FIELD EMISSION STUDY OF CVD GROWN ZnO NANOWIRES

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OF

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IN

NANOSCIENCE AND TECHNOLOGY

Submitted By

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I, Anurag, Roll No. 2K16/NST/02 of M.Tech. Nanoscience and Technology, hereby declare that the project Dissertation titled **"Field emission study of CVD grown ZnO nanowires "** which is submitted by me to the Department of Applied Physics, Delhi Technological University, Delhi in partial fulfillment of the requirement for the award of the degree of Master of technology, is original and not copied from any source without proper citation. This work has not previously formed the basis for the award of any Degree, Diploma Associateship, Fellowship or other similar title or recognition.

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CERTIFICATE

I hereby certify that the Project Dissertation titled **"Field emission study of CVD grown ZnO nanowires"** by **Anurag**, Roll No. **2K16/NST/02**, Department of Applied Physics, Delhi in partial fulfillment of the requirement for the award of the degree of Master of Technology, is a record of the project work carried out by the student under my supervision. To the best of my knowledge, this work has not been submitted or full for any Degree or Diploma to this University or elsewhere.

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Abstract

FIELD EMISSION STUDY OF CVD grown ZnO NANOWIRES GROWN VIA CVD

ZnO is an outstanding II-VI semiconductor material. ZnO as a nano material has been reported to have nanowire/nanorod, nanoribbon shapes among other types& variety of techniques are available for their synthesis. Nanowires in particular application perform better than their other nano regime counterparts due to best aspect ratio. Growth of ZnO nanowires via chemical vapor deposition (CVD) provides a good array of nanowires with appropriate sizes.

In this study we intended to grow ZnO nanowire via Thermal CVD without any inert gas environment *i.e.* under atmospheric conditions. The rationale for this choice was to device simplest method of nanowire synthesis without complexity of inert gas or vacuum requirement. Such method would be of great use for large scale industrial production.

Field emission is the phenomena of electron emission from metal, semi-conductor surface when a large electric field of the order of 10^7 V/μm is applied across them. This phenomena is being harnessed in display devices, field-emission microscopy & spectroscopy methods. The preliminary reason for interest in field emission characteristic of nanowires additional to their excellent aspect ratio is, smaller sized materials would yield higher resolution for field-emission process. Thus display devices using such materials would have resolutions which erstwhile were not possible.

In this study, ZnO nanowires of the radius in the range 15-50 nm were grown via CVD in atmospheric environment. No special pressure, gas inlet or vacuum was given to substrate. EDX characterization suggested the formation of contaminant free structure of ZnO nanowire. UV-vis & photoluminescence spectra gave idea about optical & electronic nature of as-grown nanowires.

Field emission study of the CVD grown ZnO nanowires in atmospheric conditions provide some interesting revelations. Maximum current density, turn-on voltage & field enhancement factor, the key parameters to define field-emission behavior of a material are used for identification of best candidate in terms of growth conditions. Out of all ZnO nanowire growth conditions, best ascertained by current study is found to be for nanowire which were grown at 650^{o}C for 1 hour thermal oxidation. These as-grown nanowires can be can be potential candidate for field-emission applications.

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LIST OF ABBREVIATIONS, SYMBOLS

ZnO	:	ZINC OXIDE
CVD	:	CHEMICAL VAPOR DEPOSITION
MBE	:	MOLECULAR BEAM EPITAXY
GaN	:	GALLIUM NITRIDE
PVD	:	PHYSICAL VAPOR DEPOSITION
FCC	:	FACE-CENTERED CUBIC
HCP	:	HEXAGONAL CLOSED PACKING
LED	:	LIGHT EMITTING DIODE
PEC	:	PHOTOELECTROCHEMICAL
DFT	:	DENSITY FUNCTIONAL THEORY
F-N	:	FOWLER-NORDHEIM

CHAPTER 1 : INTRODUCTION

1.1 ZnO :

Why ZnO? ZnO is a II-VI semi-conductor material which in contemporary times have gained immense popularity due to the fact that it possesses many wonderful characteristics which are regularly being employed in variety of scientific & industrial applications. ZnO crystallizes in two types of lattices, Hexagonal closed packing (HCP) & Face-centered cubic (FCC).

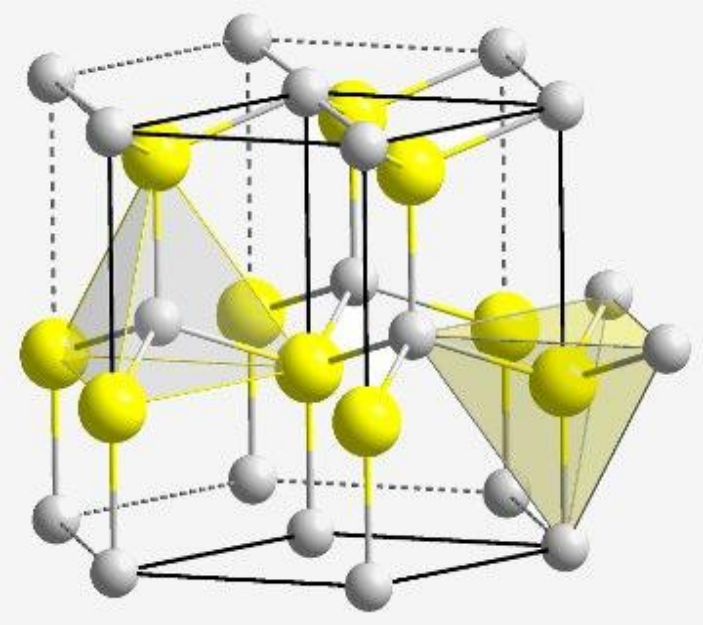


Figure 1.1 : Wurtzite structure of ZnO [2]

In above structure, yellow balls represent Oxygen atoms & white balls Zinc atoms.

Figure 1.2 provides layout of a single unit cell of Wurtzite structure.

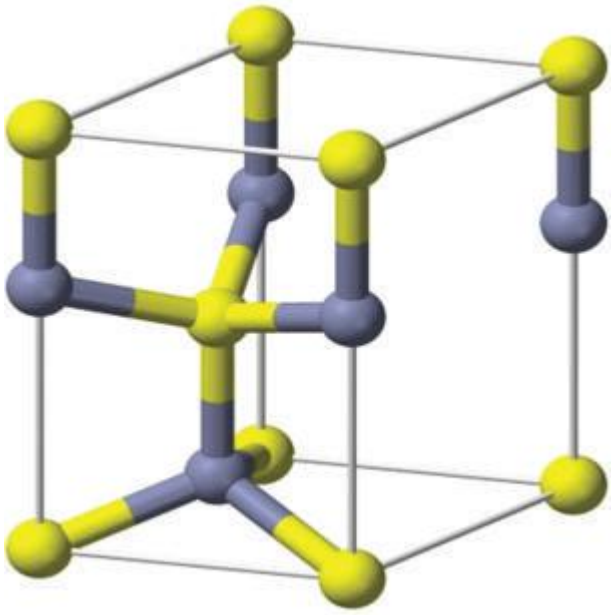


Figure 1.2 : Single wurtzite unit cell [2]

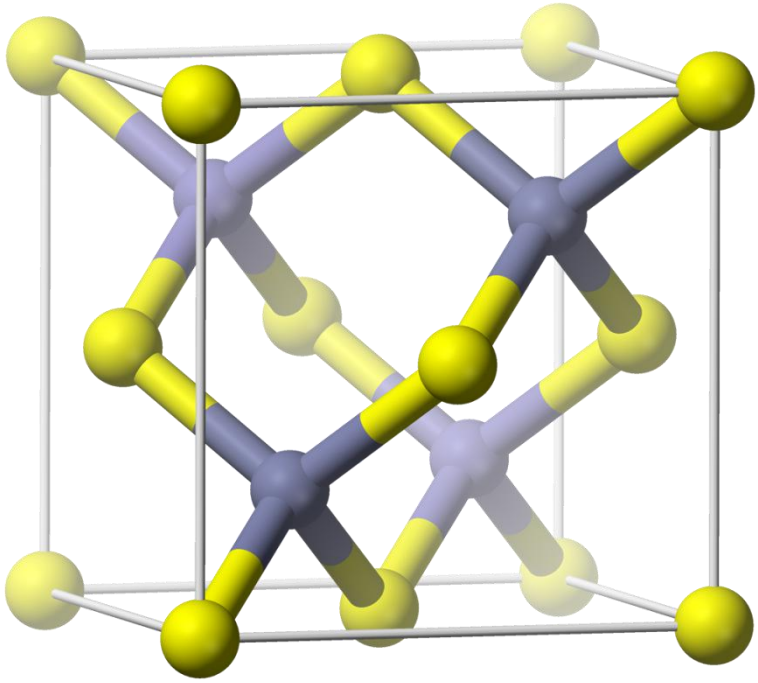


Figure 1.3 : Unit cell of Zinc blende structure [3]

1.2 :ZnO as a Semi-conductor :

ZnO is a potential candidate for semiconductor device applications. Due to a direct and wide band gap in the near-UV part of spectral region [1], & large exciton binding energy [1], it can host excitonic emissions at a range of temperatures including room temperature [1]. ZnO exhibits wurtzite crystal structure, similar to gallium nitride. But contrary to GaN, big sized single crystallized bulks of ZnO are available [1]. ZnO shows n-type semi-conductor behaviour, which at times (arguably) is attributed to availability of Oxygen vacancy defects [4]. Recently, huge advancement in the synthesis of single crystalline nanowire has been reported. This has triggered the research the research interest in the application of ZnO nanowire. Furthermore, various efforts are being made to control inherent n-type semi-conductor nature of ZnO & make p-type ZnO. This emphasis is particularly laid due to ZnO's promising candidature for GaN's alternative in carving optoelectronic devices. Significance of impurity & defects in n-type semi conductor can get better perspective by DFT study [1]. Reports of p-type semi-conductivity in ZnO:Phosphorous nanowires grown via CVD has been made in past [1]. ZnO scores over GaN in terms of availability of large single crystals as well. For instance Gallium Nitride has no native material for growth, thus it's growth in general is carried with significant proportion of defects due to non-matching structure of substrate. Yet another merit of ZnO is it's amenability to wet chemical etching, which is not shown by GaN. This feature is pivotal for fabrication of devices. In electronics & optoelectronics devices bandgap modulation is very much desired. Mixing magnesium to zinc oxide increases the it's bandgap, while mixing cadmium show decreases in bandgap, which is analogous to impact of adding aluminium & indium to gallium nitride. Despite MgO, CdO having NaCl/FCC unit cell, when in small proportion $Mg_{1-x}Zn_xO$&$Cd_{1-x}Zn_xO$ alloys attain the wurtzite geometry of host compound, & delivering large modulation in bandgap.

1.3 : Properties of ZnO:

ZnO possess large number of properties of great utilitarian value [1]. Most promising of them being a direct band gap material with 3.37 eV bandgap. This single feature makes it very desired material for realization of optoelectronic devices particularly in UV to blue parts of spectrum. Availability of large single crystals add another feather to ZnO's cap as prospective semi-conductor. Following has been enlisted it's useful properties:

• **Wide & direct bandgap**: ZnO has direct & wide bandgap of 3.37 eV while same for of gallium nitride is 3.44 [1]. This feature makes ZnO suitable for optoelectronics device (like LEDs, LASER) operating in the UV or blue spectrum [5]. Many ZnO based nano structures perform well for Optically pumped lasing.

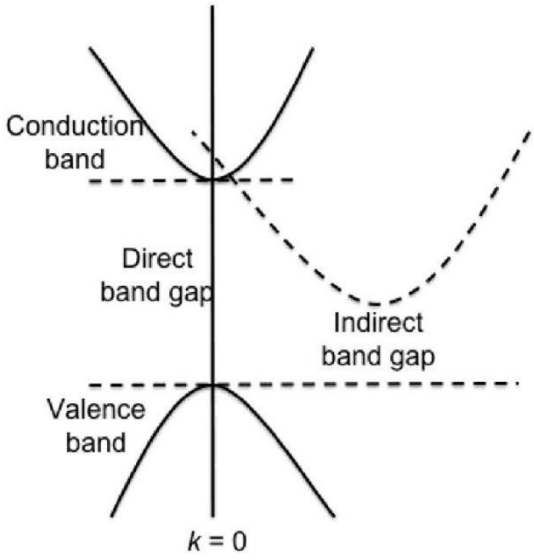


Figure 1.4 :Schematic of Direct & Indirect bandgap of energy [23]

• **Large exciton binding energy**: ZnO has large exciton binding energy of the order of 60 meV [1], which is far more than 25 meV for gallium nitride [1]. For efficient UV emission, thermal energy (k_BT) which is of the order of 25meV must be exceeded by exciton binding energy [1]. This enables considerable excitonic emission in ZnO at room temperature and higher [1].

• **Highly Piezoelectric**: Piezoelectric materials have tendency to deform when subjected to applied voltage across their crystal, & vice-versa. This property enable them to be used as sensors & transducers. The low symmetry of the wurtzite crystal structure combined with a large electro-mechanical coupling in ZnO gives rise to strong piezoelectric and pyroelectric properties. Piezoelectric films of ZnO with uniform orientation & structure have been synthesized over different substrates via various deposition techniques, including CVD, sol–gel, spray pyrolysis, MBE & sputtering [9-14].

• **Large thermal conductivity**: This property enables ZnO to be mixed with materials like rubber to enhance the thermal conductivity of automobile tires). This characteristic also ensure better performance in heat sinking during device operation. High thermal conductivity also makes ZnO a good substrate for epitaxial growth (particularly of those materials which have matching lattice constant like GaN) [1].

• **Amenability to wet chemical etching**: Amenability to wet chemical etching is a highly desired feature for semi-conducting materials.This feature is a great aid in fabrication of devices using such materials. Etching of ZnO films with acidic, basic & even mixture of reagents make it highly versatile.

• **High non-linear resistance of poly-crystalline ZnO**: This property has led to use of ZnO in synthesizing varistors of fine quality varistors. Grain boundaries are believed to be reason for resistance's non-linear behaviour. Good non-ohmic I-V characteristics of ZnO is reason for the stellar performance as varistors [1].

• **Good luminescence**: ZnO is again a suitable material for optical-electronic devices because it possess strong luminescence in the visible part of spectrum. It has emission peak around 487 & a healthy FWHM of 0.37 eV [1]. It find application in field emission displays due to n-type semi-conductor nature & for same reason in vacuum fluorescent displays. The n-type nature is generally said to be due to vacancies (O) or interstitials (Zn), [1].

• **Large single crystals**: Availability of large sized single crystals give ZnO yet another edge over competing semiconductors. This availability of substrate for native growth of

zinc oxide leads to procuring films of better quality along with minimized defect concentration. On the contrary gallium nitride has no native material for such a growth.

• **Hardness to radiation**: ZnO possesses very high radiation hardness, far more than that of gallium nitride radiation hardness is important for applications at high altitude or in space. [1].

• **High surface conduction sensitivity towards adsorbed species**: Conductivity of thin films of ZnO is very responsive the surface's exposure to large number of gases. This property has carved ZnO's way to become a suitable material for synthesis of economical smart nose or smell sensors. Trimethylamine constitute the odor, which gets along ZnO very well [1]. The sensing mechanisms involves change in electrical conductance of host species on adsorption of ambient gas over it's surface [1].

1.4 : Nanowires:

Nano particles are particles within size range of 1-100 nm. Nano wires are formed by quantum confinement of 'particle' in two dimensions & allowing delocalization only along remaining one dimension. Thus they exhibit large surface to volume ratio. Also their Debye lengths are of the order of their diameters.

The formula to calculate energy of particle confined along 2-D directions is given by

$$E = n^2\pi^2\hbar^2 / 2mL^2$$

where, n= quantum numbers,

m= effective mass,

$\hbar$= Planck's constant,

Density of states(DOS) is

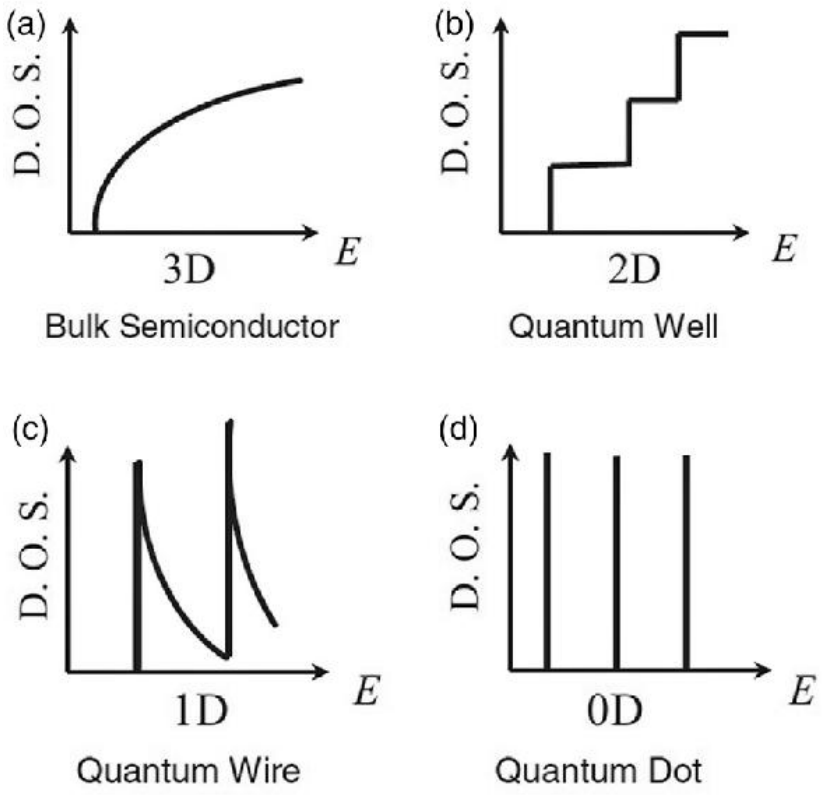


Figure 1.5 : DOS of 0-D, 1-D, 2-D & Bulk materials [6]

1.5 : Synthesis of ZnO Nanowires:

ZnO nanowires of considerable length can be synthesized using wide variety of methods. Nanowires so obtained have little to large variation in their characteristics compared to those procured via other methods.

1.5.1 : ZnO nanowire using vapor deposition : These methods of growth of nanoparticles involve two types, PVD (physical vapor deposition) & CVD (chemical vapor deposition). The essential difference between two methods is, one uses chemical reaction(CVD) while other rely over physical forces (PVD) for deposition.

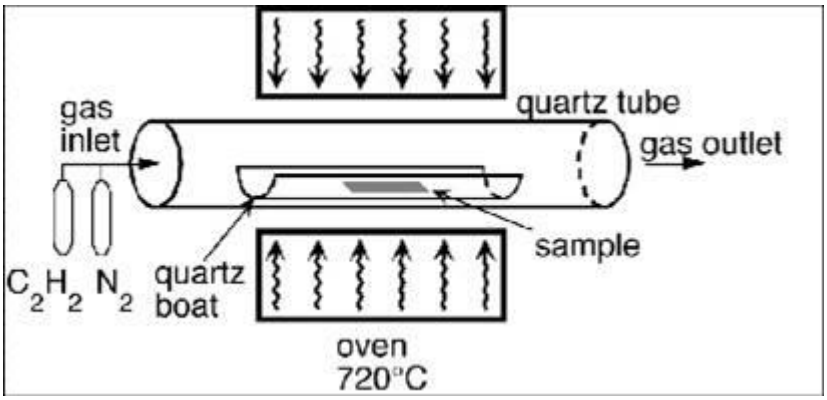


Figure 1.6 : Schematic of thermal CVD system [8]

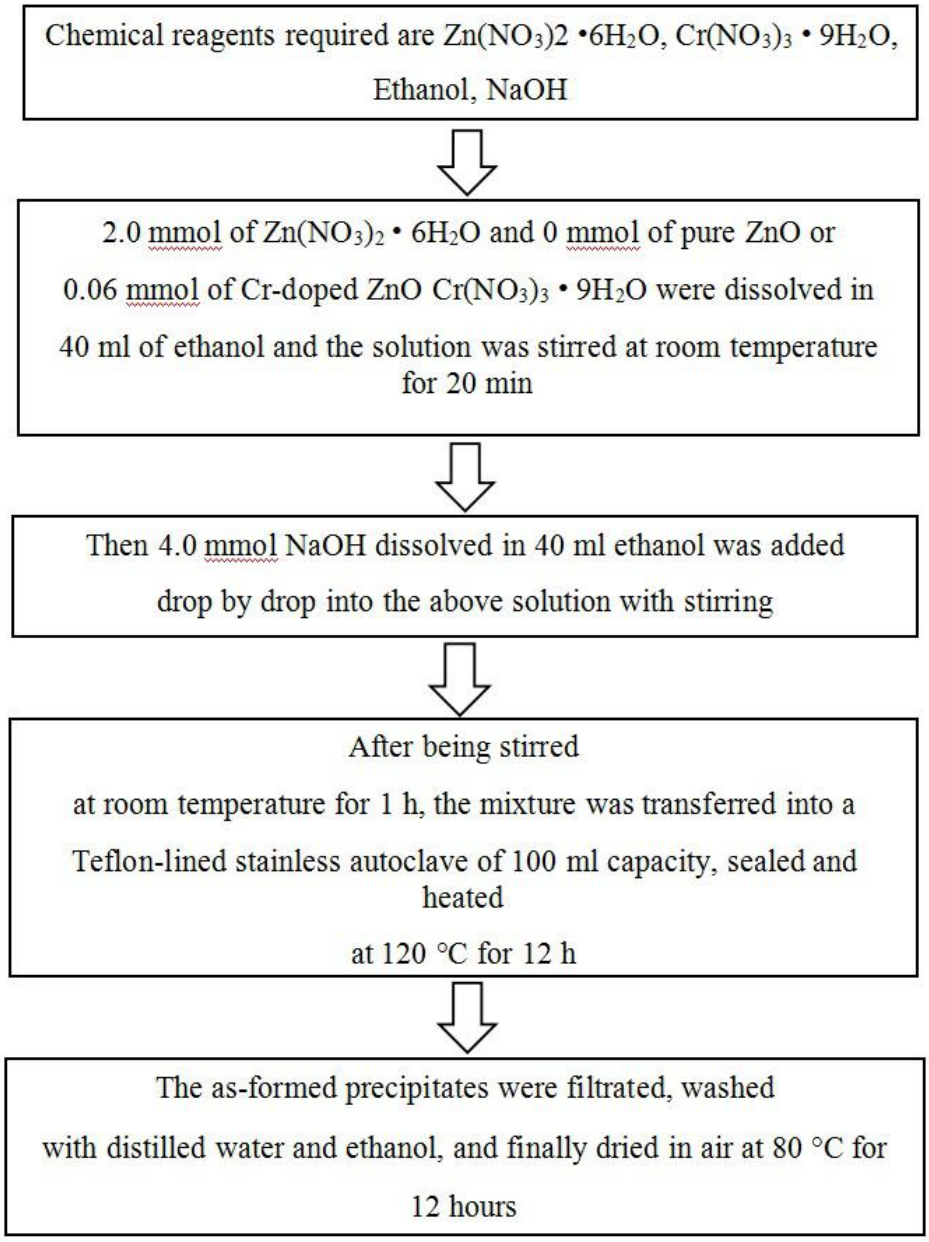
In CVD substrate is heated in presence of volatile precursors which cause desired solid formation over the substrate. Varying the condition of CVD like temperature, gas flow, pressure, mixture of gas varying physical & chemical properties of same substrate can be obtained. CVD can produce very high quality nanowires.

In PVD materials to be deposited over substrate undergoes from condensed phase to vapor phase & again convert to condensed phase to get deposited over substrate.

1.5.2 : ZnO nanowire using Solvo-thermal method :

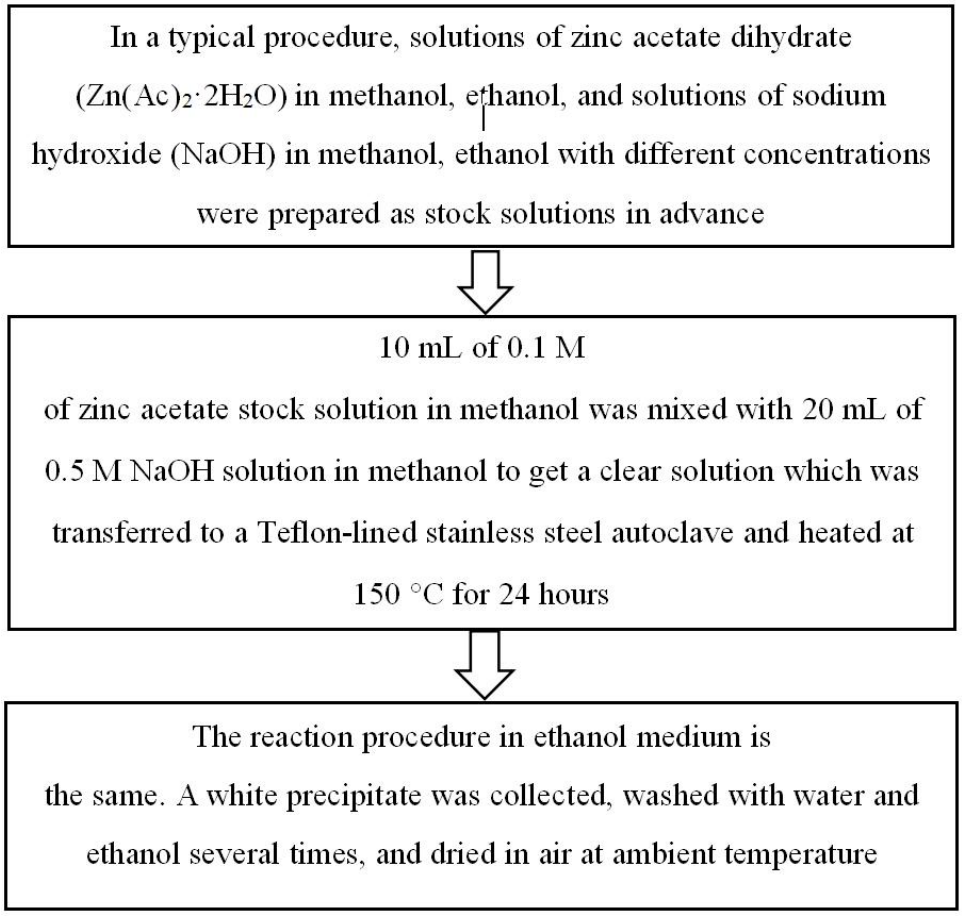
Solvo-thermal synthesis takes place inside a steel autoclave

Following method for growth of ZnO nanowire by Solvo-thermal method has been reported by [7].



1.5.3 : <u>ZnO nanowire using Hydro-thermal method</u> :

In hydro-thermal synthesis method, growth of particles take place in solution-phase in aqueous medium. This type of synthesis can take place by first growing ZnO over a seeding layer. Synthesis mechanism for ZnO nanowires is summarized below:



Hydro-thermal method has advantages of low temperature, large scale, economical synthesis. Hydro-thermal & solvo-thermal methods are both carried within an autoclave which has capacity of working with high pressure, temperature. The difference between them underlie in the solution medium which is aqueous for hydro-thermal & non-aqueous for solvo-thermal. Additionally, solvo-thermal has high pressure due to need to maintain temperature above the critical point of the solvent.

1.5.4 : ZnO nanowire synthesis using sol-gel method :

Synthesis of ZnO nanowires via sol-gel method has been reported by [31]. The reagents involved in the synthesis are Zinc-acetate-dihydrate ($Zn(CH_3COO)_2.2H_2O$), ethanol, NaOH & D.I. water. $Zn(CH_3COO)_2.2H_2O$ & C_2H_5OH were used in above synthesis method as precursor & reagent respectively. D.I. water provided medium for solvent.

Overall reaction using this Sol-gel method is single step & summarized below,

$$(Zn(CH3COO)_2.2H_2O) + 2NaOH \rightarrow ZnO + 2NaCH_2COO + H_2O$$

Sol-gel method is simplest method for synthesis of nanoparticles since it doesn't require any sophisticated equipment. It just need beaker & reagents.

1.5.5 : ZnO nanowire synthesis using Other methods :

Synthesis of ZnO nanowires using molecular beam epitaxy (MBE), electro-deposition on anodic alumina membrane (AAM) too has been reported [32].

1.6 : Application of Nanowires :

1-D nano-materials like nanowires are very versatile materials in terms of their applications. They find application in electronics, energy harnessing devices, optical devices, sensors and many more fields. Some of their amazing applications has been summarized in preceding sections

1.6.1 : Application in LASERs :

Nanowires due to flat facets provide excellent optical response in LASERs.

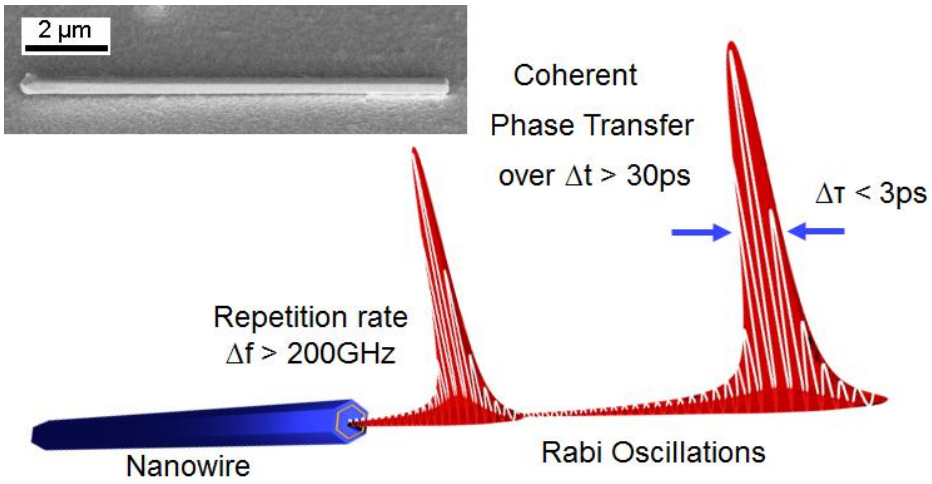


Figure 1.7 : Nanowire Laser [20]

LASERs stand for light amplification by stimulated emission of radiation. LASER is a source of monochromatic & coherent source of light. Operation of LASER require discrete energy level in material being used. Nanowire, since are quantum confined in two directions, have discrete energy levels for conduction electrons can work very well as LASER. Both electrically-pumped LASER & optically-pumped LASER has been reported [17] using nanowires.

1.6.2 : <u>Application in Batteries</u> : Nanowires are being used as electrodes in Lithium(Li) batteries [18]. Apart from nanowires other type of particles like bulk film & micro-sized particles too have been used in Li batteries. But nanowires outperform them, as is evident from the figure given below.

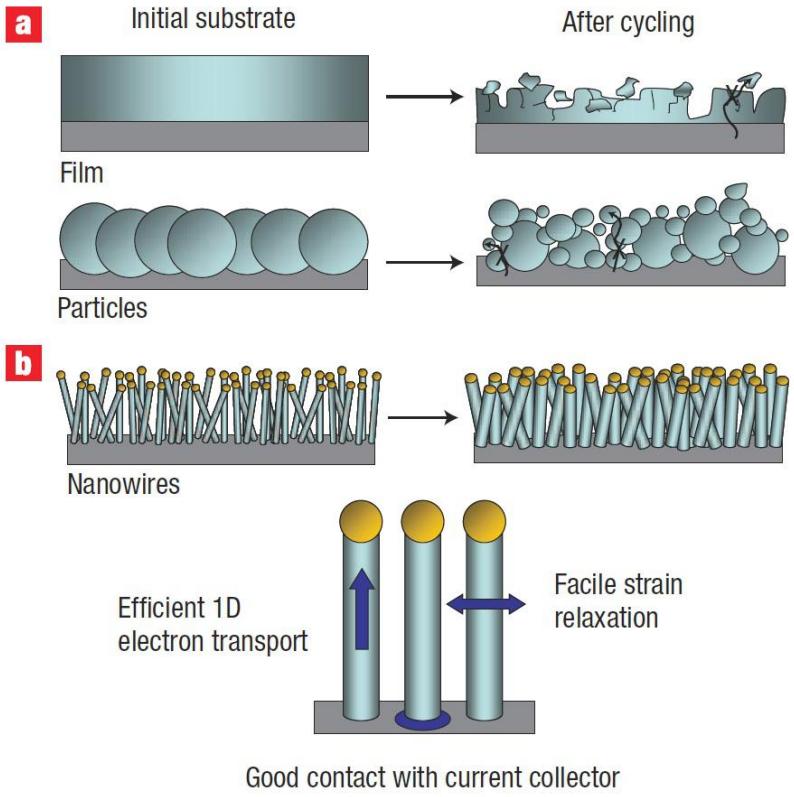


Figure 1.8 : Effect of nanowires as Battery electrode [18]

In above figure, 'a' & 'b' shows state of Li battery electrode using (bulk film & micro sized particle) & (Silicon(Si) nanowires) respectively. As is evident from the above figure that nanowire electrodes have better life after large number of cycles of charge & discharge compared to thin films & other type of nano-particles. This may be attributed to facile strength relaxation in nanowires, which is not available with other nano-scaled particles.

1.6.3 : <u>Application in optoelectronic devices</u> :

In the optoelectronic devices category, nanowires can be used for fabrication of photo-detectors.

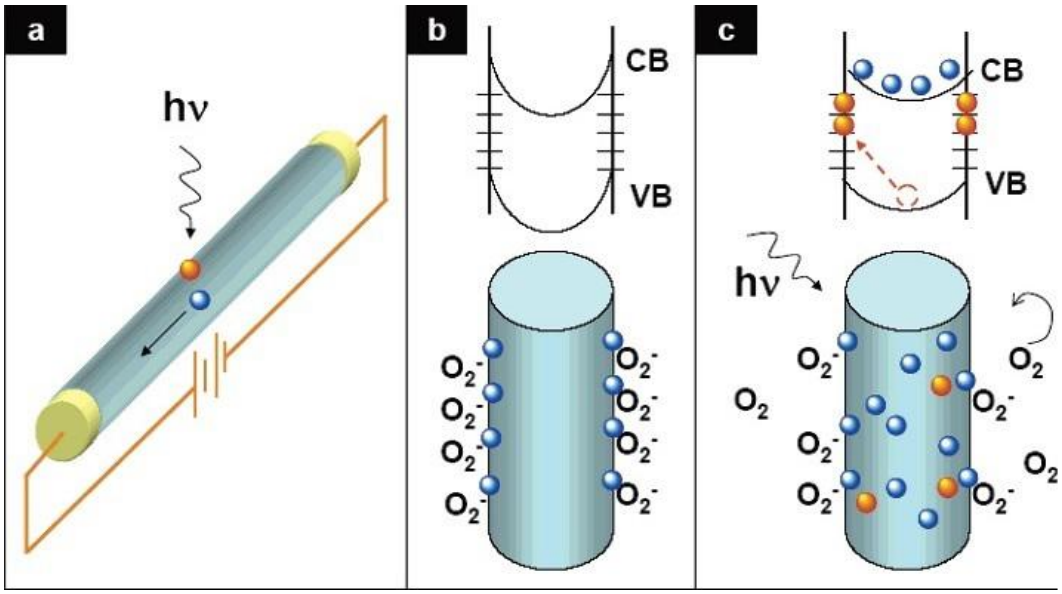


Figure 1.9 : **a**) Nanowire as Photo-detector Band structure of nanowire **b**) before & **c**) after interaction with light radiation [19]

Working principle for photo-detector is, when light with energy more than bandgap of nanowire material, fall over the detector, there is considerable change in band structure of material. This property of modulation in band structure or 'band-bending' of nanowires is used in all types of optoelectronic devices.

1.6.4 : Application in LEDs :

For desire of improved performance nanowires has found application in light emitting diode (LEDs) as well.

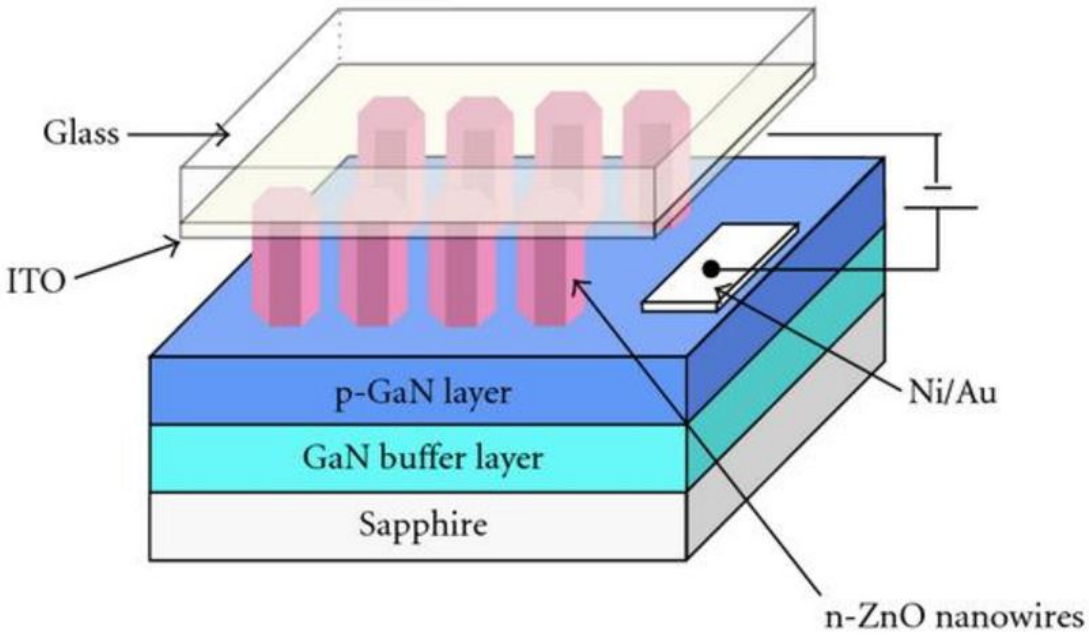


Figure 1.10 : Nanowire based light emitting diode [21]

Nanowire based light emitting diode are reported to have 50% better efficiency than ones with bulk counterpart of same material. Nanowire due to large aspect ratio not only outclass bulk materials, but also perform better than thin-films. Radiation efficiency is improved via Purcell effect in nanowire LEDs [33].

1.6.5 : <u>Application in dye-sensitized solar cell</u> : Dye-sensitized solar cells due to cost-effective manufacturing are a popular choice among solar cell category. Dye-sensitized solar cell which fall under ambit of excitonic solar cell are most efficient among other options from same category like organic, organic-inorganic hybrid solar cells. Main constituent of Dye-sensitized solar cell is a thick layer of nanoparticles over which light-harvesting species adsorb. Application of nanowires in dye-sensitized solar cell ensure direct conductive path which in turn give rise to solar generated carrier's smooth & quick collection. Thus consequently giving better efficiency.

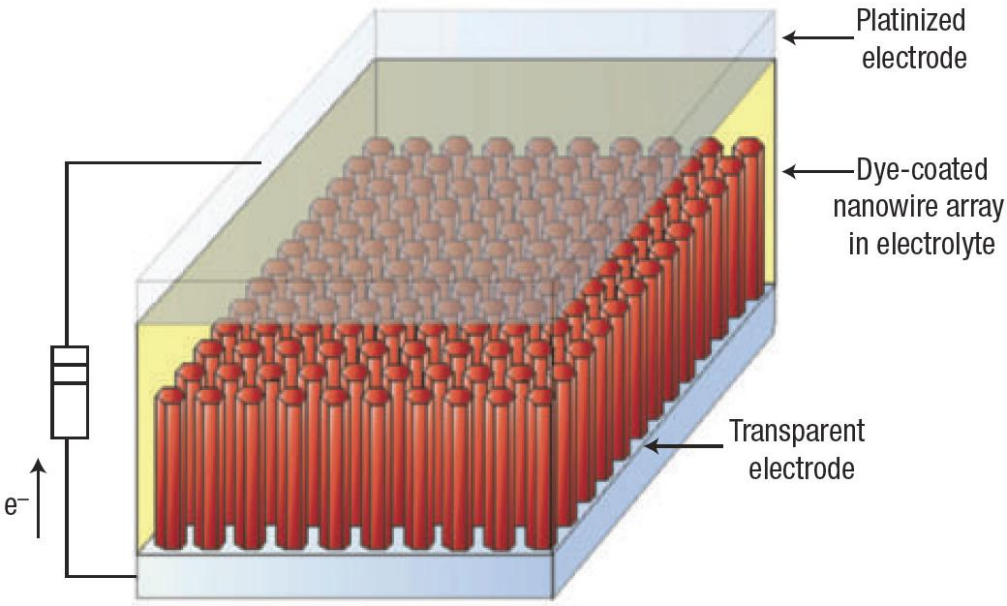


Figure 1.11 : Nanowire application in dye-sensitized solar cell [22]

1.6.6 : <u>Application in Photo-catalysis</u> : Photo-catalysis is process of speeding-up chemical reaction rate using light. Function of photocatalyst is to generate electron-hole pair after absorption of light. These electron-hole pair in turn provide their energy for expediting the chemical reaction.

Additional to speeding the reaction, photo-catalysts have environmental impact too. Effluents from various factories, are big culprit of polluting through chemical dye residue they release in environment. Using conventional method of their treatment, they got converted into another type of pollutant. Their biodegradable nature is cause for that. Semi-conducting nanowire based photo-catalyst have capability of converting these organic dyes into non-toxic product in presence of UV-vis radiation.

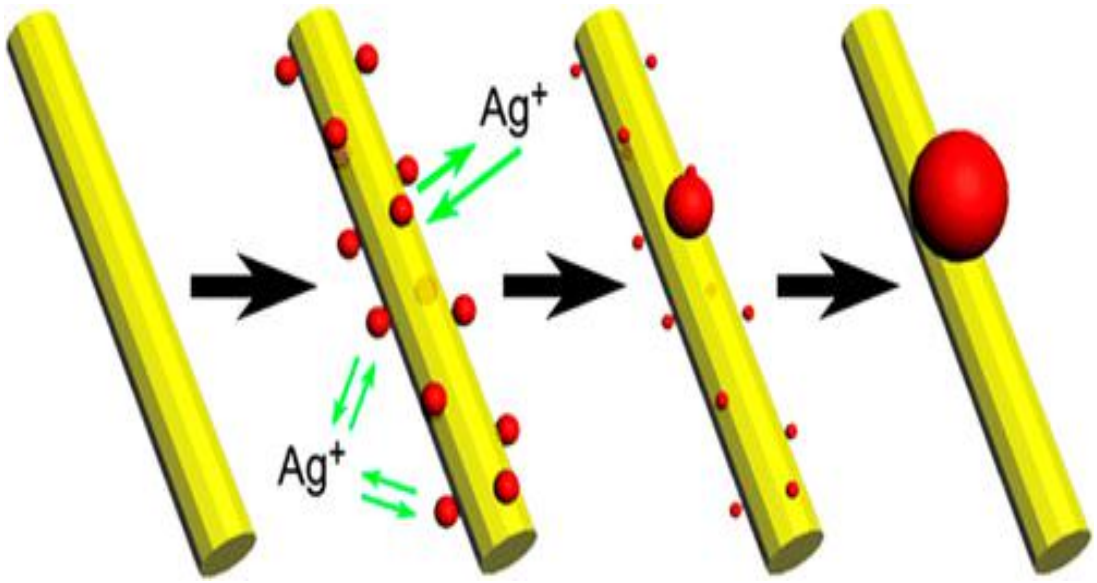


Figure 1.12 : Photo-catalysis mechanism in nanowires [23]

Fig.1.12 shows how, Ag particle present over TiO_2 nanowire surface aggregates in large when UV radiation fall over the system. Nanowire due to large surface area have better capacity of adsorption.

1.6.9 : <u>Application as sensors</u> : Wide variety of sensors using nanowires of different materials have been realized. Gas sensors, bio sensors, temperature sensors, pH sensors,etc have been realized using nanowires. ZnO is widely used oxide material in gas-based sensors.

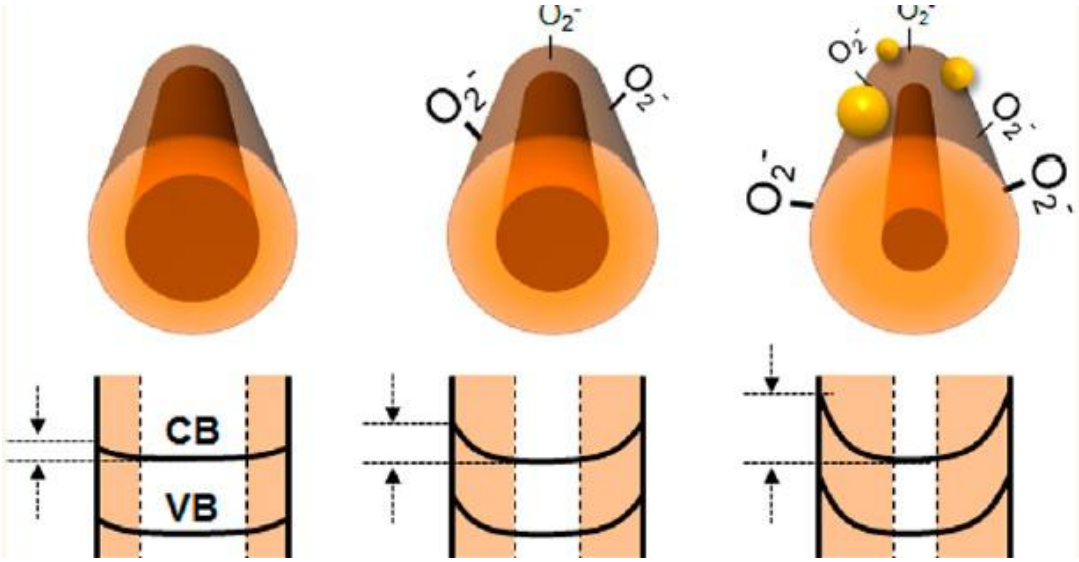


Figure 1.13 : Band diagram of ZnO wire [27]

The fundamental principle behind a gas-based sensor is that when exposed to gas their electrical conductivity is changed. This change in conductivity is measured & gives the idea about presence of certain gas in sensor's ambience.Surface band bending is the phenomena which play all important role in ZnO based gas sensor [27]. Reports of gas sensors for ethanol, CO [30]. are available.

1.7 : Field Emission :

Field emission is the phenomena of electron emission from the surface of materials when a large electric field is applied across them. Contrary to thermionic emission, field emission doesn't involve heating of the surface. Rather, the emission is caused by quantum mechanical tunneling of electrons. The applied electric field is of the order of 10^5 to 10^7 V/cm for field emission to take place. This phenomena is usually employed for luminescence in display devices.

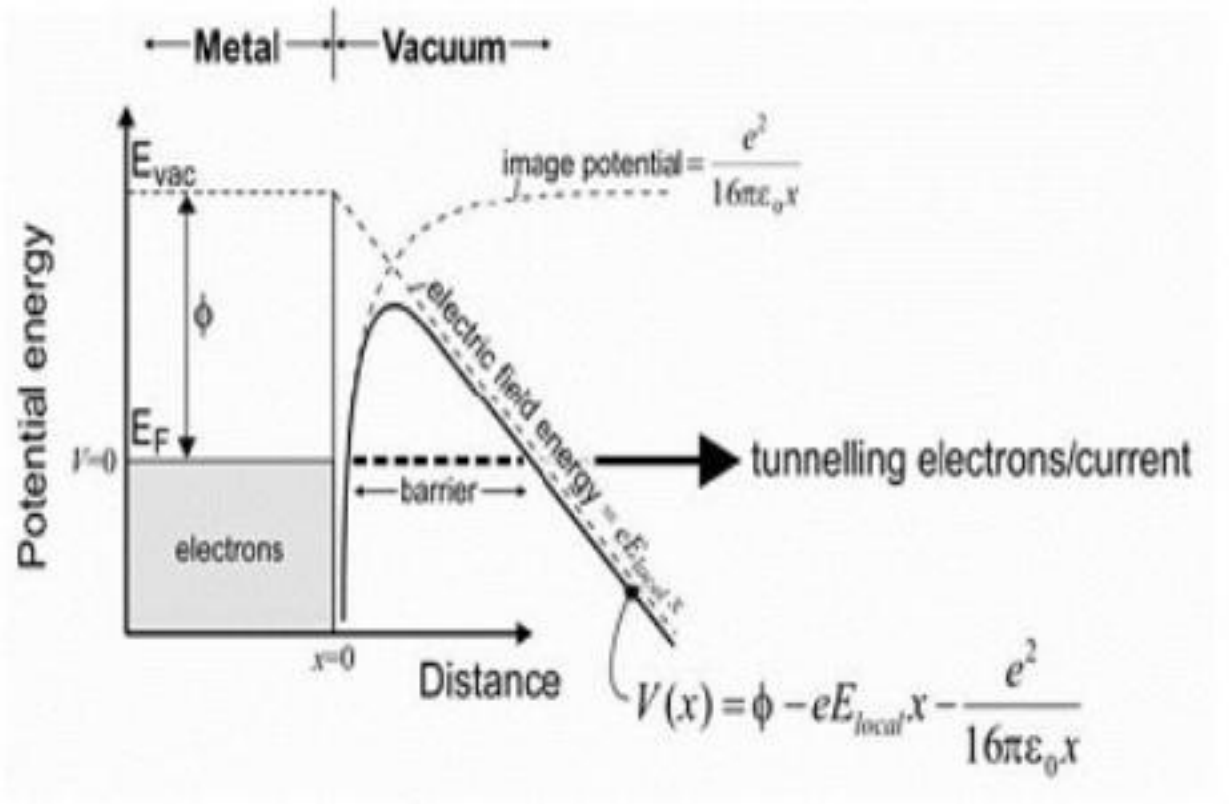


Figure 1.14 : Tunnel effect in field emission mechanism [29]

Field emission phenomena is credited to Fowler & Nordheim for their contribution to this field. As a mark of respect it is also called as Fowler-Nordheim (F-N) tunneling

Fowler-Nordheim equation provides relation between

$$J = A\phi^{-1}E^2\beta \exp\left(-B\phi^{3/2}/\beta E\right)$$

where, J = current density,

Φ = Work function,

E = Electric-field intensity,

β = Field-enhancement factor,

A =1:54 x10^{-6}AeV/V^2 &B =6.83 x 10^3 $eV^{3/2}$ Vμm^{-1} are F-N constants

Prominent parameters which define field emission are electron work function, turn-on field intensity & field-enhancement factor [28]. These factors, collectively provide statistics of all important mechanisms happening in field-emission process.

Electron work function : This is threshold energy level at which electron emission from metal conduction band to vacuum begin. Work function is denoted by ϕ.

Field-enhancement factor : Field-enhancement factor is given by β which provides enhancement in electric field . This enhancement in field is core of field emission theory. β usually has value because of high aspect-ratio & tiny tip size of emitter. This factor is calculated conveniently as slope of Fowler-Nordheim curve using following formula,

$$\beta = -B\Phi^{3/2}/slope$$

where, F-N constant B = 6.83 x 10^3 $eV^{3/2}$ Vμm^{-1}

Turn-On field intensity : Turn-on field intensity is the value of electric field at which electron emission from emitter begin in significant amount. Here in our study of ZnO nanowires, we have defined the turn-on field as 1 $\mu A/cm^2$.

CHAPTER 2 : EXPERIMENTAL

Under experimental set-up zinc foil of thickness 1.2 mm is used for growth of ZnO nanowires over it. Planar size of foil substrates were taken to be 1.3cm x1.3cm.Thermal oxidation of Zinc foil substrates was carried in Thermal CVD set up at temperature ranging from 600^{o}C to 900^{o}C for 1 hour.

2.1 : Merit of method used for synthesis : The selection criterion for used method was to have a simple method without involvement of complex reaction or hazardous reagents or gases, so that if mass production is the call, then chosen method can be employed without apprehensions.

The outcome of **First Phase** of experimental is summarized in table below:

S.No.	Temperature(^{o}C)	Time	Effect on substrate
1.	600	1 hour	No change
2.	700	1 hour	Formation of greyish-white rough patches over substrate
3.	775	1 hour	Formation of greyish-white rough patches over substrate
4.	800	1 hour	Formation of greyish-white rough patches over substrate
5.	900	1 hour	Zinc foil turns into powder

Upon observation of above outcome & their subsequent characterization, it was inferred that fine tuning of above procedure is imperative for better growth of nanowires. Scanning electron microscopy (SEM) of samples prepared at 700, 775 & 800^{o}C revealed the fair amount of growth at 700^{o}C sample. As the temperature went higher the growth receded to large extent. So, in order to fine tune in second phase, substrates were subjected to thermal oxidation at 600 to 675^{o}C for 1 hour duration. In addition to that, thermal oxidation at 500^{o}C for 3 hours was also performed.

The summary for **second phase** is given in table below:

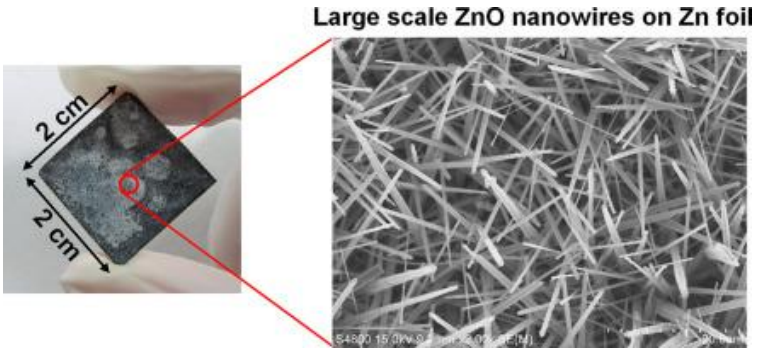
S.No.	Temperature(°C)	Time	Effect on substrate
1.	675	1 hour	Formation of greyish-white rough patches over substrate
2.	500	3 hour	Formation of greyish-white rough patches over substrate
3.	650	1 hour	Formation of greyish-white rough patches over substrate

Substrates of zinc foil were thoroughly cleaned with acetone to remove contaminant from the surface. Substrates were also Ultra-sonicated for 15 minutes to degas any foreign entity from surface.

Figure 2.1 : Thermal CVD at Nano Fabrication lab, DTU

CHAPTER 3 : RESULT

As-obtained nanowires are characterized for surface morphology using Scanning electron microscopy (SEM). Chemical composition/stoichiometric analysis is done using Energy-dispersive X-ray spectroscopy (EDX). X-ray Diffraction (XRD) is used for phase detection & particle size determination. UV-vis absorption spectroscopy is used for band gap calculation with aid of Tauc plot. Photoluminescence (PL) spectroscopy is used for Field emission study of nanowires is done using Current density-electric Field (J-E) plot & work function (Φ) is calculated using Fowler-Nordheim plot.



a) b)

Figure 3.1 : a) Bare Zinc Foil, b) after nanowire growth

3.1 : Scanning Electron Microscopy :

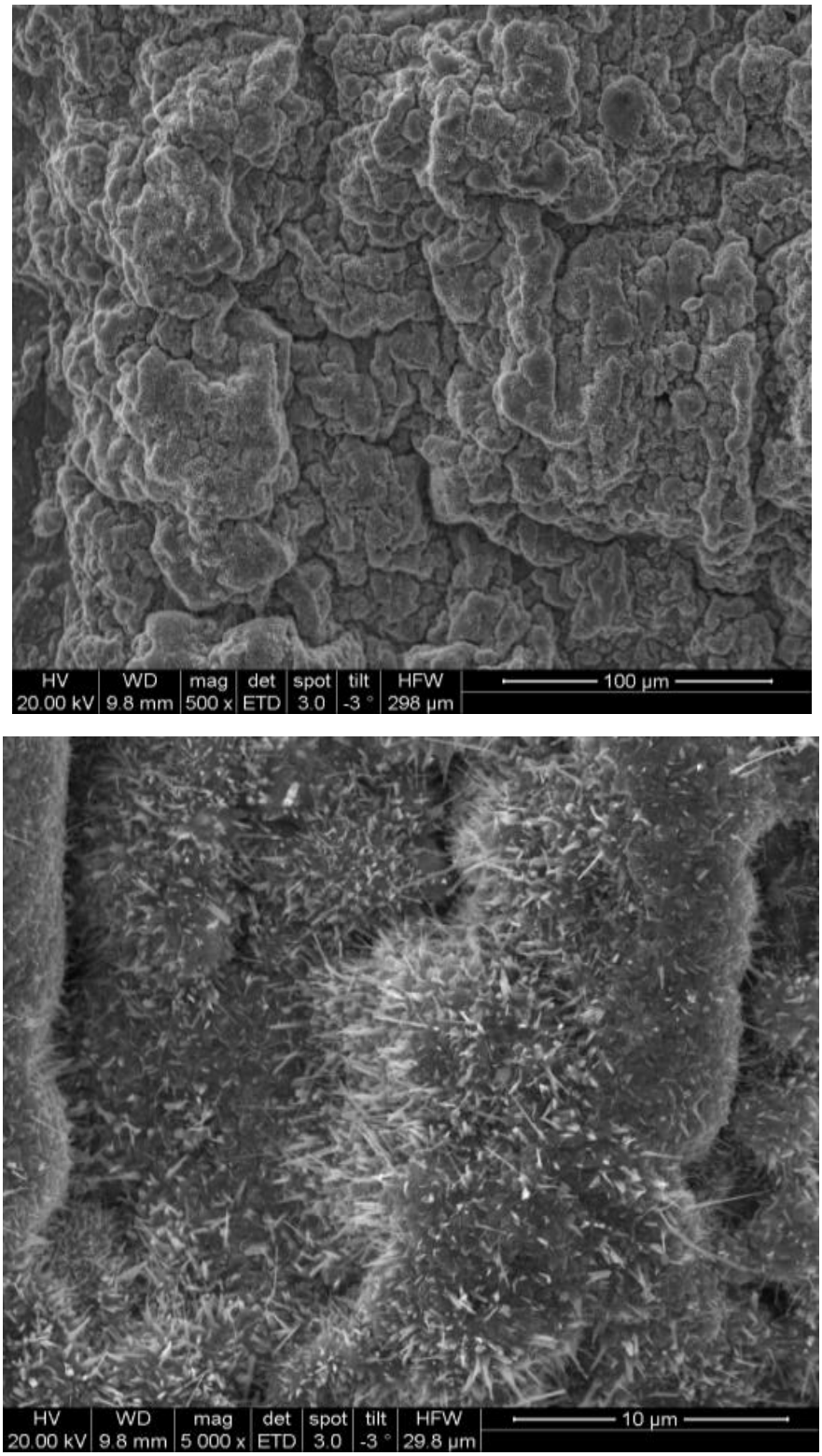
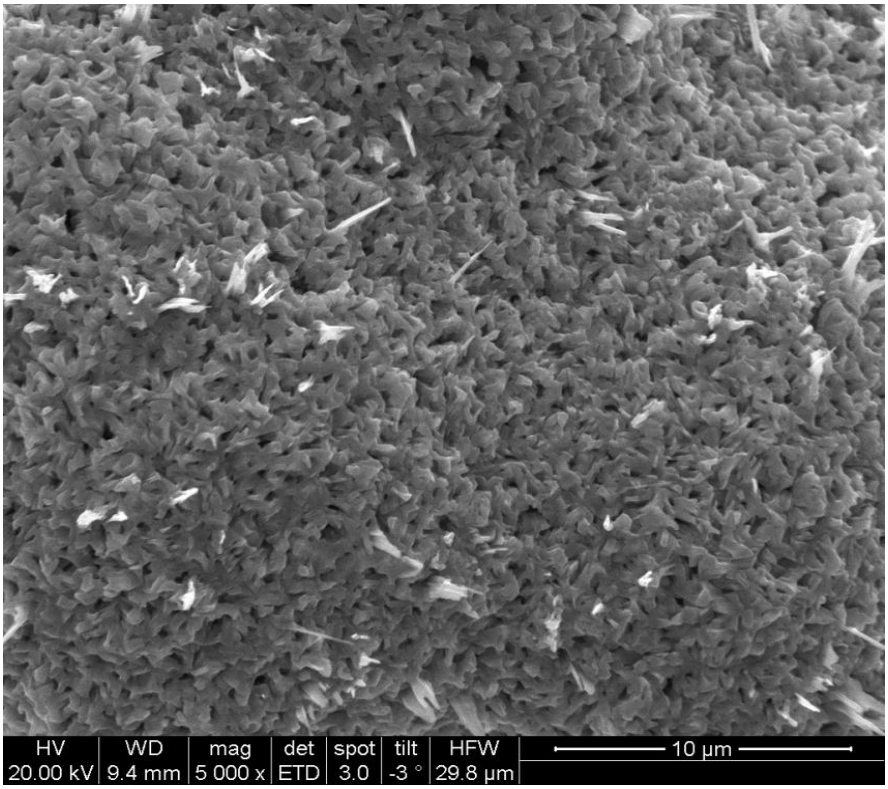


Figure 3.2 : SEM of ZnO nanowire grown at 700°C for 1 hour



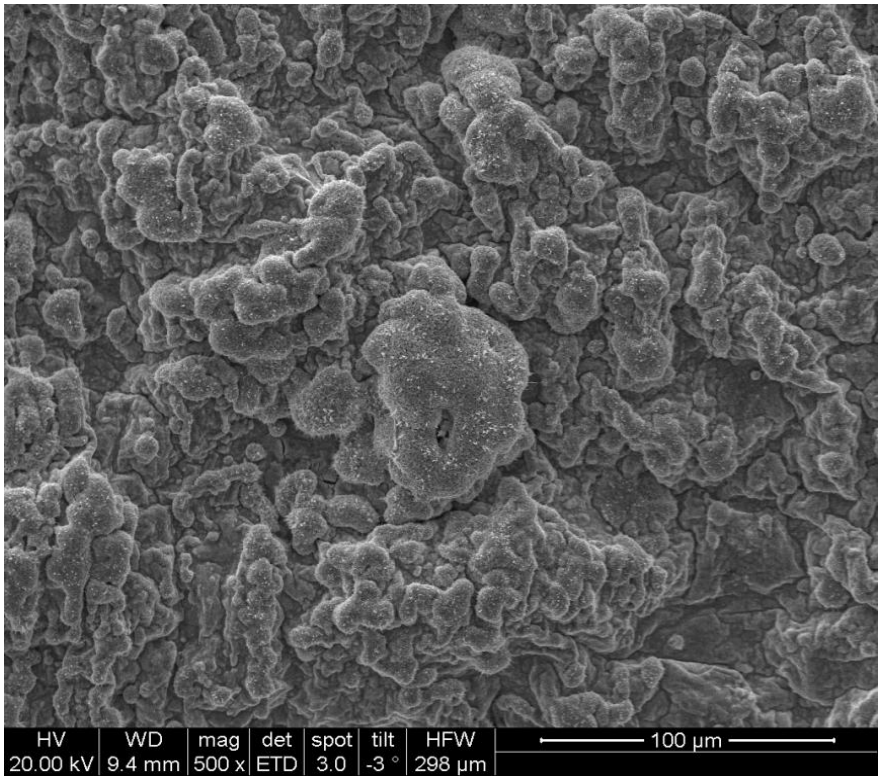
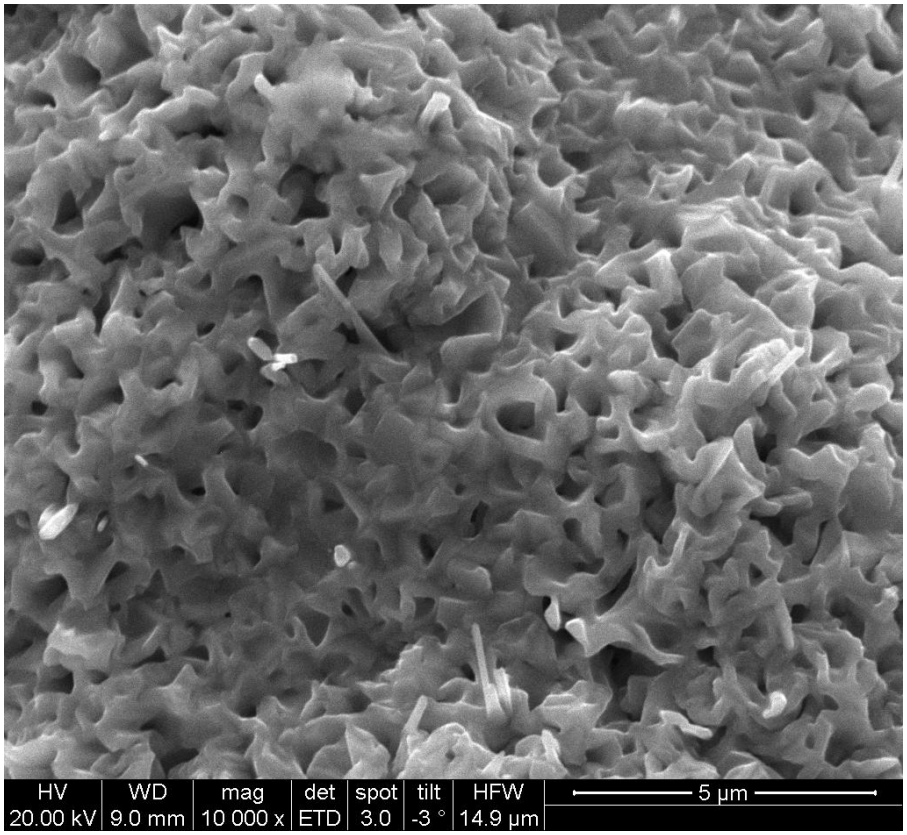


Figure 3.3 : SEM of ZnO nanowire grown at 775^{o}C for 1 hour



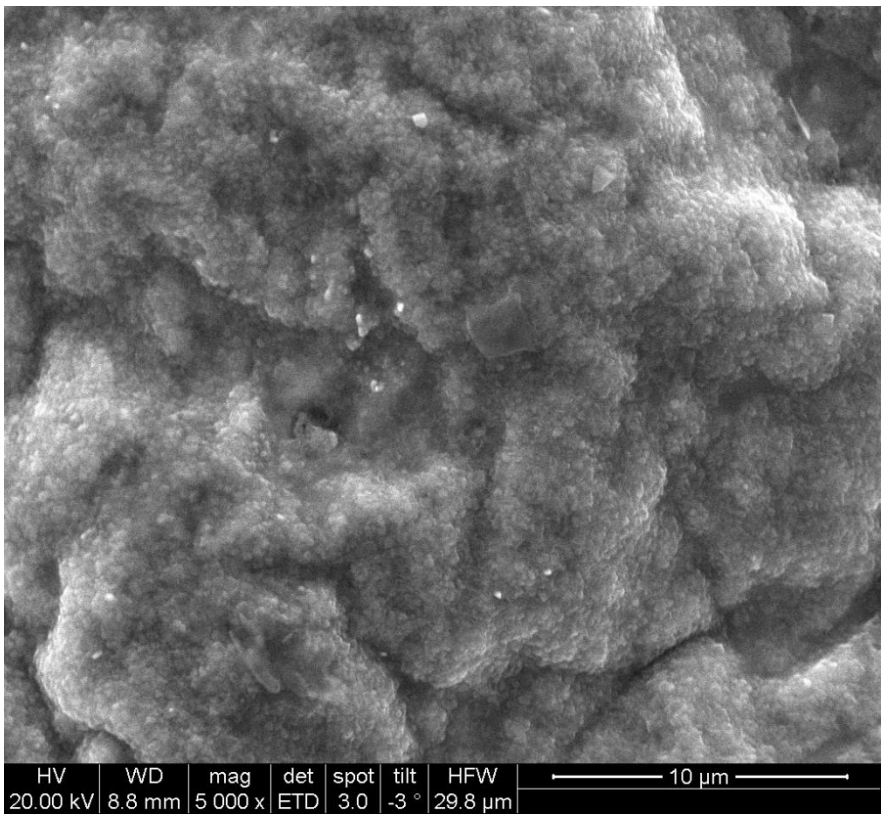


Figure 3.4 : SEM of ZnO nanowire grown at 800^{o}C for 1 hour

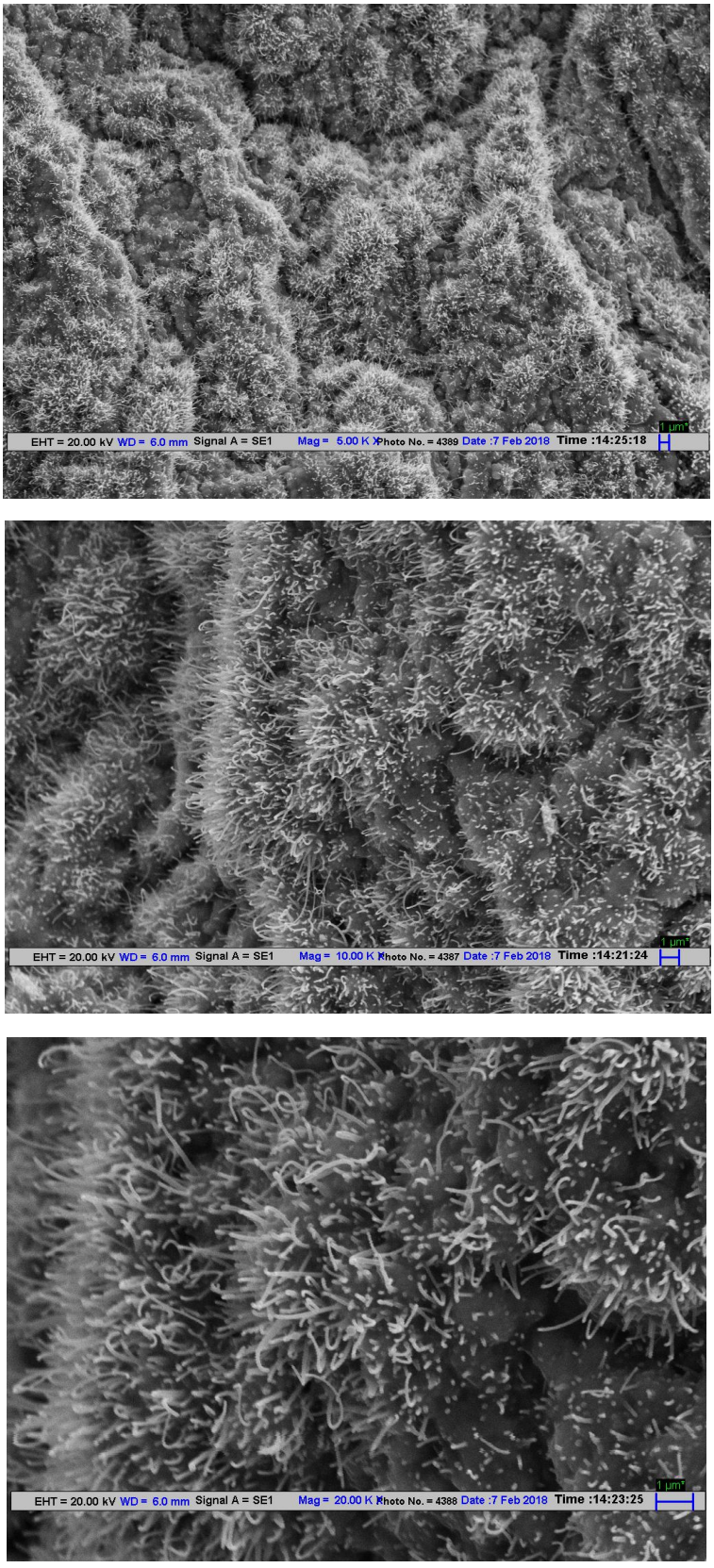


Figure 3.5 : SEM of ZnO nanowire grown at 675^{o}C for 1 hour

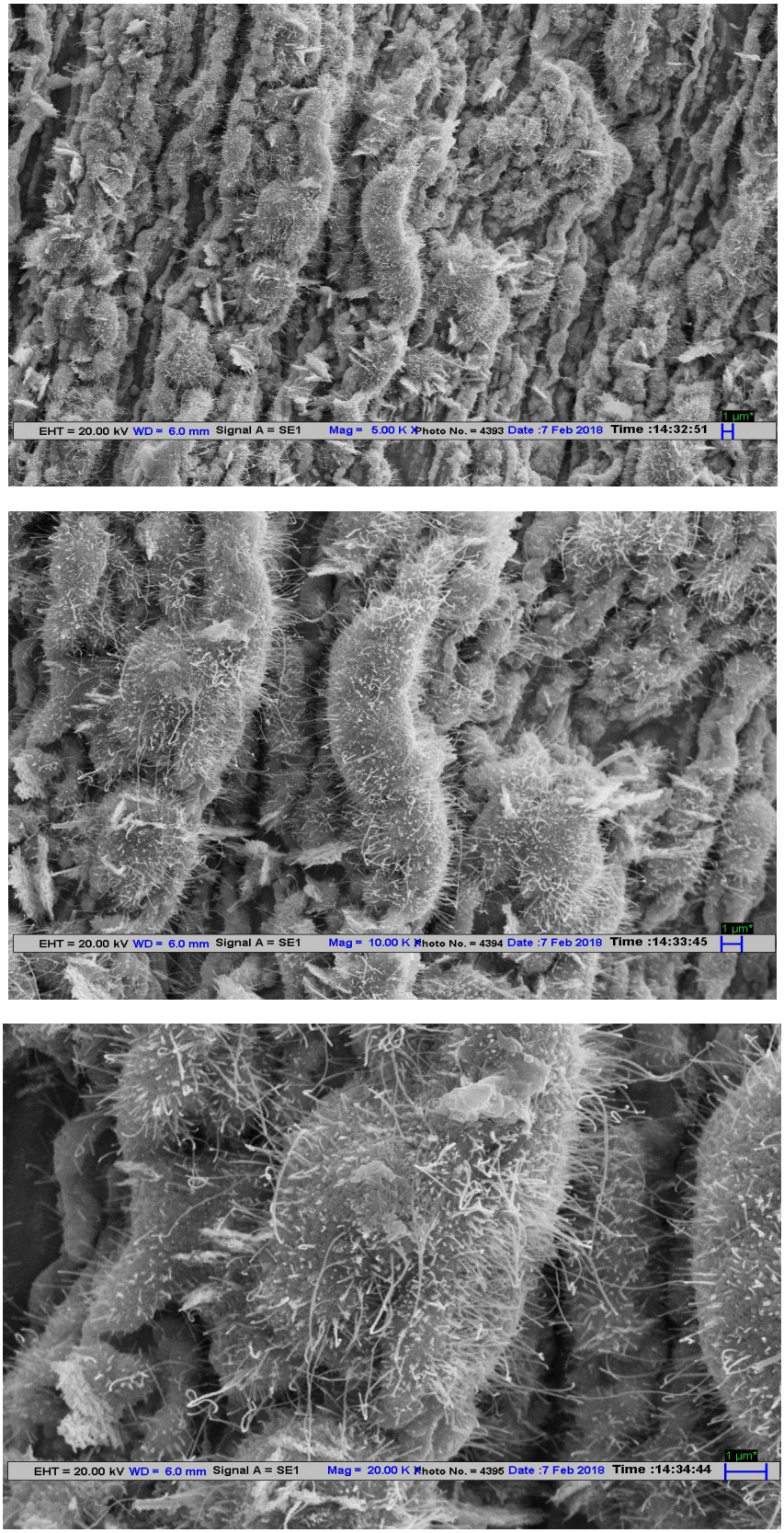
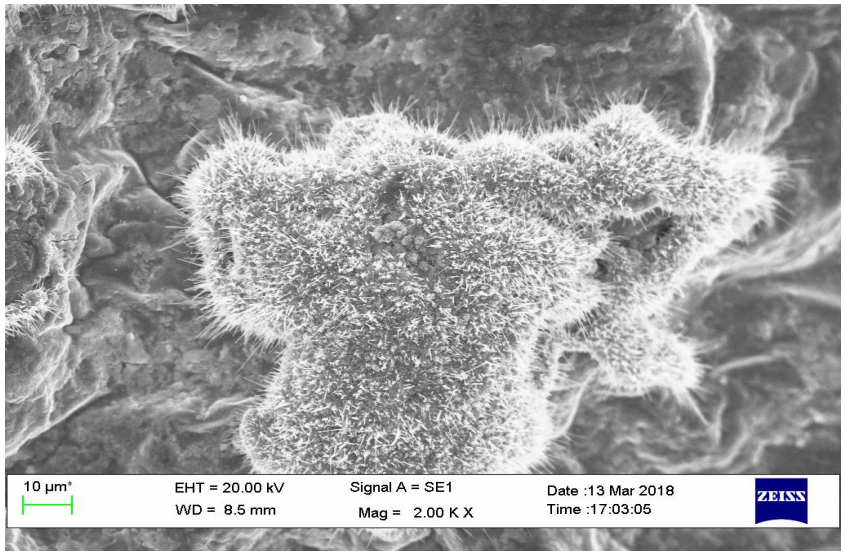


Figure 3.6 : SEM of ZnO nanowire grown at 500°C for 3 hours



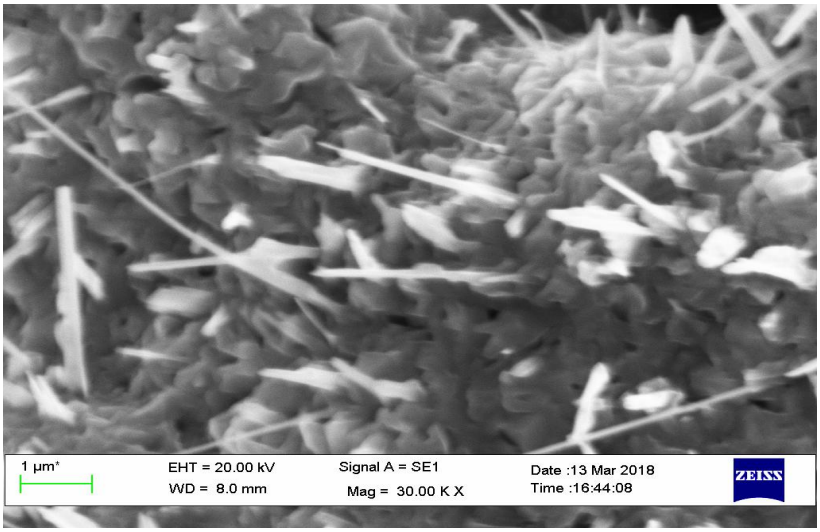


Figure 3.7 : SEM of ZnO nanowire grown at 650 ^{o}C for 1 hour

On the basis of above SEM analysis, it it found that out of all temperatures in first phase, best growth is observed at 700^{o}C for 1 hour. There is considerable density of nanowires. As the temperature increased, the density took a plunge at 775^{o}C with almost barren substrate. At 800^{o}C the damage due to heating effect can be observed.Second phase shown some outstanding growth for nanowires. At 675^{o}C for 1 hour nanowires of very high density & considerable length were observed. At 500^{o}C for 3 hours density was little lesser than that at 675^{o}C but length is longer. Growth at 650^{o}C for 1 hour again shown thick density & significant length. Thus SEM analysis of ZnO nanowire suggest that, the best temperature range for growth lie in 500^{o}C to 675^{o}C. With variation of temperature & time duration, variation in size is noticed.

3.2 : X-ray diffraction analysis :

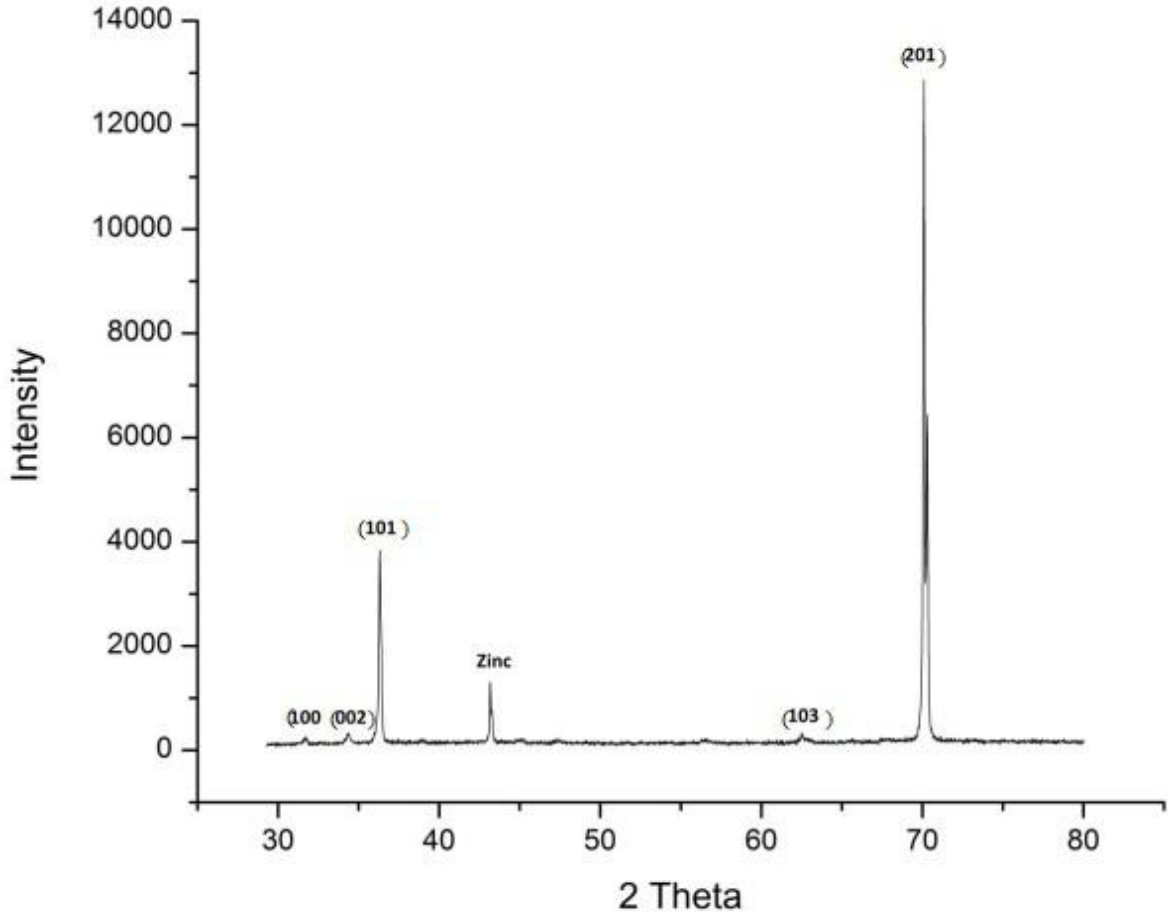


Figure 3.8 : XRD pattern of ZnO nanowire grown at 675^{o}C for 1 hour

Above XRD analysis of as-grown ZnO nanowires at 675^{o}C for 1 hour reveal presence of peaks corresponding to (100), (002), (101), (103) & (201) phases. These phases are matched to JCPDS data sheet numbered 36-1451 for Zinc Oxide. One peak corresponding to pure zinc is also part of XRD signifying presence of unconverted raw zinc in sample.

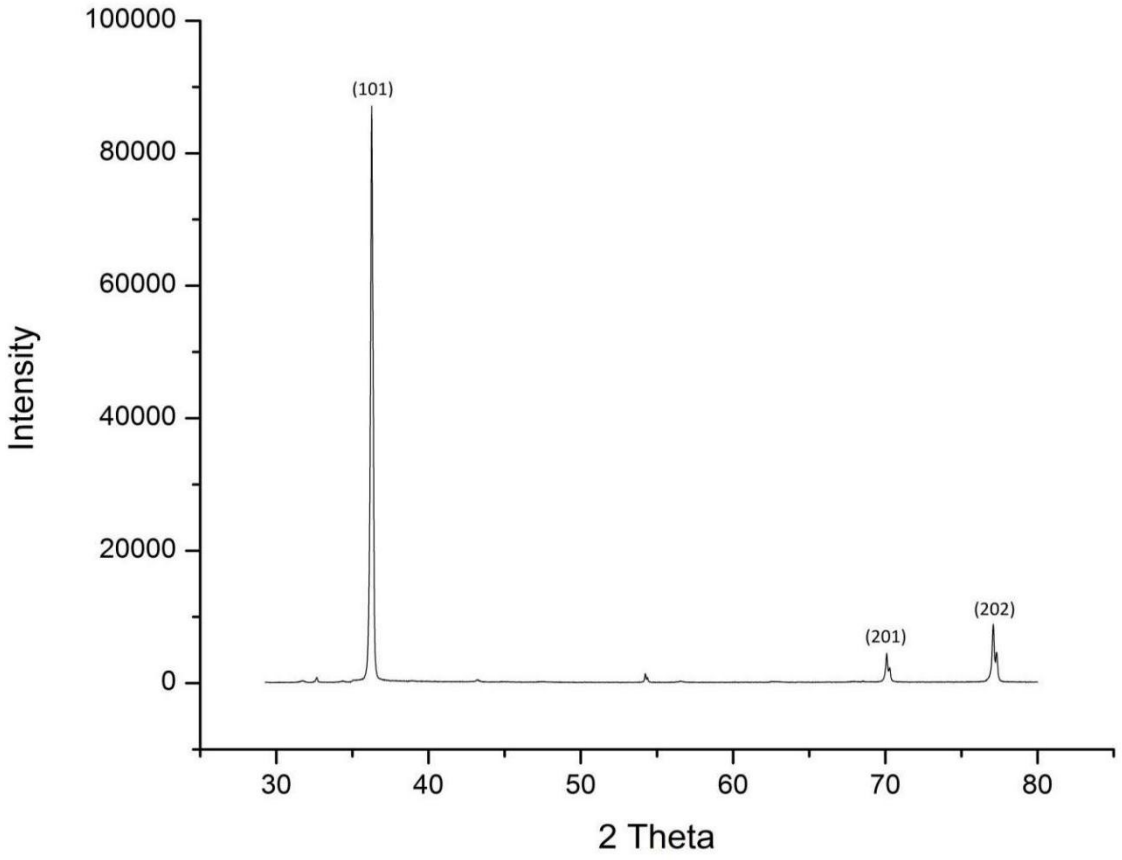


Figure 3.9 : XRD pattern of ZnO nanowire grown at 500^{o}C for 1 hour

Particle size determination using Scherrer's formula:

$$L = k\lambda/B\cos\theta$$

where, L= mean size of ordered crystalline domains,

λ= X-ray wavelength (for Cu 0.15406 nm),

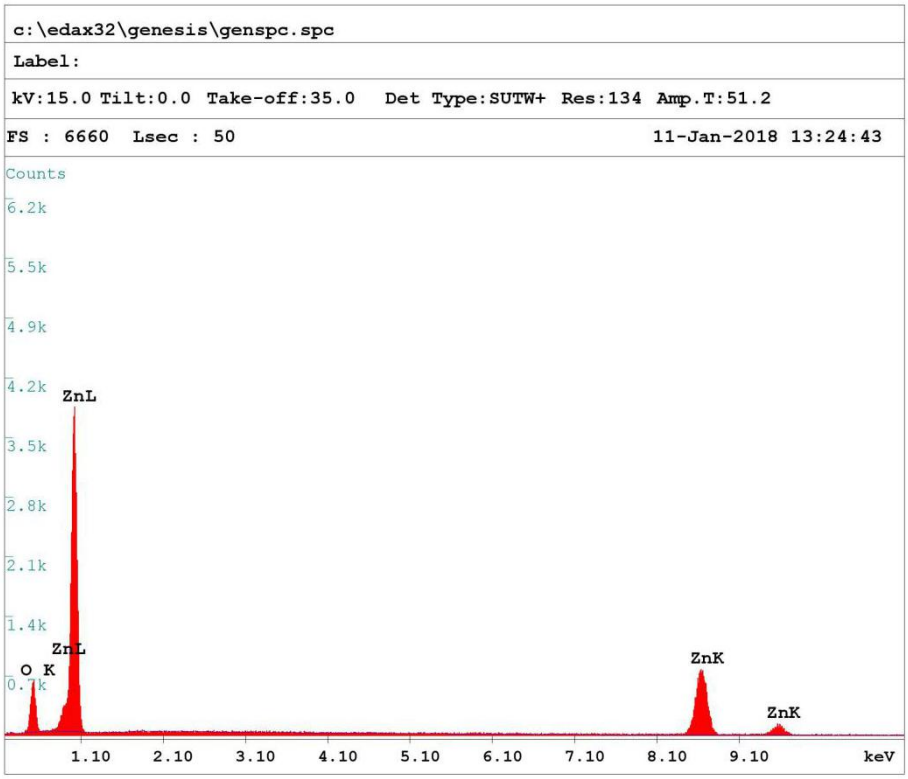
B= peak broadening at half of maximum intensity(FWHM), in radian,

θ= Bragg's angle,

k= dimensionless shape factor, has usually value of 0.9

From above formula & calculation of FWHM from Origin software, approximate average sizes of nanowires at 500^{o}C & 675^{o}C are found to be 25.0 nm & 40.5 nm respectively.

3.3 : Energy dispersive X-Ray spectroscopy (EDX)



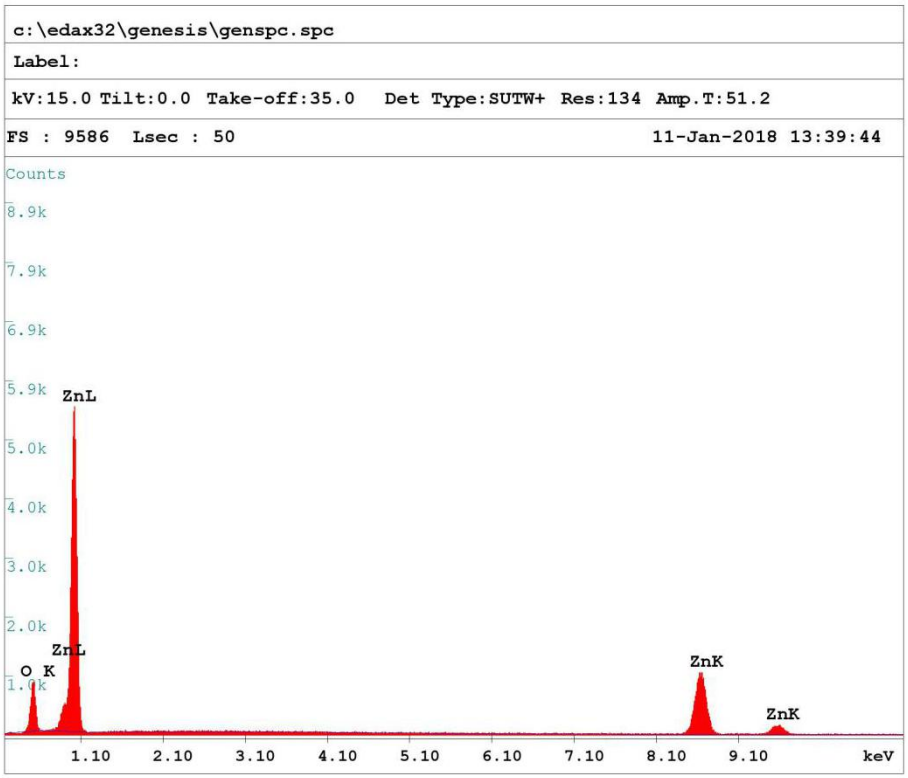
EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : User c:\edax32\eds\genuser.sec

Element	Wt %	At %	K-Ratio	Z	A	F
O K	5.40	18.92	0.0233	1.1993	0.3591	1.0023
ZnK	94.60	81.08	0.9316	0.9843	1.0004	1.0000
Total	100.00	100.00				

Element	Net Inte.	Bkgd Inte.	Inte. Error	P/B
O K	72.14	6.34	1.81	11.38
ZnK	195.40	2.88	1.03	67.85

Figure 3.10 : EDX data for ZnO nanowire grown at 700^{o}Cfor 1 hour

Above data shows presence of only Zn & O in sample signifying impurity free growth of nanowires via opted method & at given temperature condition, time duration.Even at 775^{o}C pure growth was observed, comprising only Zn & O which signify presence of ZnO or unreacted zinc.



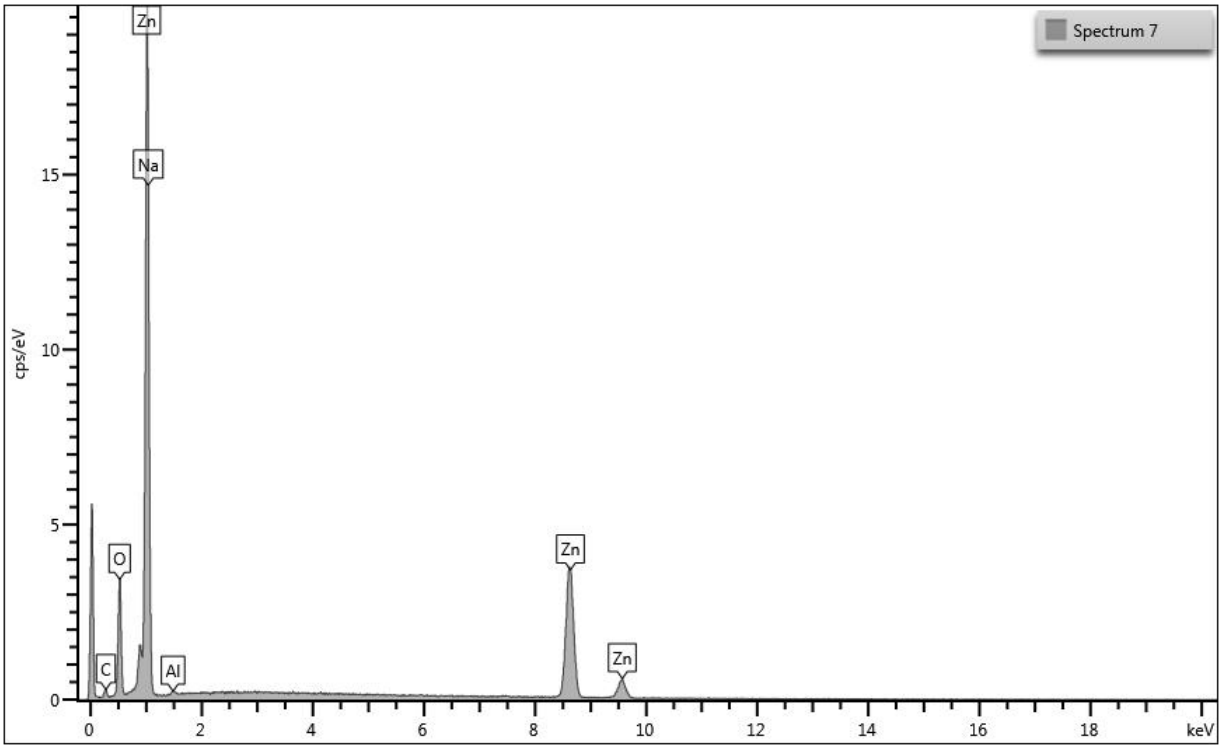
EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : User c:\edax32\eds\genuser.sec

Element	Wt %	At %	K-Ratio	Z	A	F
O K	5.64	19.64	0.0244	1.1986	0.3598	1.0022
ZnK	94.36	80.36	0.9285	0.9836	1.0005	1.0000
Total	100.00	100.00				

Element	Net Inte.	Bkgd Inte.	Inte. Error	P/B
O K	102.96	10.72	1.53	9.60
ZnK	265.72	4.48	0.88	59.31

Figure 3.11 : EDX data for ZnO nanowire grown at 775^{o}C for 1 hour

Even at 775^{o}C, nanowires grown have contaminant free synthesis comprising only Zn & O.



Result Type	Weight %
Spectrum Label	Spectrum 7
C	5.14
O	15.00
Na	5.05
Al	0.38
Zn	74.42
Total	100.00

Figure 3.12 : EDX data for ZnO nanowire grown at 650^{o}C for 1 hour

EDX at 650^{o}C shows presence of foreign elements like C, Na & Al which might be due to contamination added during either handling for SEM-EDX imaging or synthesis procedure itself. Since the synthesis took place in environmental conditions, possibility of added contaminants can't be ruled out during growth phase.

3.4 : Field Emission :

Field emission study of ZnO nanowire was the principle aim of this project. Under this scheme, Current density-Electric field (J-E) characteristics are obtained from Voltage-Current data procured from Field emission study. These characteristics further provided turn-on voltage & maximum current density values for as-grown ZnO nanowires.

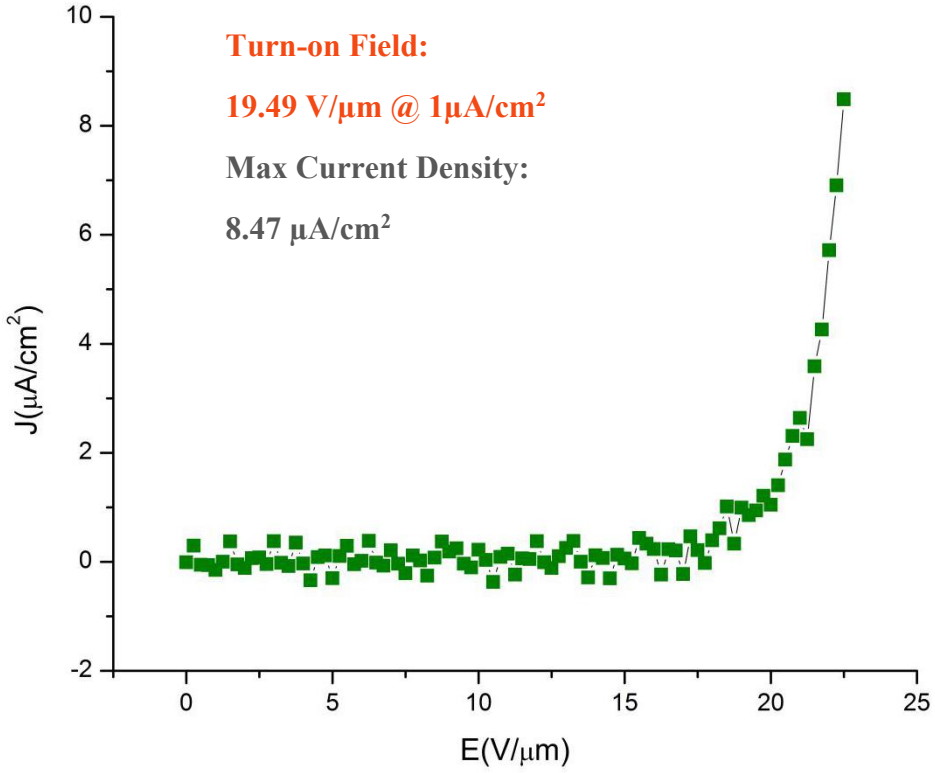


Figure 3.13 : J-E characteristics ZnO nanowire grown at 675°C for 1 hour

From above J vs E plot we obtain the value of current density as 1 µA/cm^2 at Electric field 19.49 V/µm, which is defined as turn-on field value. Maximum current density obtained was 8.47 µA/cm^2. After turn-on field the increase in current density is exponential.

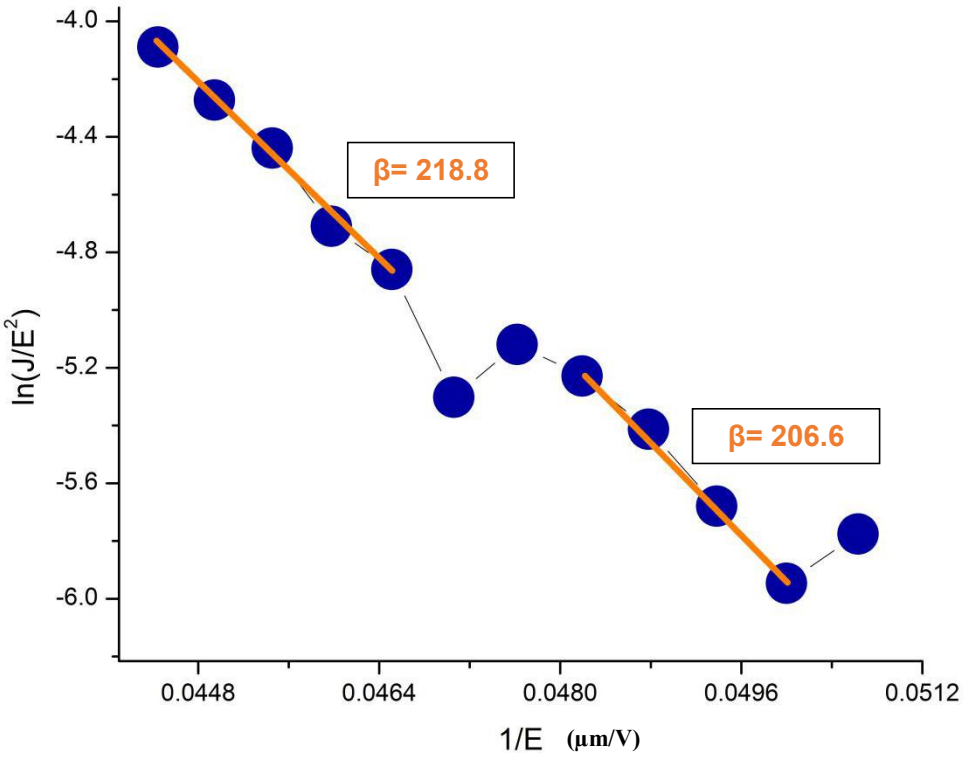


Figure 3.14 : Fowler-Nordheim plot for ZnO nanowire grown at 675°C for 1 hour

Above Fowler-Nordheim plot provides two slopes, hence two values of -378.6 & -401.05 at 675°C. Also, the work function of ZnO nanowires is determine to be ϕ = 5.28eV [35].

Further using the Fowler-Nordheim equation which relate β to ϕ by relation,

$$\beta = -B\Phi^{3/2}/slope$$

where, F-N constant B = 6.83 x 10^3 $eV^{3/2}$ $V\mu m^{-1}$

Using above relation we obtain two values of Field enhancement factor, β = 218.8 & 206.6

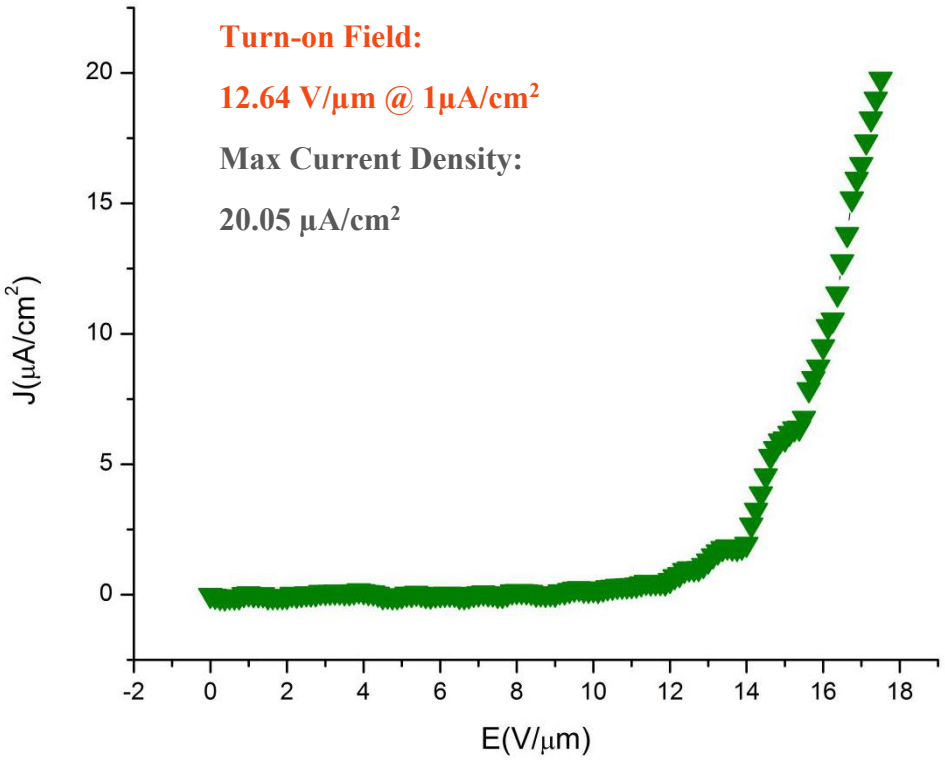


Figure 3.15 : J-E curve for ZnO nanowire grown at 500°C for 3 hours

J-E plot at 500°C for 3 hours, provide turn-on field value of . Maximum current density is obtained as 20.05 µA/cm^2. So, this is 2.5 fold growth as compared to 675°C sample. The reason may due to thinner profile of nanowires produced at 500°C. Length too might be playing role, since length & thickness of nanowires together are giving rise to better aspect ratio at this temperature & condition. The exponential growth in current density is witnessed after turn-on field point. The turn-on voltage is 12.64 V/µm which is way lower than 19.49 at 675°C.

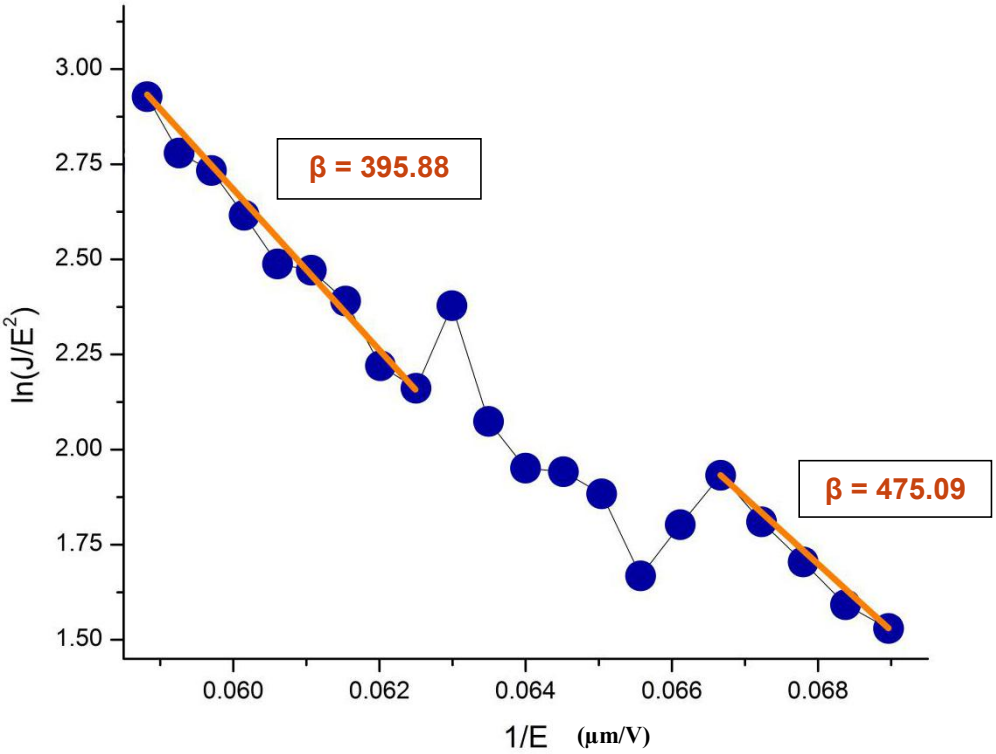


Figure 3.16 : F-N plot of ZnO nanowire grown at 500°C for 3 hours

Above Fowler-Nordheim plot provides two slopes, hence two values of -209.32 & -174.42 at 500°C.

Further using the Fowler-Nordheim equation which relate β to ϕ by relation,

$$\beta = -B\Phi^{3/2}/slope$$

where, F-N constant B = 6.83 x 10^3 $eV^{3/2}$ $V\mu m^{-1}$

Using above relation we obtain two values of Field enhancement factor, β = 395.88 & 475.09 which are considerably larger than ones at 675°C.

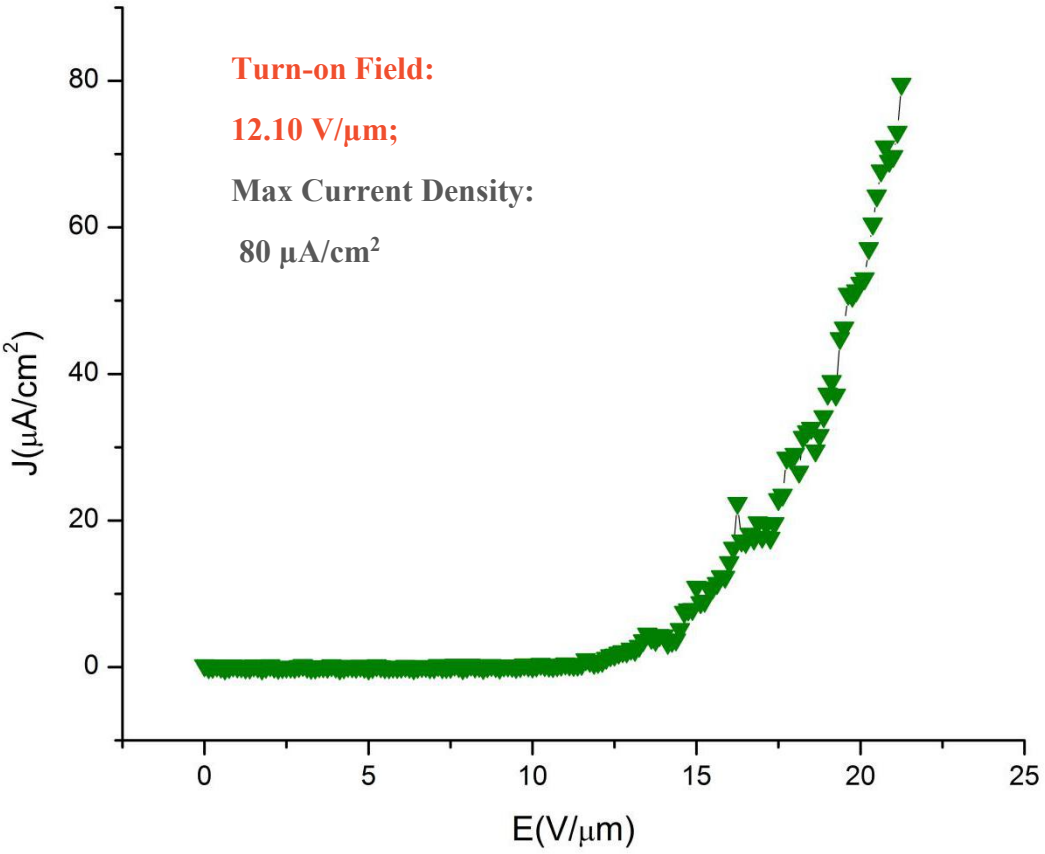


Figure 3.17 : J-E plot for ZnO nanowire grown at 650°C for 1 hour

Field emission characteristics, J vs E, of ZnO at 650°C gave significant improvement in both key parameters, turn-on field as well as maximum current density compared to ones at 675°C & 500°C. At this temperature we obtained maximum J= 80 µA/cm^2 which is almost 10 fold to one at 675°C. Similarly the tun-on field too has recorded improvement at 12.10 V/µm compared to 19.49 at 675°C. The reason for stellar performance of this sample could be due to sharp tip of nanowires in sample.

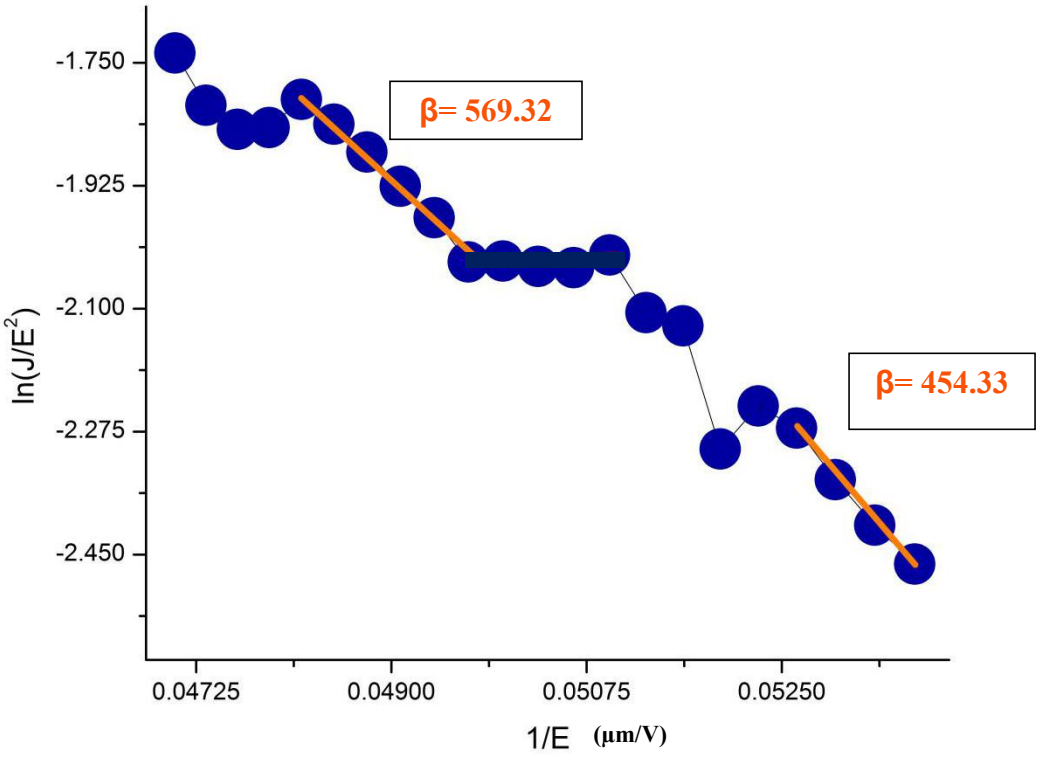


Figure 3.18 : F-N curve of ZnO nanowire grown at 650°C for 1 hour

Above Fowler-Nordheim plot again provides two slopes, hence two values of -145.55, -182.39 at 650°C.

Further using the Fowler-Nordheim equation which relate β to ϕ by relation,

$$\beta = -B\Phi^{3/2}/slope$$

where, F-N constant B = 6.83 x 10^3 $eV^{3/2}$ $V\mu m^{-1}$

Using above relation, we obtain two values of Field enhancement factor β = 569.32 & 454.33.

Thus from Field-emission plots & F-N curves of ZnO at 675°C (1 hour), 500°C (3 hours) & 650°C (1 hour), sample at 650°C has best performance in all aspects, viz, Turn-on Field, Maximum current density & Field enhancement factor.

3.5 : UV-vis absorption analysis :

Analysis of UV-vis absorption spectrum and drawing tauc plot with corresponding data leads to calculation of optical bandgap E_g

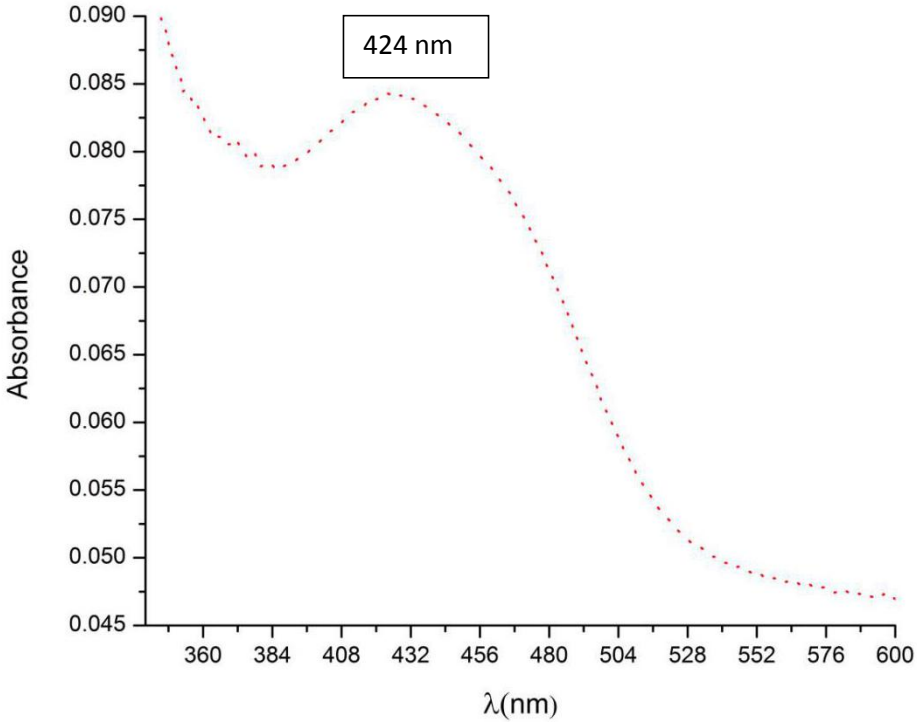


Figure 3.19 : UV-vis absorption spectra of as-grown ZnO nanowire

From the given data of absorption we obtain the Tauc plot using the relation

$$(\alpha h\nu)^n = h\nu$$

where h= Planck's constant,

ν= Frequency,

α= absorbance,

n= 2 for direct bandgap materials like ZnO

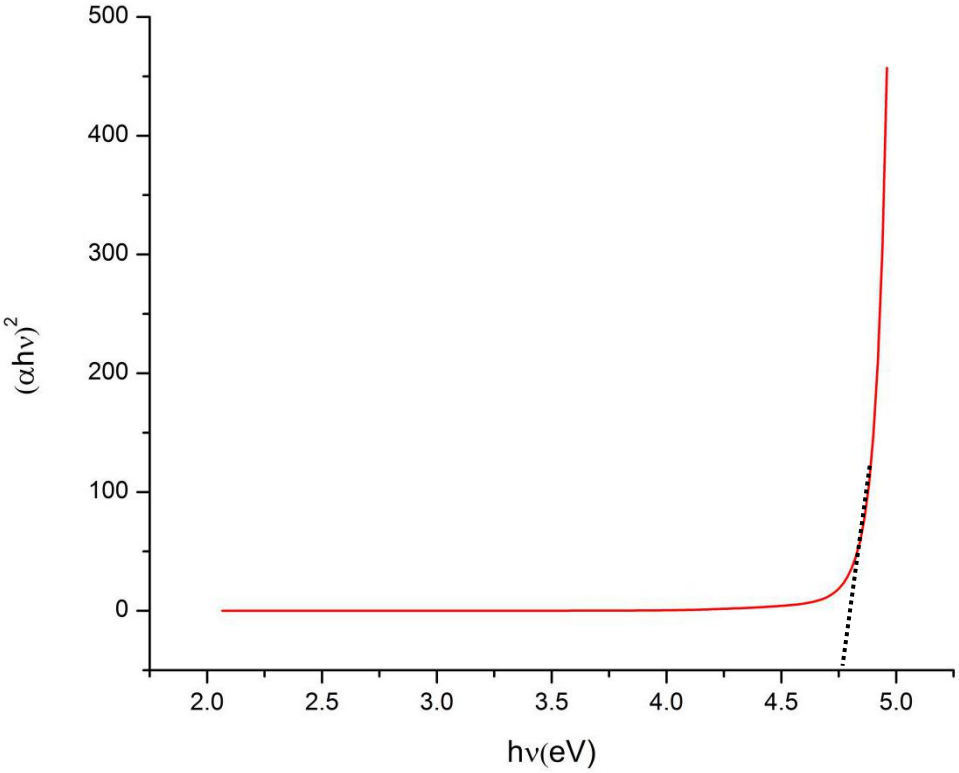


Figure 3.20 : Tauc Plot for as-grown ZnO nanowire

Optical Energy bandgap E_g is obtained from Tauc plot by extrapolating on horizontal axis. The intercept of extrapolation provided optical band gap using the UV-vis spectroscopy as 4.75 eV. This shows with decrease in particle size, the bandgap increases, For bulk ZnO bandgap is 3.37 eV & what we obtained for nanowires is significantly higher.

3.6 : Photoluminescence analysis:

Photoluminescence spectroscopy of the as-grown ZnO nanowires were done on a in dry state

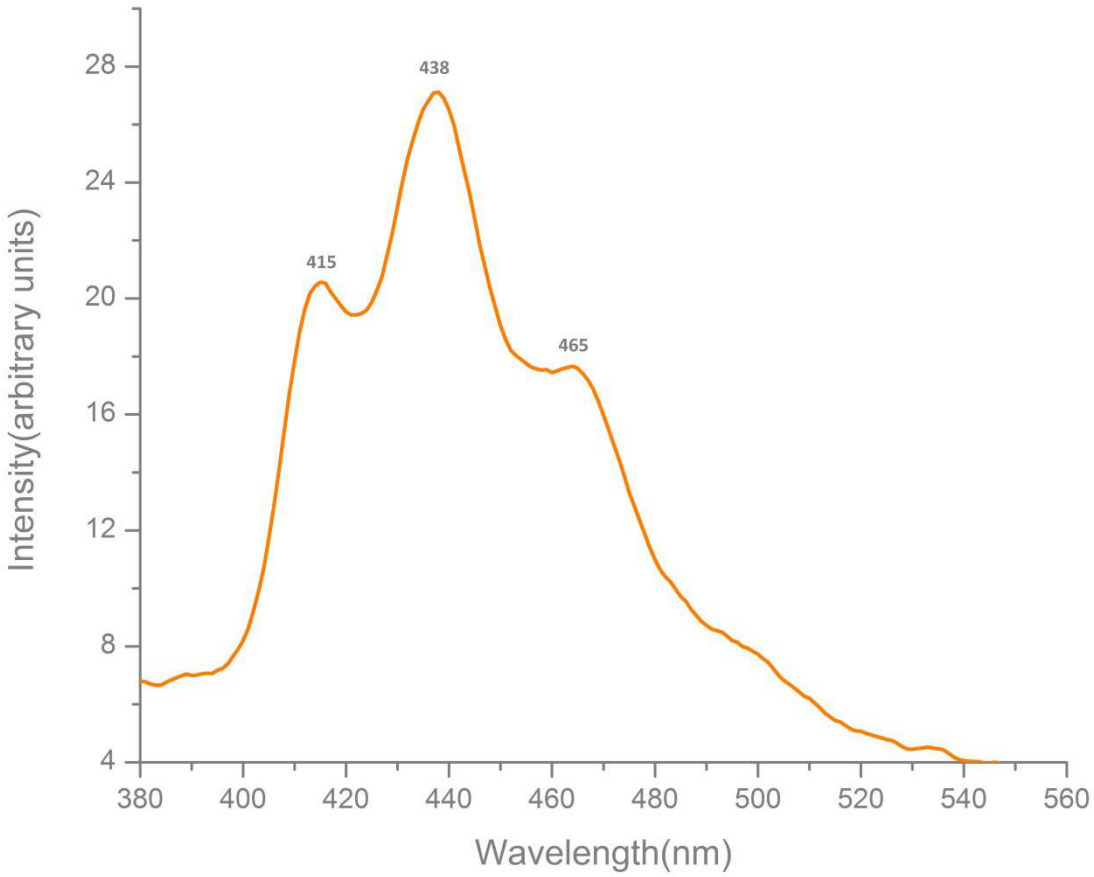


Figure 3.21 : PL Spectra of as-grown ZnO nanowire

The observed PL spectra of as-grown ZnO shows strong emission in visible range with peaks at 438, 415 & a small emission peak at 465 nm wavelength associated with violet & blue part. Usually these peaks from ZnO nanowires are attributed to deep-level defects present in nanowires. Near band edge (NBE) emission which usually has peaks near to UV range 360-370 nm [34, 36] is absent from PL of as-grown ZnO nanowires.

CHAPTER 4 : CONCLUSIONS

The objective of growth of ZnO nanowires over the surface of a zinc foil via thermal oxidation in atmospheric conditions is satisfactorily achieved. Different time duration & temperature conditions resulted into different morphology & different performance characteristics seen via variety of tools like SEM-EDX, XRD, PL & field-emission. From SEM analysis we witnessed best growth of nanowire at three temperatures 675^{o}C, 650^{o}C& 500^{o}C with time duration of synthesis from 1 hour to 3 hours. Additionally, the longer duration & lesser temperature resulted in to higher aspect ratio of nanowires. From XRD, the size of nanowires are found to be between 25nm to 50nm. EDX analysis suggested contaminant free formation of ZnO oxide, although one or two peaks of pure Zinc in XRD signal presence of unoxidized Zinc at surface. UV-vis spectra & tauc plot gave optical band gap of as-grown nanowires in access of 4.5eV which is unconventionally very higher than the electronic band gap. Photoluminescence spectra show emission peaks corresponding to violet & blue parts of visible spectrum. These peaks usually are caused by presence of deep defects present in crystal structure.

Field emission study provided some good results with as-grown nanowires. Out of three different substrates synthesized at 500^{o}C, 650^{0}C & 675^{o}C field emission was observed at all three of them. The result of 650^{o}C was found to be par excellence compared to the others. Max current density was found to be around 80 $\mu A/cm^2$ compared to 8.47 $\mu A/cm^2$ & 20 $\mu A/cm^2$ for 675^{o}C & 500^{o} C samples. Turn-on field value too was recorded best for 650^{o}C temperature as 12.10 V/μm. Field-enhancement factor too recorded maximum value for 650^{o}C temperature in range of 450 to 569.5. Thus we can conclude that as-grown ZnO nanowires can be employed for field-emission applications.

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