DEVELOPMENT OF HIGH GAIN ULTRAVIOLET PHOTO DETECTORS

BASED ON ZINC OXIDE NANOWIRES

Bhargav Mallampati

Thesis Prepared for the Degree of

MASTER OF SCIENCE

UNIVERSITY OF NORTH TEXAS

May 2014

APPROVED:

Usha Philipose, Major Professor
Kamesh Namuduri, Committee Member
Arup Neogi, Committee Member
Shengli Fu, Chair of the Department of Electrical Engineering
Costas Tsatsoulis, Dean of the College of Engineering
Mark Wardell, Dean of the Toulouse Graduate School
Mallampati, Bhargav. Development of High Gain Ultraviolet Photo Detectors Based on Zinc Oxide Nanowires. Master of Science (Electrical Engineering), May 2014, 70 pp., 1 table, 39 figures, references, 36 titles.

Semiconductor nanowires acts as an emerging class of materials with great potential for applications in future electronic devices. Small size, large surface to volume ratio and high carrier mobility of nanowires make them potentially useful for electronic applications with high integration density. In this thesis, the focus was on the growth of high quality ZnO nanowires, fabrication of field effect transistors and UV-photodetectors based on them. Intrinsic nanowire parameters such as carrier concentration, field effect mobility and resistivity were measured by configuring nanowires as field effect transistors. The main contribution of this thesis is the development of a high gain UV photodetector. A single ZnO nanowire functioning as a UV photodetector showed promising results with an extremely high spectral responsivity of 120 kA/W at wavelength of 370 nm. This corresponds to high photoconductive gain of 2150. To the best of our knowledge, this is the highest responsivity and gain reported so far, the previous values being responsivity=40 kA/W and gain=450. The enhanced photoconductive behavior is attributed to the presence of surface states that acts as hole traps which increase the life time of photogenerated electrons raising the photocurrent. This work provides the evidence of such solid states and preliminary results to modify the surface of ZnO nanowire is also produced.
ACKNOWLEDGMENTS

Many people have been a part of my graduate education and I would like to take this opportunity to thank all those kind-people who made this thesis possible. First and foremost, I would like to thank my advisor Dr. Usha Philipose for her insightfulness, patience and continuous support towards my research. Throughout my thesis-writing period, she provided encouragement, sound advice, good teaching and lots of good ideas. I would have been lost without her. I can honestly say that working with her provided me enough experience to successfully lead rest of my life for which i am indebted to her. I would also like to express my sincere gratitude to professors Dr. Arup Neogi and Dr. Kamesh Namuduri who has been part of my thesis committee.

I was fortunate to work with excellent lab mates Gopal Sapkota and Alex Bevly who provided excellent core of scientific and moral support, I need to add that they are not only good at physics but also at heart. I am thankful to Department of Physics for providing the financial support to complete my Masters degree. Along with Department of Physics, I am equally thankful to Department of Electrical Engineering for providing me the opportunity to complete thesis in my area of interest.

I would like to thank my friends for their continuous love and moral support whose presence helped make the completion of my graduate work possible. I would like to add my gratitude to Nara Chandra Babu Naidu and Gopichand Mallampati whom I always look them as an inspiration

Finally, and most importantly, I would like to my parents Indira Mallampati and Seetha Ram Babu Mallampati and my dear sister Sneha Mallampati for their unconditional tireless love and unwavering belief in my abilities. This thesis is in memory of my grand parents: Late Lakshmi Narayana Mallampati and Late Narasimha Rao Kurra.

Thanks to GOD and Bhagavad Gita, for being the driving force to the journey of my life.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>iii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>vii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>viii</td>
</tr>
<tr>
<td>CHAPTER 1 INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.1. Approaches to Miniaturization</td>
<td>4</td>
</tr>
<tr>
<td>1.1.1. Top-down Approach</td>
<td>4</td>
</tr>
<tr>
<td>1.1.2. Promise of Bottom-up Approach</td>
<td>4</td>
</tr>
<tr>
<td>1.2. Semiconductor Nanowires</td>
<td>5</td>
</tr>
<tr>
<td>1.3. Background and Development of ZnO Nanowires</td>
<td>5</td>
</tr>
<tr>
<td>1.4. Photodetectors</td>
<td>6</td>
</tr>
<tr>
<td>1.5. Nanoscale Photodetectors</td>
<td>7</td>
</tr>
<tr>
<td>1.5.1. ZnO Nanowire Photodetectors</td>
<td>8</td>
</tr>
<tr>
<td>1.6. Thesis Objectives</td>
<td>8</td>
</tr>
<tr>
<td>1.7. Outline of Thesis</td>
<td>8</td>
</tr>
<tr>
<td>CHAPTER 2 SYNTHESIS OF ZINC OXIDE NANOWIRES</td>
<td>10</td>
</tr>
<tr>
<td>2.1. Introduction</td>
<td>10</td>
</tr>
<tr>
<td>2.1.1. Physical Vapor Deposition</td>
<td>10</td>
</tr>
<tr>
<td>2.1.2. Chemical Vapor Deposition</td>
<td>11</td>
</tr>
<tr>
<td>2.1.3. Solution Based Growth</td>
<td>11</td>
</tr>
<tr>
<td>2.2. Vapor-Liquid-Solid (VLS) Growth Mechanism</td>
<td>12</td>
</tr>
<tr>
<td>2.3. VLS Growth Mechanism Applied to ZnO Nanowires</td>
<td>13</td>
</tr>
<tr>
<td>2.3.1. Experimental Details</td>
<td>14</td>
</tr>
</tbody>
</table>
CHAPTER 3 TRANSPORT PROPERTIES OF ZINC OXIDE NANOWIRES

3.1. Introduction 22
  3.1.1. Diffusive Transport 22
  3.1.2. Ballistic Transport 23
3.2. Electron Transport Properties of ZnO Nanowires 23
3.3. Two Terminal Electron Transport and Temperature Dependent Transport Measurements on ZnO Nanowires 24
  3.3.1. Different Scattering Mechanisms Contributing to Resistivity 26
  3.3.2. To Determine if Variable Range Hopping or Thermal Activation Dominates Conduction Mechanism in ZnO Nanowires 27
3.4. Three Terminal Measurements on ZnO Nanowires in a Field Effect Transistor Configuration 29
  3.4.1. Determination of Field Effect Mobility and Transconductance of the ZnO Nanowire 30
  3.4.2. Determination of Carrier Concentration in the ZnO Nanowire 32
3.5. Conclusion 33

CHAPTER 4 ZINC OXIDE NANOWIRES AS HIGH GAIN UV PHOTODETECTORS 34

4.1. Introduction 34
4.2. Sample Preparation and Experimental Setup 36
4.3. Determination of Carrier Generation Rate 37
4.4. Relationship Between Carrier Generation Rate and Electron and Hole Densities in ZnO Nanowire 38
  4.4.1. Model Explaining the Process of Trapping and De-trapping of Holes in ZnO 41
4.5. Photoresponse of ZnO Nanowire Photodetector 42
4.6. Effect of UV light Intensity on Photoresponse of ZnO Nanowires 46
4.7. Effect of Light Intensity on Rise and Fall Times of Photocurrent 47
4.8. Time Dependent UV Photoresponse of ZnO Nanowires 48
4.9. Temperature and Surface Passivation Effects on Photoresponse of ZnO Nanowires 50
4.9.1. Effect of Temperature 51
4.9.2. Effect of Surface Passivation 51
4.10. Determination of Carrier Life and Transit Times 52
4.11. Analysis of Rise and Fall Times of Photocurrent for Determination of Activation Energy 54
4.12. Conclusion 55

CHAPTER 5 CAPACITANCE AND NOISE MEASUREMENTS ON ZnO NANOWIRES 56
5.1. Capacitance Measurements on ZnO Nanowire Array 56
5.1.1. Analysis of C – V Plots at Positive and Negative Bias 59
5.2. Conclusion 61
5.3. Low Frequency Noise Measurements on ZnO Nanowires 61
5.4. Conclusion 62

CHAPTER 6 CONCLUSIONS AND FUTURE WORK 64
6.1. Conclusions 64
6.2. Future Work 66

BIBLIOGRAPHY 67
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>Activation energy estimated from temperature and intensity dependence of rise and fall times</td>
<td>55</td>
</tr>
</tbody>
</table>
### LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>(a) The first IC developed in 1958 which has 1 transistor and 4 other devices. (b) Xilinx Virtex-7 2000t which has 6.8 billion transistors.</td>
</tr>
<tr>
<td>1.2</td>
<td>Moore’s law which describes the trend of computing hardware</td>
</tr>
<tr>
<td>1.3</td>
<td>A collection of nanostructures of ZnO</td>
</tr>
<tr>
<td>2.1</td>
<td>Phase diagram with VLS growth characteristics</td>
</tr>
<tr>
<td>2.2</td>
<td>VLS growth characteristics, from Au droplet, Zn/Au liquid phase, saturation and growth</td>
</tr>
<tr>
<td>2.3</td>
<td>Diagram shows CVD furnace with quartz tube and PID controllers for temperature control and Gas flow meter</td>
</tr>
<tr>
<td>2.4</td>
<td>ZnO tetrapods</td>
</tr>
<tr>
<td>2.5</td>
<td>SEM image of as grown ZnO nanowires using CVD</td>
</tr>
<tr>
<td>2.6</td>
<td>EDX spectrum of ZnO tetrapods</td>
</tr>
<tr>
<td>2.7</td>
<td>EDX spectrum of ZnO nanowires</td>
</tr>
<tr>
<td>2.8</td>
<td>High resolution TEM image of ZnO nanowire</td>
</tr>
<tr>
<td>2.9</td>
<td>SEM image of as grown ZnO nanowires using Electrodepositon</td>
</tr>
<tr>
<td>3.1</td>
<td>SEM image of contacted ZnO nanowire</td>
</tr>
<tr>
<td>3.2</td>
<td>$I_{ds} - V_{ds}$ curves obtained at various temperatures i.e 80 K, 100 K, 140 K, 180 K, 240 K</td>
</tr>
<tr>
<td>3.3</td>
<td>Temperature dependent behavior of the resistivity of single ZnO nanowire</td>
</tr>
<tr>
<td>3.4</td>
<td>Temperature dependence conductivity measurements on a single ZnO nanowire</td>
</tr>
<tr>
<td>3.5</td>
<td>Schematic of nanowire FET</td>
</tr>
<tr>
<td>3.6</td>
<td>$I_{ds} - V_{ds}$ data plotted for a single ZnO nanowire contacted in FET configuration</td>
</tr>
</tbody>
</table>
Figure 3.7. $I_{ds} - V_{gs}$ data plotted for a single ZnO nanowire at fixed $V_{ds}$ contacted in FET configuration

Figure 4.1. Absorption of photon in semiconductor (a) $h\nu = E_g$, (b) $h\nu > E_g$, (c) $h\nu < E_g$

Figure 4.2. Figure shows the experimental setup for performing photocurrent measurements

Figure 4.3. I-V characteristics of a fabricated ZnO nanowire photodetector at dark and under UV illumination($\lambda = 370\text{nm}$)

Figure 4.4. Photoconduction mechanism in nanowire photodetectors, schematic of a nanowire photoconductor. Upon illumination with photon energy above $E_g$, electron-hole pairs are generated and holes are trapped at nanowire surface. When an electric field is applied, unpaired electrons are collected at the anode, which leads to photoconductivity [5]

Figure 4.5. (a) Shows the schematic of the energy band diagram of ZnO nanowire in dark, indicating band bending and surface trap states. VB and CB are valence band and conduction band respectively. The bottom figure shows oxygen molecules adsorbed at the nanowire surface that capture free electrons from the nanowire conducting channel. (b) Upon UV illumination, photogenerated holes migrate to nanowire surface and gets trapped, leaving behind unpaired electrons which contribute to photocurrent [5]

Figure 4.6. Photo luminescence shows that emission peak was strong at 370 nm which corresponds to energy of 3.35 eV

Figure 4.7. Photocurrent spectra of ZnO nanowire obtained in air and vacuum with a light intensity of 4.4 $\mu W/cm^2$ and an applied bias of 100 mV

Figure 4.8. Comparison of carrier generation rate with photocurrent spectra obtained from ZnO nanowires for various wavelengths (Intensity = 4.4 $\mu W/cm^2$). The photocurrent plots are measured in air and vacuum at room
Figure 4.9. Responsivity spectra of ZnO nanowire obtained in air and vacuum with a light intensity of 4.4 $\mu W/cm^2$ and an applied bias of 100 mV

Figure 4.10. Variation of the photocurrent with the intensity of illumination at 370 nm for a ZnO nanowire in air and vacuum

Figure 4.11. Variation of the time response of photocurrent with different intensities of illumination at 370 nm for a ZnO nanowire in air

Figure 4.12. Time dependent photocurrent measurements. The light is characterized by: $\lambda=370$ nm, Intensity=18.28 $\mu W/cm^2$. The measurements are in: (a) Air (b) Vacuum

Figure 4.13. Rise and decay times of photocurrent when light ($\lambda=370$ nm, Intensity=18.28 $\mu W/cm^2$) is incident on it. The photoresponse is studied as a function of temperature

Figure 4.14. Time resolved UV light($\lambda=370nm$, $Intensity = 18.28\mu W/cm^2$) photoresponse of ZnO nanowires before and after passivation

Figure 4.15. Plot of $\ln t_1$ and $\ln t_2$ vs. $1/T$ for rise and fall times of photocurrent

Figure 5.1. Figure shows highly doped $P^+$ substrate on which ZnO nanowire array was grown and then PMMA was spin coated which acts as dielectric between top and bottom electrodes

Figure 5.2. Figure shows the capacitance dependence of applied bias at different frequencies

Figure 5.3. Figure shows the capacitance dependence of frequency at fixed bias voltage

Figure 5.4. $\frac{1}{C^2}$ vs voltage characteristics of ZnO nanowire array

Figure 5.5. Figure shows the noise dependence on applied bias voltage
CHAPTER 1

INTRODUCTION

The goal of the current integrated circuit (IC) industry is to achieve significant chip size reduction, reduced power consumption, increase in processing speeds along with transistor count in a chip. The integrated circuit industry started from one transistor on a chip in 1958 which evolved into 6.8 billion transistors in a FPGA (field programmable gate array) chip which was developed by Xilinx in 2012(Figure 1.1). This indicates that the increase in transistor count is currently following the trend set by Moore’s law [19]. In 1965 Gordon Moore predicted that the transistor count on integrated circuit doubles approximately after every two years (Figure 1.2). But Moore’s law cannot hold forever, and chip manufactur-

Figure 1.1. (a) The first IC developed in 1958 which has 1 transistor and 4 other devices. (b) Xilinx Virtex-7 2000t which has 6.8 billion transistors.
ers rely on continuous scaling of transistors to achieve this exponential growth. But the scaling will soon end. There are mainly three obstacles which act as barrier; (i) the rising cost of fabrication, (ii) the limits of lithography, and (iii) the size of the transistor. For example the first transistor was invented in Bell Labs which had a size of 3-4cm, but with the advent of CMOS (complementary metal oxide semiconductor) technology, the transistor sizes were continuously scaled down to 90nm, 60nm, 45nm, and 32nm which was million times smaller than the first transistor. Currently transistors have components that are only few nanometers thick. If this miniaturization trend continues a new technology needs to be developed.

Of the many new technology’s one possible promising heir to lithography is nanotechnology. Scaling allows more devices to be integrated on a single chip, which not only reduces the size of the chip but also provides greater functionality with reduction in power consumption, thus driving new applications such as microwaves, remote controls, personal computers, laptops, and cheap mobile electronics, which we take for granted. The ultimate goal of miniaturization of these devices by scaling is to build a transistor which is smaller,
cheaper and faster, but as discussed earlier the scaling down of lithographically patterned transistor will come to end at one particular point. Using nanotechnology, the promise of device scaling can be continued. This multidisciplinary science which includes chemistry, physics and engineering is expected to provide a solution to the increasing fabrication cost of lithographically patterned ICs and will also allow the integrated circuits scaled beyond the limits of modern transistor. Diodes, field effect transistors and several electronic and opto-electronic devices can be fabricated from single nanostructures. All the above devices are only few nanometers in size and can reach a level of integration which cannot be possible with present day ICs. It is estimated that nanoelectronics can integrate $10^{12}$ devices per $cm^2$.

Nanostructured materials are those that have physical sizes in at least one dimension less than or equal to 100 nm. Observation and manipulation of these objects at atomic level is made possible by the invention of high resolution transmission electron microscopy (HRTEM), scanning probe microscopy (SPM), scanning tunneling microscopy (STM) and atomic force microscopy (AFM). Hence combined with other well developed measurement and characterization techniques it has become possible to study and manipulate nanostructures at the atomic level in great detail.

Nanoscale materials can be of three different dimensions, they can be either 0-dimensional (0-D), 1-dimensional (1-D) or 2-dimensional (2-D). Of the low dimensional nanostructures, nanowires are particularly promising for electronic device fabrication because they represent the lowest dimension that can be electrically contacted and thus can effectively transport electrons. In 1-D nanostructures such as nanowires and nanotubes, charge carriers are confined in two dimensions and have only one degree of freedom which allows exploration of new physical concepts. Nanowires exhibit aspect ratios (length-to-width ratio) generally above 1000, which means that their length is much greater than the diameter. This makes it ideas suitable for investigating the size and dimensionality dependence on electrical transport and optical properties. The uniqueness of 1-D nanowires in physical, optical, electrical and magnetic properties; attributed to size effects caused by quantum
confinement and surface effects.

Nanostructures can be synthesized by several methods such as vapor phase methods, thermal evaporation and condensation, metal-organic chemical vapor deposition, laser ablation and solution phase methods.

1.1. Approaches to Miniaturization

The two approaches that enable size reduction in materials are: 1) top-down approach, and 2) bottom-up approach.

1.1.1. Top-down Approach

Top down fabrication can be likened to sculpting from a block of stone. A piece of the base material is gradually removed until the desired shape is achieved. That is, you start at the top of the blank piece and work your way down removing material from where it is not required. The most common top down fabrication technique is photolithography [30]. In this process required portion is protected by a mask and the exposed material is etched away. This process can produce materials of size of the orders of a few microns. However this technique has a resolution limit which is defined by its resolving power (RP) as:

\[ RP = \frac{\lambda}{2n} \]

where \( n \) is related to the numerical aperture of the lens system. Considering the wavelength of light used in this set-up, device feature sizes cannot be reduced below \( \approx 100 \)‘s of nms. This is because the diffraction limit poses a fundamental restriction to the resolution that can be achieved in photolithography using light of a given wavelength. The other option is to use electron-beam lithography, but though it is possible to achieve smaller feature sizes, it increases the cost of electronic devices because it requires the use of sophisticated equipment.

1.1.2. Promise of Bottom-up Approach

This approach provides scope to go beyond size limitations imposed by top-down approach [30]. This approach is inexpensive because it uses physical and chemical forces to assemble basic units such as atoms or molecules into more complex structures. The
inspiration comes from the use of proteins to build complex living systems. Nanotechnology aims to replicate this ability to produce small clusters of specific atoms which can then be self-assembled into quantum wires (nanowires) and quantum dots. The potential of bottom-up approach is the possibility to control the growth with near atomic precession and with distinct chemical composition and structure which cannot be possible with conventional top-down approach.

1.2. Semiconductor Nanowires

Semiconductor nanowires have a wide range of applications in nanoscale electronics, chemical sensing and optoelectronic devices. With advances in techniques for synthesizing nanowires as single crystals with controlled properties (chemical composition, electronic and optical properties) and their physical dimensions, there is scope in developing nanoscale devices as sensors, light-emitting diodes, field effect transistors and solar cells. The growing interest is accompanied by increase in number of techniques to manufacture nanowires from different semiconducting materials such as silicon (Si), indium oxide ($In_2O_3$), gallium arsenide (GaAs) and zinc oxide (ZnO) to name just a few. While these proofs of concept devices support their bright future in integrated circuits, many challenges still remain; in particular though it is clear that small morphological changes at nanoscale can have drastic effect on device properties the extent of the effect is unclear. As such the experiments on assemblies of semiconductor nanowires give average results, convolving the consequences of each nanoscale fluctuation. The realization of optoelectronic devices based upon individual semiconductor nanowires depends critically upon control of material properties and parameters at nanoscale.

1.3. Background and Development of ZnO Nanowires

ZnO is one of the most prominent II-VI compound semiconductors and has been investigated since the early 1930’s. ZnO is a wide band gap semiconductor with a direct band gap of 3.37 eV at room temperature and had a large excitation binding energy of 60 meV. Thus it allows narrow excitation emission at room temperature in the ultraviolet
spectral range, Furthermore ZnO can be easily be synthesized in a wide variety of nanostructures [32, 3] as nanowires, nanorods, tetrapods, nanoribbons, nanobelts, nanotubes, nanohelices and nanosprings etc (Figure 1.3). ZnO is also environmentally safe and relatively easy to synthesize in large amounts.

![A collection of nanostructures of ZnO](image)

**Figure 1.3.** A collection of nanostructures of ZnO

Various growth techniques provide immense flexibility in choice of growth substrate [35, 3], nanostructure yield and crystalline quality. Because of all the above advantages ZnO semiconducting nanowires are emerging as promising and efficient visible blind UV photodetectors and in gas sensing applications. Nanowires have an additional advantage over thin films, because their high surface to volume ratio increases the sensitivity of sensing device.

1.4. Photodetectors

Semiconductor devices that convert optical signals into electrical signals are called photodetectors. They are used in several applications including fiber optics communication, infrared heat camera sensors, and for medical and military purposes. Photodetectors work on the principle of light absorption creating electron-hole pairs in the semiconductor. When
light (photons) of energy equal to or greater than the band gap of the given semiconductor is absorbed by it, electron-hole pairs are created within the semiconductor. There is also the possibility that photons of energy lower than the band gap will be absorbed. However, this is possible only if there are electrons occupying energy states in forbidden band gap of the semiconductor. Such defect states are due to chemical impurities and physical defects in crystal lattice.

Ultraviolet (UV) photodetectors have been point of interest for research in the last decade because of its wide range of industrial, military, biological and environmental applications. Ideal photodetectors for such applications should have high responsivity, low noise level, high visible rejection and low cost. Fast response can also be point of high interest where fast signal treatment is necessary such as UV imaging. A wide variety of UV photodetectors that fits to particular application is available today. Due to increasing interest in device miniaturization and reliable UV detection, current research is focused on developing nanoscale UV photodetectors in configurations such as Schottky photodiodes, p-i-n photodiodes and metal-semiconductor-metal (MSM) photodiodes. A new generation of wide band gap semiconductors such as diamond, SiC, GaN have emerged, with high responsivity, high thermal stability, and high response speed. More recently a new generation of one-dimensional wide band gap semiconductors such as GaN, ZnO have shown potential as high-efficiency UV photodetectors.

1.5. Nanoscale Photodetectors

Nanowire photodetectors yield high sensitivity than their bulk counterparts because of their high surface to volume ratio and high charge collection efficiency. Nanowire photoconductors are the simplest configuration of the nanowire based photodetectors. When an external bias is applied between the two ends of a nanowire that are contacted by metal contacts, and when light (which has energy equal or greater than its band gap) is incident on its surface, its electrical conductivity increases, thus providing light sensing capabilities. Nanowires have unique properties such as light polarization sensitivity, light absorption enhancement [34] and high photoconductive gain [5] which can be used in exploring the
realization of high integrated nanowire devices such as UV imagesensors.

1.5.1. ZnO Nanowire Photodetectors

Because of its wide band gap \((E_g = 3.37 \text{ eV})\), low cost and ease of manufacturing ZnO is emerging as potential alternative to GaN, CdTe, ZnTe, ZnSe and many other semiconductors in optoelectronic applications which include light-emitting diodes, laser diodes and UV photodetectors [6]. The main advantage for using ZnO as a UV photodetector is its spectral selectivity. The band gap energy of ZnO which is 3.37 eV corresponds to the light wavelength of 370 nm which is near UV, so ZnO responds to UV light, which is the required criteria for a UV photodetector.

1.6. Thesis Objectives

Five important aspects in the research and development of nanowires are high yield, simplicity in fabrication, economics, safety and real time application. The evolution of nanoscale devices not only requires the fabrication of nanoscale diameter wires but also its scope to integrate with microelectronic process. The primary objective of this thesis is to investigate a reliable and controlled approach for the bottom up synthesis of ZnO nanowires and a detailed study of factors that affect its growth and development as an efficient photodetector. To enable the successful integration of the nanowires as a real time photodetector, proper understanding of its carrier concentration, intrinsic defects and electrical transport properties such as mobility of the carriers is critical; so this thesis also highlights the results of characterization and electrical transport properties of ZnO nanowires. This thesis also presents a study of the capacitive properties of nanowires and how capacitance varies with bias voltage and with frequency.

1.7. Outline of Thesis

This thesis focuses on four different areas:
1) Synthesis and characterization of ZnO nanowires
2) Study of electron transport measurements, temperature dependent conductivity
3) Photo-sensing applications
4) Study of capacitance-voltage and capacitance-frequency measurements, along with study of noise dependence on conductivity of nanowires

Chapter 2 discusses the bottom-up approach for the synthesis of nanowires through vapor-liquid-solid (VLS) and electrochemical growth mechanisms. This chapter also emphasizes the change in morphologies of the as grown nanostructures as a consequence of change in growth parameters like oxygen gas flow-rate. Chapter 3 discusses the results of electron transport measurements on single ZnO nanowire. This chapter also discusses the fabrication of 3-terminal field effect transistor and effect of gate voltage on drain current. Results of conductivity dependence on temperature enables us to determine the intrinsic properties of ZnO such as carrier concentration, carrier mobility, resistivity as well as an understanding of the conduction mechanisms. Chapter 4 presents elaborate discussions on the results of photocurrent measurements and various factors that affects the photocurrent and how photo-sensing can be enhanced with temperature and surface passivation. This chapter also discusses the role of adsorbed and desorbed oxygen ions on the surface of nanowires and its effects on rise time and fall time on photocurrent measurements. Chapter 5 discusses the capacitance dependence on applied voltage and frequency on ZnO nanowire array, also discusses the effects of noise and explains its origin. Based on all the above results, work done in this thesis is summarized in chapter 6 and the scope of future work is presented.
CHAPTER 2

SYNTHESIS OF ZINC OXIDE NANOWIRES

2.1. Introduction

The realization of the full potential of nanoscale materials for fundamental physics studies and for fabrication of nano-electronic devices is directly dependent on the ability to fabricate such materials with preferred structure and functionalities. To achieve this goal we need to have a strict control over nanowire growth mechanisms, thus a comprehensive understanding of nanowire growth mechanisms is required. This chapter introduces the fundamentals of bottom up approach for nanowire growth, beginning with different growth methods, which were categorized into three types.

(i) Physical vapor deposition
(ii) Chemical vapor deposition
(iii) Solution based growth

2.1.1. Physical Vapor Deposition

Physical vapor deposition (PVD) is a process in which materials are directly deposited onto substrates without involving a chemical reaction. Typically, PVD can be divided into five main categories, (i) cathodic arc deposition, (ii) electron beam physical vapor deposition, (iii) evaporative deposition, (iv) pulsed laser deposition and (v) sputter Deposition. Essentially all these five methods use the same phenomena which starts with evaporating a source material without involving any chemical reaction. Cathode arc deposition uses high power electric arc to vaporize the source material from a cathode target, whereas electron beam physical vapor deposition uses a target (anode), which is bombarded with an electron beam under high vacuum, this electron beam causes atoms from the target to transforms into a gaseous phase, these atoms then precipitate into solid form. Evaporation deposition is a common method in which source metal is evaporated in high vacuum and then this vacuum allows vapor particles to travel directly to the target substrate, where it condenses.
to a solid. In pulsed laser deposition high power pulsed laser beam is focused inside a vacuum chamber to strike the target of the material that is to be deposited; vapors of this material then deposits on the required substrate. Sputtering deposition uses glow plasma discharge which bombards the material, sputtering away as a vapor for subsequent deposition. Nanowire growth by PVD depends on various factors such as vacuum level, vaporized material, substrate temperature, substrate material and vaporized partial pressures.

2.1.2. Chemical Vapor Deposition

Chemical vapor deposition [14] (CVD) is a process which involves chemical reactions during the transport of reactive gases to the substrate. CVD involves very complex reactions during the deposition process. Unlike PVD, CVD is not operated at high vacuum because of the involvement of many reactive gases, which occurs at high temperatures which further implies that even substrate has to tolerate high temperature. CVD process allows to grow a very high quality crystal film, which is relatively harder to be realized by PVD. A number of CVD methods have been developed depending on the various types of precursors used, the deposition conditions applied and forms of energy introduced in to system to activate desired chemical reactions. When metal-organic compounds are used as precursors, the process is called metal-organic chemical vapor deposition (MOCVD). If plasma is used to promote chemical reaction the process will be called as plasma enhanced CVD (PECVD). If chemical reactions takes place in normal atmospheric pressure, the process will be called as atmospheric pressure CVD (APCVD). This thesis focuses on APCVD for the growth of ZnO nanowires along with solution based growth. Also by controlling the CVD parameters such as gas flow rates, temperature it is possible to control morphology, composition and dimensions of the as-grown nanowires.

2.1.3. Solution Based Growth

Solution phase growth [35] of one dimensional nanoscale materials has gained more importance in the last decade because of its inexpensive setup and ease of growth. Solution based synthesis process can be divided into two categories; (i) low temperature wet chemical
synthesis which is performed in atmospheric pressure at slightly higher temperatures \((40 – 80^\circ C)\), and (ii) solvothermal synthesis taking place at elevated pressure and temperature which is above the boiling point of solvent. This thesis focuses on the low temperature wet chemical synthesis for the growth of ZnO nanowires.

2.2. Vapor-Liquid-Solid (VLS) Growth Mechanism

The vapor-liquid-solid (VLS) growth method is one of the many mechanisms used for the growth of one-dimensional structures such as nanowires using the CVD process. Most of the recent successful growth of semiconducting nanowire growth is based on VLS [18], growth mechanism which was first introduced by Wagner and Ellis in 1964 for Si whiskers with diameters varying from nanometers to microns. The name VLS itself reflects the pathway for the synthesis of ZnO nanowires. Zn and oxygen (O) in vapor phase diffuses into a liquid alloy droplet (reacts with oxygen forming ZnO), which subsequently supersaturates and eventually enables precipitation of a solid phase as ZnO nanowire. The liquid droplet on the substrate can be formed either by a metal (catalyst) or by a self-seeded mechanism, using Zn as the seed particle. At a particular temperature, the liquid droplet will be in equilibrium and as more growth material is supplied at this equilibrium temperature, the alloyed particle becomes supersaturated, leading to nucleation and growth. As the whole purpose of the metal is to initiate the growth it is referred as catalyst. The size of this catalyst seed determines the diameter of the as-grown nanowire.

The choice of the metal catalyst is based on its physical and chemical properties and in many cases determines the properties of nanowires. In order to use any particular metal as catalyst in VLS mechanism, the metal should be physically active and chemically stable. The eligible metal should be chosen from a phase diagram such that it forms a liquid alloy with the nanowire material with which we are interested. The source material and metal catalyst seed material forms an eutectic compound at the eutectic temperature. The vapor pressure at equilibrium point of the catalyst should be small such that the droplet will not vaporize. A catalyst which has smaller contact angle between the droplet and solid is more suitable for large growth area. Hence the equilibrium phase diagrams are particularly
helpful for estimating the optimal composition and temperature for nanowire growth. Adsorption of the vapor phase reactants onto the metal catalyst leads to the formation of a liquid metal-semiconductor alloy at the surface. The higher sticking coefficient of impinging vapor molecules on the liquid surfaces allows crystal growth to occur only where the liquid metal catalyst is present. When liquid alloys becomes saturated, additional supply of source material from gas phase results in crystallizing solid source at the liquid-solid interface. This solid-liquid interface should be well defined crystallographically in order to produce nanowires of high directionality.

In general, the VLS growth mechanism can be described by the following steps:
(i) Formation of a liquid alloy droplet between metal catalyst and the substrate used for the growth of nanowire
(ii) Deposition of source from vapor directly onto the liquid alloy droplet in the vapor liquid system
(iii) Precipitation of solid from the supersaturated liquid alloy at the liquid-solid interface

2.3. VLS Growth Mechanism Applied to ZnO Nanowires

The starting point for the growth of ZnO nanowires is deposition of the metal catalyst on the surface of the substrate using thermal evaporation. In this work, ZnO nanowires were grown using Au and also Zn as the metal catalyst. When Au is chosen as the seed layer, the Si substrate with Au is first heated. As per the phase diagram shown in Figure 2.1, at a temperature above 370°C, an alloy droplet of Au-Zn forms.

As the source temperature is raised to 800°C, solid Zn which is the source material is heated in an oxygen ambient. This produces Zn and O₂ vapors, which are transported to the molten alloy droplet. The molten Au-Zn droplet is the favorable deposition site for Zn and O₂ atoms due to its lower surface energy. VLS growth process is an isothermal process and so with the temperature held at 800°C, as more and more Zn and O₂ atoms impinge on the molten droplet, it eventually get supersaturated and a solid ZnO phase precipitates out of this droplet forming a solid-liquid interface. This crystal grows in length as more and
more atoms are added to the nucleating site. Nanowire growth will continue as long as the temperature is maintained and vapors of constituent atoms are supplied to the nucleating site. A schematic of the ZnO nanowire growth process is shown in Figure 2.2.

2.3.1. Experimental Details

ZnO nanowires were grown on Si substrate using standard VLS growth mechanism in a high temperature chemical vapor deposition (CVD) system shown in Figure 2.3.

The furnace is a three zone resistance heated furnace which was controlled by a microprocessor based self timed PID controller to minimize the overshoot and maintain an optimum set temperature. The three zone furnace is divided into two end zones which follows the central heating zone in a master-slave approach. Temperature of the master zone can be increased until 1200°C and the master and the slave zones can be set ±200°C above or below the master zone temperature. For the growth of ZnO nanowires, source is placed at one end zone and substrate is placed close to the source in an independently controlled temperature.
Pure zinc powder (alfa aesar, 99.99%) was used as solid precursor. Thin layer of Au film was evaporated on the Si substrate to initiate the growth. Zn powder was loaded into alumina boat which was placed in the constant temperature zone of high temp furnace, while the Au evaporated Si substrate was placed on a sample holder which was placed at a distance of $3 \text{ cm}$ from the source. The temperature was maintained $800^\circ C$ through the three zones and argon gas of 40 sccm is bubbled through furnace till the temperature in the furnace reaches set point temp of $800^\circ C$. Once temperature reaches set point, oxygen gas of 40 sccm is bubbled along with argon gas for a period of 90 min to facilitate growth of long ZnO nanowires.

2.3.2. Effect of Oxygen Flow Rate on ZnO Nanowires Growth

It was found that the morphology of the as-grown nanostructures were affected by the partial vapor pressure of $O_2$ [26] in the growth chamber. When the oxygen gas flow was maintained at 10 sccm, the as-grown nanostructures were tetrapods. Figure 2.4 is
Figure 2.3. Diagram shows CVD furnace with quartz tube and PID controllers for temperature control and Gas flow meter.

An SEM image of a single ZnO tetrapod nanocrystal. Each arm in the fig shown is well faceted with a hexagonal cross-section and is uniform in length and diameter. By varying growth parameters such as the \( O_2 \) gas flow content, control over the size and morphology of the tetrapod nanocrystals can be obtained. The leg of each structure is about 3–4 \( \mu \text{m} \) in length, with a diameter of about 300-500 nm. The ZnO tetrapods were fabricated without the presence of any catalysts and so it is a self-seeded growth [21]. ZnO tetrapods are grown by the vapour-solid (VS) process rather than by the vapour-liquid-solid (VLS) growth mechanism. In the VS mechanism, Zn is first self-catalyzed [21]. Ronning and Shang [4] proposed a nucleus model to explain the growth mechanism of the tetrapods. They propose that the center core of ZnO tetrapods consists of four hexagonal grains with a twin like relation, and according to this model, the four hexagonal grains nucleate as embryos during the initial growth stage. Growth then occurs along the different directions and the as-grown ZnO crystals adopt a tetrapod shape. When the grains join together to form the nucleating...
embryo, a large lattice mismatch strain occurs and this is why the nucleus is stable only for finite small sizes.

When the $O_2$ gas flow rate was maintained at 40 sccm, the as-grown nanowires were cylindrical, had lengths of 15–20 $\mu$m and diameters of about 80–100 nm (Figure 2.5).

These experiments show that the ZnO nanostructure morphology depends on the partial vapour pressure of $O_2$, with tetrapods growing at low $O_2$ vapour pressure and cylindrical nanowires growing at higher $O_2$ vapour pressures. At low vapour pressures, the crystal is non-stoichiometric and has a composition of $ZnO_{1-x}$, with relatively high pressures of zinc. The composition of the ZnO tetrapods showing Zn rich crystals is shown by the energy dispersive x-ray (EDX) spectrum shown in figure 2.6.

On the other hand, ZnO nanowires that were grown under stoichiometric conditions had Zn:O ratio of 1:1, as shown in the EDX spectrum of figure 2.7.

The as-grown nanowire is a single crystal of ZnO and has a wurtzite structure as verified by the high resolution transmission electron microscope (HRTEM) image of Figure 2.8.
**Figure 2.5.** SEM image of as grown ZnO nanowires using CVD

**Figure 2.6.** EDX spectrum of ZnO tetrapods
The four tetrapod legs are grown during the expansion of this seed. At optimum partial pressures of Zn and $O_2$, the seed is stoichiometric and cylindrical ZnO nanowires grow out of the nucleating seed.

2.4. Solution Based Growth of ZnO Nanowires

The electrodeposition of ZnO was performed in a three-electrode electro chemical cell with the aluminum substrate as the cathode. Pt wire as the counter electrode and another saturated calomel electrode (SCE) acts as reference electrode. Electrolyte was an aqueous solution of KCl and $ZnCl_2$, saturated with bubbling oxygen. $ZnCl_2$ salt acts as $Zn^{+2}$ precursor and its concentration was maintained at $5 \times 10^{-4}$ M. While KCl in the solution acts as supporting electrolyte and its concentration was maintained at 0.1 M. pH of the solution was maintained at 4.0 and zinc-acetate seeds were spin coated on the alumina substrate which acts as source of seeding particles. A constant bias of -1 V was applied between anode
Figure 2.8. High resolution TEM image of ZnO nanowire

and cathode and -2 V between reference and working electrode. Electrochemical growth [35] of ZnO nanowires occurs by $O_2$ reduction in the solution given by the following reactions:

\begin{equation}
O_2 + 2H_2O + 4e^- \rightarrow 4OH^- 
\end{equation}

and

\begin{equation}
Zn^{2+} + 2OH^- \rightarrow ZnO + H_2O
\end{equation}

The length of the nanowires grown by this technique is limited because as the nanowire grows, the concentration of $Zn^{2+}$ in the electrolyte (in the vicinity of the electrode) decreases continuously. After a certain time, no further growth is possible. KCl acts as supporting electrolyte, and it is possible to increase the concentration of the $Cl^-$ ions for dissolution of the core of ZnO nanowires, thus forming ZnO nanotubes. Figure 2.9 shows the high resolution SEM (scanning electron microscope) image of the nanowires grown for 60 min using electrochemical process.
2.5. Conclusion

ZnO nanowires were synthesized using VLS growth mechanism in a CVD system. Synthesis of high quality ZnO nanowires are sensitive to growth conditions and the effect of oxygen gas flow on the morphology of the as-grown nanostructures are discussed in this chapter. Lower $O_2$ vapour pressure favors the growth of ZnO tetrapods, while at higher pressures, stoichiometric, cylindrical nanowires are obtained. SEM images show that the nanowires have lengths of the order of 15–20 $\mu$m and diameters of 80–100 nm. EDX spectrum reveals that the ZnO nanowires have stoichiometric composition with Zn:O ratio of 50:50 wt %. Based on our experiments, the optimum growth temperature for growth of ZnO nanowires is determined to be 800°C, with argon gas flow rate of 40 sccm and oxygen gas flow rate of 40 sccm. The nanowire dimensions listed here are for a growth time of 90 min.
CHAPTER 3

TRANSPORT PROPERTIES OF ZINC OXIDE NANOWIRES

3.1. Introduction

Transport measurements on a semiconductor material provides information on the motion of electrons or holes in response to an applied electric field. The two basic properties of current conduction in any material is due to drift and diffusion of charge carriers. Diffusion of carriers is due to a gradient in carrier concentration and drift of carriers is due to the electric field applied. In 1-D electron systems such as nanowires, drift and diffusion of electrons are equally important and any charge distribution relaxes according to the diffusion law with some effective diffusion coefficient enhanced due to drift phenomenon. During transport, impurities, crystal imperfections and lattice defects affects electron scattering. In a nanowire, as the diameter of the nanowire decreases, electrons will be increasingly confined. This affects the scattering of electrons, which influences electron transport mechanism. Electron transport can occur in ballistic, diffusive or localized regimes depending on the size of system. One powerful configuration for studying electrical transport in nanowires is the field effect transistor (FET) configuration, which comprises of a nanowire response to electrical bias applied to three terminals: source and drain as the two contacts and a back gate. The change in conductance as a function of gate voltage is used to distinguish whether conductivity of a given nanowire is controlled by electrons or holes, i.e., whether it is n or p type. Depending on whether the given semiconductor is n or p-type, when a gate voltage is applied, it leads to band-bending causing the conductivity to either increase or decrease. This phenomena is explained on detail in this chapter for ZnO nanowires.

3.1.1. Diffusive Transport

If the nanowires size and diameter is more than the carrier mean free path, electrons will suffer many scattering events. In this case conduction is dominated by the scattering of carriers within the nanowire. Electrical conductivity in ZnO nanowires are controlled by the presence of impurity atoms along with the defects in the semiconductor crystal lattice. The
localized electronic states related to these defects limits the characteristics of the material by acting as scattering or recombination centers for the charge carriers. As the length of the nanowire is reduced to length of mean free path of electrons, electron transport mechanism shifts from diffusive transport mechanism to ballistic transport mechanism.

3.1.2. Ballistic Transport

Ballistic transport phenomena occurs when electrons are propagating without any scattering. This transport can be observed in nanowires where the length of nanowires is much smaller than the electron mean free path. In this case the conduction is determined by contacts between the nanowire and the external circuit and conductance is quantized into universal conductance units.

\[ G_o = 2e^2/h \]

and the other requirement for the ballistic phenomena is the thermal energy satisfies the relation \( k_B T \ll \epsilon_j - \epsilon_{j-1} \) where \( j \) and \( j-1 \) are sub band energy levels.

3.2. Electron Transport Properties of ZnO Nanowires

In bulk ZnO, the exciton Bohr radius is \( \approx 2.34 \) nm and so quantum confinement effects are not expected to be observed in ZnO nanostructures that have dimensions larger than 10 nm. The synthesized ZnO nanowires have diameters in the range of 90-100 nm, so quantum confinement effects can be ignored which further implies that electron transport in nanowires is not ballistic. Instead, the transport can be explained mostly on the basis of diffusive transport. The electron transport properties of ZnO nanowires is extensively studied and explained using temperature dependent 2-terminal measurements and gate dependent 3-terminal measurements. These measurements enable us to determine the intrinsic ZnO nanowire parameters such as carrier concentration, carrier mobility and transconductance. Temperature dependent resistance measurements were analyzed to determine the activation energy of any possible thermally activated conduction mechanisms in ZnO nanowires. In order to study the 3-terminal measurements on ZnO nanowires, a single nanowire was placed
on a highly doped (resistivity 0.001–0.005 Ω-cm) $p^+$ Si substrate covered with a 400 nm thick $SiO_2$ layer. Two Al contacts were then patterned onto the two ends of the ZnO nanowire. An SEM image of the contacted nanowire is shown in Figure 3.1. These two contacts function as the source and drain electrodes. Contact established to the $p^+$ Si is for the back gate.

![SEM image of contacted ZnO nanowire](image)

**Figure 3.1.** SEM image of contacted ZnO nanowire

3.3. Two Terminal Electron Transport and Temperature Dependent Transport Measurements on ZnO Nanowires

To determine the resistivity of the as-grown ZnO nanowires and to determine the transport mechanism, 2-terminal measurements is investigated at low temperatures. These measurements were done on a single ZnO nanowire mounted between two Al electrodes on a quartz substrate. This sample was placed in a temperature controlled cryostat from Janis which was maintained in vacuum. Continuous flow of liquid $N_2$ was maintained to get the sample to 77 K. In order to get the equilibrium temperature between the sample and the temperature controller sensor, sample was maintained in same temperature for 20-
30 minutes. Lake shore temperature controller was used to heat the sample to specific temperatures. An Agilent B1500A semiconductor parameter analyzer is used to analyze and record the variations of the drain-source current \( I_{ds} \) with drain-source voltage \( V_{ds} \); the results are as shown in Figure 3.2.

**Figure 3.2.** \( I_{ds} - V_{ds} \) curves obtained at various temperatures i.e 80 K, 100 K, 140 K, 180 K, 240 K

Considering the geometry of the nanowire, its resistivity and conductivity was then determined as a function of temperature. The results are shown in Figure 3.3(a) and (b) respectively.

As shown in Figure 3.3, the nanowire resistivity increases with \( T \) at high temperatures, from 200 K-450 K. This is expected for phonon-dominated scattering [28]. For low temperatures (below 200 K), resistivity scales exponentially in \( 1/T \). This is typical for an undoped semiconductor.
3.3.1. Different Scattering Mechanisms Contributing to Resistivity

The total resistivity of nanowires may be expressed as a sum of different contributions:

\[ \rho(T) = \rho_0 + \rho_{e-ph}(T) + \rho_{e-e}(T) \]

where \( \rho_0 \) is the residual resistivity that does not depend on temperature, \( \rho_{e-ph}(T) \) is resistivity due to electron-phonon interaction and \( \rho_{e-e}(T) \) is the contribution due to electron-electron inelastic scattering. Thus, based on our observations recorded in Figure 3.3, it can be determined that the increase in resistivity at temperatures above 200 K is due to an increase in the electron-phonon scattering. The electron-electron scattering is dominant from 80-200K and the minimum resistivity was measured to be \( 2.3 \times 10^{-4} \) \( \Omega \)-m at about 200 K. This value represents the point at which the combined resistive contributions of phonon scattering and electron scattering are at a minimum. The negative temperature coefficient of resistance in the low temperature regime (\(< 200K\)) where resistivity decreases with in-
crease in temperature (Figure 3.3) reveals the semiconductor nature of ZnO nanowire. A characteristic of semiconductors is that the carrier concentration varies exponentially with temperature. Hence, the observed increase in conductivity is attributed to an exponential increase in carrier concentration with temperature.

3.3.2. To Determine if Variable Range Hopping or Thermal Activation Dominates Conduction Mechanism in ZnO Nanowires

For electron-electron scattering, the electrons can also undergo a variable-range hopping \cite{36} process involving traps, defined by the following relation between resistivity and T.

\begin{equation}
\rho(T) = \rho_0 \exp(T_0/T)^{1/p}
\end{equation}

In this equation $\rho_0$ and $T_0$ depend on the material properties and are not strongly influenced by temperature. The parameter $p$ depends on the dimensionality of the material: $p = 2$ for one-dimensional (1D), $p = 3$ for 2D, and $p = 4$ for 3D systems. So, for 1-D nanowires, $p = 1$ and if there is variable range hopping mechanism that contributes to material resistivity or conductivity, then $\ln(\rho_0)$ should vary as $T^{-1/2}$.

On the other hand, if resistivity and hence conductivity is thermally activated, then it is defined by the equation:

\begin{equation}
\rho(T) = \rho_0 \exp(E_a/kT)
\end{equation}

To verify which of the conduction mechanism dominates, $\ln(\rho_0)$ was plotted as a function of $T^{-1}$ and also as a function of $T^{-1/2}$ (Figure 3.4). The linear fit of Figure 3.4 attests to the fact that conductivity of the ZnO nanowires in the low temperature regime followed the thermal activation process and not the variable range hopping mechanism.

An activation energy characterized by the linear region in the semi-log plot of conductivity versus $1/T$ is shown in Figure 3.4. The activation energy was obtained by fitting the
data to an exponential functional form in the limit of no compensation, using the expression:

\[ \sigma = \sigma_0 e^{(-E_a/kT)} \]  

where \( \sigma_0 \) is the pre-exponential factor, \( K \) is Boltzmann constant (8.617 \times 10^{-5} \text{eV} \text{K}^{-1}) and \( T \) is absolute temperature. This study of temperature dependent transport measurements on a single ZnO nanowire shows the conduction is thermally activated in the temperature range of 80 K to 180 K. The linear Arrhenius plot of conductivity versus \( 1/T \) suggests thermally activated condition with a single activation energy. This activation energy of conduction \( E_a \) is determined from the slope of the figure 3.4(a) using the relation

\[ \frac{d(\ln(\sigma))}{d(1/T)} = \frac{E_a}{k} \]

was calculated to be \( \approx 28 \text{ meV} \). This activation energy is consistent with reports in the literature for Zn interstitials, which act as electron donors [22].

**Figure 3.4.** Temperature dependence conductivity measurements on a single ZnO nanowire
3.4. Three Terminal Measurements on ZnO Nanowires in a Field Effect Transistor Configuration

All measurements presented using FET [9] are performed on ZnO nanowires that were dispersed onto a heavily doped $p^+$ Si substrate covered with a 400 nm thick thermally grown $SiO_2$ layer ($Si/ SiO_2$ substrate). The doped silicon serves as the back-gate electrode, while the $SiO_2$ layer serves as the gate insulator. The source and drain contacts are patterned on the two ends of the nanowire, followed by metallization of the source and drain contacts. Since the work function of Al (4.3 eV) matches with work function of ZnO (4.2 eV) the injection barrier of the electrons will be small. A schematic of the 3-terminal FET device comprising of a ZnO nanowire is shown in Figure 3.5. The nanowire length in this case is equal to the channel width which is taken to be $\approx 20 \mu m$.

![Schematic of nanowire FET](image)

**Figure 3.5. Schematic of nanowire FET**

The initial test was 2-terminal measurements, results of which are shown in Figure 3.6.
This variation of $I_{ds}$ with $V_{ds}$ was measured at $V_{gs} = 0$ V; the linear nature of this plot verifies that Al metal contacts are ohmic contacts to the ZnO nanowire. Subsequently, 3-terminal measurements using the back gate on the same device shows that as the gate voltage increased from -5 V to +20 V, the conductance of ZnO nanowire progressively increased indicating the n-type semiconducting behavior of FET. As seen in Figure 3.7, $I_{ds}$ increased more than an order of magnitude with positive $V_{gs}$ at constant $V_{ds} = 0.5$ V.

### 3.4.1. Determination of Field Effect Mobility and Transconductance of the ZnO Nanowire

The drain-source current is dependent on the drift velocity of electrons which is given by the relation:

$$I_{ds} = \int qnv_d A$$

where, $q$ is the electron charge, $v_d$ is drift velocity, $A$ is the cross sectional area of the nanowire, and $n$ is the number of carriers per unit volume. The drift velocity is related to
Figure 3.7. $I_{ds}$ – $V_{gs}$ data plotted for a single ZnO nanowire at fixed $V_{ds}$ contacted in FET configuration

the field effect mobility by the equation: $v_d = \mu_{FE}E$. The electric field is caused by the potential difference between source and drain terminals and is defined as: $E = \frac{V_{ds}}{L}$ where $V_{ds}$ is the potential difference from drain to source and $L$ is the length of channel. Hence equation 10 is re-written as:

\begin{equation}
I_{ds} = \int qn\mu_{FE}\frac{V_{DS}}{L}A
\end{equation}

$\mu_{FE}$ and $V_{DS}$ are not affected by integral, but $qn$ is affected. By defining $Q_{acc}$ to be the accumulation charge of our system defined as:

\begin{equation}
\int qnA = \frac{Q_{acc}}{L}
\end{equation}

Thus equation 11 can be transformed to:

\begin{equation}
I_{DS} = \frac{\mu_{FE}Q_{acc}V_{DS}}{L^2}
\end{equation}
where \( Q_{\text{acc}} = C(V_{gs} - V_t) \). C is the capacitance between gate and nanowire, \( V_{gs} \) is the potential difference between the gate and source and \( V_t \) is the threshold voltage. Using this analysis, the field effect mobility is expressed as:

\[
\mu_{FE} = \frac{I_{ds} L^2}{C (V_{gs} - V_t) V_{ds}}
\]

or

\[
\mu_{FE} = \frac{L^2}{C V_{ds} (\frac{V_{gs}}{I_{ds}} - \frac{V_t}{I_{ds}})}
\]

Another important parameter is the transconductance \( g_m \), which is the ratio of the current change at the output to the voltage change at the input, and is defined as:

\[
g_m = \frac{\delta I_{ds}}{\delta V_{gs}}
\]

So if we assume \( I_{ds} \) and \( V_{gs} \) are constant, \( \frac{V_{gs}}{I_{DS}} = \frac{1}{g_m} \). If we assume the contact resistance to be negligible, the field effect mobility can be expressed as:

\[
\mu_{FE} = (g_m L^2) / (C V_{DS})
\]

where \( \delta I/\delta V_g \) is the measured transconductance, \( \mu_{FE} \) is the field effect mobility, C is the capacitance of the nanowire FET and L is the length of the channel. An analytical estimate of capacitance is given by

\[
C = 2\pi \epsilon_{eff} \epsilon_0 L / \arccosh((t_{ox} + R)/R)
\]

3.4.2. Determination of Carrier Concentration in the ZnO Nanowire

The carrier concentration is determined from the equation \( Q_{\text{tot}} = Nq \), where N is the total number of charge carriers and \( n = N/V \) is the charge carrier density. Since the nanowire has cylindrical geometry, the carrier concentration can be defined as:

\[
n = \frac{Q_{\text{acc}}}{q \pi R^2 L} = \frac{C(V_{gs} - V_t)}{q \pi R^2 L}
\]
In the above equation $\epsilon_{eff} \approx 3.9$ is the effective dielectric constant for the $SiO_2$ back-gate dielectric, $\epsilon_0$ is the permittivity of the free space, $t_{ox} = 400$ nm is the dielectric thickness, $L = 20 \mu m$ the distance between the electrode contacts, and $R = 40$ nm is the radius of nanowire, using the above analysis for the determination of intrinsic ZnO nanowire parameters, the following values were determined:

Carrier concentration $= 1.3 \times 10^{17} cm^{-3}$, Transconductance $= 4.13$ nS, Nanowire resistivity at 300 K $= 0.267 \times 10^{-3} \Omega \cdot cm$, Field effect mobility $= 150 cm^2 V^{-1} s^{-1}$.

3.5. Conclusion

Transport properties of ZnO nanowires synthesized by CVD were studied by configuring into a Field Effect Transistor. Based on these studies, carrier concentration, transconductance, resistivity and field effect mobility were determined to be as $1.3 \times 10^{17} cm^{-3}$, 4.13nS, $0.267 \times 10^{-3} \Omega \cdot cm$, 150 $cm^2 V^{-1} s^{-1}$ respectively. Temperature dependent transport measurements were done in the temperature range of 80 K-440 K, the conductivity dependence on temperature in ZnO nanowires were explained by electron-electron and electron-phonon scattering phenomena. The activation energy for thermally activated conduction was estimated to be 28 meV from the linear Arrhenius plot of conductivity.
CHAPTER 4

ZINC OXIDE NANOELIRES AS HIGH GAIN UV PHOTODETECTORS

4.1. Introduction

Photoconductivity is a well-known property of semiconductors in which conductivity of the semiconductor increases when light of energy equal or greater to band gap energy of the material is incident upon it. Figure 4.1 shows the schematic which is used to explain the photoconductivity process. A semiconductor is characterized by two bands, the conduction and valence band which is separated by the energy band gap of the semiconductor. When the semiconductor is illuminated with light, photons with energy equal to or greater than its band gap is absorbed by the semiconductor resulting in the formation of electron-hole pairs [16]. Thus, photons can be absorbed by the electrons in the valence band if their energy $E_{ph} = h\nu$ is either equal to or greater than the band gap energy $E_g$ of the semiconductor. By absorbing these photons electrons from the valence band are excited to the conduction band thus creating electron-hole pairs which increase the conductivity of the material. However there is a possibility to even create electron-hole pair with a photon energy $h\nu < E_g$, if electrons occupies energy states in the energy band gap due to impurities and physical defects in crystal lattice.

Photoconductivity involves several other successive or simultaneous phenomena such as photogeneration of carriers, carrier trapping [23, 5], carrier detrapping and carrier recombination when light is incident on the material. The magnitude of photocurrent changes induced by light radiation depends upon several factors [34] like number of carriers generated upon absorption of photons and mobility of the photogenerated carriers. The duration of photoconduction change depends on the factors like life time of the carriers and the time for carriers to encounter a trap. Therefore, photoconductivity is also a valuable phenomena that can provide information on the electronic properties of semiconductors relating to the charge carrier life time and mobility. Photoconductive semiconductors are important in a variety of applications such as photodetectors and photovoltaic devices.
In this chapter, an experiment design to measure photocurrent in ZnO nanowires will be presented. An extremely high photocurrent gain was measured, which agrees with earlier reports [5] in terms of surface states contributing to conductivity of nanowires. The basic concepts related to photoconductivity in ZnO nanowires, including light absorption, carrier photogeneration, and carrier trapping is explained. The effect of temperature and surface passivation on all the above mentioned phenomena is also studied and explained. The reason for using ZnO nanowires as ultraviolet (UV) Photodetectors is because of its many advantageous properties such as wide direct bandgap (3.37 eV), ease of manufacturing these nanowires at low cost, and the fact that ZnO is an environmentally friendly material with high spectral selectivity in UV region. Based on our experiments, we conclude that ZnO nanowires have high photoconductive gain which is a very promising result for use in
real time applications.

4.2. Sample Preparation and Experimental Setup

The as grown ZnO nanowires which has high stoichiometry (Zn:O is 1:1 at wt%) from CVD growth are transferred on to a quartz substrate and these nanowires were contacted by two Al electrodes. An image of the experimental set-up showing all equipment used in this experiment is shown in Figure 4.2. The quartz substrate with the contacted ZnO nanowire is mounted in a Janis liquid nitrogen cryostat. Agilent B1500A semiconductor device analyzer which is connected to cryostat is used to study the I-V characteristics. A tungsten halogen lamp (100 W, oriel series, quartz tungsten) is used as the excitation light source; providing light in the wavelength range from 280 nm to 2700nm. Light from this source is made to pass through monochromator which provides wavelength selectivity. Light coming from

![Experimental setup](image-url)
monochromator is made to pass through two plano convex lenses which are used to converge the beam and focus the light on the sample in the cryostat. The lamp is connected to a voltage source; by changing the voltage applied to the light source, the intensity of light can be varied. The focused light beam is aligned such that the light passes through a transparent quartz window in the cryostat and is incident on the sample containing the nanowire. The cryostat is designed to operate in the temperature range 77K to 450K. Lake shore temperature controller is used to control the sample temperature with high precession. The outer vacuum chamber thermally isolates the sample space area from surrounding room temperature. The vacuum chamber is pumped to a vacuum of $10^{-3}$ Torr before performing the photocurrent measurements in vacuum. Photocurrent measurements were measured under a constant DC bias of 100 mV applied by Agilent B1500A semiconductor device analyzer. Photocurrent under dark and UV illumination were recorded by switching 100W halogen lamp on and off.

4.3. Determination of Carrier Generation Rate

The rate at which carriers are generated in the semiconductor depends on the absorption coefficient of the material, which is dependent on the wavelength of light. Carrier generation rate ($G$) is defined as the rate at which carriers are generated when UV light is illuminated on the ZnO nanowire and is defined by the equation:

$$G = \frac{I_o}{\hbar \omega R} [I_1(2\alpha R) - L_1(2\alpha R)]$$

$R = 0.5 \times 10^{-5}$ cm, and at 370 nm wavelength $\alpha R = 2 \times 10^5 \times 0.5 \times 10^{-5} = 1$, and incident intensity $I_o$ is 4.4 $\mu W/cm^2$ and $\hbar \omega$ is energy of photon, at 370 nm wavelength the energy of photon is 3.35 eV and $L_1$ is modified Struve function and $I_1$ is modified Bessels function both of them were functions of order 1, whose values were 1.047 and 1.531 respectively. By using all the above values carrier generation rate is calculated to be $G = 7.95 \times 10^{17}/(cm^3.s)$

There are two cases for limiting values of carrier generation rate: case (i) If $\alpha R \ll 1$
then $G$ is given by

$$G = \frac{I_o}{h\omega} = 1.64 \times 10^{18}/cm^3.s$$

Case (ii) If $\alpha R \gg 1$ then $G$ is given by

$$G = \frac{I_o}{\pi h\omega R} = 10^{18}/cm^3.s$$

The analysis described below is based on the assumption that every photon absorbed by the material results in the generation of an electron-hole pair.

4.4. Relationship Between Carrier Generation Rate and Electron and Hole Densities in ZnO Nanowire

Figure 4.3 shows the results of photocurrent measurements performed on ZnO nanowire device in standard ambient conditions; in dark and under UV illumination ($\lambda = 370 nm$). At a bias of 100 mV dark room current was about 51 nA. However, when the nanowire was illuminated with UV light of 370 nm, the current was measured to be 221 nA. This shows that the magnitude of the photocurrent increased about four times due to UV illumination. As photons are absorbed by the nanowire, an excess electron density exists within the ZnO nanowire, which is related to the hole density (both trapped and free holes) by the relation:

$$n_e = n_{h}^f + n_{h}^t$$

where $n_e$ is excess electron density in conduction band, $n_{h}^f$ is free hole density in valence band and $n_{h}^t$ is the trapped hole density. A schematic of the photoconduction process showing a single nanowire that is electrically biased and that produces electron hole pairs as a result of light absorbed by it is shown in Figure 4.4. Thus, when light is incident on the ZnO nanowire, there is an increase in the electron and hole concentration. The rate equations that define the change in free and trapped hole density as well as change in excess electron
Figure 4.3. I-V characteristics of a fabricated ZnO nanowire photodetector at dark and under UV illumination ($\lambda = 370\text{nm}$)

density is expressed [7] as:

(24) \[ \frac{dn_f}{dt} = G - \frac{n_{h,t}}{\tau_{tr}} - \frac{n_{h,f}}{\tau_r} \]

(25) \[ \frac{dn_h}{dt} = \frac{n_{h,t}}{\tau_{tr}} - \frac{n_{h,f}}{\tau_d} \]

(26) \[ \frac{dn_e}{dt} = G - \frac{n_{h,t}}{\tau_r} - \frac{n_{h,f}}{\tau_d} \]

In the above equation $G$ is photogeneration rate and $\tau_{tr}$ is trapping time and $\tau_r$ is radiative decay time and $\tau_d$ is de-trapping time. $n_e$ and $n_{h,t}$ can be increased by increasing generation rate $G$. Free holes either decay radiatively at a rate of $\frac{1}{\tau_r}$ or get trapped on nanowire surface
Figure 4.4. Photoconduction mechanism in nanowire photodetectors, schematic of a nanowire photoconductor. Upon illumination with photon energy above $E_g$, electron-hole pairs are generated and holes are trapped at nanowire surface. When an electric field is applied, unpaired electrons are collected at the anode, which leads to photoconductivity $[5]$

at a rate $\frac{1}{\tau_{tr}}$. Radiative decay of each hole also annihilates an electron. Let the trapped holes get detrapped at a rate of $\frac{1}{\tau_d}$. The detrapping process involves capture of a free electron by
the trapped hole, rather than the hole returning to the valence band. This means that each
detrapping process eliminates a trapped hole and a free electron.

The photocurrent density ($\rho$) can be expressed in terms of the excess electron density
(using equation 23) by the equation:

\begin{equation}
\rho = en_e\mu E = e(n_h^f + n_h^t)\mu E
\end{equation}

4.4.1. Model Explaining the Process of Trapping and De-trapping of Holes in ZnO

In dark oxygen molecules are adsorbed [5, 20, 23, 8] on the surface of ZnO nanowires
which captures free electrons from nanowire conducting channel and forms depletion layer
near the nanowire surface. The generation of photoelectrons in ZnO nanowires upon UV
illumination is attributed to the desorption of oxygen molecules from the surface of ZnO
nanowires.

\begin{equation}
O_2 + e^- \rightarrow O_2^-(ad)
\end{equation}

When these nanowires were subjected to UV illumination with energy greater than
the band gap of ZnO, electron and hole pairs are generated and these photogenerated holes
migrate to adsorbed oxygen molecules on the surface of ZnO nanowire. These migrated
holes neutralize the adsorbed oxygen molecules which allows them to desorb them from ZnO
nanowire surface. As a result the photocurrent increase due to photogenerated unpaired
electrons until desorption and readsorption of oxygen molecules reach an equilibrium state.

\begin{equation}
e^- + h^+O_2^-(ad) \rightarrow e^- + O_2(g)
\end{equation}

Figure 4.5 explains the hole trapping and photoconduction mechanism in ZnO nanowire.
From the above discussions we can observe that surface of the nanowire is placing very cru-
cial role in photocurrent measurements, which provides scope to us to alter nanowire surface
by different methods such as surface passivation and compare their characteristics such as carrier lifetime with earlier measurements.

**Figure 4.5.** (a) Shows the schematic of the energy band diagram of ZnO nanowire in dark, indicating band bending and surface trap states. VB and CB are valence band and conduction band respectively. The bottom figure shows oxygen molecules adsorbed at the nanowire surface that capture free electrons from the nanowire conducting channel. (b) Upon UV illumination, photogenerated holes migrate to nanowire surface and get trapped, leaving behind unpaired electrons which contribute to photocurrent [5]

4.5. Photoresponse of ZnO Nanowire Photodetector

Figure 4.7 shows the photocurrent spectra recorded in air and vacuum, for a light intensity $4.4 \, \mu W/cm^2$ and an applied electrical bias of 100 mV. The photocurrent shows a sharp cut-off around 375 nm, corresponding to the energy band gap of ZnO nanowire. From the figure 4.6 Photo luminescence spectra on ZnO nanowire also reveals that band gap is 3.37 eV. Above the band gap energy (wavelengths below 375 nm), the photocurrent is almost
Figure 4.6. Photo luminescence shows that emission peak was strong at 370 nm which corresponds to energy of 3.35 eV constant in both air and vacuum. The photocurrent is negligible at higher wavelengths above 390 nm (the measured current is simply the dark current that exists as a result of the 100 mV electrical bias). The absence of photocurrent in this wavelength region is because the energy of light is not sufficient to excite the electrons to conduction band. So this high spectral selectivity combined with high photosensitivity shows the possibility of using ZnO wires as UV photodetectors. From figure 4.7 it is also evident that photocurrent of ZnO nanowire increase by about 4 times in magnitude when compared with dark room current and in vacuum the increase was about 9 times in magnitude which is because of increase in electron life time as explained earlier. The figure 4.7 also shows the spectral similarity of photocurrent measured in air and vacuum which indicates that same physical process is responsible for photoconduction.
Figure 4.7. Photocurrent spectra of ZnO nanowire obtained in air and vacuum with a light intensity of 4.4 $\mu W/cm^2$ and an applied bias of 100 mV.

In order to confirm that the photocurrent arises from the generation of electron and hole pairs that were produced as a result of light absorption, the variation of photocurrent and carrier generation rates with wavelength was plotted. Figure 4.8 shows the calculated generation rate vs wavelength and the measured photocurrent in air and vacuum. It is evident from this plot that the photocurrent in both air and vacuum arises from carriers that are generated as a result of photon absorption.

Responsivity [11] is one of the most important characteristics of photodetectors. It is defined as the ratio of electrical output to optical input. It is expressed in Amperes/Watt (A/W) of incident radiant power. Responsivity is a function of wavelength and the intrinsic properties of the material like its band gap. For this purpose spectral response measurements were done between the wavelengths of 300-420 nm under a applied bias of 100 mV.
Figure 4.8. Comparison of carrier generation rate with photocurrent spectra obtained from ZnO nanowires for various wavelengths (Intensity = 4.4 µW/cm²). The photocurrent plots are measured in air and vacuum at room temperature obtaining the spectral photoresponsivity spectrum, the intensity of incident radiation was kept constant at about 4.4 µW/cm² for all wavelengths of incident radiation. Responsivity (R) can be estimated from Figure 4.7, using the equation:

\[ R = \frac{I_{ph}}{P} \]  

The incident power (P) is determined by the equation:

\[ P = I_o(2RL) \]
where $I_o = 4.4 \times 10^{-6}$; $L = 20 \ \mu \text{m}$, and nanowire radius $R = 0.5 \times 10^{-5} \ \text{m}$ The detector responsivity is thus estimated to be $12.5 \times 10^4 \ \text{A/W}$

Figure 4.9 shows the responsivity spectrum obtained in both air and vacuum.

![Responsivity spectra of ZnO nanowire](image)

**Figure 4.9.** Responsivity spectra of ZnO nanowire obtained in air and vacuum with a light intensity of $4.4 \ \mu\text{W/cm}^2$ and an applied bias of $100 \ \text{mV}$

For the measured light intensity, the responsivity of the ZnO photodetector was extremely high, of the order of several kA/W. The reason for this high responsivity is the high photocurrent in the circuit.

4.6. Effect of UV light Intensity on Photoresponse of ZnO Nanowires

Photoconductivity of ZnO nanowire can be increased by increasing the intensity [12] of illuminating UV light. With increasing light intensity, more photons are absorbed by the nanowire, which causes an increase in the number of electron hole pairs generated. So
with increasing the intensity of UV light, the concentration of electron-hole pairs increases,
which leads to increase in excess electron density and hence an increase in the magnitude of
photocurrent. Figure 4.10 shows the intensity dependence of photocurrent of ZnO nanowire
for a applied bias of 100 mV for air and vacuum. As expected, the increase in photocurrent
is higher in vacuum than in air; attributed to longer lifetime of electrons in vacuum. As

![Graph showing the variation of photocurrent with intensity in air and vacuum.](image)

**Figure 4.10.** Variation of the photocurrent with the intensity of illumination
at 370 nm for a ZnO nanowire in air and vacuum

see in Figure 4.10, the increase in photocurrent with light intensity is not as significant at
higher intensities, which could be attributed to the presence of traps in the nanowire. More
detailed experiments are required to analyze this dependence.

4.7. Effect of Light Intensity on Rise and Fall Times of Photocurrent

It was also experimentally observed that the rise and fall-times of photocurrent in
the ZnO nanowire photodetector depended on the intensity [17] of illumination. Figure 4.11
shows the time response of photocurrent under different illuminated intensities. From the figure 4.11 we can observe that at higher intensities when UV light was turned ON, the photocurrent rises rapidly followed by a slow increase. When the light intensity is reduced, the rapid increase of rise-time of photocurrent decreases, while the slow increase of rise-time of photocurrent increases. The same trend follows for decay of photocurrent when UV light is turned off.

This dependence of rise and fall-times on light intensity can be explained by saturation of traps. When the intensity of light is high, more number of electron-hole pairs are generated. This could lead to a saturation condition where all the photogenerated holes will be trapped at the surface. At such high intensities, there is a possibility that a large number of un-trapped holes exist. Thus, the free holes will readily combine with the excess electrons and cause a rapid decrease in photocurrent when the light is turned OFF. However, when the surface is illuminated with lower light intensities, the number of generated electron-hole pairs will be lower, causing most of them to be trapped at the surface. Consequently, the excess electrons will remain available for photoconduction for a longer time. The sluggish response of photocurrent at lower light intensities is thus attributed to the trapping and de-trapping mechanism of holes when light is turned ON and OFF.

4.8. Time Dependent UV Photoresponse of ZnO Nanowires

The rise and fall-times of photoresponse provides important information about the surface of ZnO nanowires, which in turn controls the photoresponsivity. The desorption and re-adsorption of oxygen on the surface of nanowire mainly governs current rise and decay profile. Figure 4.12 shows that increase in magnitude of current is much higher in vacuum [8] than in air under illumination of same UV light that is $\lambda = 370\text{nm}$, Intensity $= 18.28\mu\text{W/cm}^2$ which can be explained with the consistent increase of electron life time under oxygen-deficient environments. From the figure 4.12 we can observe that when UV illumination was turned off, the time taken to reach the dark room current that is decay time is too long [20, 23, 8] in both cases and even much higher in vacuum which is attributed to a longer life time of electrons as explained before. Figure(4.12a) shows the response of
Figure 4.11. Variation of the time response of photocurrent with different intensities of illumination at 370 nm for a ZnO nanowire in air.

Photocurrent in air. Upon exposure to UV light, photocurrent rises rapidly followed by a slow increase reaching a steady state value in several minutes. However, when UV light is turned off, the current decays slowly [15, 8] following a short rapid decay. The current takes more than 120 min to return to dark value. A very different photoresponse is observed in vacuum. Figure( 4.12b) shows the response time of photocurrent in vacuum. Upon exposure to UV light, a short rapid photocurrent increase is observed followed by a slow increase, and photocurrent in vacuum is much higher than in air because of longer electron life time. When the UV light is turned off, the current follows a slow decay path because of the slow detrapping rate of holes. This difference in the photoresponse behavior of the ZnO nanowire in air and in vacuum is attributed to the fact that under vacuum the desorbed oxygen molecules are swept out of the cryostat, which causes the holes to be trapped for a longer
Figure 4.12. Time dependent photocurrent measurements. The light is characterized by: $\lambda=370$ nm, Intensity=$18.28 \mu W/cm^2$. The measurements are in:

(a) Air (b) Vacuum

time. The electrons are thus unable to recombine [1] with the holes and this leads to an increase in photocurrent and a very slow rate of decay to its dark value when the light is turned off.

4.9. Temperature and Surface Passivation Effects on Photoresponse of ZnO Nanowires

As seen in fig 4.12 the rise and fall time of photocurrent are influenced by the trapping/detrapping mechanism due to the presence of surface states on the nanowire surface. Figure (4.12a) shows two step relaxation process, which consists of an initial sharp drop in photocurrent followed by a slow decline. The fast drop in photocurrent relaxation is explained by the fast recombination of free electron-free hole pairs, and the slow relaxation of
The photocurrent is controlled by holes being detrapped (oxygen desorption) from the nanowire surface, followed by the free electrons recombining with the previously trapped holes. The primary goal of the experiment presented in this section was to reduce this slow relaxation time to make these ZnO nanowires useful in fast sensing applications. So we conducted the same time response measurements by varying the conditions such as temperature and also by modifying the nanowires by surface passivation by using \((NH_4)_2S\) solution which gives us best results for rise and decay times.

4.9.1. Effect of Temperature

Time dependent photoresponse measurements on ZnO nanowires were done by varying the temperature of the sample environment and illuminating the light (\(\lambda=370\) nm, Intensity \(I_o = 18.28\mu W/cm^2\)). The results are as shown in figure 4.13, which shows that the decay time reduces with increase in temperature and the magnitude of photocurrent is also reducing with temperature. This is because when the sample is heated, the carriers are thermally activated, which accelerates the trapping and de-trapping process as light was turned ON and OFF. At high temperatures, when the light is turned OFF for study of decay times, the holes that are trapped by surface states are released faster and they capture the free electrons, thus causing the photocurrent to decay at a faster rate at higher temperatures. The significant reduction in photocurrent could also be attributed to the fact that there might be thermally active traps within the band gap of ZnO, that captures the free electrons and reduces the magnitude of photocurrent.

4.9.2. Effect of Surface Passivation

The presence of surface states (adsorption of oxygen molecules) on the ZnO nanowire surface results in the long lifetime of photogenerated carriers and thus influences ZnO NW-based ultraviolet photodetectors. But the slow adsorption process also leads to slow detector response time. Here we show that \((NH_4)_2S\) solution is effective in passivating surface trap states of ZnO nanowires. As a result, ZnO nanowire photodetectors devices exhibit significantly improved response time. Figure 4.14 shows the rise and decay time for sample
Figure 4.13. Rise and decay times of photocurrent when light ($\lambda=370$ nm, Intensity=$18.28$ $\mu W/cm^2$) is incident on it. The photoresponse is studied as a function of temperature

Sample before and after passivation for 1 min, we can observe that after passivation the magnitude of current reduced drastically and the rise and decay times also reduced because of the passivation of surface traps by $(NH_4)_2S$.

4.10. Determination of Carrier Life and Transit Times

Since the ZnO nanowire is contacted by two Al electrodes and a bias of 100 mV is applied between the two electrodes, the electric field (E) between the ends of the nanowire can be estimated by using the equation: $E = \frac{V}{d}$ where $V$ is the applied voltage = 100 mV; and $d$ is the length of the channel = 20$\mu m$. Therefore $E = 50$ V/cm.

The minority carrier life time is given by formula $\delta n = G\tau$ where $\delta n$ is photo induced excess carrier concentration. The current density ($J$) where $J = \frac{I_{ph}}{A}$, where $A$ is the cross-
Figure 4.14. Time resolved UV light ($\lambda = 370\text{nm}, \text{Intensity} = 18.28\mu\text{W/cm}^2$) photoresponse of ZnO nanowires before and after passivation section. The performance of the ZnO photodetector is measured in terms of its Gain defined as: $\text{Gain} = \tau/t_{tr} = 2150$. This high gain is attributed to the high photocurrent and the presence of surface states in the ZnO nanowire.
4.11. Analysis of Rise and Fall Times of Photocurrent for Determination of Activation Energy

The temperature dependence of rise and fall times were analyzed to obtain activation energy. As seen in Figure 4.13 the rise and fall time curves could be fitted to a bi-exponential and from this two times $t_1$ and $t_2$ were extracted. The plot of $\ln(t_1)$ and $\ln(t_2)$ with $1/T$ is shown in Figure 4.15. From the slope, the activation energy was estimated by assuming a temperature activated mechanism and using the equation: $\text{Slope} = E_a/k$, where $k$ is Boltzmann constant.

**Figure 4.15.** Plot of $\ln t_1$ and $\ln t_2$ vs. $1/T$ for rise and fall times of photocurrent

The slow process in rise and the fast process in decay have similar activation energy.
Table 4.1. Activation energy estimated from temperature and intensity dependence of rise and fall times

<table>
<thead>
<tr>
<th>Process</th>
<th>Activation energy from $t_1$</th>
<th>Activation energy from $t_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rise</td>
<td>0.05 eV</td>
<td>0.27 eV</td>
</tr>
<tr>
<td>Decay</td>
<td>0.15 eV</td>
<td>0.23 eV</td>
</tr>
</tbody>
</table>

and so could be caused by the same process. This activation energy of 0.25 eV could be related to a shallow hole trap, which is temperature activated. Further experiments are required to confirm this fact.

4.12. Conclusion

This chapter focused on the fabrication and characterization of a ZnO nanowire based UV photodetector. The suitability of nanowires as photodetectors was demonstrated and they showed an extremely high responsivity of the order of several kA/W. The gain of the photodetector was estimated to be over 2000. The high gain is attributed to the presence of surface states which act as hole traps, thus increasing the magnitude of the photocurrent through the device. This work also shows the effect of temperature, light intensity and surface passivation on the measured photocurrent. Surface passivation is a promising strategy for the reduction or elimination of surface states. This result is therefore considered very encouraging, since it opens up the possibility of producing high speed, nano photo-detectors, which can detect light in the ultra-violet spectral region. Current-voltage measurements on a single ZnO nanowire in the presence and absence of UV light suggests its possible use as UV light detectors, sensors and switching devices for nanoscale optoelectronic applications.
CHAPTER 5

CAPACITANCE AND NOISE MEASUREMENTS ON ZNO NANOWIRES

Electrical and opto-electronic measurements on individual wires require that single nanowire to be contacted by metal electrodes. This requires lithography where patterns are made to the two ends of a single nanowire, followed by metalization. This is a time-consuming and very often difficult process. An alternative approach is to study the behavior of an array of nanowires, by contacting the entire array by a metal electrode. In this case, the system of parallel nanowires should be grown on a conducting substrate which serves as one of the electrode. Prior to deposition of the top electrode, the voids between the nanowires in the array of nanowires must be filled with a suitable dielectric. Such a device architecture has some principal advantages. Firstly, it makes electrical transport measurements much easier, avoiding the highly sophisticated technology of contact fabrication to individual nanowires. Secondly, it increases multi-fold the amplitude of various phenomena, such as current.

In this chapter, the transport measurements are extended to study the effect of device capacitance on applied bias as well as the effect of noise measured on a single ZnO nanowire. The CV measurements were made on an array of nanowires, since a single nanowire has extremely low capacitance.

5.1. Capacitance Measurements on ZnO Nanowire Array

ZnO nanowire array used in this experiment were grown on a highly doped $p^+$ substrate using CVD. On this vertically grown array, a thin layer of PMMA (poly methyl-methacrylate) was spin coated at 2000 rpm for 30 sec. The PMMA fills the voids between the nanowires, electrically isolates them and also provides mechanical support for the top electrode. the device thus consists of a dielectric medium (PMMA) embedded with nanowires. The spin rate and viscosity of the PMMA was adjusted such that after spin coating and drying the tips of the nanowires were exposed. Aluminum (Al) contact is evaporated on the top surface of this device, which functions as the top electrode making electrical contact to one end of an array of nanowires. The areal density of the ZnO nanowires is estimated by
SEM to be about 2-3 wires /µm². The bottom electrode is the heavily doped substrate. The dielectric thus insulates the top and bottom electrodes. Figure 5.1 shows the schematic of ZnO nanowire array device. In order to measure the capacitance of the array of nanowires at different frequencies, the bias voltage was varied between -10 V and +10 V. The measured capacitance has contributions from the dielectric as well as from the space charge region in the nanowires which varies as the bias is changed. Thus the total measured capacitance includes the capacitance between the substrate and the upper electrode and the contribution of nanowire array. ZnO nanowires are n-type which we concluded from the three terminal measurements in chapter 3. For n-type semiconductors, positive voltage at the top electrode corresponds to an accumulation of electric charge and negative voltage at top electrode corresponds to an depletion of electric charge. As the bias voltage was swept from -10 V to +10 V, the variation in capacitance of the nanowire array is shown in Figure 5.2.
Figure 5.2. Figure shows the capacitance dependence of applied bias at different frequencies

When the voltage applied to the top electrode is negative, the majority carriers (electrons) are pushed away from the negatively biased top electrode. Thus, there will be a higher concentration close to the highly doped Si substrate. Thus, under negative bias, the nanowires are depleted and acquire a space charge region beginning at nanowire tips and extending towards the substrate with increase in negative bias. When the applied voltage to the top electrode is positive, electron concentration will increase towards the top electrode and at large voltage bias, there is a tendency for saturation as most of the electrons are at the nanowire tip. It is thus concluded that for the n-type ZnO nanowire, a positive bias at the top electrode corresponds to an ‘accumulation’ of electric charge and a negative voltage at the top electrode corresponds to a ’depletion’ of electric charge in the nanowires.

Figure 5.2 also shows the frequency dependence of capacitance. As seen in this measurement, the capacitance is fairly unaffected at high frequencies. This is most likely due to the fact that when biased at high frequencies, the carriers do not have enough time to
redistribute. Figure 5.3 shows the capacitance dependence of frequency at fixed applied bias of 8V, from which we can notice the capacitance is decreasing with increase in frequency. From Figure 5.2, it is also noted that there exists a strong dispersion of capacitance at positive $V$, when the charge is concentrated mostly near the nanowire tips.

![Figure 5.3](image)

**Figure 5.3.** Figure shows the capacitance dependence of frequency at fixed bias voltage

5.1.1. Analysis of $C - V$ Plots at Positive and Negative Bias

When the voltage applied to the top electrode is negative, the space charge region within the nanowire extends from the nanowire tips toward the substrate. In the nanowire array, the nanowire length $L$ exceeds the separation $d$ between the nanowires. In this case, the mutual interaction between the nanowires becomes important and the capacitance can be estimated using the formula for Schottky layer in a bulk semiconductor with effective doping of $N n_0$, where $n_0$ is one-dimensional impurity density in the nanowire and $N \approx d^{-2}$ is the density of nanowires ref[25]. As the length of the space charge region ($l$) increases such
that as $l \to L$, $\Delta C \to 0$ at $V \approx -50 \, V$. With this approximation, the Schottky equation for the space charge region length can be written as

$$l = \left[ \frac{\varepsilon \varepsilon_0 V}{2\pi e N n_0} \right]^{1/2}$$

$\varepsilon$ is the dielectric constant of PMMA ($\sim 3.0$). Considering the length of the nanowires to be $\approx 10 \, \mu m$, Equation 33 gives $N n_0 = 1.34 \times 10^{13} \, cm^{-3}$. The areal density ($N$) of the array of nanowires is estimated to be $\approx 10^8 \, cm^2$. Hence, $n_0 \approx 10^5 \, cm^{-1}$, which corresponds to a non-compensated carrier density (due to defects) of $\sim 10^{15} \, cm^{-3}$.

When the voltage applied to the top electrode is positive, electron concentration in the nanowires increases and at large $V$, the situation approaches that of metallic nanowires considered theoretically in [2]. Strong frequency dispersion of capacitance is related to a finite time $\tau$ of recharging nanowires by the applied voltage. Thus, $\tau$ is the time of electron transport to the distance $L$. In the regime of strong accumulation, the equation for the time constant can be written as

$$\tau \approx \frac{L^2}{D},$$

where $D$ is the electron diffusion coefficient. The frequency dependence of capacitance shown in Figure 5.3 shows an absence of a frequency dispersion below 1 MHz. This would imply that $\tau \approx 10^{-6} \, s$. Using equation 34, the electron diffusion coefficient is $D \approx 1 \, cm^2/s$. Einstein’s equation, relating diffusion coefficient to mobility is expressed as

$$\mu = \frac{e D}{kT},$$

Using equation 35, the estimated electron mobility is in the range of $50 - 100 \, cm^2/Vs$. this value of mobility is lower than that calculated in Chapter 3 and is attributed to the fact that this is an averaged mobility taken over multiple ZnO nanowires, while the mobility
estimated from 3-terminal gate measurements is on a single ZnO nanowire and hence is more accurate. Carrier Density due to defect states in a ZnO nanowire array can also be calculated from the $\frac{1}{C^2}$ vs voltage plot as shown in the figure 5.4 as $2.20 \times 10^{15} cm^{-3}$ using the following equation.

$$n_o = \frac{-2}{q\epsilon_o(d/dV1/C^2)}$$

5.2. Conclusion

5.3. Low Frequency Noise Measurements on ZnO Nanowires

Low frequency noise measurements were carried out to in order to study the current fluctuation by examining the correlation bias and amplitude of the 1/f noise. Figure 5.5 shows the drain current vs noise spectrum of a ZnO nanowire two terminal device, when drain bias is increased the drain current increases which in turn leads to increase in drain
current noise [13, 27]. The 1/f noise in a nanowire may contain contributions from the interaction of carriers. According to Hooge’s empirical model, 1/f noise is given by

\[
S_I(f) = \frac{\alpha_H \times I_d^\beta}{f \times N}
\]

In the above equation \(I_d\) is the drain current, \(\alpha_H\) is Hooge’s constant, \(N\) is the total number of carriers and \(\beta\) is current dependent component. From this equation we can tell that noise increase with increase in drain current which is exactly what we observed from our noise spectra shown in figure 5.5

\[\text{Figure 5.5. Figure shows the noise dependence on applied bias voltage}\]

5.4. Conclusion

Chapter 5 focuses on the capacitance measurements on an array of free-standing ZnO nanowires. Capacitance-voltage measurements on the nanowire array gives an estimate of defect density in the nanowires and frequency dispersion of capacitance at low frequencies
could be attributed to the presence of deep level traps. Effect of applied bias on the capacitance of ZnO nanowire array is plotted at different frequencies explained. Mobility and carrier concentration are determined from the above data and compared with data obtained from chapter 3. Finally low frequency noise measurements on ZnO nanowires were explained.
6.1. Conclusions

The primary objective of my thesis was to synthesize high quality ZnO nanowires with controlled properties such as stoichiometric composition and physical dimensions with high yield and low cost. All these objectives were successfully achieved by synthesizing high quality ZnO nanowires by chemical vapor deposition using vapor-liquid-solid (VLS) growth mechanism, and also by solution based low temperature electrochemical deposition method. The as-grown nanowires were about 15–20 $\mu m$ long and had diameters in the range of 60 – 100 nm. In all cases, the nanowires had a Zn:O ratio of 1:1 at.wt%.

Following synthesis, the next objective (discussed in chapter 3), was to develop a high performance field effect transistor, to determine the electrical properties of ZnO nanowires and the transport phenomena. This was achieved by dispersing ZnO nanowires onto a heavily doped $p^+$ Si substrate covered with a 400 nm thick thermally grown $SiO_2$ layer. The doped silicon served as the back-gate electrode, while the $SiO_2$ layer served as the gate insulator. Following metallization (evaporating Al) of source and drain contacts at the two ends of single ZnO nanowire, the transport properties were determined. Using the nanowire in an FET type of configuration, the ZnO nanowires were found to exhibit n-type semiconducting behavior. From the analysis of results on the FET ZnO based device, the intrinsic ZnO nanowire parameters such as carrier concentration, transconductance and field effect mobility were determined to be $1.3 \times 10^{17} cm^{-3}$, 4.13 nS and $150 cm^2 V^{-1} s^{-1}$ respectively. Temperature dependent transport measurements in the temperature range from 80 K - 440 K showed that the conductivity increased with increase in temperature in the range from 80 k - 200 K. This increase in conductivity within the low temperature regime is a characteristic of semiconductors and is attributed to an exponential increases in carrier concentration with temperature. However, in the temperature range from 200 K - 440 K, a slight decrease in conductivity was observed. This decrease in conductivity at higher
temperatures is attributed to increased electron-photon scattering. In the low temperature regime, conduction was found to be thermally activated by an activation energy of 28 meV, attributed to the presence of Zn interstitials in the as-grown ZnO nanowires.

The final objective of this thesis work was to develop a high gain UV photodetector. This objective was achieved (discussed in chapter 4) by fabricating a ZnO nanowire photodetector which showed high responsivity and high gain of about 2000. The reasons for this high gain was successfully explained on the basis of the presence of surface states which acts as hole traps which increases the electron life time which ultimately leads to increase in photocurrent. The effect of temperature, light intensity, and surface passivation on the measured photocurrent was also studied and the results were successfully explained. Results indicate that as-grown wires when illuminated by UV light showed slow response in both air and vacuum, the response time was improved by passivation of sample with \((NH_4)_2S\) solution. From all the results discussed indicates the potential use of ZnO wires as high gain visible blind UV photodetectors.

In Chapter 5, measurements were done on a ZnO nanowire array. The array of vertical nanowires were grown on highly doped \(p^+\) substrate which served as the top electrodes; the bottom electrode was the heavily doped Si substrate. Prior to deposition of the top electrode, the voids between the nanowires in the array of nanowires were filled with a suitable dielectric (PMMA). Capacitance-voltage measurements were done on this nanowire array along capacitance-frequency measurements which were presented in this chapter along with low frequency noise measurements which gives us information about noise dependency on the applied bias.

Experiments described in this thesis establish a reliable way for synthesizing high quality ZnO nanowires along with n-type based FET. In this thesis we also developed an effective ZnO nanowire photodetector which yields very promising results, a step forward in the realization of nanowire photodetectors.
6.2. Future Work

In this thesis, growth and applications based on ZnO nanowires were discussed. Future work could include doping [29, 31] of ZnO nanowires with different metals followed by investigation of their electrical and opto-electronic properties. Doping will influence parameters like electrical conductivity, field effect mobility and carrier concentration. It is also possible to dope with p-type [31] and n-type dopant to create p-n junctions within the same nanowire. Thus single nanowires can function as diodes and an array of such p-n junctions can be used in the fabrication of light emitting diodes (LEDs).

This thesis analyzed photocurrent properties of single nanowires. Further research is required for a full understanding of the high photoconductive gain that was measured. The photoresponse properties of the nanowire array can also be investigated and a working device constructed. ZnO offers tremendous potential in future applications of electronic, optoelectronic, piezoelectric [24, 33] and magnetoelectronic [10] devices. There are still important issues which need to be further investigated, one key aspect is the growth of p-type ZnO nanowires and fabrication of nanoscale p-n junctions for electrically driven nano led or laser. Integration of ZnO nanostructured building blocks for large scale device applications is another important issue. Continuous effort is dedicated to achieve large arrays of programmable structures for building reconfigurable architectures. Room temperature ferromagnetism is another important area for future research in ZnO nanowires. Overall this thesis Encourages the progress on the research of nanostructured ZnO materials.


67


probed from zno nanowire films by photocurrent measurements, APPLIED PHYSICS LETTERS 86 (2005).


