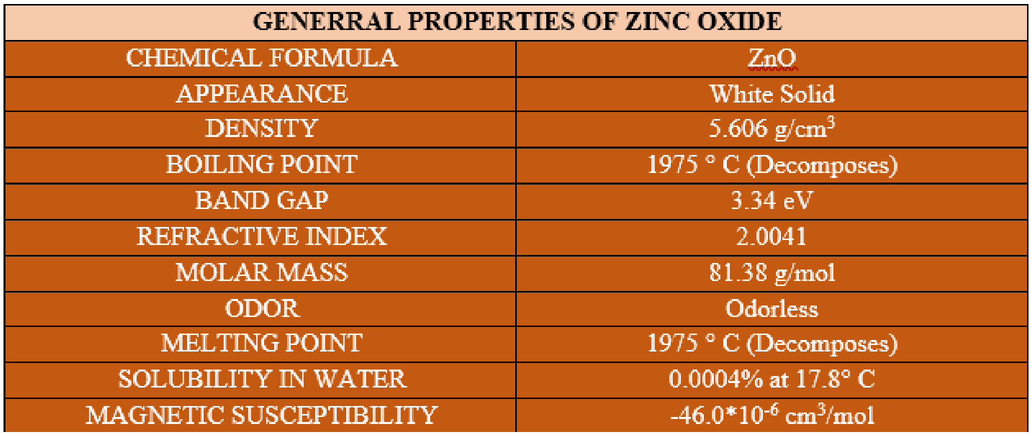
The most important application of gas sensors is to sense lethal gases leakages in industries. CO, CO_2 and NO_2 are some of the most fatal gases present in most of the chemical industries. Inhaling these gases even in the ppm concentration can be leaded to serious health issues and even death on spot. So, sensing these gases and for their removal on time gas sensors plays a very important role.

Another most important application of gas sensor includes the detection of some poisonous and flammable gases present in the environment of the homes. During combustion of CH_4 it produces CO_2 as by product which will dissociates into CO in less oxygenated areas which leads toward the sudden death. To prevent this, gas sensor can be used which will indicate the presence undesirable gases if they exceed the fatal limits.

CHAPTER 2: LTERATURE REVIEW

2.1) INTRODUCTION

Zinc oxide is inorganic material of group II – VI which consist of Zinc and Oxygen. Due to the size atomic size difference between both the atoms lots of abnormal charge distribution is created in the crystal structure and vacancies and interstitials starts to form which make it n-type wide band gap semiconductor. Some of the basic important properties of the ZnO is mentioned in the table.



GENERRAL PROPERTIES OF ZINC OXIDE	
CHEMICAL FORMULA	ZnO
APPEARANCE	White Solid
DENSITY	5.606 g/cm^3
BOILING POINT	1975 ° C (Decomposes)
BAND GAP	3.34 eV
REFRACTIVE INDEX	2.0041
MOLAR MASS	81.38 g/mol
ODOR	Odorless
MELTING POINT	1975 ° C (Decomposes)
SOLUBILITY IN WATER	0.0004% at 17.8° C
MAGNETIC SUSCEPTIBILITY	$-46.0*10^{-6}$ cm^3/mol

Table# 1

2.2 CRYSTALLOGRAPHIC FEATURES OF ZINC OXIDE

Zinc oxide is a n type semiconductor material belongs to II – VI group of periodic table and due to this special combination its ionic character lies in between the ionic and covalent semiconductors making it a wide band gap semiconductor. There are three polymorphs of ZnO usually known as Wurtzite (B4), Zinc Blend (B3) and Rochelle Salt commonly known as Rock Salt. Among the above three crystal structures Wurtzite is the most stable one due to its thermodynamics. Whereas, Zinc Blend and Rock salt are accounted for metastable phases of ZnO. [13] A detailed description of each of the above mention crystal phases is mentioned below;

2.2.1 WURTZITE

It is the most stable structure of zinc oxide to be found. It has hexagonal closed packed (HCP) geometry having a and c lattice parameters. A perfect crystal of ZnO have c/a ratio of about 1.633. [13] There are atoms of oxygen O and zinc Zn present in the sublattices of overlapping HCP crystal structures. [14] in this overlapping each Oxygen ion is surrounded by the tetrahedral of Zn ions and vice versa. Because of this sp^3 hybridization properties like piezoelectricity and polarity is found in the system. [15]

In case of perfect lattice each sublattice is displaced to an amount of u=0.375 in fraction coordinates. This internal parameter "u" is defined as the anion-cation bond length divided by the c lattice parameter. These values refer to the ideal cases in real cases there are slight diversions in the values due to the presence of impurities and vacancies. [15]

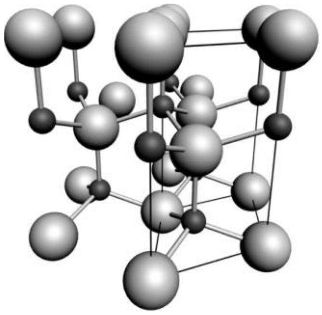


Figure 8 Wurtzite Crystal Structure

2.2.2 ZINC BLEND

It is overlapped structure of two face centered cubic (FCC) lattices. It is also one of the metastable phases of zinc oxide. This structure can be stabilized by the epitaxial growth over a cubic substrate. Its unit cell consists of equal atoms of zinc and oxygen that is four atoms of each element. It is formed by displacing FCC unit cells of zinc and oxygen to one quarter to each other diagonally. [13]

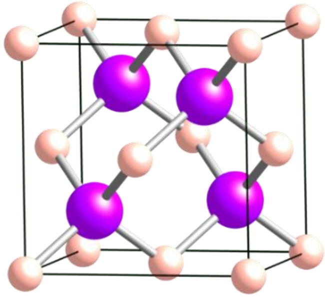


Figure 9 Zinc Blend Crystal Structure

2.2.3 ROCK SALT

Rock salt is FCC structure and a metastable form of ZnO. It can't be formed as that of Zinc Blend by epitaxial growth but can be transformed from wurtzite by the application of external pressure and i.e. 10 GPa and by shrinking the wurtzite to about 17%. During shrinking the ionic characters tends to increase due to inter-ionic columbic interaction. [13]

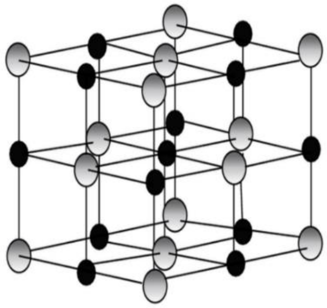


Figure10 Rock salt Crystal Structure

2.3 MECHANICAL PROPERTIES:

Mechanical properties of the bulk zinc oxide are anisotropic in nature for example the hardness at the c-axis is approximately 5 GPa at the penetration depth of 300 nm but at a-axis the value for hardness is almost 2 GPa with the penetration depth of 200nm so the it is softer than the previous one. ZnO is considered as a soft material. Deformation only occurs at pyramidal and basal planes. [15]

Literature also shows that mechanical properties changes by growing ZnO epitaxially. In this case hardness value reaches to approximately 5.7 GPa at the c-axis. [3] Devices utilizing electromechanical coupling can use zinc oxide because of its piezoelectric applications and its piezoelectric tensor is much higher than AlN and GaN. [14]

2.4) PROPERTIES AND APPLICATIONS

ZnO is very important material because its renders so much important applications that it can be used in many devices. These important properties along with their applications are discussed below;

2.4.1 BINDING ENERGY

ZnO show excellent exitonic emission at room temperature as well as at higher temperatures that is the reason behind its application in optical devices. ZnO show this property because of its high free-exciton binding energy of 60 meV which is much more as compared to GaN i.e. 25 meV. [16]

2.4.2 SENSITIVITY AND SURFACE CONDUCTIVITY

ZnO is very sensitive to small amount odor when it is exposed to various gases. So, it can be used as a sensor to differentiate between the fruits by their freshness due to its high sensitivity towards the presence of trimethylamine's odor. The mechanism of the sensors is not studied yet, but it is think that the absence of the electron layer on the vacuum annealed samples on exposure to air is the cause of sensing. [16]

2.4.3 OPTICAL COEFFICIENTS

ZnO thin-films show second and third order non-linear optical behavior which confirms its applicability in non-linear optical equipment. The crystallinity and the process of growth of the ZnO governs the linearity of the optical properties. Second order linearity can be achieved using spray pyrolysis, reactive sputtering laser deposition techniques. For non-linear optical devices polycrystalline ZnO can also be used which shows third order linearity. [16]

2.4.4 AVAILIBITY OF LARGE CRYSTALS

ZnO is also available in the form of single large crystal. To obtain such microstructure vapor phase transport and hydrothermal growth techniques can be opted. Chemical Vapor Deposition, Ultrasonic Spray deposition and Sputtering techniques are utilized to form thin-films. Deposition of ZnO on the substrate is also an important technique to reduce defect concentration and to increase its efficiency than GaN. [16]

2.4.5 AMENABILITY TO WET CHEMICAL ETCHING

ZnO has Special ability to be etched by different kind of alkaline mixtures or acids making it a flexible material for processing, designing and fabricating it for integrated devices. [16]

2.4.6 RADIATION HAZARDS

As compared to GaN, ZnO possess very high radiation resistance making it a suitable material to be used in outer-space equipment due to the importance of radiation hardness in this region. [16]

2.4.7 BAND GAP

ZnO is a wide and direct band gap semiconductor material. It's value of changes with temperature. At room temperature its band gap value is 3.37 eV. Whereas, at low temperature value increase to 3.44 eV. Due to this shift in band gap it is a potential material to be used in laser diodes, optoelectronics, photodetectors and light emitting diodes. Studies have shown that ZnO in the form of platelets, thin-films, nanocrystals and nanowires have applications in optically plumbed lasing. [16]

2.4.8 LUMINESCENCE

Due to its luminescence properties in the green-white region of the spectrum and emission at 495 nm and a very broad half width of 0.4 eV it can pe utilized in fluorescent displays and field emission displays. This is ensued because ZnO is n-type semiconductor material. The emission of green light is not yet studied but due to acceptor Zn ions they make it n-type semiconductor. [16]

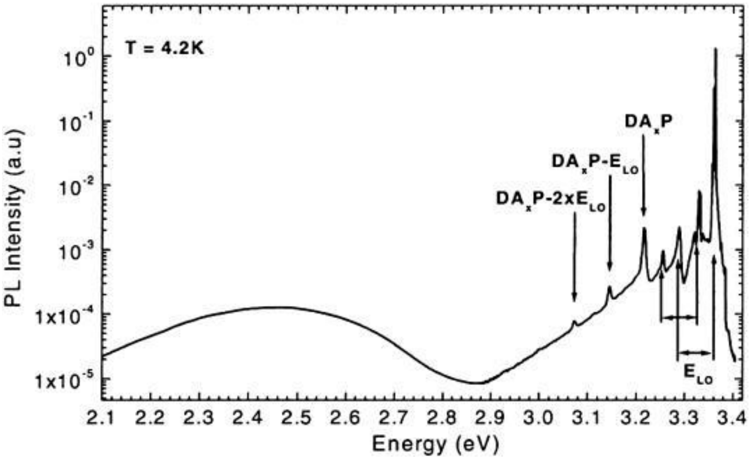


Figure 11 Luminescence plot of ZnO

2.4.9 NON-LINEAR RESISTANCE OF POLY CRYSTALLINE ZINC OXIDE

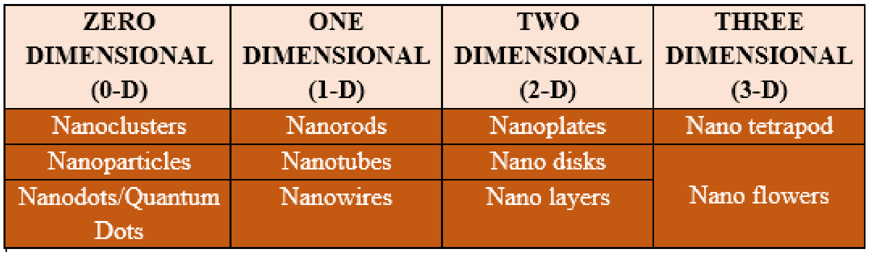
ZnO in polycrystalline forms shows non ohmic IV characteristics. So, based on this it can be used as Voltage Dependent Resistor (V.D.R). research is being under progress to understand the phenomena behind the non ohmic IV characteristics of ZnO. [16]

2.4.10 THERMAL CONDUCTIVITY

Due to high thermal conductivity of ZnO, it can be used in high temperature devices. Point defects present in the stacking of ZnO are the reason behind its high value of thermal conductivity. Rotational, vibrational and electronic movement governs the thermal conductivity κ (W cm−1 K −1) of the material. ZnO is used in rubbers as an additive because polar faces of ZnO shows very high thermal conductivity and this rubber can be used to make tires. [16]

2.5) NANO STRUCTURES OF ZINC OXIDE

Due to ease of fabrication ZnO is available in several Nano-structures. So, based on their geometry they can be divided into following categories;



ZERO DIMENSIONAL (0-D)	ONE DIMENSIONAL (1-D)	TWO DIMENSIONAL (2-D)	THREE DIMENSIONAL (3-D)
Nanoclusters	Nanorods	Nanoplates	Nano tetrapod
Nanoparticles	Nanotubes	Nano disks	Nano flowers
Nanodots/Quantum Dots	Nanowires	Nano layers	

Table# 2

2.5.1 NANO PARTICLES

The particles having diameter in the range of 1-100 nm are known as nanoparticles. Nanoparticles have huge spectrum of applications in field of environment protection, medicine, optics and sensing due to their optical, magnetic and electrical properties. In literature, there is high variety of nanoparticles of different materials but based on application and properties most important of them are metal oxide nanoparticles. In the recent years ZnO nanoparticles gain huge importance due to their applications in sensors, electrical devices and solar cells. [14]

Among the various routes Sol-Gel method is usually adopted to fabricate nanoparticles. Sol- Gel methods is cheap, environment friendly and easy to adopt. ZnO nanoparticles have extensive application in the cosmetic industry because their efficiency to block UV radiation is higher than traditional TiO_2. [14]

2.5.2 NANORODS

Nanorods are usually grown at the c-axis of the crystal structure in case ZnO the crystal structure is wurtzite. The aspect ratio (length/diameter) of the nanorods are very high but relatively lower than the nanowires.

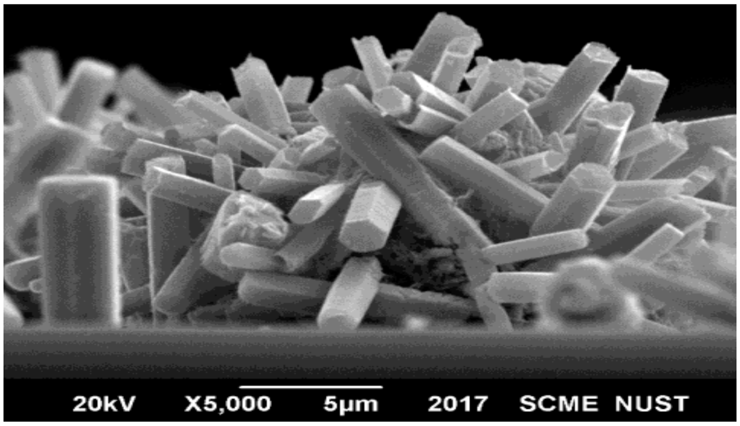


Figure 12 SEM Image of ZnO Nanorods

2.5.3 NANOWIRES

Nanowires have very high value of aspect ratio even greater than the aspect ratio of the nanorods. The diameter for nanowires is much less than one micron and the length are in the 10s of micron. [17] nanowires have potential applications in solar cells and gas sensors and can be fabricated using hydrothermal growth, metalorganic chemical vapor deposition or thermal oxidation techniques. [18]

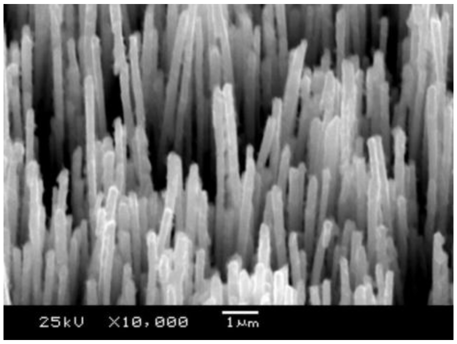


Figure 13 SEM Image of ZnO Nanowires

2.5.4 NANOTUBES

Nanotubes have same structure as that of nanorods, but main difference is that they are hollow and tabular. This special structure renders high surface area and great porosity into them. That is why they can be used as biosensors, intramolecular junctions and in the process of catalysis. [19]

The basic mechanism behind the growth of nanowires is not understand yet but to fabricate them plasma assisted growth, thermal oxidation and evaporation and hydrothermal decomposition techniques can be used. [20]

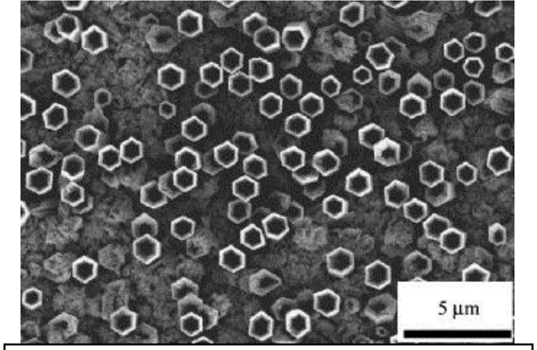


Figure 14 SEM Image of ZnO Nanotubes

2.5.5 NANOBELTS

Nanobelts are the nanowire with side surfaces and well-defined geometry. It ZnO powder is sublimed without catalyst nanobelt will be obtain as a result. Nanobelts have uniform lengths and rectangular cross-section having width to thickness ratio of about 5 to 10. Literature shows that the thickness and width of nanobelts are in the range of 10-30 nm and 50-300 nm respectively. [19]

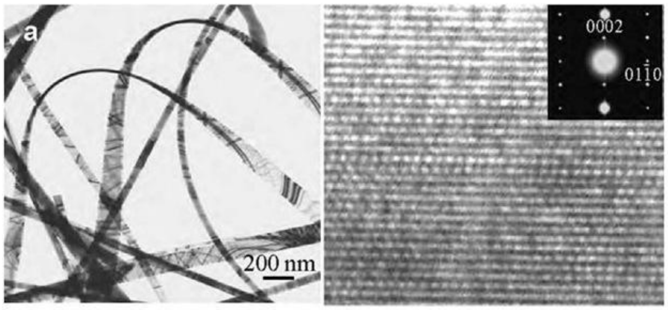


Figure 15 TEM Image of ZnO Nanobelts

2.5.6 HIERARCHICAL NANOSTRUCTURES

Hierarchical nanostructure obtains by changing the composition of the parent material. Change in composition effect the morphology of the structure and complex results are obtained. For example, when ZnO and SnO_2 are mixed in the weight ratio of 1:1 central axial nanowires with Nano branches begins to grow. This mechanism is known as VLS (vapor-liquid-solid) mechanism. This process has two steps. The first step is faster and nanowire growth takes place in it. In the second step epitaxial growth of Nano ribbons occurs at the sic crystallographic directions at an angle of 60° to each other. [19]

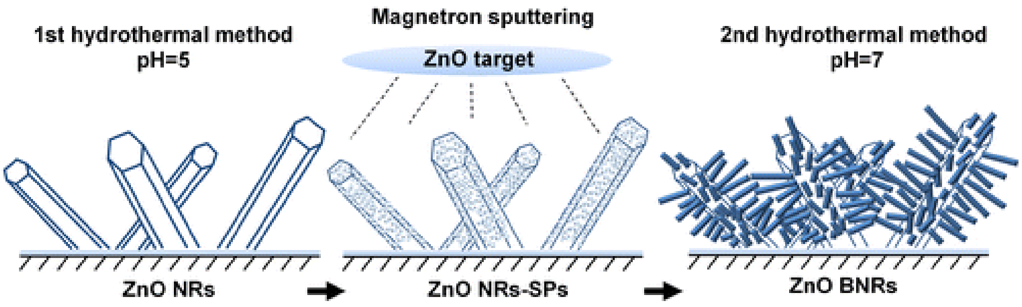


Figure 16 Step by step Growth of ZnO Hierarchical Structures

2.5.7 NANOCOMBS AND NANOSAWS

Asymmetric growth along Zn [1000] gives comb structure due to the anisotropy found in wurtzite structures. Two surfaces of ZnO are responsible for such growth. (0001) surface of Zn is Positively charged and chemically active and the other surface (000 ¯1) of Oxygen is negatively charged and relatively inert. As experiments suggests inert surface never grows so it will not help in the growth of nanobelts. So, the active surface leads the self-catalyzed growth due to the presence of Zn clusters. [19]

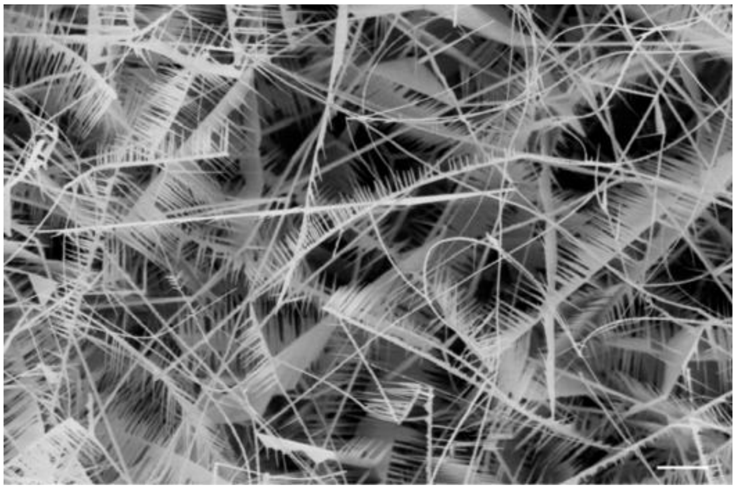


Figure 17 SEM Image of ZnO Nanocombs

2.5.8 NANOSPRINGS AND NANOSPIRALS

Reduction in the electrostatic energy of the polar nanobelts tend them to form a spiral shape. Similarly, Nano helixes are formed in a result of the reduction of electrostatic energy and dipole moments of the polar faces of the nanobelts. Nano springs have uniform cross section of single crystal ZnO with the radius of approximately 500-800 nm. [19]

2.6) POTENTIAL APPLICATIONS OF ZINC OXID

2.6.1 DOMESTIC APPLICATIONS

ZnO has wide range of application in domestic area. It is being extensively used in the healthcare industry for the skin care products. It is also being used in anti-aging products. It is also a source of minerals in food industry.

2.6.2 INDUSTRIAL APPLICATIONS

To produce anti-abrasion rubber ZnO is used as additive to increase its efficiency and hence used by the rubber industry. ZnO is used as white dyestuff in ceramics to lower the sintering temperature. Due to its anti-bacterial and deodorant properties it is being utilized in chemical industry. Paint industry also uses ZnO to improve shielding and anti-static material. [21]

2.6.3 SOLAR CELLS

Being a n-type semiconductor, ZnO nanowires are used as charge collectors in solar cells. ZnO nanowires provide better charge collection and separation along with enhances light entrapment by reducing reflection as compared to simple thin-film of ZnO. nanowire increases the short circuit current due to large p-n junction area hence increases the efficiency of energy conversion. Short circuit current density of Cu_2O/ZnO nanowire cells deposited over ITO substrate is 8.2 mA/cm^2 which is double than the planer thin-film junction i.e. 4.3 mA/cm^2. [21]

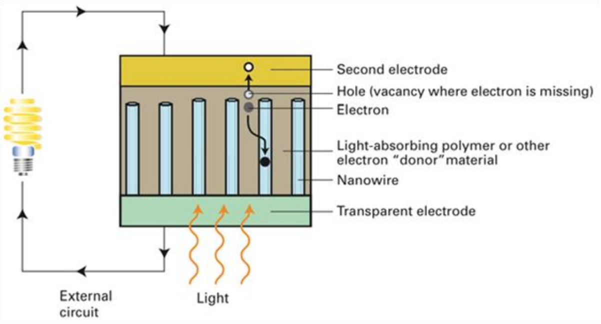


Figure 18 Schematic Image of ZnO Nanorods Solar cells

2.6.4 PHOTO DETECTORS

In the modern research facilities in the world reduction of background noises and to avoid erroneous detection, finding of UV light is really very important for spectroscopy and sensing. Due to high luminescence properties ZnO can be used as photodetector. The reason to use ZnO as a photodetector are as follows;

1. Wide band gap of 3.3 eV.
2. Irresponsive to infrared and visible spectrum of light.
3. Temperature independent high exciton binding energy.
4. High value of saturation velocity.
5. Highly resistant to radiations.
6. High spatial resolution.

Nanowire have high spatial resolution than thin-film structures. [21]

2.6.5 ZINC OXIDE METHANE SENSORS

Literature show that ZnO thin-films are highly immune to CH_4 gas. For sensing material ZnO with Pd as a catalyst required. ZnO at high temperature of 200° C have small response time i.e. approximately 1 minute and low recovery time i.e. 3 minutes. Sensitivity of ZnO methane sensor is 86%. [16]

2.6.6 NANOCANTILEVER

Cantilevers are used in scanning probe microscopy SPM for imaging and to study surface properties of the material. Tradition cantilevers are made up of Si_3N_4 or SiC. By growing nanotubes or nanowires at the surface of these cantilevers can enhance the working efficiency of SPM by imaging sudden minute changes in the structural morphology.

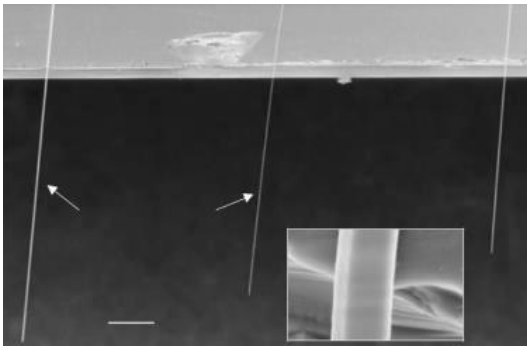


Figure 19 SEM Image of ZnO Nanorods on AFM Cantilever

Cost effective and more sensitive cantilevers can be made by the combining nanobelts with the micro-electromechanical systems (MEMS) technology. Due defect free nature of nanobelts along with superior mechanical properties they are considered ideal nanostructure to produce cantilevers. Sensitivity of the cantilever can further be improved by reducing the cross-section of the nanobelts. Micromanipulation of the above-mentioned techniques can be used to align nanobelts horizontally over the silicon chips. Aftermath resonating frequencies of the cantilevers are tuned to be used in atomic force microscopy AFM. [19]

2.7) INDUSTRIAL MANUFACTURING OF ZINC OXIDE

ZnO is very important material in modern industries its application covers a broad spectrum of products. So, to overcome its demand its is important manufacture ZnO at

Industrial level. There are three different kind of industrial methods to form ZnO in bulk. These three methods are listed below;

- **DIRECT PROCESS:**
  In this process reduction by carbon of oxidized zinc takes place. After reduction Zinc metal is heated by burning air to get vaporized and oxidized by it to produce ZnO. This process is also known as American Process.

- **INDIRECT PROCESS:**
  In this process zinc is extracted using different metal sources by vaporizing the metals and then it got oxidized by air to produce Zinc Oxide. This process is also known as French Process.

- **WET CHEMICAL PROCESS:**
  In this process salts of zinc are utilized to produce zinc oxide. First, precipitations from the salts are carried out using alkaline solutions. Then these solutions are filtered. After filtration zinc oxide is produced by dehydration and calcination.

2.8) SYNTHESIS OF ZINC OXIDE NANOSTRUCTURES

Nanostructures of ZnO can be synthesized in verity of ways. To discuss them in detail we have divide them into two categories as follows;

1. Solution Phase Synthesis.
2. Gas Phase Synthesis.

Both the categories have been discussed below;

2.8.1 SOLUTION PHASE SYNTHESIS

In this type aqueous solutions are utilized to form ZnO nanostructures. Some of the solution phase synthesis methods are listed below;

1. Sol-Gel Route
2. Spray Pyrolysis Method
3. Electrophoresis
4. Hydrothermal Method
5. Chemical Bath Deposition

2.8.1.1 SOL-GEL METHOD

Sol-gel method is an easy way to synthesize ZnO nanostructure. For this Zinc Acetate Dihydrate and Sodium Hydroxide is required in a weight ratio of 1:4 along with distilled water in the volume ratio of 2:3 respectively. Both salts are then dissolved in their respected volume of distilled water and stirred for 5 minutes. After proper mixing Sodium Hydroxide solution is poured into Zinc Acetate Dihydrate solution with proper stirring continued. After this drop wise addition of 100 ml ethanol is carried out. After all this white precipitate of ZnO starts to form indicating the end of the reaction. [22]

2.8.1.2 SPRAY PYROLYSIS

It is a very simple and cost-effective method to deposit thinfilm of ZnO over a cross-section of large area. One the most important aspect of this technique id that it can be used for mass production due to ease of adoption and high yield. In this process atomizers are used as carrier to transport solution in the form of a spray. This increases the wettability of the particles and the layers to be deposited and prevent the formation of large droplets.

To grow nanostructures from this technique constant temperature and along with continuous stirring is requires that is why magnetic stirrers and thermocouples are being utilized in this process. Spray distance is fixed according to requirements of the coating on the substrate. Spraying is done in steps to homogenize the temperature. The reaction using $ZnCl_2$ as a precursor solution is as follows [23];

$$\mathrm{ZnCl2 + H2O \Rightarrow ZnO + 2HCl}$$

2.8.1.3 ELECTROPHORETIC DEPOSITION

Nanoparticles of ZnO can be deposited by using electrophoretic deposition EPD. The process takes place in a cell known as electrophoretic cell. The substrate act as an electrode against a counter electrode of platinum foil. These two electrodes are separated by a known distance depending upon coating quality required. The important parameters to be considered for EPD are galvanostatic conditions, current densities and time of deposition. After EPD substrate is dried and cooled to room temperature. [24]

2.8.1.4 HYDROTHERMAL METHOD

Hydrothermal method is used for the synthesis of highly oriented nanostructures of ZnO even at higher temperatures than 100° C. to make nanorods out of this method, Zinc Nitrate Hexahydrate and Hexamethylenetetramine HMTA are dissolved in the distilled water for 30 minutes with continuous stirring. [25] After this autoclave vessel lined with Teflon is utilized for further processing. The vessel is remained closed for the specific time on a particular temperature for the growth of the nanostructure. After the reaction cleaning of the sample takes place by distilled water and ethanol. [26] The set of reaction taking place between Zinc Nitrate Hexahydrate and Hexamethylenetetramine HTMA are as follows [27];

I. **Decomposition Reaction;**

$$(CH_2)_6N_4 + 6H_2O \longrightarrow 6HCHO + 4NH_3$$

II. **Hydroxyl Supply Reaction;**

$$NH_3 + H_2O \longleftrightarrow NH_4^+ + OH^-$$

III. **Supersaturation Reaction;**

$$2OH^- + Zn^{2+} \longrightarrow Zn(OH)_2$$

IV. **ZnO Growth Reaction;**

$$Zn(OH)_2 \longrightarrow ZnO + H_2O$$

2.8.1.5 CHEMICAL BATH DEPOSITION (CBD)

Chemical bath deposition CBD is a cheap and low temperature synthesis method for the synthesis of ZnO. Due to low temperature deposition can be done on cheap substrate like glass. CBD method employs two steps to produce nanostructure i.e. nucleation and growth. The important parameters to considered for CBD are seed layer, precursor concentration, growth time and buffering agent. To form nanorods of ZnO onto the substrate 25 mM solution of Zinc Nitrate Hexahydrate is formed in distilled water. This solution is then kept at 90° C for 2.5 hours along with the substrate immersed into the solution bath. As the time complete the sample are then annealed at 450° C with a ramp rate of 5° C/min. [28]

2.8.2 GAS PHASE SYNTHESIS

These synthesis methods are carried out at high temperature in closed vessels with gaseous environment. Some of the methods utilized to for nanostructures of ZnO are as follows;

1. Vapor Transport Method
2. Microwave Assisted Heating
3. Metal Organic Chemical Vapor Deposition MO-CVD
4. Ultrasonic Spray Chemical Vapor Deposition US-CVD

2.8.2.1 VAPOR TRANSPORT METHOD

ZnO nanoparticles are grown in this method by using quartz tube inside a thermal furnace. The substrate material is placed at a specific distance at the center of the quartz tube. The whole process is divided into four steps as follows;

1. Flow of Ar gas in the tube for half an hour.
2. Increase in the furnace temperature to 800° C along with the flow of Ar gas.
3. Maintaining the temperature for 1 hour and replacement of Ar with Ar/H_2O or Ar/O_2 gas.
4. Cooling of the sample to room temperature.

The pressure of the quartz tube is maintained at 0.03-0.05 MPa. The Cooling rate should be 7° C/min. following are reaction occurring inside the chamber. [29]

$$Zn_{(g)} + H_2O_{(g)} \rightarrow ZnO_{(s)} + H_{2(g)}$$

$$2Zn_{(g)} + O_{2(g)} \rightarrow 2ZnO_{(s)}$$

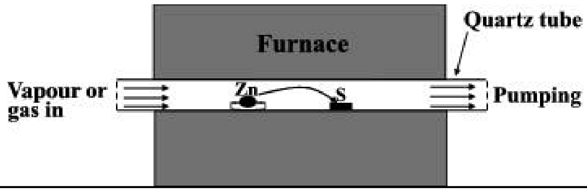


Figure 20 Schematic Image of Vapor Transport Method

2.8.2.2 ULTRASONIC SPRAY CHEMICAL VAPOR DEPOSITION US-CVD

For the synthesis of multilayer and doped nanostructures of ZnO US-CVD technique is utilized. It is an advance form of spray pyrolysis technique. As to form thin-films, spray pyrolysis is considered easy to use technique similarly US-CVD is an easy way to synthesize doped nanostructures. [18]

ZnO synthesis required gold as a catalyst. ZnO grows on Vapor-Liquid-Solid VLS mode. Due to VLS Au particles starts to grow on the thin-film of Au when heated at the growth temperature. The source of ZnO is a solution of Zinc Acetate Dehydrate in water and acetic acid in the ration of 9:1. Temperature for the growth is 750° C-950° C and the reaction time is 30 minutes. [30]

2.8.2.3 MICROWAVE HEATING

The process is also known as microwave chemical bath deposition CBD. The precursors salts and solvent are same. In this method a solution of Zinc Nitrate Hexahydrate ($Zn(NO_3)_2.6H_2O$), Hexamethylenetetramine HMTA ($C_6H_{12}N_4$) in a de ionized water and let them dissolve for 30 minutes at room temperature. The solution is the heated to 95° C with continuous stirring. As the temperature of the solution reaches 95° C it is then heated in microwave oven for almost 2 hours. Reaction occurring in the whole process are given below [31];

$$(CH_2)_6N_4+6H_2O \rightarrow 6HCHO+4NH_3$$

$$NH_3+H_2O \rightleftarrows NH_4^{+}+OH^{-}$$

$$2OH^{-}+Zn^{2+} \rightleftarrows ZnO+H_2O$$

As the reaction proceed the solution become translucent indicating the formation of nanorods. In the reaction dissociation of Zinc Nitrate Hexahydrate takes place to form Zn^{2+} ions. These positive ions react with OH^{-} to form nanorods. Then the substrate is washed with distilled water and dried. [19]

CHAPTER3: EXPERIMENTAL DESIGN AND PROCEDURE

For the efficient working of the project it is distributed among the following phases;

1. Synthesis phase
2. Sensing phase

3.1) SYNTHEIS PHASE

For better and reliable results, optimization of synthesis process is an important tool which can leads toward more energy and cost-effective synthesis route for any chemical or material production. Optimization for the ZnO nanorods/ thin-films synthesis process is done to control the following parameters;

- Uniform array of nanostructure.
- Higher aspect ratio.
- Reproduceable routes of synthesis.

Synthesis phase is distributed among the following steps.

3.1.1) SUBSTRATE SELECTION

One of the most important part for synthesis phase is the choice of substrate. Substrate is selected based on its inertness with the coated material which is in our case is ZnO. The other important factor to consider while choosing a suitable substrate is ease of growth of nanorods of ZnO on the substrate surface and the adhesion of seed layer on the substrate surface is also an important parameter to consider while decide a substrate material. Some general influential factors for selecting a substrate material are;

- Availability.
- Chemical Inertness.
- Its electrical conductivity.

So, after considering above mention properties we decided to choose single crystal Silicon (Si) wafer as substrate for our gas sensor.

3.1.2) CHOICE OF SYNTHESIS ROUTE

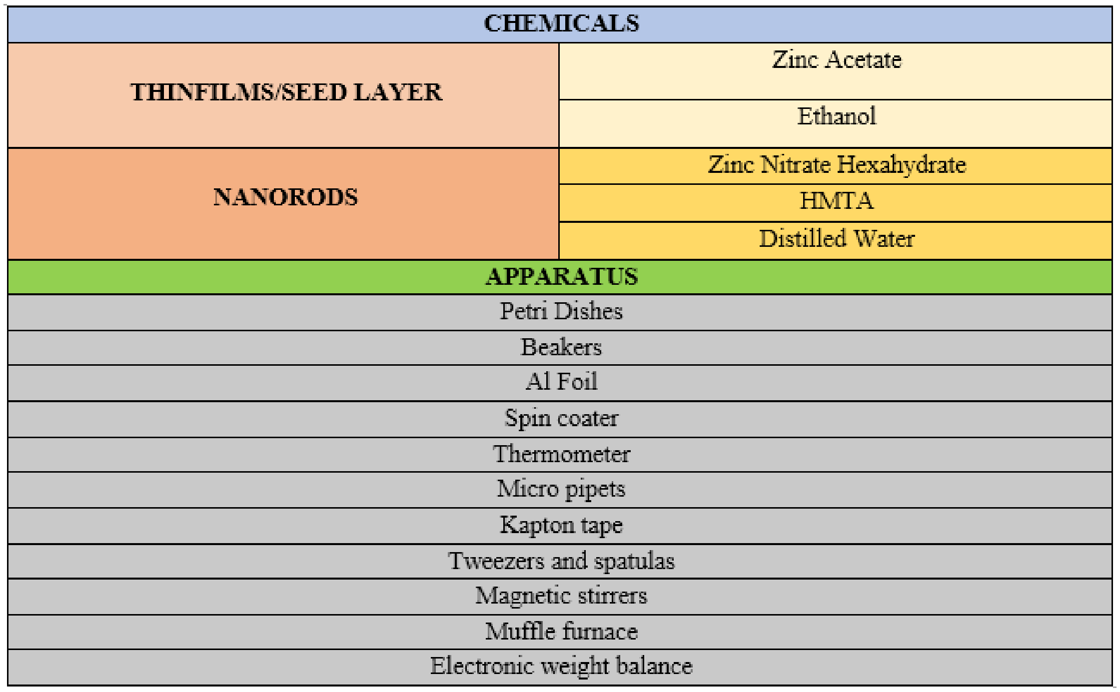
The choice of synthesis route is an important aspect of any project. There are certain parameters on which it is decided to choose between different synthesis routes these parameters are listed below.

- Ease of reaction.
- Availability of reactants (chemicals).
- Environmental compatibility.
- Economical suitability.
- Resources available.
- Optimum conditions.

Keeping the above parameters in consideration spin coating of seed solution is selected for thin films of ZnO and for ZnO nanorods chemical bath deposition (CBD) method is selected.

3.1.3) REQUIRED APPARATUS AND CHEMICALS

Apparatus Is the basic equipment required to run an experiment or reaction and chemicals are the basic ingredients of result. The required apparatus and chemical to run above mention experiments are listed below;



CHEMICALS	
THINFILMS/SEED LAYER	Zinc Acetate
	Ethanol
NANORODS	Zinc Nitrate Hexahydrate
	HMTA
	Distilled Water
APPARATUS	
Petri Dishes	
Beakers	
Al Foil	
Spin coater	
Thermometer	
Micro pipets	
Kapton tape	
Tweezers and spatulas	
Magnetic stirrers	
Muffle furnace	
Electronic weight balance	

Table# 3

3.2) SYNTHESIS PROCEDURE

Synthesis of ZnO is the most crucial stage of the project. For gas sensing applications two types of synthesis reactions are carried out, one for the thin-films/seed layer and other one is to grow nanorods for both reactions chemicals and conditions are totally different. Detailed description of both processes is given below.

3.2.1) THIN-FILMS/SEED-LAYER

To form a thin film of a gas sensor, 5mM solution of zinc acetate is required in ethanol. To achieve this molarity 5.48 mg of zinc acetate dihydrate is required and it must be dissolved in 5 mL of ethanol and it is then stirred for some time to ensure complete mixing of the two ingredients.

After the formation of the solution it is deposited on the surface of the substrate i.e. Si wafer. Before deposition wafer is masked using a masking tape such that a slot of width of few of micron is remain open for deposition. After masking the sample is placed on the spin coater for coating of the solution. For coating 40 microliter of solution is dropped on the surface of the substrate and then coated on it with the spin of 3000 RPM. Sample is coated two time for 30 seconds for each coat to ensure the uniform spread of the coating solution.

After coating sample is annealed at 350° C with a ramp rate of 10° C/min and socked for 20 mins.

3.2.2) GROWTH OF NANORODS BY CBD METHOD

After forming a thin-film/seed layer, nanorods of ZnO are grown above that seeded surface of the substrate. To grow nanorods the best method to use is chemical bath deposition (CBD). For this 25mM solution is formed of Zinc Nitrate hexahydrate and Hexamethyletetramine (HMTA) in distilled water. The conditions for the growth of nanorods are as follows;

- Temperature should be maintained at 90° C.
- Time required for growth is approximately equal to 2.5hr.

As the temperature of the solution reaches the 90° C seeded samples are placed inside the chemical bath comprises of the 25mM solution of Zinc Nitrate hexahydrate and Hexamethyletetramine (HMTA) in distilled water. After that temperature is maintained at 90° C for 2.5 hours to ensure maximum growth. HMTA is added because it assists the growth at the direction of (0001) plane of hexagonal wurtzite.

After CBD sample is annealed at 450° C with a ramp rate of 5° C/min and soaked for 1 hour.

3.3) ADDITION OF DOPANTS

Introduction of dopants into the lattice parameters of ZnO can enhance the sensitivity and selectivity of the gas sensor. Furthermore, it also effects the ultraviolet (UV) detection of ZnO hence decreasing the response time of gas sensors. Taking account of the above applications following dopant materials are selected based on sensitivity and selectivity.

- Graphene.
- Sodium (Na).

Detailed procedure of doping of these materials into the lattice of ZnO is given below.

3.3.2) GRAPHENE DOPING

Graphene is a single atomic layer of graphite and considered as a first 2D material. Doping zinc oxide with graphene leads towards the better sensitivity of the gas sensors towards NO_2 gas. Doping of graphene can be done in various concentrations of graphene to testify which will be a best concentration for the application of gas sensing. The graphene used for synthesis purpose are centrifuged at 500 RPM and 1000 RPM for 48 mins. There are two different methods to dope graphene into the thin-films and nanorods respectively.

- **Doping of Thin-film/Seed layer with graphene:**

  To dope zinc oxide with 1 wt.% of graphene, 100 µL of a suspension of graphene in N-methyl pyrrolidone (NMP) is mixed with the seeding solution i.e. zinc acetate and ethanol and after thorough stirring a solution of ZnO with 1 wt.% doped graphene is ready. ZnO doped with 0.5 wt.% and 5 wt.% are prepared similarly by adding 50 µL and 500 µL graphene and NMP suspension into the seeding solution respectively.

- **Doping of nanorods with graphene:**

  To form nanorods of zinc oxide doped with graphene a solution is made which consist of two equal parts. First part is a 25mM solution of Zinc Nitrate and HMTA in distilled water and the second part is a suspension of graphene in NMP. After mixing these two parts in equal proportion a mixer is heated to 90° C and samples are placed inside the solution after proper masking. Temperature is then maintained at 90° C for 2.5 hours for proper growth and doping of graphene into the lattice of zinc oxide.

3.3.3) SODIUM (Na) DOPING

Doping Na into the lattice of zinc oxide enhances the sensitivity of the gas sensor also improve its selectivity for CO_2. Na Doped samples are highly sensitive to all gases but when the mixture of gases is introduced they show selective nature towards CO_2.

- **Doping of Thin-film/Seed layer with Na:**

  To form seeding layer 5 mM solution of Zinc Acetate Dihydrate is form in ethanol along with 40 mol% of Sodium Acetate Dihydrate. The solution is then stirred continuously till the dissolution of the salts. After proper mixing the solution is coated over ITO substrate using Spin Coating technique. The coatings are then annealed at 350° C with a ramp rate of 10° C/min.

- **Doping of nanorods with Na:**

  To grow nanorods doped with Na, 25 mM solution of Zinc Nitrate Hexahydrate and Hexamethylenetetramine HMTA is formed in distilled water along with 40 mol% of Sodium Nitrate Hexahydrate. The seeded substrate is then immersed in this Chemical Bath and heat it up to 90° C and then maintained at this temperature for 2.5 hours. These samples are then annealed at 450° C at a ramp rate of 5° C/min.

3.4) CHARACTERIZATION

To determine the final properties of the prepared nanostructures following characteristics of the test sample are judged;

- Uniformity
- Morphology
- Orientation
- Alignment
- Crystallinity
- Electrical Conductivity

X Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and IV characteristics techniques are used to judge the above mention characteristics of the samples.

3.5) SENSING PHASE

Sensing phase of this project is divided into the following 3 steps;

1. Sensor Design
2. Gas Chamber Design
3. Gas sensing Assembly

3.5.1) SENSOR DESIGN

Sensor is based on ITO coated glass substrate which is then covered in such a way that there at the center of the substrate is uncovered slot of few microns is present. In that uncovered region growth of ZnO nanostructures takes place which will be the main sensing part of the sensor.

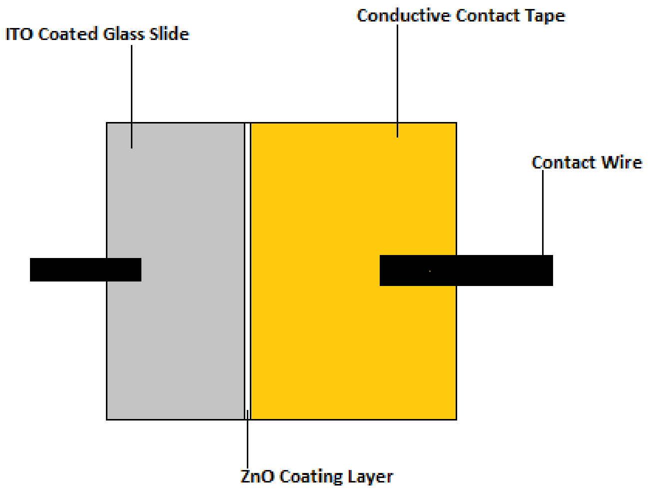


Figure 21 Schematic Sample Design

3.5.2) GAS CHAMBER

For keeping the gas volume constant and to determine the IV characteristics of the gas sensor a special chamber was designed and assembled by Mr. Muzammil Ahmed a student of MS program at SCME. There are clamps in that chamber that can be used to hold the sensor and to connect it with the external circuit to determine the change in its properties.

3.5.3) GAS SENSING ASSEMBLY

Gas sensing assembly comprises of many parts which includes gas cylinders, flow meters, gas sensing chamber, electrical station and a display system. Each of which has its own purpose and functionality.

First, gases from the cylinder enters the flowmeters. Flowmeter controls the flow of gases and allows only desired SCCM of gases to enter the sensing chamber where sensor is placed. Due to the introduction of the gases into the sensing chamber sensor starts to change its properties which will be determine by the electrical station and result will be displayed on the display center.

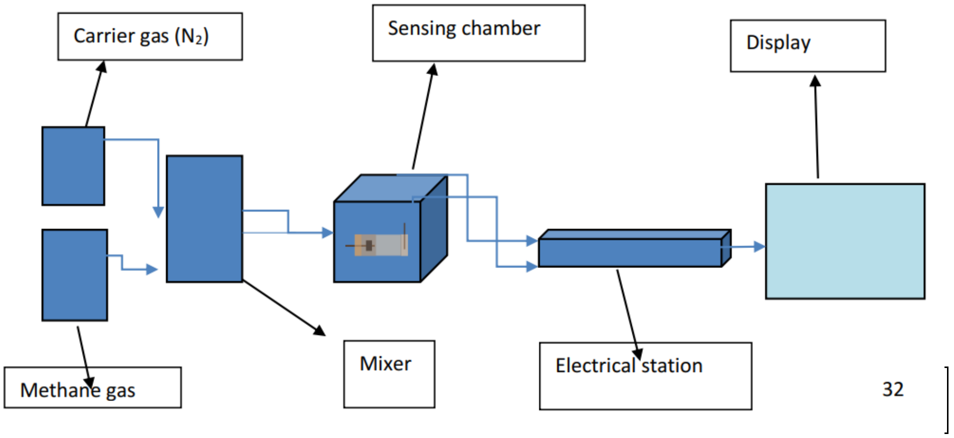


Figure 22 Sensing Assembly Design

CHAPTER 4: CHARACTERIZATION, RESULTS AND ANALYSIS

The following characterization techniques were used to find different properties and results

1. Scanning electron microscopy
2. X-ray diffraction and crystallography
3. IV Characteristics

4.1. SCANNING ELECTRON MICROSCOPY

The scanning electron microscope (SEM) is used for observation of specimen surfaces. When the specimen is irradiated with a fine electron beam (called an electron probe), secondary electrons are emitted from the specimen surface. The basic purpose of SEM is to study the morphology topography, chemical composition, crystal structure and electrical behavior of very small samples can be observed by two-dimensional scanning of the electron probe over the surface and acquisition of an image from the detected secondary electrons.

4.1.1. CONCTRUCTION OF SEM

The SEM requires an electron optical system to produce an electron probe, a specimen stage to place the sample, a secondary electron detector to collect secondary electrons, an image display unit and an operating system. Electron optical system consists of an

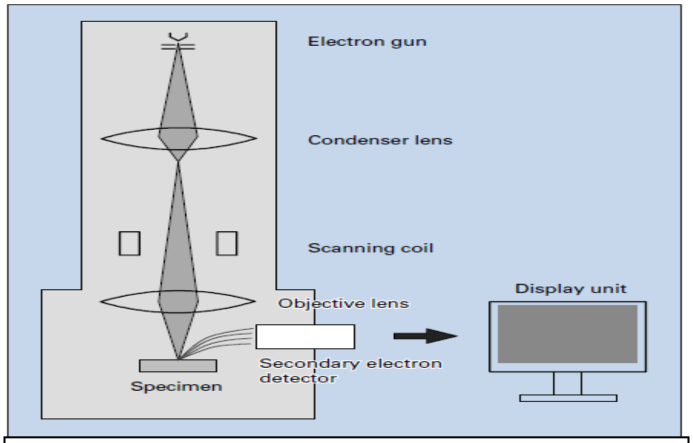


Figure 23 Schematic representation of SEM machine.

electron gun, an objective lens and a condenser lens to produce an electron probe.

4.1.2. IMAGE FORMATION IN SEM

The SEM images are quite different from the images taken by the light microscope. Th electron optical system contains two or more electromagnetic lenses which are operated in vacuum and electron gun. The electron gun accelerates the electrons with the high energies in the range of 1-40KV. When electrons enter the specimen, the electrons are scattered within the sample and gradually it loses their energy and after that they are absorbed in the specimen. The scattering range of electron is different inside the sample depending on the electron energy, atomic number and density of the atoms. As the energy is higher the scattering range is larger and if the atomic number and density are large, the scattering range is smaller.

The SEM utilized these signals to observe and analyze the sample surface and it performs different elemental analysis and state analysis. Signals in the form of electromagnetic radiations are generated when sample is struck to high speed electrons. Out of these radiations, back scattered electrons are secondary electrons are collected by the detector and then signal is amplified, and image is displayed on the monitor screen. Usually the quality of SEM images depends on three important parameters:

- Performance of the instrument
- Imaging parameters
- Nature of the specimen

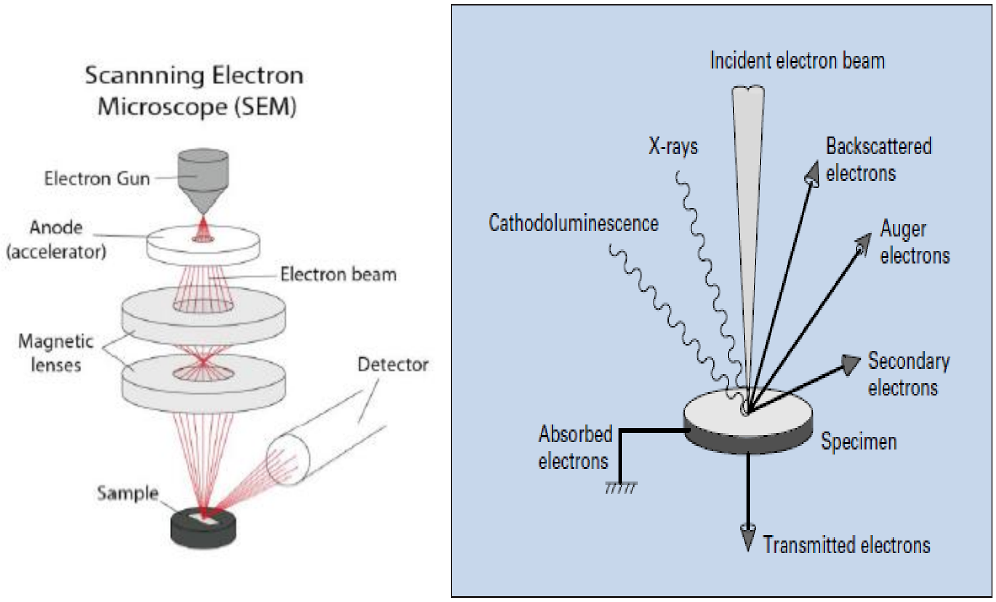


Figure 24 Schematic of SEM and Emission of Electrons

4.1.3. TYPES OF ELECTRON GUN

There are two types of electron guns: FE gun and SE gun

➢ FIELD-EMISSION ELECTRON GUN

FE gun is use for high resolution in SEM. It utilizes the field-emission effect when high electric field is applied to a metal surface. A single crystal of tungsten is welded to a tungsten wire and its tip is in a curvature shape with a radius of about 100 nm. This is called the emitter. To generate a field emission, the tip of emitter must be very clean. Thus, FE guns needs to be placed in an ultrahigh vacuum of about 10^{-8} Pa. The energy spread of FE gun is small because of no heating of emitter. In low accelerating voltage observation, this energy spread determines the resolution (Chromatic aberration)

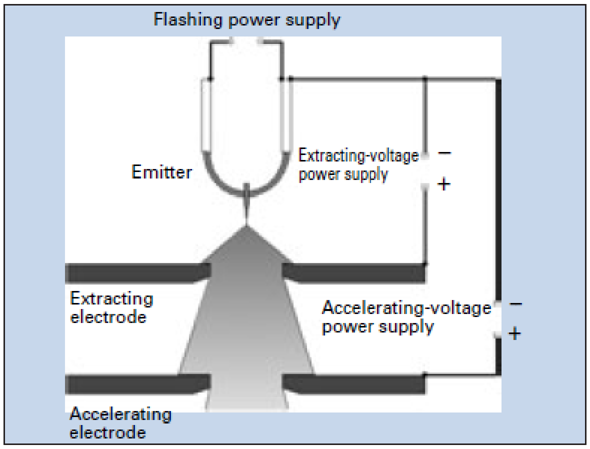


Figure 25 Schematic of Field Emisson Electron Gun

➢ SCHOTTKY-EMISSION ELECTRON GUN

SE gun uses the Schottky-emission effect when a high electric field is applied to heated metal surface. The emitter is cathode made of ZrO/W. A single crystal of tungsten is coated with ZrO, with a tip curvature radius of a few hundred nanometers. In SE gun a large emission current can be obtained at relatively low cathode temperature of about 1800k because of decrease in work function of ZrO coating. Its advantage is that electron beam current is highly stable because of the emitter, which is placed in an ultrahigh vacuum of about 10^{-7} Pa, and no gas absorption occurs. Compared to the FE gun, the energy spread of SE gun is larger and it produces larger probe current,

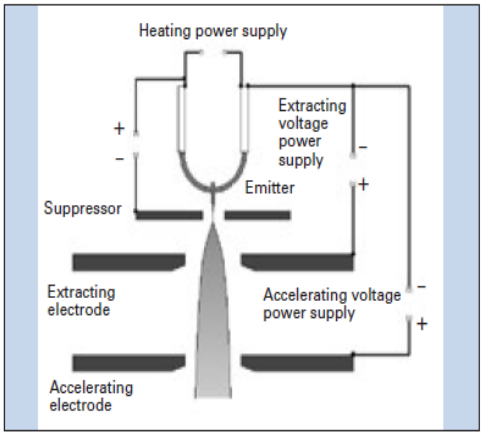


Figure 26 Schematics of Schottky Emission Electron Gun

and these features are very effective for various analysis that occurs simultaneously with morphological observation.

4.1.4. LENSES

The function of lens is to converge electron beam, so that a beam of desired diameter is obtained. They are in a form of metal cylinders operating in vacuum. A magnetic field is generated inside the lens to focus or defocus the electron beam.
Lenses have three basic designs

- Conical lens or pinhole: specimen is outside the lens and magnetic field
- Immersion lens: specimens are very small and placed inside the lens
- Snorkel lens: specimen is inside the magnetic field, but outside the lens

4.1.5. MAGNIFICATION

The magnification is defined in the ratios of the scan line length on monitor to the scan line length of the specimen. Mostly the screen length is fixed, and the magnification is only changed by increasing or decreasing the scan length of specimen.
Mathematically it is shown by,

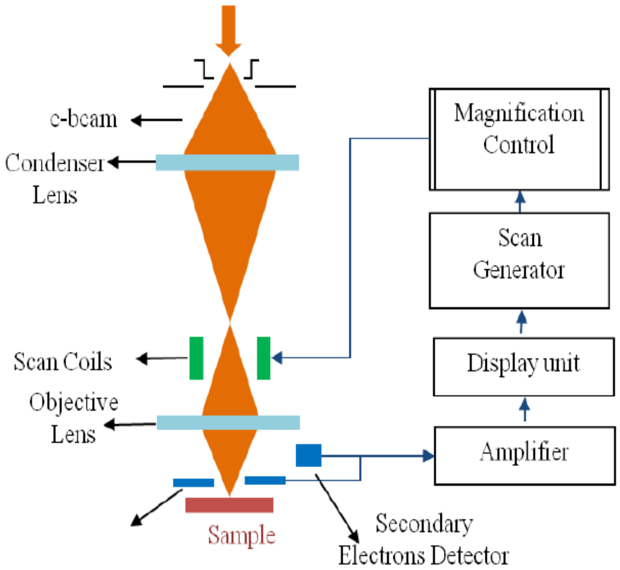


Figure 27 Configuration of Lenses in SEM

$$M = D/d$$

4.1.6.IMAGE QUALITY.

The SEM images are controlled by a detector. The signal measurement is controlled by the amount or quantity of electrons at the detector, while presence of noise can decrease the quality of image, thus the image quality is defined as the ratio of the signal to noise i.e. S/N

The contrast is defined as the ratio of the difference of signals detected at two points divided by one of them.

$$\textbf{Contrast} = (S_2 - S_1)/S_2$$

Where S_2 and S_1 are signals detected at two arbitrary points, and $S_2>S_1$, that means contrast can always be positive ranges from 0 to 1.

4.1.7. COMPOSITIONAL CONTRAST

It is also called atomic number contrast and it occurs due to the difference in atomic number at respective areas, due to which intensity of signals from those areas differs. High atomic areas appear bright as compared to low atomic areas. Mathematically it is given by;

$$C = (n_1 - n_2)/n_2$$

Where n_1 and n_2 are the back scattered coefficients of two regions. The more is the difference in the atomic numbers, the more is the contrast and vice versa.

4.1.8. TOPOGRAPHICAL CONTRAST

This includes all those effects which play role in the imaging of the shape and morphology of the samples. Trajectories and number of secondary electrons and back scattered electrons depends on the angle of incidence between the specimen’s surface and the beam, due to which topographic contrast is developed. The angle of incidence depends on the specimen surface. When the beam strikes at each point, the detector gets direct information on the inclination as due to secondary and back scattered electrons. Finally, the interpretation and analysis of image does not require the information regarding the mechanism of image formation.

4.1.9. DEFECTS IN SEM

- **CONTAMINATION**

  The deposition of some unwanted or external molecules on the specimen surface. Due to this deposition, the scattered electron coefficient changes and contrast is developed. Imaging at low magnification, and then by increasing the magnification can reduce the effect. The beam is mostly contaminated by hydrocarbon molecules, and they can affect the signals even at high magnification. By increasing the vacuum, you can minimize the effect of contamination. Some anticontamination devices can also be installed near the specimen.

- **CHARGING**

  Not all the incident electrons are scattered back from the specimen, but many of them penetrate the specimen and remain there as their kinetic energy is reduced. Now if the specimen is not properly ground, these impart a net charge to the sample, due to which the specimen's surface potential rises. Usually, insulator materials undergo this charging effect, because electron does not flow properly, so they cannot reach the ground. The field line of the detector get disturbs when there occurs a local charging and surface potential is altered. These all affect the collection of secondary electrons. Also, due this local charging, voltage contrast is developed, and the potential distribution is imaged. Some areas appear darker and some areas appear bright due to localized opposite charges.

4.1.10. SAMPLE REQUIREMENTS

The Specimen must meet the following requirements before it is placed on the stage

a) The surface to observe is exposed
b) The specimen is firmly fixed to the specimen mount
c) The specimen has conductivity in principle

When you want to observe the internal structures, it is necessary to prepare a cross section. And following methods are required [32]

i. Fracturing
ii. Cutting

iii. Mechanical Polishing
iv. Milling by ion beam
v. Contrast enhancement
vi. Mounting specimen
vii. Coating

4.1.11. RESULTS

SEM was done to study the surface morphology and dimensionality of the nanorods. The following images are the SEM images of various samples grown on ITO substrate. The images show a uniform density, homogeneity, smoothness and misaligned nanorods along the c-axis

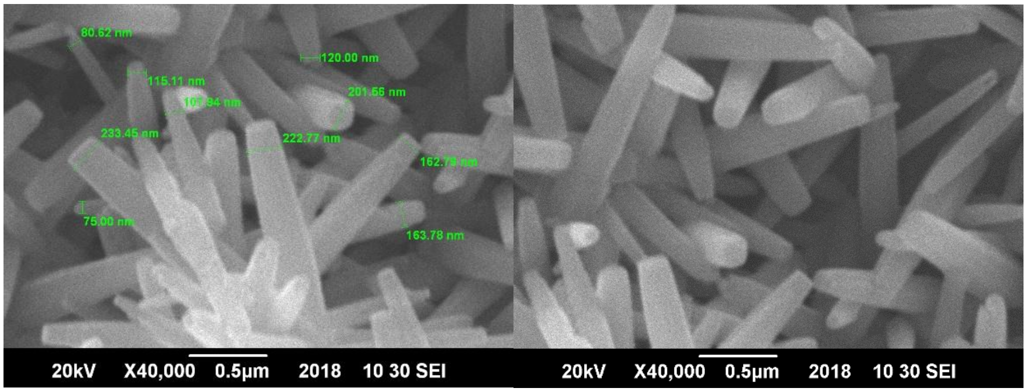


Figure 28 SEM results of 40 mol% Na in ZnO

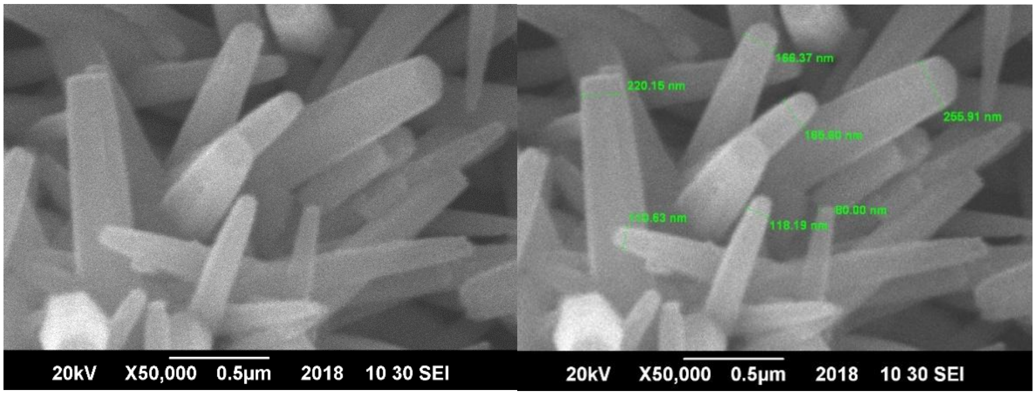


Figure 29 SEM results of mol% of Graphenen in ZnO

4.2. X-RAY DIFFRACTION AND CRYSTALLOGARPHY

X-RAYS:

X-rays are electromagnetic waves which have high frequency and very short wavelength, with high energies. They can penetrate or pass through an object.

CRYSTALLOGRAPHY:

The determination of crystal structure of any substance using x-ray diffraction technique is called crystallography.

X-RAY DIFFRACTION:

An incident beam of X-rays is caused by the atomic planes of a crystal structure to interfere with one another as they leave the crystal is called X-ray Diffraction.

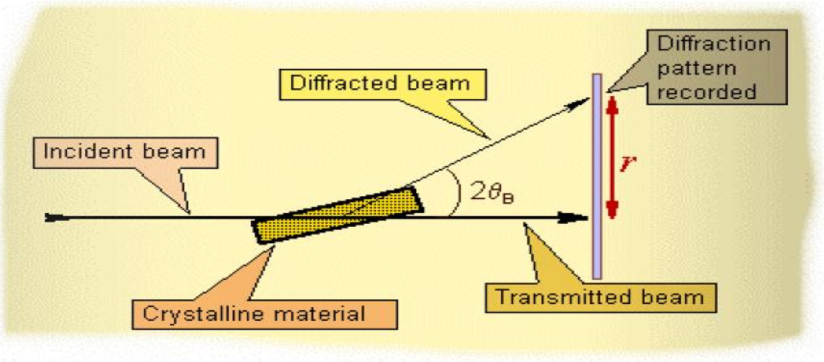


Figure 30 Schematics of XRD

4.2.1. WHY XRD

X-ray Diffraction is important due to the following reasons

- Determine the orientation of a single crystal or grain.
- Find the crystal structure of an unknown material.
- Measure the size, shape and internal stress of small crystalline regions.
- Measure the average spacings between layers or rows of atoms.
- Phase identification

4.2.2. BRAGG'S LAW AND X-RAY DIFFRACTION

Diffraction occurs only when Bragg's law is satisfied condition for constructive interference.

Bragg's law tells us that how waves reveal the atomic structure of crystals.

Mathematically it is shown as

$$n\lambda = 2d\sin\theta$$

The variable d is the distance between the atomic layers in a crystal, and lambda λ is the wavelength of the incident X-ray beam, n is an integer.

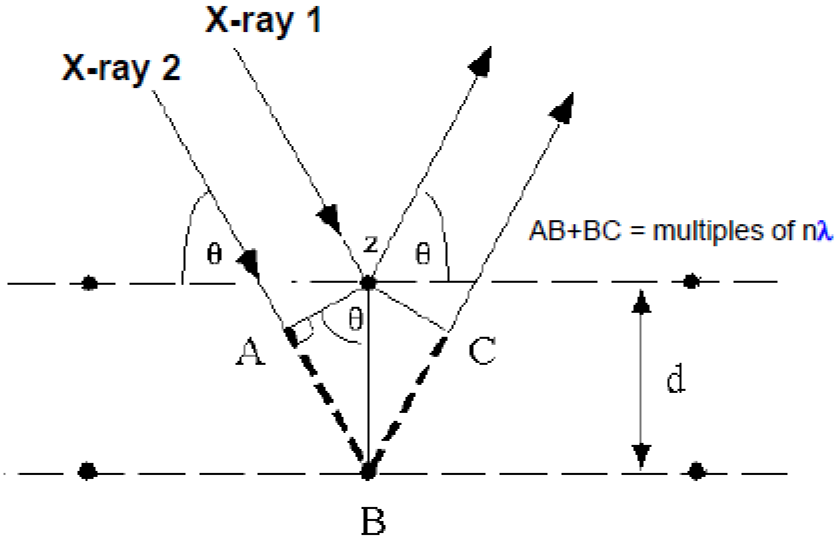


Figure 31 Representation of Bragg's law

4.2.3. XRD EXPERIMENT AND WORKING PRINCIPLE

Some of the basic features of XRD experiment are following:

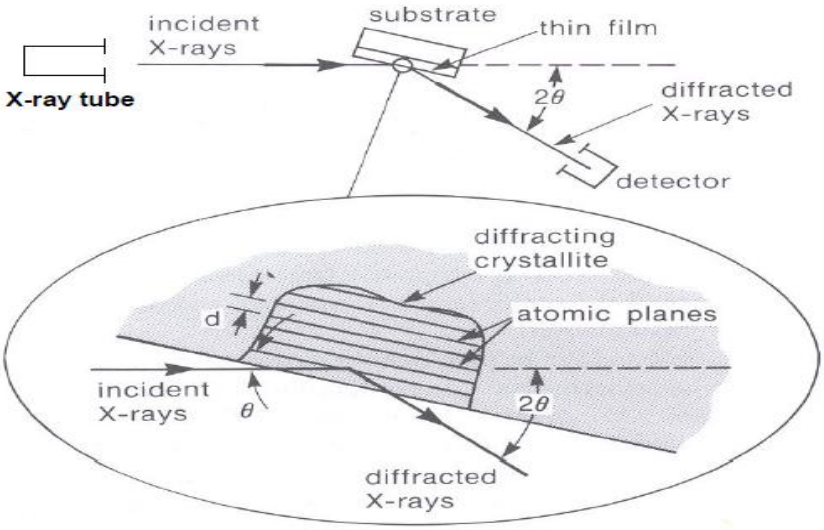
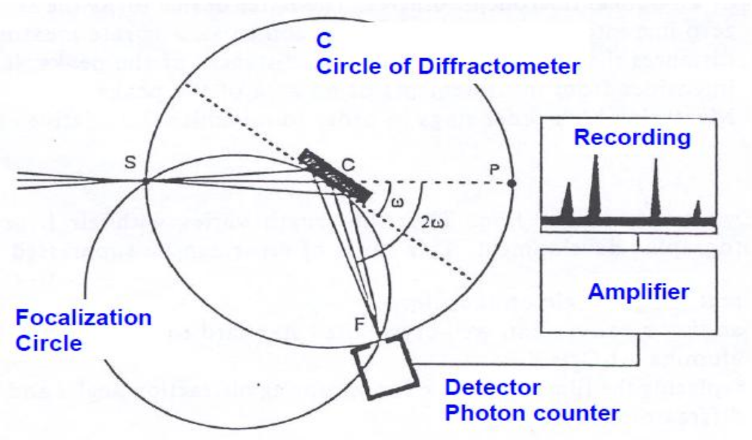


Figure 32 Diffractrometer

i. Production
ii. Diffraction
iii. Detection
iv. Interpretation

Detection of Diffracted X-rays by a Diffractometer



Bragg - Brentano Focus Geometry, Cullity

Figure 33 Schematics of Diffractometer

Peak position is determined by d-spacings and lattice parameters

$$\lambda = 2d\sin\theta$$

4.2.4. XRD PATTERN

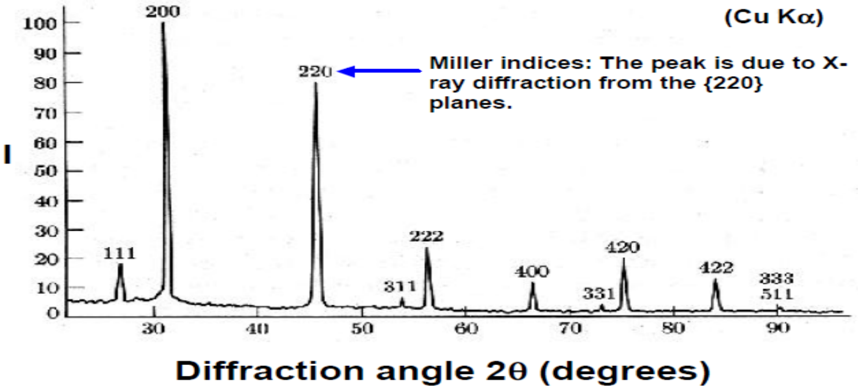


Figure 34 XRD PLOT

Significance of peak shape in XRD

- Peak position
- Peak width
- Peak intensity

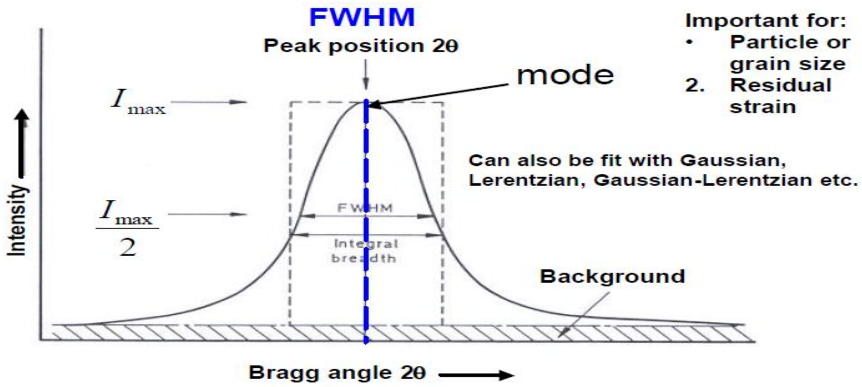


Figure 35 XRD peak Characteristics

4.2.5. PROPERTIES OF X-RAYS

X-rays have four types of properties:

- **PHYSICAL PROPERTIES**

- X-rays are electromagnetic in nature
- X-rays always travel in straight line
- Wavelength ranges from 0.5 Å to 10 Å
- They cannot have seen from naked eyes or heard
- Refraction, diffraction and interference are shown by X-rays
- In the presence of magnetic or electric field, they cannot show deflection
- They are absorbed by some materials

- **CHEMICAL PROPERTIES**

- Many substances show a change in color when X-rays are passed through them
- In case of solution, X-rays produce OH radical which react with the solute and thus chemical changes occur
- Enzymes lost their fermenting power when gets exposed to X-rays

- **BIOLOGICAL PROPERTIES**

- Malignant lesion or cancerous patients are treated by using the excitation property of X-rays
- They also used as bactericidal or germicidal

- **PHYSIOLOGICAL PROPERTIES**

- X-rays can produce an image on the photographic films, even of the internal parts [33]

4.2.6. RESULTS

The crystal structure of ZnO nanorods was studied by using XRD. The plots indicate that they correspond to polycrystalline hexagonal ZnO nanorods, by showing the peaks at 32°, 34.4° and 36.5°, which exactly match with the peak positions of ZnO. All peaks are indexed to ZnO, while some extra peaks at 30° and 52 ° belong to the substrate i.e. as the XRD plot of ITO is shown below. In case of 40 mol% Na into the lattice of ZnO slight shift in the peaks of ZnO is observed but for the case of Graphene, no shift in the peaks have been noticed. The reason behind this should be low amount of addition of

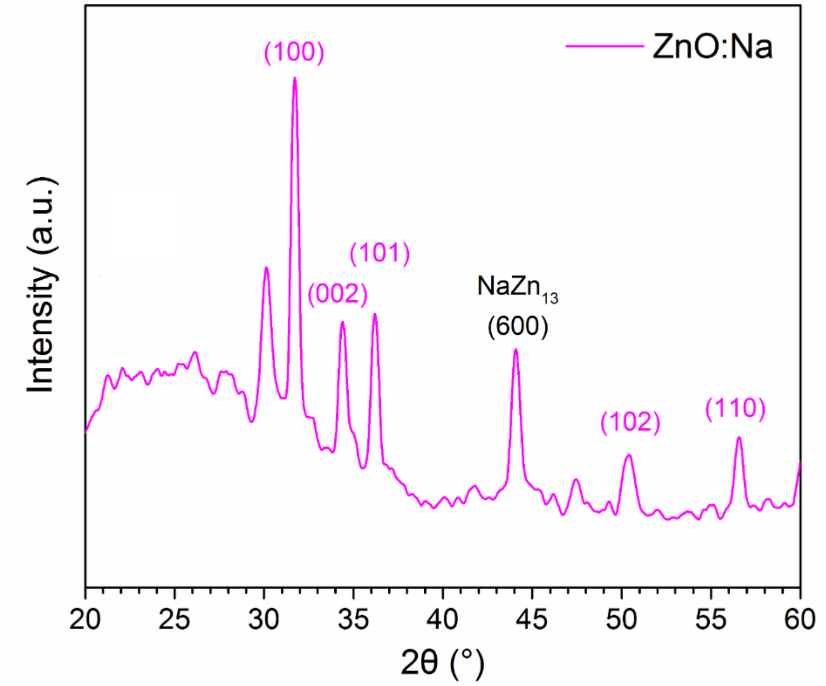


Figure 36 XRD Result of 40mol%Na in ZnO Nanorods

graphene i.e. 1 mol%. The reason to observe the peaks of ITO is that the x-rays have high penetrating power which is up to 3mm, so they reached ITO too. The reference code against which the sample was compared is 00-036-1451. In figure both the plots reveal that the three major peaks belong to ZnO, while the extra peaks are indexed for ITO.

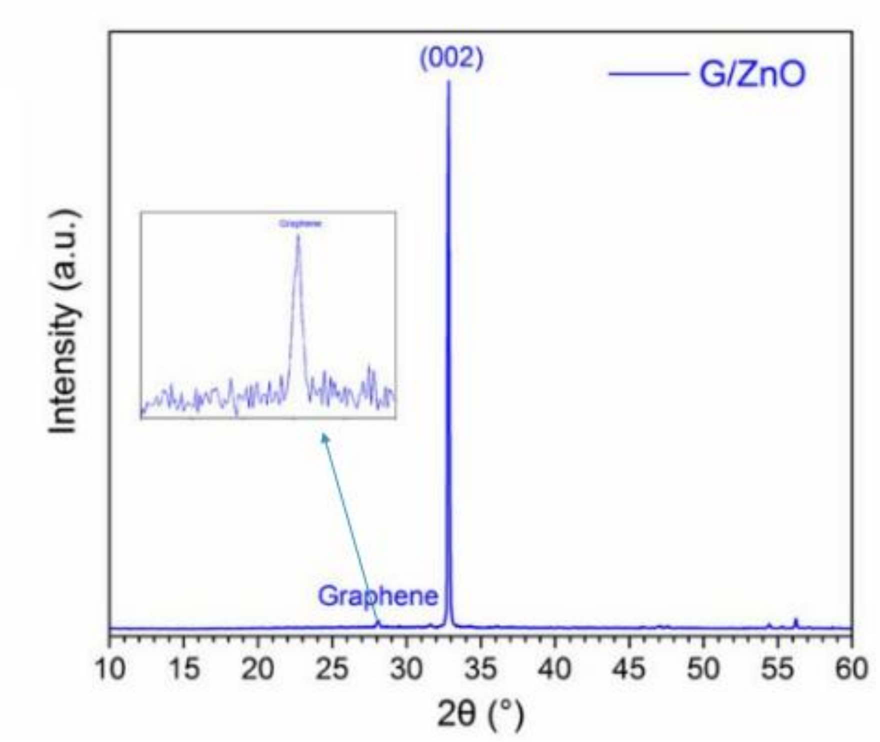


Figure 37 XRD plot of 1mol% graphene in ZnO Nanorods

4.3. IV CHARACTERISTICS

As ZnO is an n-type semiconductor, and the gas sensing properties are due to its surface resistance. In air, oxygen is absorbed or chemisorbed on the surface and it acts as trap while capturing electrons from the conduction band, due to its high electro negativity. As a result, depletion region produces on the surface. Now it depends on the gas to be sense, if it is oxidizing it will decrease the conductivity of increase the resistivity. Similarly, in case of reducing gas, the resistivity will decrease, and conductivity will be enhanced

We studied the IV characteristics on the electrochemical station. The IV characteristics of ZnO were studied in vacuum, in open air, in nitrogen, in ethanol (also in UV), and when the substrate was exposed to methane. The area of the substrate or sample was 1.5cm^2 i.e. (1x1.5) cm^2.

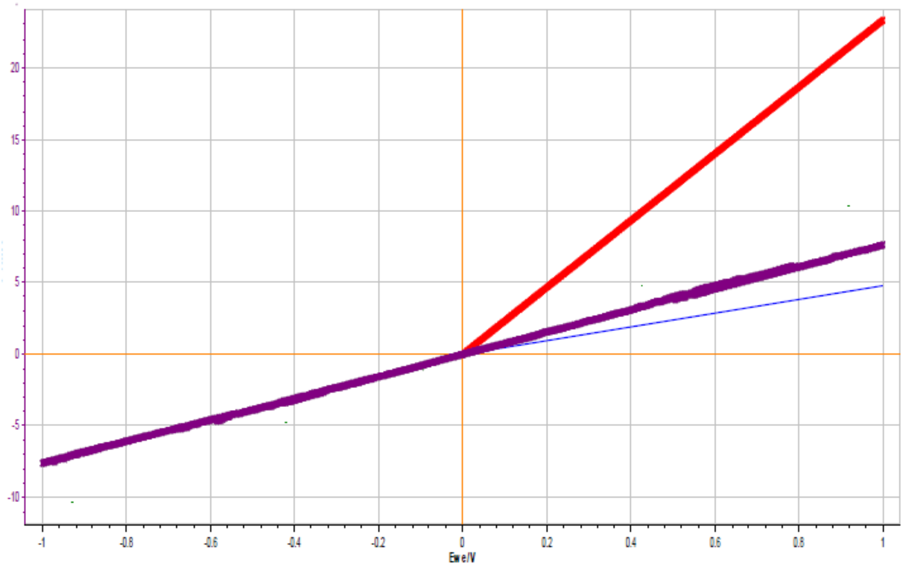


Figure 38 Standard Plot of IV Characteristics

The IV plots in the figure xx show that their slops change as the medium is changed, in case of pure ITO the conductivity is very high as it is obvious from the slope. It is because the ITO is conductor. But when the ITO substrate having ZnO nanorods on it is exposed to air, the conductivity decreases or its resistance increases, because the oxygen from the air gets adsorbed on the surface of ZnO and it captures the conduction electrons of the ZnO, due to which the charge carriers decreases in amount. Hence the resistance increases.

When the sensor was exposed to UV light, the conductivity increased because UV light can excite the charge carriers. Further when the distance between the UV source and the sensor was decreased, the conductivity further increased that indicates that the high intense UV light increases the sensitivity of the sensor.

The UV detection mechanism depends on the intrinsic defects like oxygen vacancies and zinc interstitials. It is already mentioned that the chemisorbed oxygen molecules on the surface confine the free electrons of the ZnO sensor.

$$\mathbf{O_2 + e \longrightarrow O_2\text{ - ads.}}$$

When UV light of energy greater than the band gape of ZnO is incidented, electron-hole pairs are formed. Adsorbed oxygen combines with the hoe to form oxygen molecule and then desorbed, decreasing in the width of depletion region, thus increasing the conductivity.

$$\mathbf{h + h + O_2\text{ - ads.} \longrightarrow O_2}$$

After the UV light, the oxygen gets reabsorbed until the equilibrium is regained. This is slow process which increases the relaxation time constant for the device.

4.3.1. METHANE SENSING

Methane is one the reducing gas, hence its increases the conductivity of ZnO nanorods. The adsorbed oxygen increases the surface resistance of the sensor by capturing the conduction electrons. Methane reacts with the adsorbed oxygen and the trapped electrons are sent back to the conduction band [34] due to which the resistance decreases and the conductivity increases. The entire reactions are shown as

$$\mathbf{O_2(g) \rightarrow O_2(ads)\ O_2(ads)+e^- \rightarrow O_2\text{ - }(ads)}$$

$$\mathbf{O_2\text{ - }(ads)+e^- \rightarrow 2O\text{ - }(ads)\ O - (ads) + e^- \rightarrow O_2\text{ - }(ads)}$$

$$\mathbf{CH_4(gas) + 2O_2\text{ - }(ads) \rightarrow CO_2(gas) + 2H_2O(gas) + 2e^-}$$

$$\mathbf{CH_4(gas) + 4O - (ads) \rightarrow CO_2(gas) + 2H_2O(gas) + 4e^-}$$

$$\mathbf{CH_4(gas) + 4O_2\text{ - }(ads) \rightarrow CO_2(gas) + 2H_2O(gas) + 8e^-}$$

4.3.2 CARBONDIOXIDE SENSING

Carbon dioxide CO_2 has linear molecular structure. According to Literature there are water molecules present at the surface of the MOS gas sensor, at low temperature these molecules form hydroxyl and hydrogen ions which react with metal oxide to form carbonates and bicarbonates. In the case of high temperatures CO_2 reacts with surface adsorb oxygen atoms to form CO^{3-} ion directly. All these reactions requires an electron from the surface hence reduction in the conductivity of the Metal Oxide occurs. [35]

$$\mathbf{CO_2(g) + OH^-(ads) \rightarrow HCO_3^-\ (surface)}$$

$$\mathbf{CO_2\ (g) + H^+(ads) + 2e^-\ (surface) \rightarrow HCO_2^-\ (surface)}$$

$$\mathbf{HCO_2^-\ (surface) \rightarrow CO(gas) + OH^-\ (surface)}$$

$$\mathbf{HCO_3^-(surafce) + OH^-\ (ads) \rightarrow CO_3^{2-}(bulk) + H_2O(gas)}$$

$$\mathbf{CO_2(gas) + O^{2-}\ (ads) \rightarrow CO_3^{2-}}$$

4.3.3. RESULTS

IV characteristics for methane sensing clearly show the shift of the peaks according to the concent ration of the gases for both ZnO samples. Sample with 40 mol% Na show high activity toward the as can be analyzed by the results. On the other hand, sample with 1 mol% Graphene shows rather selective effect toward CH_4 gas.

Conc. of Methane	Sensitivity Ra/Rg	% Sensitivity w.r.t Air
20 sccm	1.62	162
30 sccm	1.74	174
40 sccm	1.88	188

RESPONSE TIME	3-5 sec
Recovery time	65 seconds
Error	+/- 1.2%

Table#4

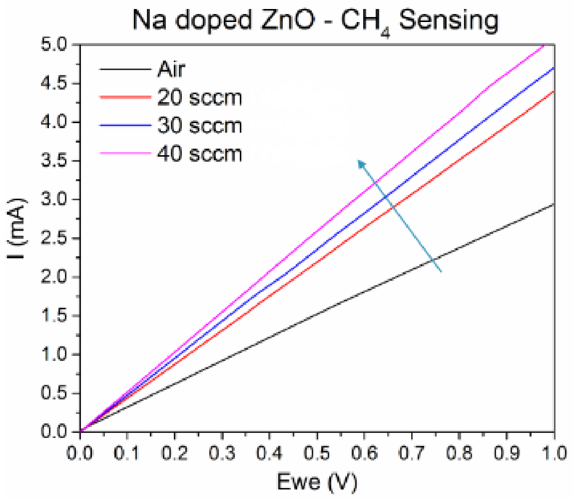


Figure 39 CH_4 Sensing of 40 mol% Na with ZnO

Conc. of Methane	Sensitivity Ra/Rg	% Sensitivity w.r.t Air
10 sccm	1.11	162
30 sccm	1.44	174

RESPONSE TIME	10 sec.
Recovery time	240 seconds

TABLE# 5

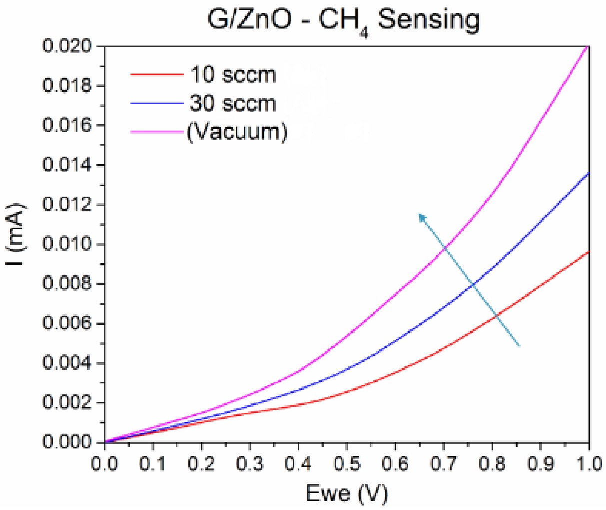
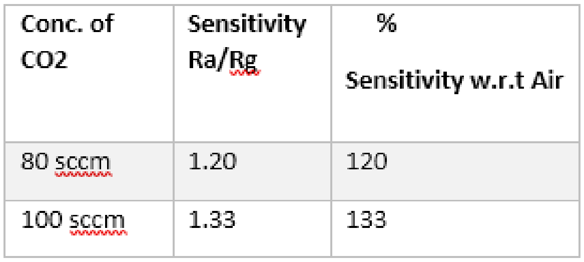
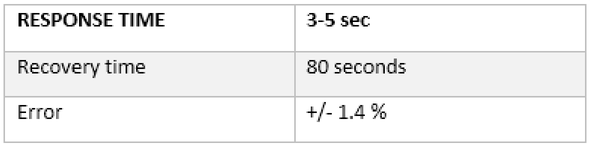


Figure 40 CH_4 Sesning of 1 mol% graphene in ZnO



Conc. of CO2	Sensitivity Ra/Rg	% Sensitivity w.r.t Air
80 sccm	1.20	120
100 sccm	1.33	133



RESPONSE TIME	3-5 sec
Recovery time	80 seconds
Error	+/- 1.4 %

TABLE# 6

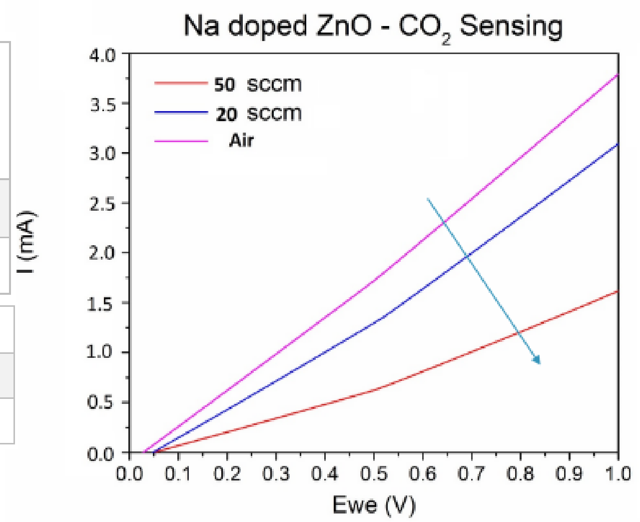
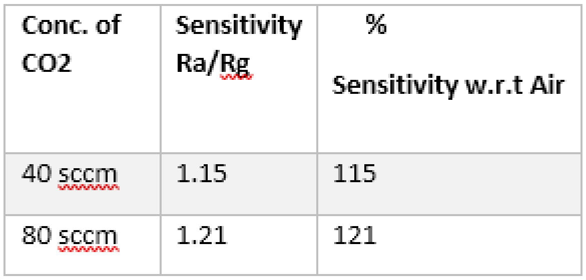
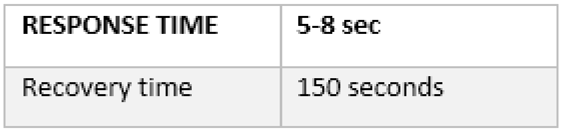


Figure 41 CO_2 Sesning of 40 mol% Na in ZnO



Conc. of CO2	Sensitivity Ra/Rg	% Sensitivity w.r.t Air
40 sccm	1.15	115
80 sccm	1.21	121



RESPONSE TIME	5-8 sec
Recovery time	150 seconds

TABLE# 7

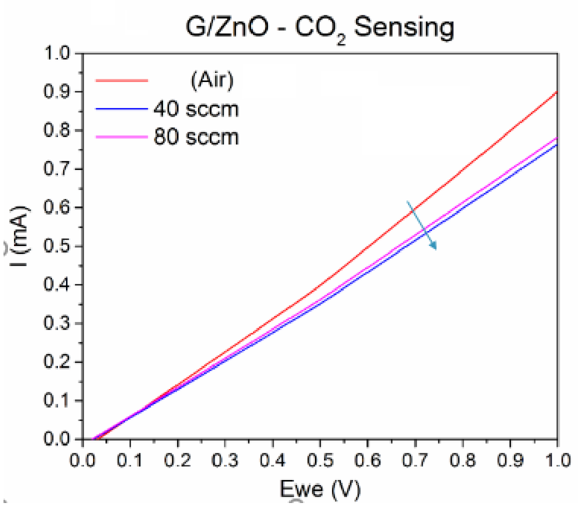


Figure 42 CO_2 Scensing of 1 mol% Graphene in ZnO

CHAPTER 5: CONCLUSION

The experimentation in both phases produced results, revealed via the characterization techniques discussed above, that can be concluded as follows:

1. Spin coating is a more effective method for seed layer deposition
2. For better results and growth following conditions are optimum:

- Growth Time: 2.5 hrs
- Growth Temperature: 90° C

3. CBD method provides better uniformity.
4. ZnO’s conductivity varies when in exposure to UV light
5. ZnO’s conductivity is sensitive to gas molecules’ interaction with the surface
6. Na Doped samples are more selective towards CO_2 gas but also show results for CH_4 gas.
7. Sample with 1mol% Graphene shows highly selective nature for CO and show very small change in the resistivity in the case of CH_4

All these conclusions verify that the objectives of our final year project were successfully achieved.

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