SYNTHESIS OF ZINC OXIDE NANORODS: SEED LAYER ANNEALING EFFECT ON ELECTRICAL CONDUCTIVITY

YOUNAS IQBAL

A thesis is submitted in fulfillment of the requirement for the award of the
Doctor of Philosophy of Science

Faculty of Applied Sciences and Technology
Universiti Tun Hussein Onn Malaysia

APRIL 2018
I would like to dedicate this thesis to my beloved parents, brothers, sisters, wife and my daughter for their endless support and encouragement.
ACKNOWLEDGEMENT

All praise goes to Almighty ALLAH, the Most Gracious and the Most Merciful, who created the universe and appointed the man as His vicegerent. I offer humble thanks to ALLAH who blessed and give me the courage and power to complete this dissertation. All the blessing to His Prophet Muhammad (peace be upon him), who is the source of knowledge and guidance for humanity.

Special appreciation goes to my supervisor Assoc. Prof. Dr. Mohd. Kamarulzaki Mustafa for his supervision, and prestigious guidance, kindness, patience, constant motivation and supports during my entire educational journey. His invaluable help of constructive comments and suggestions throughout this work which have contributed to the success of this research.

Special thanks to my Mother and my Father for their immense support, love and prayers. I would essentially have not been able to achieve this noble goal without their kindness and prayers. I wish to express my appreciation for their love and affection on me in every aspect of life. I would like to express my profound admiration to my eldest Brother Javed Iqbal. It is impossible to describe in words how much you have done for me to go this far without your support. I can never forget his love and support for me even more than his children. I would like to acknowledge a valuable pat on my back of my brother Inam Iqbal and my sisters.

My sincere thanks go to Dr. Habib Shah who provided me the opportunity to start my PhD, Dr. Fazli Wadood and Haslinda Abdul Hameed who introduced me to UTHM and Malaysian lifestyle. Many thanks to my fellow lab mates Dr. Uzair Majeed and Dr. Mahmood Awual Adamu for berating and incented me all the times for my right track in the last 3 years.

These acknowledgements wouldn’t be completed without express my sincere appreciation to my wife Kulsoom Iqbal and daughter Afia Iqbal for their patience, support, cares and understanding.
Orientation of zinc oxide nanorods has a vital role in the performance of nanoscaled-based optoelectronic devices and biosensing. In spite of a lot of research, there is no clear mechanism for the growth and orientation of ZnO nanorods during hydrothermal deposition. Beside the other properties of ZnO nanorods the electron transport properties and electron conduction are very important, in successful immobilization of various biomolecules in the field of biosensing. In current study the orientated ZnO nanorods were fabricated through hydrothermal method from a lowest possible precursor concentration. The precursors concentration was varied from 1 to 9 mM at constant deposition time (6 hours) and temperature (90°C), on annealed (500°C) and un annealed gold seed layers. The mean square roughness of annealed and un annealed seed layers are 6.711 and 8.839 nm respectively. The morphological study of the prepared ZnO nanorods revealed a clear improvement in orientation of ZnO nanorods grown on annealed seed layer compared to un annealed seed layer. The structural characterization through XRD reveals that there is a clear peak (002) in all the concentrations on annealed seed layer. The elemental analysis showed the presence of zinc and oxygen in all concentration along with gold, which was detected from the glass substrate coated with gold. The FTIR analysis revealed very less number of bands for oriented ZnO nanorods compared to the un oriented nanorods. These analyses were confirmed by conductivity test conducting using four point probe, which shows the conductivity of oriented ZnO nanorods grown on annealed gold seed is very much higher (up to 90.909 S/m) than the un oriented ZnO nanorods (maximum value 11.574 S/m) grown on un annealed gold seed layer. From the results it is concluded that the seed layer roughness has a vital role in orientation of ZnO nanorods which has a good effect on the electrical conductivity of ZnO nanorods.
Orientasi zink oksida (ZnO) batang nano memainkan peranan penting berasaskan prestasi peranti optoelektronik dan nano pengesan bio. Penyelidikan kebanyakan tidak menunjuk mekanisma yang jelas untuk pertumbuhan dan orientasi ZnO batang nano semasa pemendapan hidroterma. Ppengangkutan elektron dan pengaliran elektron juga sangat penting dalam kejayaan imobilisasi terhadap biomolekul yang pelbagai di dalam bidang pengesan bio. Kajian semasa menunjukkan saiz ZnO batang nano yang direka melalui kaedah hidroterma daripada kepekatan prekursor yang terendah. Kepekatan prekursor adalah berbeza-beza daripada 1 sehingga 9 mM pada masa pemendapan yang berterusan (6 jam) dan suhu (90°C), suhu pemanasan haba (500 °C) dan tidak dipanaskan lapisan benih emas. Purata kekasaran lapisan yang licin dan tidak licin adalah 6.711 nm dan 8.839 nm. Kajian morfologi daripada penghasilan ZnO batang nano menunjukkan peningkatan yang jelas pada permukaan yang berhaba berbanding dengan lapisan benih yang tidak berhaba. Pencirian struktur melalui XRD mendedahkan bahawa terdapat puncak yang jelas (002) di semua kepekatan pada lapisan benih yang berhaba. Analisis unsur menunjukkan kehadiran zink dan oksigen pada semua kepekatan bersama-sama dengan saduran emas. Manakala, analisis FTIR menunjukkan jumlah jalur yang sangat sedikit berorientasi ZnO batang nano berbanding batang nano yang tidak berorientasi. Analisis ini telah disahkan oleh ujian kebolehaliran yang dijalankan menggunakan prob empat titik, yang menunjukkan kebolehaliran berorientasikan ZnO batang nano yang bertambah pada suhu pemanasan hababeni emas adalah lebih tinggi (sehingga 90.909 S/m) daripada tidak berorientasi ZnO batang nano (nilai maksimum adalah 11.574 S/m) yang dan tidak dipanaskan lapisan benih emas. Daripada keputusan ini dapat disimpulkan bahawa benih yang mempunyai lapisan kasar memainkan peranan penting dalam orientasi ZnO batang nano, di mana ia mempunyai kesan baik terhadap kebolehaliran elektrik.
# CONTENTS

<table>
<thead>
<tr>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>TITLE</td>
<td>i</td>
</tr>
<tr>
<td>DECLARATION</td>
<td>ii</td>
</tr>
<tr>
<td>DEDICATION</td>
<td>iii</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENT</td>
<td>iv</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>v</td>
</tr>
<tr>
<td>ABSTRAK</td>
<td>vi</td>
</tr>
<tr>
<td>CONTENTS</td>
<td>vii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>x</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xi</td>
</tr>
<tr>
<td>LIST OF SYMBOLS AND ABBREVIATIONS</td>
<td>xv</td>
</tr>
<tr>
<td>LIST OF PUBLICATIONS</td>
<td>xvii</td>
</tr>
</tbody>
</table>

## CHAPTER 1 INTRODUCTION

1.1 Nanotechnology and ZnO nanostructures  
1.2 Characteristics and crystal structures of Zinc Oxide (ZnO)  
1.3 Nanostructured Zinc Oxide  
1.4 ZnO nanorods synthesis techniques  
1.5 Problem Statement  
1.6 Objectives  
1.7 Scope of the study  
1.8 Outline of thesis

## CHAPTER 2 LITERATURE REVIEW

2.1 Introduction  
2.2 Synthesis of ZnO nanorods by chemical methods  
2.2.1 Synthesis of ZnO nanorods by hydrothermal method  
2.2.2 Alignment of ZnO nanorods  
2.3 Physical mechanism for nanorods growth
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.4</td>
<td>Applications of ZnO nanorods</td>
<td>29</td>
</tr>
<tr>
<td>2.5</td>
<td>Electrical properties of ZnO nanorods</td>
<td>31</td>
</tr>
<tr>
<td>2.6</td>
<td>Native point defects in ZnO</td>
<td>33</td>
</tr>
<tr>
<td>2.6.1</td>
<td>Surface defects</td>
<td>33</td>
</tr>
<tr>
<td>2.6.2</td>
<td>Point defects</td>
<td>34</td>
</tr>
<tr>
<td>2.6.3</td>
<td>Complex defects</td>
<td>36</td>
</tr>
<tr>
<td>2.7</td>
<td>Doping in ZnO nanorods</td>
<td>37</td>
</tr>
</tbody>
</table>

**CHAPTER 3 METHODOLOGY** | 39 |
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Introduction</td>
</tr>
<tr>
<td>3.2</td>
<td>Substrate cleaning</td>
</tr>
<tr>
<td>3.3</td>
<td>Seed layer preparation</td>
</tr>
<tr>
<td>3.4</td>
<td>Preparation of zinc oxide (ZnO) nanorods by hydrothermal method</td>
</tr>
<tr>
<td>3.5</td>
<td>Alignment of ZnO nanorods</td>
</tr>
<tr>
<td>3.5.1</td>
<td>Annealing of Cr/Au Seed layer</td>
</tr>
<tr>
<td>3.6</td>
<td>Temperature optimization</td>
</tr>
<tr>
<td>3.7</td>
<td>Optimization of deposition time</td>
</tr>
<tr>
<td>3.8</td>
<td>Characterization techniques</td>
</tr>
<tr>
<td>3.8.1</td>
<td>Field emission-scanning electron microscope</td>
</tr>
<tr>
<td>3.8.2</td>
<td>Energy dispersive x-rays analysis</td>
</tr>
<tr>
<td>3.8.3</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>3.8.4</td>
<td>Atomic Force Microscopy (AFM)</td>
</tr>
<tr>
<td>3.8.5</td>
<td>Fourier Transform infrared spectroscopy</td>
</tr>
<tr>
<td>3.8.6</td>
<td>Four point probe</td>
</tr>
</tbody>
</table>

**CHAPTER 4 RESULTS AND DISCUSSIONS** | 60 |
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>Introduction</td>
</tr>
<tr>
<td>4.2</td>
<td>Effect of precursors concentrations on surface microstructure</td>
</tr>
<tr>
<td>4.3</td>
<td>Elemental composition analysis</td>
</tr>
<tr>
<td>4.4</td>
<td>Effect of precursors concentrations on crystal structure</td>
</tr>
<tr>
<td>4.5</td>
<td>FTIR analysis</td>
</tr>
<tr>
<td>4.6</td>
<td>Electrical Conductivity Test</td>
</tr>
</tbody>
</table>
4.7 Effect Seed layer annealing on morphology of ZnO nanorods 72
4.8 Crystal structure 79
4.9 FTIR analysis 81
4.10 Electrical Conductivity 82
4.11 Effect of deposition time 83
4.12 Effect of deposition temperature 84

CHAPTER 5 CONCLUSION AND RECOMMENDATION 86
5.1 Conclusion 86
5.2 Future work 87

REFERENCES 88
VITA
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Comparison of percentage of surface atoms for Au nanoparticles</td>
<td>3</td>
</tr>
<tr>
<td>1.2</td>
<td>Summary of the various deposition and synthesis techniques to produce nanomaterials</td>
<td>4</td>
</tr>
<tr>
<td>1.3</td>
<td>Physical properties of bulk ZnO</td>
<td>8</td>
</tr>
<tr>
<td>2.1</td>
<td>Summary of different results and methods for aqueous solution growth of ZnO nanorods and nanowires adapted from (Weintraub, 2010)</td>
<td>23</td>
</tr>
<tr>
<td>3.1</td>
<td>Preparation and Characterization Techniques of ZnO Nanorods using Hydrothermal Method</td>
<td>44</td>
</tr>
<tr>
<td>4.1</td>
<td>Atomic percentage of Zn and O in ZnO at different concentrations</td>
<td>66</td>
</tr>
<tr>
<td>4.2</td>
<td>Lattice parameters and crystalline structure of ZnO nanorods</td>
<td>67</td>
</tr>
<tr>
<td>4.3</td>
<td>Conductivity of ZnO nanorods at various concentrations at un annealed seed layer</td>
<td>70</td>
</tr>
<tr>
<td>4.4</td>
<td>The surface roughness parameters of annealed and un- annealed seed layer by AFM</td>
<td>73</td>
</tr>
<tr>
<td>4.5</td>
<td>Atomic percentage of Zn and O and Au in ZnO at various concentrations</td>
<td>79</td>
</tr>
<tr>
<td>4.6</td>
<td>Lattice parameters and crystalline structure of oriented ZnO nanorods</td>
<td>80</td>
</tr>
<tr>
<td>4.7</td>
<td>The resistivity and conductivity results of ZnO nanorods on annealed seed layer at various concentrations</td>
<td>83</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

1.1 Schematic of top down and bottom up approaches 4
1.2 Crystalline forms of ZnO (a) Hexagonal wurtzite (b) Zinc blend (c) Rock salt (Ashrafi, 2007) 6
1.3 The hexagonal wurtzite of ZnO crystal structure 7
1.4 Number of publications on ZnO nano and gas or chemical sensor according to web of knowledge database 9
1.5 ZnO nanostructures. (a) Randomly distributed nanorods produced by hydrothermal process, (b) Flower like nanorods produced by hydrothermal process, (c) Vertically aligned nanorods produced by chemical vapor deposition process, (d) Hierarchical dendrites produced by vapor-phase transport process (Arafat et al., 2012). 10
2.1 The process of hydrothermal synthesis, reviling the importance of pressure and heat (Ngqondo, 2008) 19
2.2 Illustration of ZnO nanorods and its common facets of ZnO. 27
2.3 Oxygen vacancies in ZnO (a) 2 charge state (b) 1 charge state (c) 0 charge state 34
2.4 Substitutional defects in ZnO 35
2.5 Sulfur interstitial defects in ZnO 36
2.6 Zn interstitial in ZnO 37
3.1 Flow chart of synthesis, orientation and characterization of ZnO nanorods 40
3.2 Flowchart of summary 41
3.3 Ultrasonic cleaning apparatus (Power sonic 405, Hwashin, Korea)

3.4 Double Target Sputter Coater Used to Deposit Cr-Au seed layer

3.5 Preparation flowchart of zinc oxide (ZnO) nanorods by hydrothermal method.

3.6 Hydrothermal growth of ZnO nanorods in (a) pre-heating (b) Growth sample

3.7 Schematic process to obtain ZnO nanorods

3.8 A schematic of FESEM internal structure

3.9 Field emission- scanning electron microscopy (Mint-Src UTHM, 2017)

3.10 A schematic of EDX internal structure

3.11 A typical EDX spectrum of ZnO nanorods

3.12 A typical EDX spectrum of ZnO nanorods

3.13 A schematic of XRD equipment

3.14 X-ray diffracto-meter (Mint-Src UTHM, 2017)

3.15 A schematic of AFM

3.16 A typical 3D AFM image of annealed gold seed layer

3.17 Atomic force microscopy system (UTHM, 2017)

3.18 Schematic of Michelson Interferometer

3.19 Fourier Transform infrared spectroscopy (FTIR)

3.20 Schematic of four point probe setup

3.21 Four point probe

4.1 FESEM images of ZnO nanorods on un annealed seed layer synthesized at (a) 1 mM (b) 2 mM (c) 3 mM (d) 4 mM (e) 5mM (f) 6mM (g) 7 mM (h) 8mM (i) 9mM (50,000 magnification)

4.2 Low magnification FESEM images of (a) 4 mM (b) 5 mM (c) 6 mM (d) 7 mM (e) 8 mM (f) 9 mM (1000 Magnification)

4.3 EDX spectrum of ZnO nanorods synthesized at (a) 1 mM (b) 2 mM (c) 3 mM (d) 4 mM
4.4 EDX spectrum of ZnO nanorods synthesized at (a) 5 mM (b) 6 mM (c) 7 mM (d) 8 mM (e) 9 mM

4.5 Graphical representation of Zn and O atom with precursor concentration

4.6 X-ray diffraction patterns of ZnO nanorods various concentrations (1 -9 mM)

4.7 FTIR spectra of ZnO nanorods on un annealed seed layer at various precursors concentrations

4.8 Graphical representation of electrical conductivity of ZnO nanorods at various concentrations

4.9 AFM image of (a) un annealed (b) annealed seed layer

4.10 FESEM images of ZnO nanorods at annealed seed layer synthesized at (a) 1 mM (b) 2 mM (c) 3 mM (d) 4 mM (e) 5mM (f) 6mM (g) 7 mM (h) 8mM (i) 9mM. (50,000 magnification)

4.11 Surface morphology for 8mM at magnification (a) 1000x (b) 5000x (c) 10,000 (d) 25,000 (e) 50,000 (f) 100,000

4.12 Cross section image of ZnO nanorods at 8 mM precursor solution

4.13 EDX spectrum of ZnO nanorods grown on annealed gold seed layer synthesized at (a) 1 mM (b) 2 mM (c) 3 mM (d) 4 mM (e) 5mM

4.14 EDX spectrum of ZnO nanorods grown on annealed gold seed layer synthesized at (a) 6 mM (b) 7 mM (c) 8 mM (d) 9mM

4.15 Graphical representation of Zn, O and Au atom with precursor concentrations

4.16 X-ray diffraction patterns of ZnO nanorods various concentrations (1 -9 mM) at annealed seed layer

4.17 FTIR spectrum of ZnO nanorods at annealed seed layer various precursors concentrations

4.18 Graphical representation of electrical conductivity of oriented ZnO nanorods at various concentrations
4.19 FESEM images at 25,000 magnification at (a) 2 hours (3) hours (4) hours (5) hours

4.20 FESEM images at 25,000 magnification at (a) 50 °C (3) 60 °C (4) 70 °C (5) 80 °C
**LIST OF SYMBOLS AND ABBREVIATIONS**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Å</td>
<td>Angstrom</td>
</tr>
<tr>
<td>hν</td>
<td>Photon energy</td>
</tr>
<tr>
<td>β</td>
<td>Temperature coefficient</td>
</tr>
<tr>
<td>µm</td>
<td>Micrometer</td>
</tr>
<tr>
<td>GaN</td>
<td>Gallium nitride</td>
</tr>
<tr>
<td>SiC</td>
<td>Silicon carbide</td>
</tr>
<tr>
<td>Gv</td>
<td>Gibb's free energy</td>
</tr>
<tr>
<td>Si</td>
<td>Silicon</td>
</tr>
<tr>
<td>Gs</td>
<td>Surface energy</td>
</tr>
<tr>
<td>r*</td>
<td>Critical radius</td>
</tr>
<tr>
<td>k</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>J</td>
<td>Rate of nucleation</td>
</tr>
<tr>
<td>Au</td>
<td>Gold</td>
</tr>
<tr>
<td>Ef</td>
<td>Formation energy</td>
</tr>
<tr>
<td>Cr</td>
<td>Chromium</td>
</tr>
<tr>
<td>meV</td>
<td>Mega electron volt</td>
</tr>
<tr>
<td>Gpa</td>
<td>Gaga Pascal</td>
</tr>
<tr>
<td>F</td>
<td>Mechanical force</td>
</tr>
<tr>
<td>P</td>
<td>Polarization</td>
</tr>
<tr>
<td>α</td>
<td>absorption co-efficient</td>
</tr>
<tr>
<td>λ</td>
<td>Wavelength</td>
</tr>
<tr>
<td>GaN</td>
<td>Gallium nitride</td>
</tr>
<tr>
<td>SiC</td>
<td>Silicon carbide</td>
</tr>
<tr>
<td>Si</td>
<td>Silicon</td>
</tr>
<tr>
<td>GOx</td>
<td>Glucose oxidase</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Resistivity</td>
</tr>
<tr>
<td>$\Omega$</td>
<td>Ohm</td>
</tr>
<tr>
<td>Min</td>
<td>Deepest peak value</td>
</tr>
<tr>
<td>Max</td>
<td>Highest peak value</td>
</tr>
<tr>
<td>Rpv</td>
<td>Peak to valley value</td>
</tr>
<tr>
<td>Rq</td>
<td>Root mean square roughness</td>
</tr>
<tr>
<td>Rz</td>
<td>Ten point average</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Absorption coefficient</td>
</tr>
<tr>
<td>W</td>
<td>Tungsten</td>
</tr>
<tr>
<td>WC</td>
<td>Tungsten carbide</td>
</tr>
<tr>
<td>Os</td>
<td>Osmium</td>
</tr>
<tr>
<td>Eg</td>
<td>Energy band gap</td>
</tr>
<tr>
<td>mM</td>
<td>Millimolar</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>FESEM</td>
<td>Field emission scanning electron microscopy</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray diffraction</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometer</td>
</tr>
<tr>
<td>PVD</td>
<td>Physical vapor deposition</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra-Violet</td>
</tr>
<tr>
<td>Eg</td>
<td>Energy band gap</td>
</tr>
<tr>
<td>MOCVD</td>
<td>Metal organic chemical vapor deposition</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive x-rays spectroscopy</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>HMT</td>
<td>Hexamethylenetetramine</td>
</tr>
<tr>
<td>VLS</td>
<td>Vapor liquid solid</td>
</tr>
<tr>
<td>RMS</td>
<td>Root mean square</td>
</tr>
<tr>
<td>US $</td>
<td>United states dollar</td>
</tr>
<tr>
<td>MBE</td>
<td>Molecular beam epitaxy</td>
</tr>
<tr>
<td>PZT</td>
<td>Lead Zirconium titanate</td>
</tr>
<tr>
<td>NRs</td>
<td>Nanorods</td>
</tr>
</tbody>
</table>
LIST OF PUBLICATIONS


CHAPTER 1

INTRODUCTION

1.1 Nanotechnology and ZnO nanostructures

In 1959 Richard Feynman of California Institute of Technology delivered a lecture what is considered to be the first lecture on technology and engineering at the atomic scale. In his lecture he mentioned that “there is plenty of room at the bottom” suggesting manipulating things at the atomic level (Feynman, 1960). Feynman pointed out that there was a real possibility to design materials by manipulating individual atoms, as it would not violate any physical laws.

Nowadays this lecture is referred to as the origin of nanotechnology paradigm. However, because of the restriction in equipment capability, the boost of nanotechnology was observed in 1900s. In this decade, the, sophisticated equipment’s such as scanning electron microscope, X-ray diffraction, atomic force microscopy and etc. have become more available for scientists to explore nanoworld. The word “nanotechnology” was first introduced by N. Taniguchi in 1974 at an international conference on industrial production in Tokyo in order to describe the super thin processing of materials with nanometer accuracy and the creation of nanosize mechanism. In the second half of 1980s and the early 1990s important discoveries and inventions were made which created an essential impact on the further development of
nanotechnology. Since then a number of publications on nanotechnological subjects and practical application of nanotechnology expanded sharply.

Fundamentally nanotechnology is the study of producing and operation of typical functional materials, devices and systems that fall in the range of 1-100 nm (Wang, 2005). In other words nanotechnology is a field of applied science that deals with synthesis, designing, characterization and application of nanoscale devices and materials (Abeer, 2012). Materials show a remarkable change in their fundamental properties (electrical and thermal conductivities, absorbance, photoluminescence, mechanical etc) when they are engineered at the nanoscale (Dubbaka, 2008). This is because of two major influences (i) high surface to volume ratio and (ii) quantum effects. High surface to volume ratio means that there will be a significant friction of atoms at the surface of the materials, which affects the electrical and mechanical properties, and high surface reactivity (Sirelkhatim, 2015), whereas the quantum effect is the confinement of charge carrier motion in small volume of material which affects the optical, electrical, magnetic, and thermoelectric properties of the materials (Gabrielyan, 2013). For example, opaque substance becomes transparent (copper); insulators become conductors; solids turn into liquids at room temperature (gold); and stable material turns into unstable materials (aluminum) (Yu, 2009). The electronic and optical properties of nanomaterials could be modified by modifying the charge carrier density and band structure in different way from their bulk counterpart. Nanoscale designing varies material’s macro and microscopic properties such as charge capacity, magnetization, and melting temperature with unchanged chemical composition (Mathews, 1978). This means that as the particle size decrease the number of active atoms on the surface is significantly increase as shown in Table 1.1 (Chang, 2013; Hostetler, 1998).

In recent years a tremendous amount of research efforts has gone towards studying synthesis, fundamental properties, manipulation, characterization, device fabrication and testing. These new materials have a vital role and applications in industry sectors including medicines, security, transport energy and communication.

In year 2006, an estimated US $50 billion worldwide were amalgamated for nanotechnology, and was expected to reach US$1-2.6 trillion until 2011-2016. It is projected that the production of nanoparticles will increase from the estimated 2,300 tons today to 58,000 tons by 2020. Therefore, it is believed that nanotechnology will ultimately affect what the people eat, how they communicate, how long they live and
how they work. It will change their energy sources, medical care, water and environment (Schaefer, 2010).

Table 1.1: Comparison of percentage of surface atoms for Au nanoparticles

<table>
<thead>
<tr>
<th>Particle radius (nm)</th>
<th>Total number of atoms</th>
<th>Percentage of surface atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.65</td>
<td>79</td>
<td>76</td>
</tr>
<tr>
<td>0.71</td>
<td>116</td>
<td>67</td>
</tr>
<tr>
<td>0.81</td>
<td>140</td>
<td>69</td>
</tr>
<tr>
<td>0.87</td>
<td>201</td>
<td>64</td>
</tr>
<tr>
<td>0.98</td>
<td>225</td>
<td>62</td>
</tr>
<tr>
<td>1.10</td>
<td>309</td>
<td>52</td>
</tr>
<tr>
<td>1.20</td>
<td>459</td>
<td>51</td>
</tr>
</tbody>
</table>

Nanotechnology is considered to be the next industrial revolution and will cause tremendous impacts on the society, economy, and generally in future. It has wide applications in biotechnology, medicine, information technology, material technology, manufacturing, energy production and storage, instrumentation, environmental applications and security (Aneesh & Jayaraj, 2010).

In the world of nanotechnology, there are two schemes for making nanostructures and devices: Top-down approach and bottom-up approach. In top-down approach a bulk piece of material is divided and subdivided until it finally falls in the nanometer regime, whereas in bottom-up approach is building of a material from the bottom, i.e. self-assembly of atoms and molecules into nanostructure: atom-by-atom, molecule-by-molecule or cluster-by-cluster. The schematic of top down and bottom up approaches are shown in Figure 1.1. These various techniques are summarized in Table 1.2 (Khan, 2012). By comparing bottom-up and top-down techniques, the bottom-up techniques are far preferable as they exceed the limits of top-down technology regarding future applications, therefore the bottom up approach should be utilized as it is capable of producing nanoscale features (Wan, 2011). The other superiority of bottom-up approach over the top down is in terms of photolithography and is capable of producing variety of nanostructures with high yield, less defect and better range ordering, and is the reason that ZnO nanostructures fabricated through bottom-up approach possessed unique physical, electrical and optical properties which are highly applicable for downstream applications (Perumal, 2016).
Table 1.2: Summary of the various deposition and synthesis techniques to produce nanomaterials

<table>
<thead>
<tr>
<th>Serial No.</th>
<th>General techniques</th>
<th>Sub techniques</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Physical vapor deposition (PVD) methods</td>
<td>Magnetron sputtering, Thermal evaporation, Pulse laser deposition, Radio-frequency, Resistive, Focused ion beam, RF induction, Electron beam, Sputtering</td>
</tr>
<tr>
<td>2</td>
<td>Chemical vapor deposition (CVD) methods</td>
<td>Plasma-enhanced CVD, Thermal CVD, Metal-organic CVD, Low-pressure CVD, Molecular Beam Epitaxy (MBE), Atomic layer deposition</td>
</tr>
<tr>
<td>3</td>
<td>Solution based synthesis</td>
<td>Sonochemical method, Sol-gel chemical process, Hydrothermal/solvothermal method, Micro-emulsion method, Co-precipitation, Template-assisted synthesis</td>
</tr>
<tr>
<td>4</td>
<td>Electrochemical synthesis</td>
<td>Electrochemical deposition, Electrophoretic deposition</td>
</tr>
<tr>
<td>5</td>
<td>Physical methods</td>
<td>High energy ball milling process</td>
</tr>
</tbody>
</table>

![Figure 1.1: Schematic of top down and bottom up approaches](image-url)
1.2 Characteristics and crystal structures of Zinc Oxide (ZnO)

ZnO is a wide direct band gap (3.37 eV) and a large exciton binding energy (60meV) semiconducting material at room temperature (Zhang., 2012). Materials are considered to be wide band gaps if their band gap energy is incomparably greater than that of common semiconductors like silicon (1.1 eV), and gallium arsenide (1.4 eV) (Yoder, 1996). The advantage of wide band gap material is that they are more efficient in high power and high temperature applications and can withstand high power because the electric breakdown voltage for wide band gap materials tends to be much higher (Rahmani, 2010). Furthermore, the large exciton binding energy (60 meV) than the thermal energy (25meV) at ambient temperature is responsible for stable electron-hole pair recombination, which paves a good way for the good luminescence behavior of ZnO (Lv et al., 2007).

Due to the large difference in electronegativity value (Zn=1.65, O= 3.44) the bonding between Zn atoms and O atoms is highly ionic (Jagadish & Pearton, 2011). ZnO belongs to II-VI semiconducting-materials and is found in two crystalline forms i.e hexagonal wurtzite and face centered cubic. In stable state ZnO usually exists in wurtzite while it can be turned into the zinc blend and rock salt phase by applying appropriate growth conditions (Alghamdi & Alzahrani, 2013). The rock salt phase of ZnO gives a smaller equilibrium volume than wurtzite phase because of the more tightly packed atoms in rock salt phase. In these crystalline structures, each anion is surrounded by cations at the corners of tetrahedrons. Each oxygen anion is surrounded by four zinc cations at the corner of the tetrahedron, and vice versa (Carpenter et al., 2012). There is a case when ZnO crystallizes in rocksalt structure when exposed to high pressure condition. Under compression at high pressure relatively 5-7Gpa, the lattice parameters reduce due to the interionic coulombic interaction to favor the iconicity more over the covalent nature and the wurtzite crystal structure transfer to the rock-salt type structure (Solozhenko et al., 2011). The rocksalt structure cannot be stabilized by the epitaxial growth (Morkoç, 2008). The zinc blende structure has lower iconicity as compared to the wurtzite structure and leads to lower carrier scattering and higher doping efficiencies (Ashrafi, 2007). Wurtzite is the more stable structure than rocksalt and zincblende, and it has been found theoretically that this crystal structure
is energetically more favorable in comparison to the other two structures. All these structures are shown in Figure 1.2.

![Diagram of ZnO crystalline forms](image)

Figure 1.2: Crystalline forms of ZnO (a) Hexagonal wurtzite (b) Zinc blend (c) Rock salt (Ashrafi, 2007)

The structure of ZnO consists of alternating planes composed of tetrahedrally coordinated O-2 and Zn+2 stacked alternately along C-axis (Wang, 2004). Its structure is formed by alternating planes of tetrahedrally coordinated O-2 and Zn+2 ions along the c-axis as shown in Figure 1.3, which makes the entire structure without central symmetry, which result in a piezoelectric effect by which a mechanical stress/strain can be converted into electrical voltage, owing to the associative displacement of cations and anions in the crystal (Wang, 2008). Due to the specific distribution of cation (Zn2+) and anions (O2-) the entire unit cell of ZnO is neutral,
some surfaces are terminated entirely with cations or anions (Bing et al., 2014), which leads ZnO possesses positively or negatively charged on the surface (Birkholz, 2006).

Figure 1.3: The hexagonal wurtzite of ZnO crystal structure

The wurtzite structure of ZnO consists four common surfaces; two of them are polar i.e Zn (001) and O (00-1) whose faces are terminated along c-axis and two are non polar i.e (11-20) and (10-10) faces. The non polar surfaces possess an equal number of Zn and O atoms (Ali, 2012). The primitive translation vectors a= 0.3249 nm and b=0.3249 nm lay in the X-Y plane are of equal length and include angle of 120˚ while c=0.5206 nm is parallel to z-axis. The other possible lattice parameters of the hexagonal unit cell obtained in various methods range from 0.32475-0.32501 nm for “ a” and from 0.52042-0.52075 nm for “ c” (at room temperature) (Ramashia, 2015). ZnO has a high melting point 1975 °C which determine its high thermal and chemical stability. The other properties of ZnO (bulk) are given in table 1.3. The conduction band minima and valance band maxima appear at the same axis Brillouin zone, indicating that ZnO is direct semiconducting material (Tobin, 2005). The direct and wide band gap properties also suggest that ZnO may have a high breakdown voltage and may have lower noise which can be used in high-temperature and high-power applications. The number of articles published on ZnO has been increasing every year and in 2007-2008 and ZnO becomes the second popular semiconductor after Si due to improvements in growth related techniques of single crystalline ZnO.
Table 1.3: Physical properties of bulk ZnO

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>5.67526 g/cm³</td>
</tr>
<tr>
<td>Molecular mass</td>
<td>81.389</td>
</tr>
<tr>
<td>Point group</td>
<td>6 mm (Wurtzite)</td>
</tr>
<tr>
<td>Lattice constants at room temp.</td>
<td>a=3.250Å, c=5.205Å</td>
</tr>
<tr>
<td>Melting point</td>
<td>2250K</td>
</tr>
<tr>
<td>Electron mass</td>
<td>0.28</td>
</tr>
<tr>
<td>Hole mass</td>
<td>1.8</td>
</tr>
<tr>
<td>Band gap energy at room temperature</td>
<td>3.37 eV</td>
</tr>
<tr>
<td>Exciton binding energy</td>
<td>60 meV</td>
</tr>
<tr>
<td>Specific heat</td>
<td>0.125 cal/gm</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>0.006 cal/cm/K</td>
</tr>
<tr>
<td>Thermoelectric constant at 573 K</td>
<td>1200 mV/K</td>
</tr>
</tbody>
</table>

1.3 Nanostructured Zinc Oxide

Zinc oxide is a compound semiconductor which consists of Zn+2 and O-2. Zinc belongs to group II of transition metals and oxygen to group VI element; therefore, it is called a metal oxide semiconductor. The nanostructured materials have been broadly studied due to their potential uses in fabricated micro and nanoscale devices. Since the discovery of carbon nanotubes in 1911 many experimental and theoretical investigations have been conducted on nanoscale ZnO such as nanowires, nanorods and nanotubes (Iijima, 1991). Nanostructured ZnO has a large surface to volume ratio that can be used to enhance the performance of devices. As the sizes are reduced, devices become faster. The reduction in size also contributes to the quantum confinement phenomenon. Quantum confinement traps electrons in a small area in such a way that controlling the moment of electron in particular direction becomes easier. Confinement of electrons within the small-sized material also renders the band gap tunable; additionally, confinement increases the optical bandgap and promotes a faster operation speed (Lu et al., 2006). Nanostructured ZnO has achieved particular consideration due to its distinguished performance in photonics, optics and electronics, ZnO is the richest nanostructured material, i.e can be formed in nanocomb, nanorings, nanospring/nanohelix, nanobelt, nanowires and nanocages form (Wang, 2004).
ZnO is a unique material and it is extensively researched by scientists for its potential in a wide range of applications such as dielectric, piezoelectric, pyroelectric, plate panel display sensor devices, field effect transistors and ultraviolet light emitting devices (Kim, 2011). In nanostructured form ZnO has been researched extensively over the past few decades due to their exclusive properties compared to its bulk form. Nanostructured ZnO consists of the structures with diameter not more than 100nm (Pei et al., 2009). A lot of nanostructures were produced by scientists; however, it cannot be determined that which nanostructure is best for electronic, optoelectronic device applications (Buhro & Colvin, 2003). From 1960, synthesis of ZnO thin film has been an active field because of their applications as sensors, transducers and catalysts. In Figure 1.4 the research studies available over the previous year’s regarding ZnO nanomaterial indicates that among the other nanomaterials ZnO is the most attractive and its applications in chemical/gas sensors is substantially increased (Galstyan, et al., 2016).

![Figure 1.4: Number of publications on ZnO nano and gas or chemical sensor according to web of knowledge database](image)

The distinctive properties of 1-D ZnO nanostructures grant a promising combination for chemical selectivity electrochemically and chemically tunable platform is crucial for tailor sensor response. For that reason, 1-D ZnO nanostructure NRs/NWs are comprehensively applied in a variety of sensing applications e.g biomarkers, biosensors, chemical sensors, gas sensors, humidity sensors, pH sensors pressure/force/load sensors and UV sensors. In the last few decades nanotechnology
REFERENCES


Chithra, M. J., Sathya, M., & Pushpanathan, K. (2015). Effect of pH on crystal size and photoluminescence property of ZnO nanoparticles prepared by chemical


properties of ZnO nanowires. Journal of Alloys and Compounds, 467(1), 342-346.


Ram, S. G., Ravi, G., Manikandan, M., Mahalingam, T., & Kulandainathan, M. A. (2011). Controlled hydrothermal growth of ZnO nanostructures by sequestering the Zn metal ions with the chelating agent EDTA. Superlattices and Microstructures, 50(4), 296-302.


Weintraub, B. A. (2010). One-dimensional zinc oxide nanomaterials synthesis and photovoltaic applications: Georgia Institute of Technology.


