



OPTIMISATION OF ZnO NANORODS FOR IMPROVED CARRIER EXTRACTION IN ORGANIC-
INORGANIC HYBRID PHOTOVOLTAIC CELLS

By

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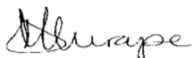
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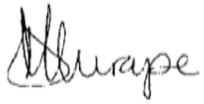
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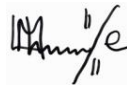
CERTIFICATION

The undersigned certifies that he has read and hereby recommends for acceptance by the Faculty of Science a dissertation titled: **OPTIMISATION OF ZnO NANORODS FOR IMPROVED CARRIER EXTRACTION IN ORGANIC-INORGANIC HYBRID PHOTOVOLTAIC CELLS**, in fulfilment of the requirements for the degree of Master of Science (*Physics*) of the Botswana International University of Science and Technology.



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DEDICATION

This research work is dedicated to my family and close friends.

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LIST OF ABBREVIATIONS

1 D: One Dimension

Å: Angstrom

Al₂O₃: Aluminium Oxide

BHJ: Bulk Heterojunction Polymer

BPC: Botswana Power Corporation

CBD: Chemical Bath Deposition

CeO₂: Cerium (IV) Oxide

D: Crystallite size

DSSCs: Dye-sensitized solar cells

EDX: Energy Dispersive X-ray Spectroscopy

E_g: Band Gap

eV: Electron Volts

Fe₂O₃: Iron (III) Oxide

FOM: Figure of Merit

FWHM: Full Width at Half Maximum

GaAs: Gallium Arsenide

hrs: Hours

In₂O₃: Indium (III) Oxide

k: Extinction coefficient

K: Kelvin

LED: Lower Electron Detector

LO: Longitudinal Optical

ml: Millilitres

mm: Millimeters

mM: Millimolar

MOCVD: Metal–Organic Chemical Vapor Deposition

n: Refractive index

Nb₂O₅: Niobium Pentoxide
OPV: Organic Photovoltaics
P3HT: Poly(3-hexylthiophene)
PCBM: [6,6]-phenyl-C61-butyric acid methyl ester
PCE: Power Conversion Efficiency
PSCs: Perovskite cells
PV: Photovoltaic
SADC: South African Development Community
SEM: Scanning Electron Microscopy
Si: Silicon
SILAR: Successive Ionic Layer Adsorption and Reaction
SnO₂: Tin (IV) Oxide
SrTiO₃: Strontium Titanate
TCO: Transparent Conductive Oxide
TiO₂: Titanium Dioxide
TO: Transverse Optical
USP: Ultrasonic Spray Pyrolysis
WO₃: Tungsten Trioxide
XRD: X-ray Diffraction
ZnO: Zinc Oxide
 δ : Dislocation Density
 ϵ : Strain
 ϵ_1 : Real dielectric constant
 ϵ_2 : Imaginary dielectric constant
 λ : Wavelength
 ρ : Electrical resistivity
 σ : Stress

RESEARCH OUTPUT

Publication

1. **K. Mosalagae**, D. M. Murape, L. M. Lepodise. Effects of growth conditions on properties of CBD synthesized ZnO nanorods grown on Ultrasonic Spray Pyrolysis deposited ZnO Seed Layers. **Submitted to Heliyon Journal (Elsevier) and accepted 10 July 2020.**
2. **Koketso Mosalagae**, Davison M. Murape. Potential for solar dryer application for food processing in Botswana. **Submitted to BIUST Research Innovation Symposium (RDAIS 2017) and published.**
<https://drive.google.com/file/d/0B1Jc4P8baYEPVGlicm94b2F4UE0/view?usp=sharing>

Conference Presentations

3. **K. Mosalagae**, D. M. Murape, L. M. Lepodise, Z. N. Urgessa. “ZnO nanorod structures grown by chemical bath deposition on a seed layer prepared by a successive ionic layer adsorption and reaction (SILAR) method” at the 9th International Conference of African Materials Research Society (AMRS), Gaborone, Botswana from 11th – 14th of December 2017.
4. **K. Mosalagae**, D. M. Murape, L. M. Lepodise. “Synthesis of ZnO nanorods by Chemical Bath Deposition on ZnO seed layers deposited by Ultrasonic Bath Deposition”, NANOSMAT-AFRICA 2018 International Conference on Surfaces, Coatings and Nanostructured Materials, Cape Town, South Africa from 19th -23rd November 2018.
5. **Koketso Mosalagae**, Davison M. Murape. “Potential for solar dryer application for food processing in Botswana”, at the BIUST Research Innovation Symposium (RDAIS 2017), Botswana International University of Science and Technology, Palapye, Botswana from 12th – 14th of June 2017.

ABSTRACT

Zinc Oxide (ZnO) is a promising semiconductor material suitable for the application in electronic and optoelectronic systems. ZnO tailored into nanorods has a potential to be used in photovoltaic cells due to its large surface area to volume ratio that allows for maximum light harvesting and improved electron transportation efficiency. ZnO nanorods that are less compact, thin and long with fewer defects can be used for organic/inorganic solar cells application. In this study chemical bath deposition (CBD) was used to grow ZnO nanorods on a glass substrate coated with a seed layer. The seed layer was deposited using the ultrasonic spray pyrolysis (USP) technique prior to growth of nanorods. The influence of seed layer thickness on the alignment, distribution and homogeneity of the subsequently grown nanorods was explored. A KLA Tencor D-100 surface profilometer was used to measure the seed layer thickness. The effects of varying the growth time, temperature and precursor concentration on the morphological, structural, optical, vibrational and electrical properties of the subsequently grown nanorods were explored. X-ray diffraction (XRD) revealed structural properties under different growth parameters. Scanning Electron Microscopy (SEM) was used to observe the arrangements, distribution and uniformity of the ZnO nanorods as the growth conditions were varied. Confirmation of Zn and O elements in the seed layers and nanorods was done by Energy Dispersive X-ray Spectroscopy (EDX). UV/Vis/NIR spectrophotometer measurements revealed an optical transmittance of between 50 – 70 % for the nanorods. Optical properties such as the band gap (E_g), the extinction coefficient (k), the refractive index (n), and the real (ϵ_1) and imaginary (ϵ_2) dielectric constants were derived from the transmittance spectra. Raman spectroscopy results confirmed the presence of phonon modes belonging to the hexagonal ZnO phase in consistency with the XRD results. The Four Point Probe set up was used to determine electrical resistivity (ρ) and figure of merit (FOM) of the grown nanorods. This work shows that the orientation, structural, optical, vibrational and electrical properties of the grown nanorods are controlled by alteration of the growth parameters. Well aligned, less compact and long ZnO nanorods with high aspect ratio suitable for working as a photoanode in solar cells were obtained under optimized growth conditions of: a precursor concentration of 25 mM, bath temperature of 90 °C and growth time of 2 hrs.

CHAPTER 1: INTRODUCTION

1.1 Overview of solar technology

The need for clean renewable energy options all over the world is uncontested. Whilst notable advances have occurred in the area of green renewable energy sources such as photovoltaic (PVs), wind, biomass, biogas and solar thermal, these technologies have remained on the periphery when it comes to utilization compared to the conventional/traditional energy resources because of challenges like low efficiencies, the sophistication of technologies and low acceptance levels [1].

It is prudent to keep increasing the impetus of attempts to increase efficiency whilst making renewable energy technologies cheaper to compete economically with their up until now cheaper fossil fuels counterparts. Solar energy has the potential to be the ultimate energy source of choice to solve the energy and environment nexus challenge that threatens to destroy mother earth through global warming [2].

The sun as we know, has a life span of billions of years [3] and it is therefore an inexhaustible source of clean energy. Solar PV and solar thermal technologies are capable of converting solar energy into electrical and heat in pollution free processes that will not harm the environment.

Solar cells are semiconductor devices known to convert energy of sunlight to electrical energy via the PV effect. Although many devices that utilize the PV effect have technologically advanced over the past five decades [2, 4], two major challenges that have impeded their use are lower conversion efficiency and higher cost compared to their fossil fuel counterparts [5]. Figure 1.1 shows the progress in solar conversion efficiencies of different solar cells.

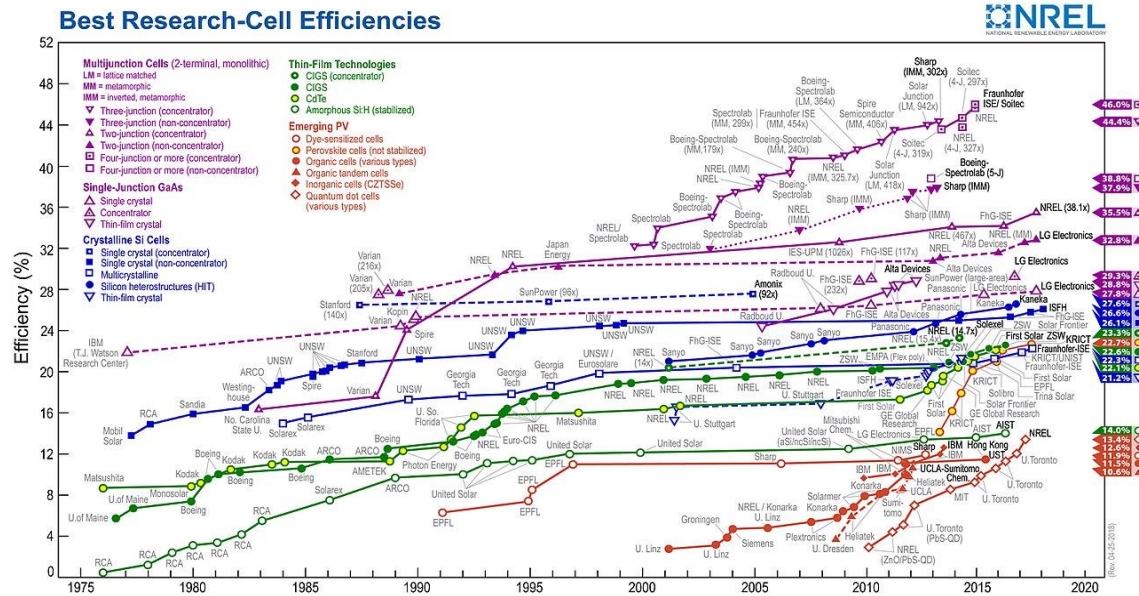


Figure 1.1: The progression of conversion efficiencies of different solar devices [6].

The bedrock of PV devices is a solid state single crystal solar cell which was invented some half a century back and currently constitutes 94 % of the PV market [7]. Solid state solar cells work by using the principle of p–n junctions designed from the p-type and n-type semiconductors. The photogenerated electrons and holes at the p–n junction interface are swept away from the junction by the electrical field across it, then routed through external circuits. The conversion efficiency of solar cells made of single crystalline silicon (Si) is around 25 % in commercial designs [8].

Poly-crystalline, amorphous Si [9] and compound semiconductors such as cadmium telluride (CdTe), gallium arsenide (GaAs), copper indium gallium selenide (CIGS) [10] etc PV solar cells have also been developed but later than the mono-crystalline Si ones. Monocrystalline and polycrystalline silicon solar cells were the first-generation solar cells, while amorphous silicon and other thin films solar cells like CdTe, GaAs, CIGS etc were the second generation. In particular, the compound semiconductor based devices such as tandem solar cells have demonstrated efficiency as high as 44 % in three-junction concentrator cells under laboratory conditions [11]. Although both Si and compound semiconductor PV solar cells have achieved relatively high efficiencies for commercial use, major breakthroughs are still required to achieve the long-lasting goals of low production and operating cost [9].

The development of third generation solar cells is a promising approach to improve solar-energy conversion efficiencies. These solar cells include: organic/inorganic perovskite cells (PSCs) [12], organic photovoltaic (OPV) cells namely dye-sensitized solar cells (DSSCs) [13, 14] and bulk heterojunction polymer (BHJ) solar cells [15]. They use organic and inorganic materials such as semiconductors and polymers for transportation of charge and absorption of sunlight. Among these solar cells, DSSCs and BHJ solar cells are attractive candidates because of their relatively simple solution production techniques which could lead to low cost being incurred. In addition, they possess special features such as lightweight, flexibility, low toxicity, and better performance in diverse light conditions [13, 14].

The general working principle of OPV based cells is an imitation of the natural process of photosynthesis which is different from crystalline Si-based ones. This is different from traditional PV cells where semiconductors assume both functions of light absorption and charge transportation. OPV solar cells consist of an absorber, photoanode and the counter electrode (cathode). The incident photons from the sun are absorbed by an absorber producing free hole-electron pairs known as excitons [16]. Separation of the hole-electron pairs occur due to the built-in field, hence migration to the electrodes. The electrons are conveyed via the photoanode while the holes reach the counter electrode for the production of external current. The configuration and working principle differ slightly from one solar cell to another. The dye and conjugate polymer in DSSCs and BHJ cells function as absorbers of sunlight while semiconductor films such as titanium dioxide (TiO_2) or zinc oxide (ZnO) act as photoanodes.

Ideally, all the hole and electron pairs produced by the incident light should be able to reach the external circuit via the electrodes. In reality, charge recombination losses occur in each stage of the PV process thus hindering successful collection of all the electrons and holes by the electrodes [17]. At the first stage, known as the photogeneration, the produced electrons have a chance of recombining with the holes before reaching the collecting electrodes if the exciton coefficient length is smaller than the material's domain size. This kind of recombination is referred to as geminate recombination [17, 18]. Other recombination losses occur after separation of hole and electron pairs at the interface of the acceptor and donor materials. The dissociated free electrons and holes are likely to recombine before migrating to the respective

electrodes. This recombination is known as non-geminate recombination [17, 18]. It also includes combination of the electrons and holes trapped in the nanomaterial network. The recombination of electron-hole pairs affects the conversion efficiency of the solar cells hence remains a major challenge [19].

1.2 Role and properties of the photoanode in solar cells

The photoanode, also referred to as the working anode plays a vital part in the functioning of the hybrid solar cells. Figure 1.2 shows structural representation of solar cells constructed with the working anode. The photoanode basically, acts as a supporter or bridge for sensitizer loading and conveyer of the electron to the external circuit. Ideally, a photoanode should possess a large surface area for maximum dye loading and a high electron transportation rate in order to produce high charge collection efficiency and minimum losses [13]. It should also be able to absorb and scatter light for effective functioning of the dye and must be highly resistant to photo-corrosion. The band gap energy should also be engineered to match that of the sensitizer for improved photoelectron injection [20]. All these features are required for the fulfillment of the role of the photoanode for efficient functioning of the solar cell.

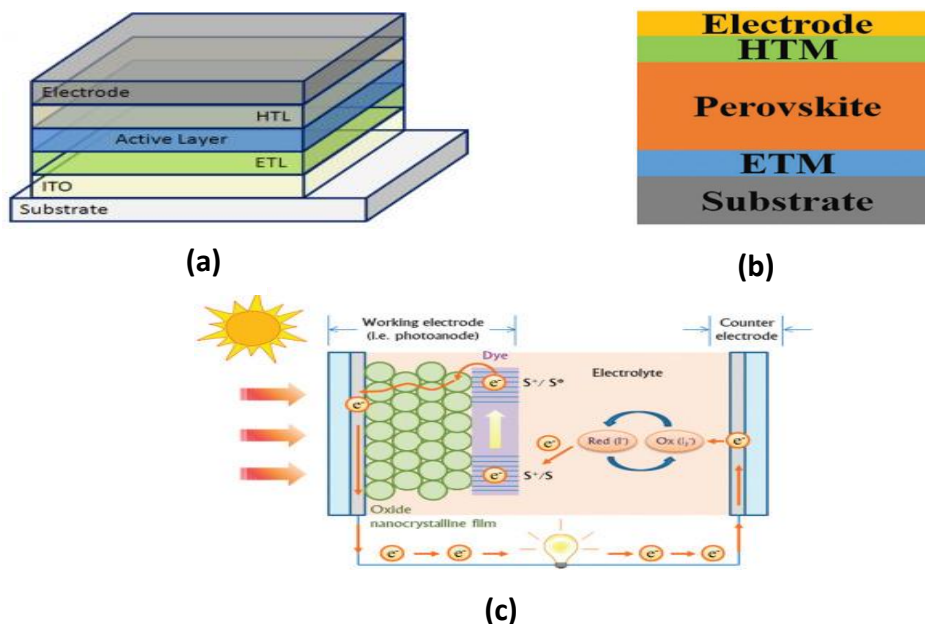


Figure 1.2: Photoanode in (a) Bulk heterojunction solar cell [21], (b) Perovskite solar cell and (c) DSSC [22].

1.3 Nanostructured materials for the photoanode in solar cells

Several materials especially metal oxide nanostructures have been investigated as photoanodes. Among these metal oxides, TiO_2 , ZnO and niobium pentoxide (Nb_2O_5) are the prominent ones for photoanode application in PV solar cells because of their similar unique properties especially the band energy structures as shown in Table 1.1 [23].

Table 1.1: Special features of the photoanode materials [24, 25].

Properties	ZnO	TiO ₂	Nb ₂ O ₅
Band gap (eV)	3.2-3.3	3.0-3.2	3.4-3.5
Crystal structure	Wurtzite, zinc blende, and rock salt	Anatase, rutile and brookite	Pseudo hexagonal, orthorhombic and monoclinic
Electron mobility in bulk ($\text{cm}^2\cdot\text{V}\cdot\text{s}^{-1}$)	205-300	0.1-4.0	-

TiO_2 has been mostly investigated and proved to be the most effective material for the fabrication of the photoanode. It possesses unique characteristics such as high chemical stability, less toxicity, high electron affinity, high surface area and a suitable band gap which are required for an ideal photoanode in solar cells. TiO_2 photoanode based DSSC has achieved highest recorded efficiency of 13-15 % [26, 27, 28]. Perovskite solar cells developed with TiO_2 anodes have achieved an efficiency of 22.1 % [29]. The high efficiency is due to the large surface area of the TiO_2 nanoparticles allowing increased dye particles adsorption. One disadvantage is that high annealing temperatures of up to 500 °C are normally required for TiO_2 synthesis and this hinders the development of flexible PSCs [24]. Low annealing temperatures are vital in the production of flexible modules of solar cells as the most used polymer substrate cannot withstand temperatures higher than 250 °C [30]. Another challenge with TiO_2 is that it can only absorb in the ultraviolet region hence limiting its light harvesting capacity. Additionally, its electron mobility is rather low [31]. Charge recombination also occurs in TiO_2 based DSSC due to low electron mobility and transportation rate. These challenges adversely affect the TiO_2 based solar cells.

ZnO is another prominent semiconductor with similar unique properties such as a wide band gap as those of TiO₂ and has been widely studied for photoanode fabrication. It is relatively cheap, possesses a large exciton binding energy of 60 meV and is resistant to photo-corrosion [32]. The maximum efficiencies of 17.6 % and 7.5 % of ZnO based perovskite solar cells and DSSC respectively have been achieved [33, 34]. In DSSC with ZnO based photoanode, the efficiency is lower than that of TiO₂ based photoanode because of less dye adsorption and instability in acidic conditions of ZnO [35].

Nb₂O₅ is also an alternative metal oxide that has not received much attention from researchers as compared to ZnO and TiO₂ especially as a photoanode for DSSCs [36]. This is because it is hard to prepare thermally stable Nb₂O₅ at temperatures of 500 °C as all the polymorphs of Nb₂O₅ present large crystalline unit cells [37]. Nb₂O₅ has unique features such as low internal resistance, a higher conduction band hence a higher open circuit voltage, and improved chemical stability. However, less research has been done on studying electron mobility of this metal oxide [38]. An efficiency of 3.04 % was achieved by using one dimension (1 D) nanofibers as a photoanode for DSSCs [39]. This efficiency is lower than that of 0 D peanut-shaped particles based DSSCs with 3.4 % [36]. Other semiconductor oxides which include tungsten trioxide (WO₃), tin (IV) oxide (SnO₂), strontium titanate (SrTiO₃), aluminum oxide (Al₂O₃), vanadium pentoxide (V₂O₅), zirconium dioxide (ZrO₂), cerium (IV) oxide (CeO₂) and Iron(III) oxide (Fe₂O₃), have also been studied, however the solar cells efficiency is still low [24].

1.4 Statement of the problem

The highest recorded conversion efficiency of organic/inorganic based devices is still way below the conversion efficiency of the Si based solar cells [11]. The low efficiency of organic/inorganic solar cells is due to the losses that occur at every step of the photogeneration, separation, and collection processes [13, 15, 40]. The recombination losses in the OPV cells are due to the inefficient transportation of carriers by the photoanodes.

ZnO and TiO₂ nanostructures prepared using solution-based methods have often been used as candidates for extraction of electrons due to their unique properties. The higher electron mobility, crystallite quality and low temperature synthesis of ZnO nanostructures makes them an alternative material to TiO₂ for the use in solar cells [41]. The limitations with ZnO nanostructures such as nanoparticles arise from the surface defects due to the presence of grain boundaries. These defects tend to trap electrons leading to recombination losses. ZnO nanorods have less grain boundaries thus allowing direct channel for improved electron transportation. As such, there is a need to grow ZnO nanorods using simple methods for improved electron transportation in solar cells.

1.5 General Objectives/ Aims

The main objective of this study is to grow vertically aligned ZnO nanorods that are less compact, thin and long with fewer defects which can be used for organic/inorganic solar cells application. This is expected to be achieved through:

- Growing ZnO seed layers using ultrasonic spray pyrolysis (USP) for the growth of vertically aligned nanorods.
- Synthesizing ZnO nanorods by chemical bath deposition (CBD).
- Studying the structural, morphological, optical, vibrational and electrical properties of ZnO nanorods.
- Studying the effects of varying the bath temperature, time and solution concentration on the growth and properties of ZnO nanorods.
- Deriving the optimal growth conditions for vertically aligned ZnO nanorods that are less compact, thin and long and have few defects.

1.6 Hypothesis

- The variation of the CBD parameters to obtain optimized growth conditions lead to improved structural, morphological, optical, vibrational and electrical properties of ZnO nanorods allowing their application in PV cells as electron transporters.

1.7 Significance of the study - Energy situation in Botswana

Botswana is a landlocked country at the centre of Southern Africa with an area of about 582 000 km². It has a semi-arid climate and about 75 % of its area is covered by the Kgalagadi desert. According to the 2011 Population and Housing Census, the country had a population of about 2.02 million [42]. Botswana has to meet the basic human needs of its increasing population through the exploration and utilization of the available natural energy resources. Provision of energy services is an essential ingredient of socio-economic development of any country. The energy supply profile of Botswana is comparable with other developing countries, particularly the Southern African Development Community (SADC) region, and is mainly dominated by wood and coal fuel [43]. As a developing country, Botswana relies heavily on coal as a major energy source due to its abundance estimated at about 212 billion tonnes. Coal is being mined solely by Morupule Colliery located close to Palapye in the Central District of Botswana. Botswana Power Corporation (BPC) is running Morupule Power Station using the coal from the adjacent Morupule Colliery and provides the greatest portion of the country's domestic power generation [44, 45]. Energy generation from natural resources in Botswana is not sufficient to meet the demand [46]. As such, Botswana is highly dependent on imports from neighbouring countries, primarily South Africa to meet its energy demand [44]. Even though Botswana is significantly working towards meeting the electricity demand in all the sectors, the situation remains constrained. The power supply is less than the country's demand, hence the need to import electricity from neighbouring countries.

The use of coal for generation of energy has a well-documented significant negative impact on the environment from the emission of pollutants [47]. Botswana, in the meantime has potential

renewable energy resources that can be tapped into. These include solar, wind and various forms of bioenergy. Wind as source of renewable energy is inadequate, specific to a location and randomly distributed during the year [48]. However, there is wind energy project that will install wind turbines to generate electricity in the Kweneng District, Botswana. Biomass energy is another source of renewable energy being utilized in Botswana for various purposes. The available biomass resources are not sufficient to generate electricity on a sustainable basis. Limited perennial rivers in the country has ruled out potential for hydro power. The Okavango and Chobe rivers found in the northern part of Botswana remain centers of tourism attraction hence making them inaccessible to building hydropower stations. In a year, an average of 320 clear, sunny days and solar insolation of 21 MJ/m²/day on average are received all over the country [49]. Therefore, there is a need for Botswana to shift to solar energy through the utilization of excellent solar conditions using various PV-based electricity generation technologies. PV-based systems including solar home systems, solar mini grids and battery charging stations are used in few regions of the country.

The major challenge has been the high costs of PV-based systems in Botswana hence only few people in both rural and urban are connecting to the PV-based systems. In addition, less research has been done on the development of a solar cell and its components in Botswana. Most of the work is of theoretical nature and is mainly of academic interests only. As such, there is a need to research on nanomaterial based solar devices so as to come up with new cheap, durable, efficient and environmentally friendly nanomaterials to convert the heat and light energy from the sun to electricity. The utilization of solar energy using these devices will reduce greenhouse gases emissions which contribute to global warming resulting in climate change. This study will contribute to the development of unique nanostructures to be used in solar cells.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

The application of nanostructured based technology in different fields is of high interest [50, 51, 52, 53, 54, 55]. One of the nanomaterials that have been explored for different applications is ZnO. Research has been conducted on ZnO as a unique material in different fields. The interest in this material arises due to the development of synthesis methods enabling tailor making into high quality nanostructures hence addressing challenges faced in the industry. In the field of solar technology, the main challenge is low conversion efficiency in photovoltaic cells due to charge recombination. As a way to address the challenge, ZnO based solar cells have been developed. In this chapter, background information on ZnO basic properties which include structural, optical, vibrational and electrical properties is presented. A depth review on ZnO nanorods synthesis methods and photovoltaic cell applications is also given.

2.2 ZnO

ZnO is a (II–VI) compound semiconductor and one of the most promising materials in the field of nanotechnology being actively researched on today due to its interesting properties [56]. As a transparent conductive oxide (TCO) with special features such as controllable electrical properties and high transparency within the visible range, it finds a broader application in electro-optical devices [57]. Its application in optoelectronic devices include transistors, light emitting diodes, chemical and gas sensors, room-temperature UV lasers, optical wave guide and solar cells [50, 51, 52, 53, 54, 55]. It is also used in the field of Biomedical and Environmental Sciences as it is non-toxic and environmentally friendly [56]. Research and development activities are ongoing for various metal oxide semiconductor based solar cells e.g. TiO_2 , SnO_2 and In_2O_3 . However, ZnO is still to be fully explored as an alternative semiconductor material with marked crystal quality, higher electron mobility and low crystalline temperature allowing simple and affordable synthesis process [41].

ZnO as a very fascinating material with potential for many applications is particularly attractive in its nanostructure form for photovoltaic applications. ZnO can be simply tailored into various nanostructures such as nanobelts, nanowires, nanorings, nanoflowers and nanorods using several methods. Among these nanostructures, 1D ZnO nanostructures especially nanorods promise to be more suitable for photovoltaic cell applications due to their large surface area to volume ratio allowing improved electron transportation efficiency [58, 59]. For the past few decades, nanotechnology has been dominated by the 1D nanostructures [60]. The nanosized 1D structures have significantly improved the properties and performance of the nanodevices.

2.3 Crystal structure of ZnO

ZnO can either possess the hexagonal wurtzite or cubic zinc blende or cubic rock salt crystal structures as it crystallizes. However, ZnO naturally crystallizes in wurtzite structure with a hexagonal unit cell belonging to the space group C_{6v}^4 (Schoenflies notation) and $P6_3mc$ (Hermann–Mauguin notation) under ambient conditions as shown in Figure 2.1 (a). At relatively high pressures the ZnO crystals may exhibit the rock salt phase indicated in Figure 2.1 (b). However, ZnO exhibiting rock salt structure cannot stabilize on crystalline substrates. Figure 2.1 (c) illustrates the cubic zinc blende structure exhibited by ZnO when grown on cubic substrates. The wurtzite structure as a hexagonal lattice is composed of Zn^{2+} cations each tetrahedrally bonded to four O^{2-} anions and vice versa. The tetrahedral fraction coordinated Zn^{2+} and O^{2-} ions are stacked along the threefold C-axis in an alternating manner. The tetrahedral symmetry is pivotal for the polarity along the hexagonal axis, which ultimately gives rise to the piezoelectric property.

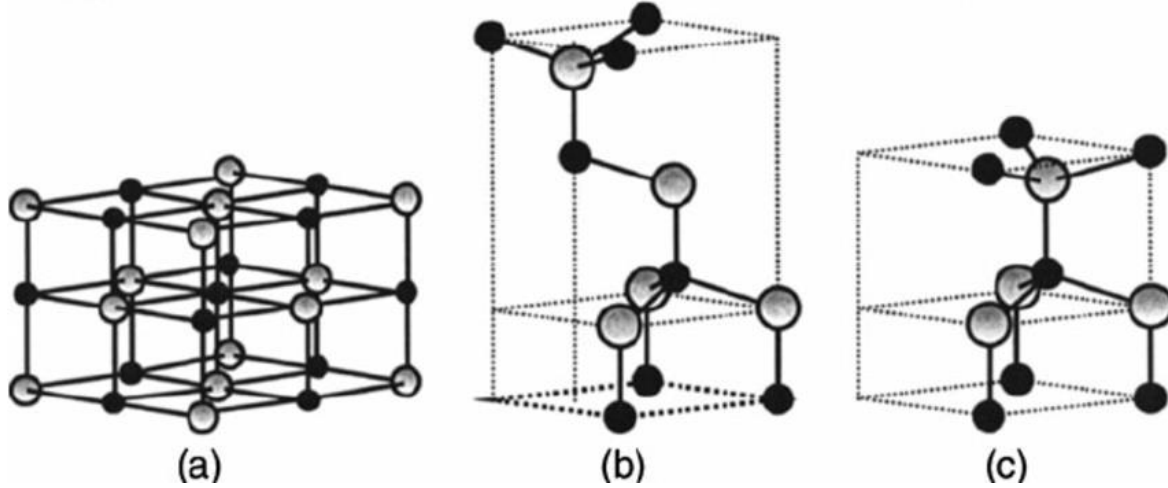


Figure 2.1: Representation of ZnO crystal structures: (a) cubic rock salt (b) cubic zinc blende (c) Hexagonal wurtzite. Shaded grey is Zn atoms while O atoms are shaded black [61].

The arrangement of zinc and oxygen atoms in ZnO in a tetrahedral manner positions zinc and oxygen atoms at 0001 and $000\bar{1}$ surfaces of the wurtzite symmetry respectively. The wurtzite ZnO consists of four common face terminations which include two polar faces and two non-polar faces each containing the same number of Zn and O atoms. The Zn^{2+} (0001) terminated face and O^{2-} ($000\bar{1}$) terminated face are the polar faces while $(11\bar{2}0)$ and $(10\bar{1}0)$ are the non-polar faces. The planes normal to the c -axis are referred to as basal planes. The tetrahedral coordination of ZnO in its crystal lattice denotes the natural sp^3 hybridization covalent bonding, however the ionic character belonging to Zn-O bond tends to make ZnO to exhibit strong ionic bonding. The strong ionic character tends to widen the energy band gap of ZnO.

A schematic representation of the hexagonal wurtzite structure of ZnO including the lattice parameters is shown in Figure 2.2. The lattice constants or parameters of the hexagonal close-packed lattice type are $a = 3.2495 \text{ \AA}$ and $c = 5.2069 \text{ \AA}$ at 300 K [62]. The c/a ratio for ZnO is 1.602 which is close to the ideal ratio of 1.633 assigned to the hexagonal close packed structure. The length of the anion-cation bond parallel to the c -axis is denoted as b . The off c -axis cation-anion bond length is denoted by b_1 while other additional bond lengths include b'_1 (along the c -axis), b'_2 and b'_3 [63]. The b lattice parameter divided by the c lattice parameter (b/c) gives the internal parameter u . There is a strong relationship between the c/a and b/c ratios such that when

internal parameter, u increases, the c/a ratio decreases. α and β represents the bond angles. The lattice parameters can be affected by several factors which include free charge, temperature, impurities, interplanar spacing dislocations, strain and stress [64]. X-ray diffraction (XRD) technique is normally used to study the lattice parameters [65].

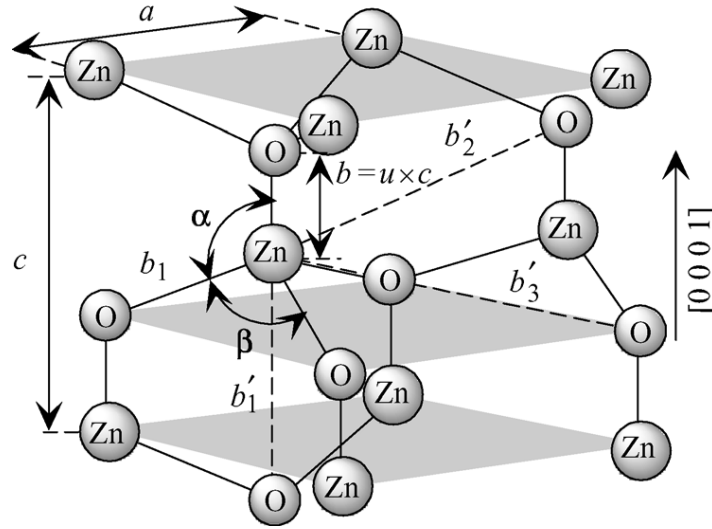


Figure 2.2: Representation of the hexagonal wurtzite structure of ZnO with the lattice parameters [61].

2.4 Fundamental properties of ZnO

2.4.1 Physical properties of ZnO

It is vital to investigate and understand the physical properties of ZnO for the development of innovative and interesting applications. ZnO has generated a lot of attention in different fields for a variety of applications due to its special physical properties. Table 2.1 presents a summary of the important physical properties of ZnO.

Table 2.1: Properties of ZnO.

Properties	Values	References
Stable phase at 300 K	Wurtzite	[66]
Lattice constant (300 K)	$a = 3.2475 - 3.2501 \text{ \AA}$; $c = 5.2042 - 5.2075 \text{ \AA}$; $u = 0.375$	[60, 61]
Density (300 K)	5.605 g/cm^3	[67]
Volume	23.8	[67]
Exciton binding energy	60 meV	[60, 62]
Band gap (300 K)	3.4 eV	[62]
Thermal conductivity	$0.6-1.0 \text{ Wcm}^{-1} \text{ K}^{-1}$	[68]
Thermal expansion coefficient	$a = 6.5$; $c = 3.02 (10^{-6} \text{ m /K})$	[66, 69]
Refractive index	2.008, 2.029	[69]
Hardness	$\sim 5.0 \text{ Gpa}$	[67]
Electron mobility (300 K)	$200 \text{ cm}^2/\text{Vs}$	[66, 69]
Melting point	2250 K	[67]
Solubility in water	0.0004 %	[67]

2.4.2 Optical properties

The optical properties of ZnO strongly depend on its energy band structure [62]. Intrinsic and extrinsic optical transitions occurring in the energy band structure are used for studying the optical properties of the semiconductor. Intrinsic optical transitions occur between the holes in the valence band and electrons in the conduction band. Such transitions also occur when the group velocities of the electron-hole pair is equal and thereby constituting an exciton. On the other hand, extrinsic optical effects are associated with the defects present in ZnO. Normally, these defects lead to formation of electronic states in the band gap hence influencing the processes of optical absorption and emission. ZnO has a band gap of 3.37 eV and a larger exciton binding energy of 60 meV at room temperature as listed in Table 2.1 [70, 71]. The high exciton binding energy enables efficient exciton emission due to ultraviolet luminescence at room temperature.

Basic optical properties such as refractive index, band gap, dielectric constant and extinction coefficient have been comprehensively studied from the transmittance spectra of ZnO nanorods

obtained from the UV/VIS spectrometer [72]. The ability to tune these properties of ZnO nanorods and their high transparency enable performance in optoelectronic devices. It has been revealed by several studies that the nanorods diameter variation can be used to tune band gap of ZnO [73, 74].

In solar cells, ZnO nanorods as TCOs allow maximum transmittance of photons to reach the absorber material. As such the need to determine the transparency of the nanorods is imperative. Optical properties of the nanorods synthesized on a glass substrate have been studied [75, 76, 77]. Ideally, the nanorods allow 100 % of incident light in the visible window to be transmitted. However, the transmittance is affected by the reflection, interferences and optical properties of the substrate used. A summary of the optical parameters of wurtzite ZnO based on literature survey is presented in Table 2.2.

Table 2.2: Review on optical properties of ZnO.

Optical parameters	Values	References
Band gap	3.21-3.42 eV	[78]
Refractive index	1.64-2.60	[79, 69, 80, 81]
Real Dielectric constant	4.0-7.0	[80, 82]
Imaginary Dielectric constant	0.2-0.3	[80, 82]
Extinction coefficient	0.04-0.075	[80, 82]

2.4.3 Vibrational properties

Vibrations occurring in crystals are useful in providing crucial information on optical confinement effect, lattice defects, crystal quality, stress and strain of the nanostructures. The vibrations of the atoms or molecules in a crystal is also known as phonons or normal modes. When the atoms are moving perpendicular to the wave propagation, the phonons are considered to be longitudinal. However, when atoms are moving parallel to the wave motion, a term transverse is used to denote the phonons. Phonons can either move in phase or out of phase. Those phonons

moving in phase are referred to as acoustic while out of phase phonons are named optical modes [61].

Raman scattering technique has been used to study the vibrational properties of ZnO [61, 83, 84]. The inelastic scattering of photons by the electrons in a lattice is known as Raman scattering. The photons interact with the electron by the process of Hamiltonian interaction [85]. A hole-electron pair resulting from this interaction leaves the material in a virtual state. The excitation of the hole-electron pair into another state as a result of electron-photon interaction lead to the emission or absorbing of a photon. The pair then recombine to the ground state radiatively, and a scattered low energy photon is emitted during the process [86].

In the case of wurtzite structured ZnO, which has four atoms per primitive cell, 12 phonon modes are present. Among these phonon modes, 9 are optical and 3 belong to the acoustic group. According to the group theory, the phonon modes observable at the Γ point of the Brillouin zone are [61]:

$$\Gamma = 2A_1 + 2B_1 + 2E_1 + 2E_2 \quad (2.1)$$

Among these modes, A_1 and E_1 are both Raman active and infrared active while $2E_2$ modes are Raman active only. The $2B_1$ are silent modes. Both the A_1 and E_1 modes divide into longitudinal optical (LO) and transverse optical (TO) phonons [61, 87]. A_1 (TO), E_1 (TO), A_1 (LO) and E_1 (LO) modes are related to the impurities and defects such as dopants, Zn interstitials and oxygen vacancies or their complexes. $2E_2$ modes branch into low and high frequencies. The E_2 (high) modes are linked to the vibration of oxygen atoms while the E_2 (low) are related to the vibration of the Zn sublattice. The E_2 modes are non-polar because the ions in each sublattice move in opposite directions leading to zero net polarization [85]. On the other hand, A_1 and E_1 are polar modes since the ions move in such a manner that the oxygen displaces Zn sublattice resulting in induced polarization. When incident light is perpendicular to the c-axis of ZnO nanorods, only the E_2 (high) and A_1 (LO) phonon modes appear [83]. A typical Raman spectrum of wurtzite ZnO consists of E_2 (low), A_1 (TO), E_1 (TO), E_2 (high), A_1 (LO), and E_1 (LO) corresponding to 101, 380, 407, 437, 579 and 583 cm^{-1} [36]. Table 2.3 compiled from literature survey lists the Raman modes with

their corresponding frequencies. Figure 2.3 shows an illustration of the vibrational behavior of the Zn and O atoms.

Table 2.3: Raman modes with frequency ranges of ZnO [61, 88, 89, 90, 91, 92].

Normal modes	Frequencies (cm ⁻¹)
E ₂ (low)	98-101
A ₁ (TO)	376-390
E ₁ (TO)	409-413
E ₂ (high)	436-438
A ₁ (LO)	574-579
E ₁ (LO)	580-591

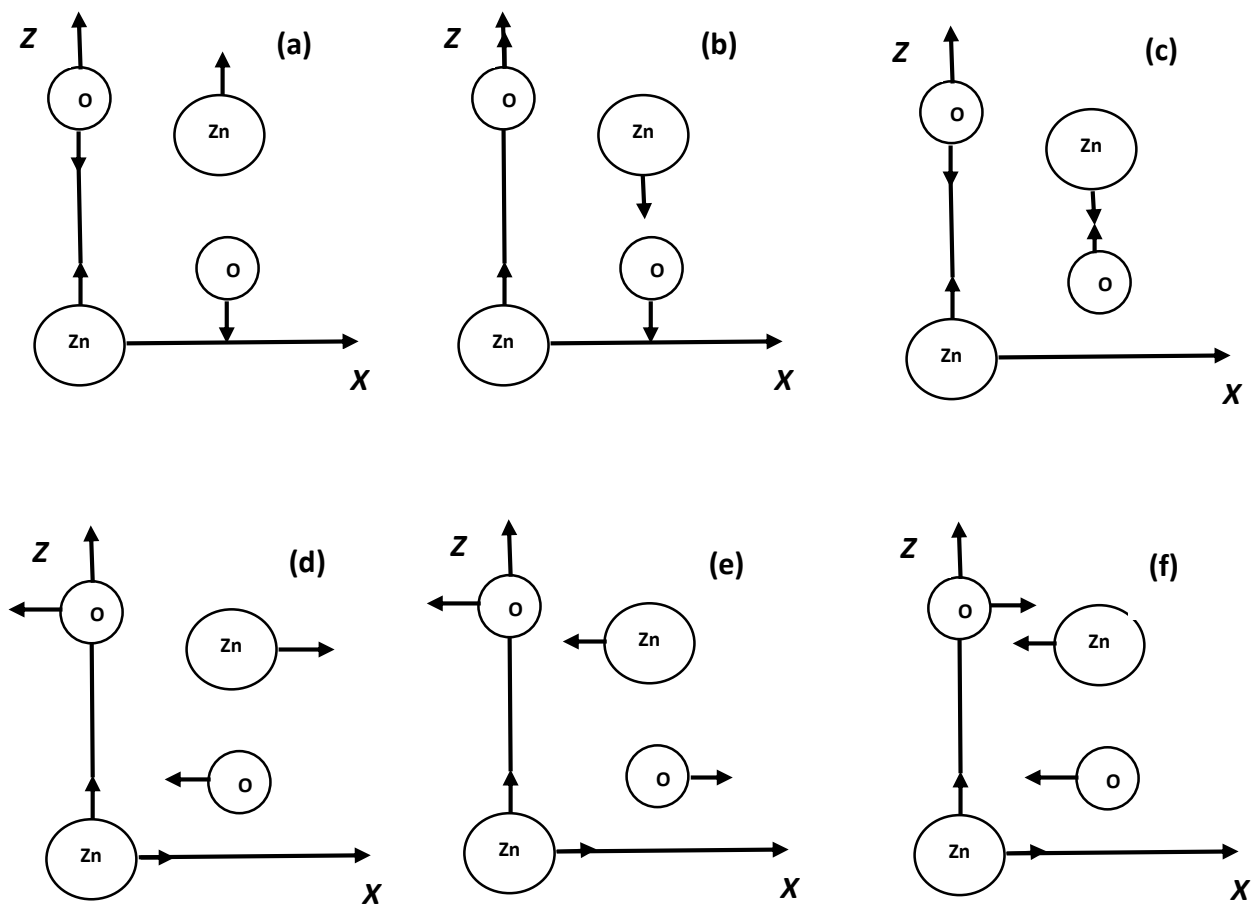


Figure 2.3: General Zn and O atoms vibrations: (a) A₁ mode, (b) B₁ (1) mode, (c) B₁ (2) mode, (d) E₁ mode, (e) E₂ (1) mode and (f) E₂ (2) mode [61].

2.4.4 Electrical properties

The novelty of the electrical properties of ZnO semiconductors lead to their applications in optoelectronic devices. In these devices, ZnO in different nanostructure forms allow charges to flow hence acting as the electrodes. The presence of crystal defects for instance oxygen vacancies and zinc interstitials justify the n-type state of ZnO nanostructures. These defects affect the electrical conductivity of the nanostructures, for example in a perfect crystal an oxygen vacancy formed produces two electrons leading to increased carrier concentration hence less resistivity of the nanostructures [93]. Due to low concentration of these vacancies, pure ZnO nanostructures or thin films are normally highly resistive. As such there is need to increase the carrier concentration of ZnO nanostructures so as to reduce the resistivity for enhanced electrical conductivity. Research work has proven that ZnO nanostructures can be grown using different techniques to enhance their electrical conductivity [94]. The lowest resistivity of $15 \text{ } \Omega \text{ cm}$ was achieved in a study in which ZnO nanorods were fabricated by sol-gel and CBD method [94]. A similar value was reported, with the CBD method used for the fabrication of the nanostructures on seedless substrates [95]. In another work, the resistivity of ZnO nanorods fabricated by CBD on a substrate coated by dip coating technique was $1.24 \times 10^4 \text{ } \Omega \text{ cm}$ [96]. Low values of resistivities to the order of $10^{-4} \text{ } \Omega \text{ cm}$ were recorded from ZnO nanorods prepared by wet chemical approach and vapor phase transport [97]. Experimental reported values of electrical resistivity ranges between the orders of magnitude of 10^{-3} to $10^5 \text{ } \Omega \text{ cm}$ [94, 98, 99, 100, 101, 102]. Several factors such as doping crystal structures, measuring techniques and surface contact resistances contribute to the variation of the previously reported resistivities of ZnO nanorods. Furthermore, ZnO naturally lacks the surface passive layers which exposes it to environmental conditions which can lead to random absorption of species resulting in the change of the occupied surface state density [103]. These absorbed species are responsible for the variation of resistivity and sensitivity of the ZnO nanostructures.

The figure of merit (ϕ) is a quantity used scale to the applicability of the ZnO nanostructures in solar cells as photoanodes. Haacke's equation is widely used by several researchers to measure the suitability of the transparent conductive oxide in solar cell applications [104, 105]. A figure of

merit value of the order $10^{-6} \Omega^{-1}$ was reported suitable for the nanostructures to be used as a photoanode in optoelectronic devices [106, 107].

2.5 ZnO nanorods for organic/inorganic solar cells

Organic/inorganic solar cells which include perovskite solar cells, DSSCs and BHJ solar cells are low cost promising devices for improved solar energy conversion efficiency [108, 109]. These solar cells consist of an organic and inorganic materials combined together for harvesting light and generation of charges for electricity [110]. Research is ongoing on finding a better combination of the organic/inorganic materials mainly because the power conversion efficiency (PCE) still remains low. One of the major challenges contributing to low PCE values is charge recombination due to discontinuous transportation of electrons [111]. As a way of improving electron transport efficiency, ordered single-crystalline nanorods can be used as a replacement of a nanoparticle layer [109]. It has been demonstrated experimentally that electron flow is tens to hundreds of times quicker in nanorods as compared to electron flow in nanoparticles [112, 113]. Studies are being carried out to deal with the challenge, by proposed development and utilization of inorganic nanostructures in the form of nanorods [114, 115, 116, 117], tetrapods [118, 119], nanoporous structures [120, 121] and nanotubes [122, 123] acting as electron acceptors for improved charge separation and carrier extraction efficiency. These inorganic nanostructures use materials that include, ZnO, CdS, CaTe, TiO₂, PbSe, CaSe etc. ZnO in nanorods form is among the promising semiconductors possessing good optoelectronic properties suitable for hybrid photovoltaic solar cells [118, 119].

Several research groups are working on fabricating ZnO based solar cells. ZnO based perovskite solar cell recorded PCE of around 17 % [34]. An efficiency of up to 16.1 % was found from solution-processed ZnO based perovskite solar cells by Yang's group [124]. Song et al [125] further improved the efficiency to 18.9 % by using triple cation perovskite absorber. In 2005, a ZnO nanorod-based DSSC was first fabricated using low cost hydrothermal process achieving an efficiency of 0.5 % [109]. Ever since then, efforts have been made to investigate and utilize ZnO nanorods as electron acceptors for improving the performance of the DSSCs [126, 127, 128]. The

maximum PCE reported is around 7.5 % for DSSCs fabricated with pure ZnO while that of TiO₂ is 12.3 % [129]. Xu et al [130] fabricated a multi layered nanowire based DSSC achieving an efficiency of 7 %. Several studies have been made on fabrication of ZnO nanorods based BHJ solar cells as a way of improving electron extraction and ultimately the PCE [131, 132, 133]. The performance of ZnO nanorods/Poly(3-hexylthiophene) (P3HT) with [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) added is still lower than the highest recorded PCE now over 10 % for PCBM polymer solar cells (BHJ) [134, 135]. The variation of the efficiencies maybe due to the fact that the currently used methods are insufficient to tune the nanostructures to the desired quality [16].

2.6 Review on synthesis of ZnO nanorods

Several methods have been developed for ZnO nanorods fabrication which include metal–organic chemical vapor deposition (MOCVD) [66, 136], CBD [137, 138, 139, 140], spray pyrolysis [141], hydrothermal deposition [100, 142, 143], chemical vapor deposition [66, 136], Vapor-liquid-solid phase deposition [144, 145, 146] among others. All these synthesis processes fall under either physical and chemical deposition methods or gas phase and solution-based methods [137, 147]. Each of these methods possess different advantages and disadvantages. Gas-phase methods are generally expensive; require complex equipment and catalysts; high temperatures; and are substrate limited. However, these methods produce ZnO nanorods with high aspect ratio; offer better control of deposition parameters and high growth rates [148]. On the other hand, solution-based methods such as CBD are simple, use low temperatures, suitable for large scale production of uniform growth on a variety of substrates and require no catalyst.

For the growth of vertically ordered nanorods, pre-coating the substrate with a seed layer contributes a lot in minimizing crystal mismatch between the substrate and the nanostructures. Several methods have been utilised for the deposition of the ZnO seed layers which include spray pyrolysis [149, 150], sputtering [100], spin coating [137, 151], dip coating [152], successive ionic layer adsorption and reaction (SILAR) [153] among others. Table 2.4 gives data on previous research on the growth of ZnO seed layers and nanorods by CBD method. The characteristics of

the nanorods synthesized by CBD depend on the great extent of the preparation conditions such as the seed layer deposition method and CBD growth parameters. It can be observed from Table 2.4 that with different preparation conditions, the aspect ratio of the nanorods obtained were different. A detailed description of CBD and spray pyrolysis methods will be given in the next chapter on methodology.

Table 2.4: Review on ZnO nanorod synthesis by CBD.

Methods	Temperature (°C)	Precursors	Growth time (hrs)	Aspect ratios (nm)		ref
				Length	Diameter	
SILAR and CBD	80	Zn (NO ₃) ₂ .6H ₂ O and HMTA	8	-	40-450	[92]
	80	Zn (CH ₃ COOH).2H ₂ O and HMTA	2	600	200	[154]
Spin coating and CBD	85	Zn (NO ₃) ₂ .6H ₂ O and HMTA	1.5	900	45	[155]
Dip coating and CBD	90	Zn (NO ₃) ₂ .6H ₂ O and HMTA	2	Several micrometers	80-1200	[156]
Spray pyrolysis and CBD	95	Zn (NO ₃) ₂ .6H ₂ O and HMTA	-	-	-	[150]
	90	Zn (NO ₃) ₂ .6H ₂ O and NaOH	1-9	-	90-150	[157]
	85	Zn (NO ₃) ₂ .6H ₂ O and HMTA	7	400-4000	20-500	[158]
Sputtering and CBD	90	Zn (NO ₃) ₂ .6H ₂ O and HMTA	1	542-695	70-83	[159]
	95	Zn (NO ₃) ₂ .6H ₂ O and HMTA	9	2500	-	[160]
	85	Zn (NO ₃) ₂ .6H ₂ O, HMTA and PEI	6	2200	79	[161]

CHAPTER 3: METHODOLOGY

3.1 Introduction

In this study, the growth of the ZnO nanostructures is achieved by a two staged process: The first stage is the synthesis of the seed layer and its integration on a cleaned substrate. This is followed by the synthesis of ZnO nanorods. Ultrasonic spray pyrolysis (USP) method was used to deposit ZnO seed layers. The ZnO nanorods were produced by the solution-based method CBD. This chapter focuses on the materials, procedures and methods used in the preparation for the synthesis of ZnO nanostructures. It also describes the techniques used for characterization of the grown nanostructures.

3.2 Cleaning of experimental apparatus

It is vital to clean all materials to be used in the process to prevent contamination of the samples that are to be prepared. The beakers (80 ml) and magnetic stirrers were cleaned using concentrated acid to etch out any organic and inorganic materials on their surfaces. The beakers were then rinsed with de-ionized water, before being left to dry under ambient conditions. Microscope glass slides with dimensions; (76 mm×26 mm×1 mm) were used as substrates. A Branson Ultrasonic bath shown in Figure 3.1 was used to clean the glass substrates. The ultrasonic bath utilizes transducers to produce high frequency sound waves to agitate the liquid for removal of dirt particles. The substrates were ultrasonically cleaned using acetone, followed by ethanol and then de-ionized water for 30 minutes each. Acetone and ethanol act as solvents to dissolve oils and organic residues on the substrates. Finally, the substrates were rinsed with de-ionized water, before being blown dry using nitrogen gas.



Figure 3.1: A Branson ultrasonic bath.

3.3 Ultrasonic spray pyrolysis (USP)

USP is a chemical method used for the synthesis of nanomaterials. It involves the use of an ultrasonic atomizer vibrating at high frequency to produce fine particles from the precursor solution which are then carried by the flowing air through the nozzle to a preheated substrate [162]. Upon deposition onto the substrate, the fine particle forms a stable crystalline compound. Other by-products from the reaction evaporate away. The design of the atomization chamber is such that large particles cannot be carried by the gas to the substrate lying flat on the hot plate. Basically, USP consists of a precursor solution (a) an ultrasonic atomizer (b), a substrate heater (c), a rotameter (d) and a nozzle (e) as shown in Figure 3.2.

USP is a simple technique offering several advantages which include; low cost, better control of deposition rate and thin film thickness, moderate deposition temperatures (300-500 °C) and wide coverage of uniform adherent films or nanoparticles [163, 164, 165, 166]. However, the major challenges of this technique are the presence of cracks and pores as the quality of the film vary with substrate temperature [167].

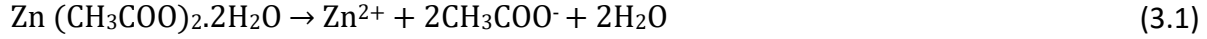


Figure 3.2: The Ultrasonic Spray Pyrolysis (USP) setup.

3.3.1 Preparation of ZnO seed layers by USP

The USP technique was used for the deposition of ZnO seed layers on cleaned glass substrates. The ZnO seed layer solution was prepared by ultrasonically dissolving 0.15 M concentration of Zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) in a mixture of ethanol and de-ionized water. The optimized volume ratio of ethanol to di-ionized water was kept at 1:3 [157]. The prepared solution was atomized using an ultrasonic nebulizer and delivered to the target substrate by compressed air. The flow rate and nozzle-substrate distance were maintained at 4.5 L/min and 1.5 cm respectively. The substrate temperature was kept at 400 °C. The temperature was monitored by the digital multi-meter and a K-type thermocouple thermometer. The precursor solution was continuously sprayed on each substrate for a specified time. The spraying time was varied from 10 minutes to 40 minutes so as to optimize the seed layer thickness. After the deposition process, each substrate was left on the hot plate for 5 minutes to allow for

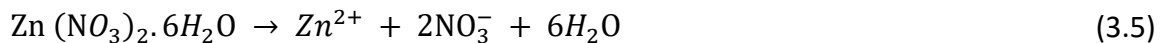
evaporation of residual water content [150, 168]. The substrates were finally allowed to cool down to room temperature. The chemical reactions involved in the deposition of the ZnO seed layers are given by the equations (3.1) - (3.4):



3.4 Chemical bath deposition

The CBD method has been used since 1869 for deposition of the thin film of different semiconductors [169]. It is defined as the process of synthesizing nanostructures by the use of at least two precursors in a solution. CBD is a solution-based method commonly used for the synthesis of ZnO nanorods due to its several advantages. It is economical as it utilizes simple equipment, requires no catalyst, offers uniform area growth for large scale production, utilizes low temperature and flexibility of substrates [170, 171]. However, this technique also possesses a drawback of wasting precursor solution after the bath deposition [161].

The growth mechanism of nanostructures using CBD involves two stages, nucleation followed by growth of the particles in a solution. Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and hexamethylenetetramine (HMTA, $\text{C}_6\text{H}_{12}\text{N}_4$) were dissolved in de-ionized [92, 154, 155, 158]. In most cases, HMTA is used as a base to act as a pH buffer to control the solution pH to around 6 - 7 for the supply of hydroxyl (OH^-) ions [172]. Zinc nitrate hexahydrate is responsible for the supplying of Zn^{2+} ions while the de-ionized water provides O^{2-} ions for the formation of ZnO [173, 174]. HMTA hydrolyses in water yielding formaldehyde (HCHO) and ammonia (NH_3). NH_3 then dissolves in water (H_2O) resulting in ammonium (NH_4^+) and hydroxyl (OH^-) ions. OH^- reacts with Zn^{2+} producing Zinc hydroxide ($\text{Zn}(\text{OH})_2$). Finally, the $\text{Zn}(\text{OH})_2$ decomposes into ZnO and water. The chemical reactions for the formation of ZnO are given in the equations (3.5) - (3.9) [175, 176]:





During deposition, coating the substrate with ZnO nanoparticles as a seed layer minimizes the thermodynamic barrier by forming nucleation sites thereby improving the aspect ratio, optical properties and ensures uniformity in the development of ZnO nanorods [177, 178, 179, 180]. In general, deposition parameters for the synthesis of ZnO nanorods on different substrate are well established. Deposition parameters which includes growth time, temperature and precursor concentration are used to govern the growth of ZnO nanorods by CBD. Figure 3.3 shows the CBD set up used for the synthesis of ZnO nanorods.

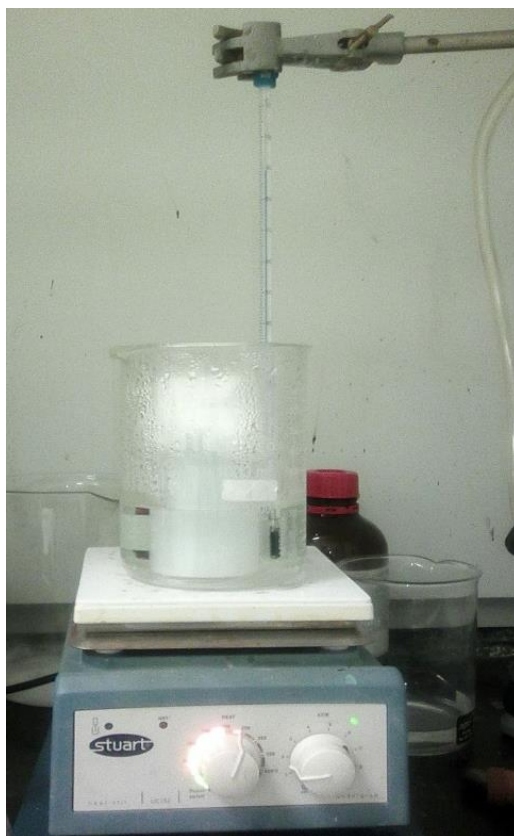


Figure 3.3: The CBD set up that was used for the synthesis of ZnO nanorods.

3.4.1 Effects of growth parameters on ZnO nanorods

The growth solution for ZnO nanorods fabrication was made by mixing equimolar zinc nitrate hexahydrate and hexamethylenetetramine in 100 ml of di-ionized water under stirring. The seeded substrates were vertically immersed into the growth solution being heated at temperatures ranging from 60 °C to 90 °C for 1.5 hrs to 3.0 hrs.. After the deposition process, a sample was rinsed with distilled water and blown with nitrogen gas for drying. All the samples were annealed on a hot plate at 400 °C for one hour to improve the crystallinity, minimize structural defects and to remove organic ligands resulting from the growth solution [181, 182, 183]. The samples were stored in clean labelled containers for characterization. A series of experiments were carried out by varying one parameter while keeping other parameters constant to investigate their effect on the properties of the nanorods. The growth parameters were varied to investigate their effects on the ZnO nanorods as shown in Table 3.1

Table 3.1: Growth parameters variation.

Growth time (hrs)	Concentration (mM)	Temperature (°C)
1.5	10	60
2.0	15	70
2.5	25	80
3.0	30	90

3.5 Characterization techniques

The structural, morphological, optical, vibrational and electrical properties of ZnO nanorods were characterized. A surface profiler was used to measure the thickness of the seed layer nanoparticles. An X-ray diffraction (XRD) machine was used for studying the crystalline structure of the nanorods. The nanostructure morphologies were investigated by a field emission scanning electron microscopy (FE-SEM) equipped with energy dispersive spectroscopy (EDS). A UV/VIS/NIR spectrophotometer was used for studying optical properties. Raman spectroscopy was used as a tool for studying the vibrational modes of the nanorods. Electrical measurements were obtained using the Four-point probe equipment.

3.5.1 Thickness determination

The thickness of the ZnO seed layers play a vital role in their vertical alignment. A KLA Tencor Alpha-step D-100 surface profiler was used for thickness measurements of the ZnO seed layers deposited by USP at various duration. The profilometer measures the 2D topology of the surfaces within a 30 mm scanning length. It consists of a 140 mm x-y sample positioning stage and detector (diamond stylus). The stage holds the sample while the diamond stylus tip detects the step on the surface of the sample. A step is normally made on the sample by scratching the film with a steel pin. The diamond stylus is lowered vertically downward to ensure contact with the sample surface on the substrate. The stylus is then moved along the surface with a constant force hence giving the surface height information along the scan line. The height between the sample surface and substrate surface due to the created step will be the thickness of the film. Figure 3.4 shows the surface profiler used in this study.



Figure 3.4: A KLA Tencor D-100 surface profilometer.

3.5.2 Structural characterization

The use of X-ray diffraction (XRD) techniques is one of the vital and powerful tools for studying the crystalline orientation of nanostructures. This technique involves aiming the crystal lattice with an X-ray beam in such a manner that the diffracted beam reaches the detector. As the crystal

lattice is struck by a beam of X-rays, several planes will be revealed satisfying Bragg's law indicated in the following equation (3.10):

$$n\lambda = 2d\sin\theta \quad (3.10)$$

Where,

n is an integer,

λ is the X-ray wavelength,

d is the spacing between atomic planes in the crystalline phase and

θ is the scattering angle.

The diffracted beam of X-rays collected by the detector is normally measured as a function of the diffraction angle (2θ). The output results are then recorded as counts per second against the diffraction angle (2θ). The diffraction patterns obtained are used for the identification of the crystalline phases of the sample [184]. For this study, orientation and crystal structure of ZnO nanostructures were studied using an X-ray diffractometer (XRD, D8 Advance, Bruker, Germany) shown in Figure 3.5. The diffractometer consists of a 3-kW generator, Cu K α radiation source and Lynx Eye XE energy dispersive strip detector. The working principle of the XRD is presented in Figure 3.6. The Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) was scanned over the samples in the range $2\theta = 20 - 70^\circ$. A voltage of 40 kV and a current of 40 mA were set for the operation of the X-ray generator.



Figure 3.5: A Picture of the X-ray diffractometer (XRD, D8 Advance, Bruker, Germany).

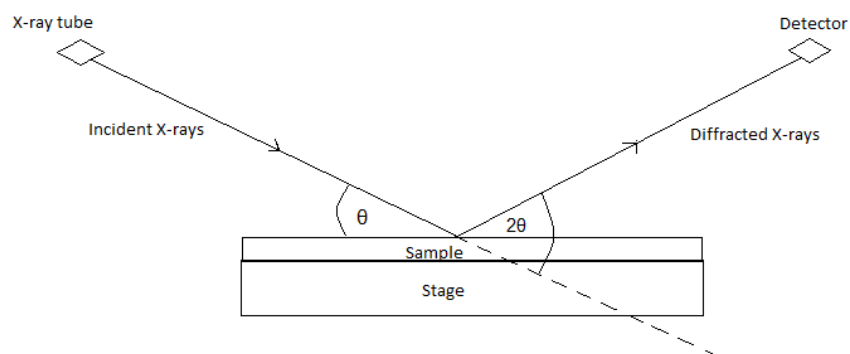


Figure 3.6: A Schematic diagram of an XRD [185].

3.5.3 Morphological and elemental characterization

It is imperative to make an observation of the morphology and elemental composition of the nanostructures so as to confirm the arrangement, shape, size and chemical composition of the desired structures. Of recent, scanning electron microscopy (SEM) emerged as a useful tool for studying the nanostructures via imaging, diffraction and elemental analysis. An SEM uses electromagnetic lenses to de-magnify the size of the electron beam produced by an electron source into a probe. The probe enables scanning of the surface of the samples in a raster manner [186]. Several kinds of emissions are produced from the interaction of the sample and electron probe. These emissions are then captured by the detectors.

Morphological and elemental composition information of the samples are independently gathered by the utilization of certain types of the emitted electrons. These emitted electrons can either be secondary or backscattered electrons. The secondary electrons possessing energies less than 50 eV are used for morphological studies while backscattered electrons with energy greater than 50 eV plays a role in elemental analysis [186]. Characteristic X-rays captured using the X-ray detector can be used for detailed elemental analysis using Energy Dispersive X-ray Spectroscopy (EDX or EDS). EDS is normally coupled to the SEM thus allowing identification of the elemental composition of the sample under observation. This technique is non-destructive and highly sensitive to elements heavier than carbon. Basically, EDS operates by detecting X-rays produced from the interaction of the sample with an electron beam. A beam of electrons hits and excites

the atoms making up the sample leading to the production of X-rays as the excess energy released. This excess energy of the X-ray is typical of the atoms producing them, hence peaks form in the EDS spectrum.

SEM offers many advantages which include: broad observable z-axis with better resolution and higher magnification as compared to optical microscopy. For this study, a field emission scanning electron microscopy (FE-SEM, JEOL JSM-7100F, Japan) equipped with energy dispersive spectroscopy (EDS) shown in Figure 3.7 was used for studying the composition, orientation and morphology of the ZnO nanorods. A JEOL JSM-7100F consists of the in-lens thermal field emission electron source producing electron beam. The FE-SEM was operated at accelerating voltages ranging from 0.1 kV to 30 kV. The vacuum pressure level in the observation chamber was maintained at 10^{-3} to 10^{-5} Pa. A lower electron detector (LED) located under the objective lens was used for capturing images. All the ZnO samples on glass substrates were firmly mounted on the sample holders using carbon conductive adhesive and coated with a thin layer of carbon using carbon sputter. Coating with carbon is necessary as it minimizes the charging effect which affects the image quality.



Figure 3.7: A Field emission scanning electron microscope (FE-SEM, JEOL JSM-7100F, Japan) equipped with energy dispersive spectroscopy (EDS).

3.5.4 Optical properties

Several optical properties of materials are used to fabricate optoelectronic devices, for example; transmittance, absorbance and reflectance must be known so as to predict the device properties. ZnO nanomaterial has emerged as a better candidate for optoelectronic application due to their special properties such as high transmission of light within the visible and near infra-red wavelength range [60, 72]. A Varian Cary 500 Scan UV-VIS-NIR Spectrophotometer was used to measure the optical transmittance of ZnO nanorods in the UV-VIS and NIR regions. The spectrophotometer is connected to the computer with Cary WinUV Software installed. The software enables control and operation of the spectrophotometer. A double beam and double pass monochromator system is one main component that enables improved photometric efficiency of the spectrometer. The monochromator device selects specified wavelengths from the incident light beam. Tungsten or deuterium lamp act as the source of incident light with a wavelength range of 175 nm - 3300 nm. The basic working principle of the spectrometer is to pass a beam of light through the sample firmly held by the holder resulting in electronic transitions of the particles while absorbing and transmitting light in the UV, VIS and NIR ranges of the electromagnetic spectrum. A detector is used to receive the rest of the transmitted beam of light. Figure 3.8 shows a UV-VIS-NIR spectrophotometer used in this study.

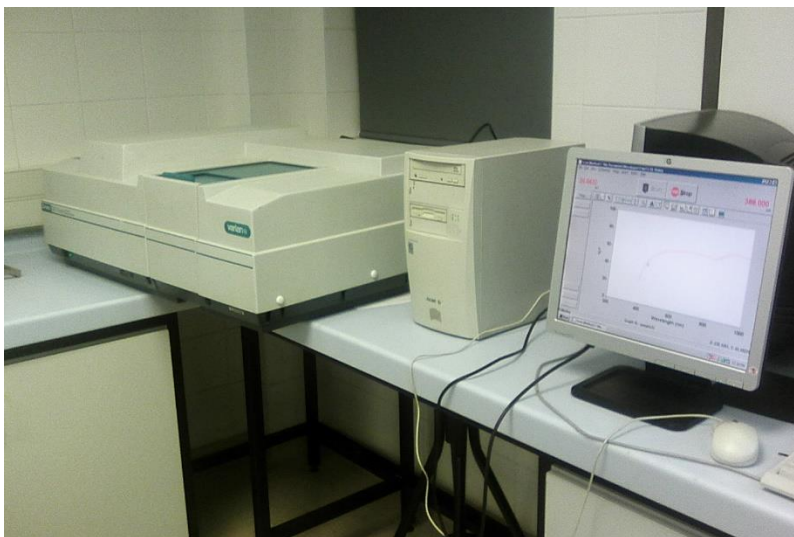


Figure 3.8: A Varian Cary 500 Scan UV-VIS-NIR spectrophotometer.

3.5.5 Raman studies

The understanding of vibrational properties of molecular structures using Raman spectroscopy is important in the field of nanomaterials as it enables identification of the molecules. Raman spectroscopy technique relies on inelastic scattering of light from the laser source upon interacting with the sample. When incident light interacts with the sample, light is scattered. Scattering of the light can either be elastic (Rayleigh) or inelastic. Elastic scattering takes place when the energy of the incident light is equal to the energy of the scattered light while inelastic takes place when the energy of the incident light is not equal to that of scattered light. During the interaction, most of the scattering is elastic. Only a small fraction of the scattering is inelastic with the scattered light having different energy from the incident light. This inelastic scattering of light is called Raman effect or scattering after it was discovered by CV Raman [187]. This technique is used for identification of molecules through the fingerprint patterns in a Raman spectrum presented as intensity against wavelength shift. It also enables studying the crystallinity, orientation and stress of materials. Figure 3.9 shows a Horiba-Jobin Yvon Raman Spectrometer consisting of a 532 nm excitation line of a solid-state laser used to study the nanostructures in this study.



Figure 3.9: Picture of a Horiba-Jobin Yvon Raman Spectrometer.

3.5.6 Four-point probe equipment

The examination of the electrical properties of nanostructures or thin films especially semiconductors is commonly done using the typical method of the four-point probe. This method offers advantages such as better electrical tests accuracy and less work on the preparation of the sample [188]. In this study, the four-point probe set up shown in Figure 3.10 was used to determine the resistivity of the grown ZnO nanorods.



Figure 3.10: Picture of the Four-point probe setup consisting of the power supply, voltmeter, ammeter and connecting wires.

The circuit used for the measurements is illustrated in Figure 3.11. It comprises of four spaced probes made up of tungsten which prevents electrical contacts hence minimizing errors. The four-point probe works using the collinear measurement mode, where the current is applied via the outer probe pair from the power supply and voltage across the sample is measured by the inner probe pair using the voltmeter. The sheet resistance is then calculated using the following equation:

$$R_s = \frac{V}{I} \quad (3.11)$$

where, V is the voltage across the sample and I is the applied current. The sheet resistance is then used for calculation of resistivity which is defined as a measure of how a material opposes the movement of electric current.

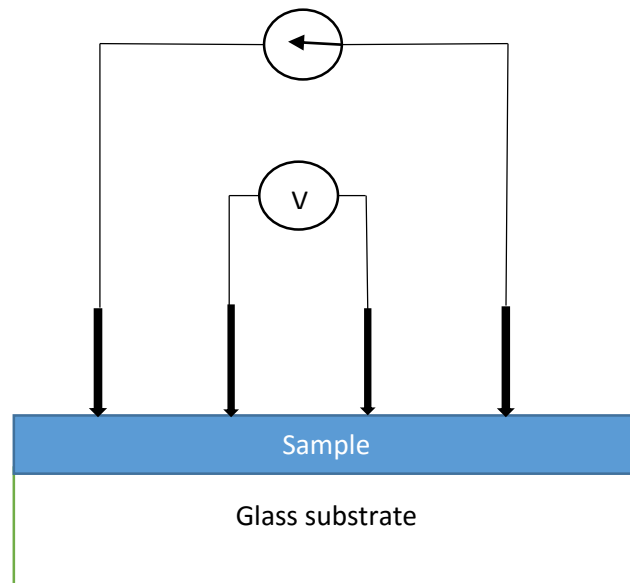


Figure 3.11: Schematic representation of the Four-point probe circuit.

CHAPTER 4: RESULTS AND DISCUSSIONS

4.1 Introduction

This chapter presents the results and in-depth analysis of the results of the work done. The structural, morphological, elemental, optical, vibrational and electrical results of the grown nanostructures are discussed in detail. Section 4.2 looks at the effect of ZnO seed layer thickness on the vertical arrangement, length, diameter and aspect ratios of the ZnO nanorods. Section 4.3, 4.4 and 4.5 gives results on the effect of CBD parameters on the growth of nanorods.

4.2 Effect of ZnO seed layer thickness on ZnO nanorods growth

4.2.1 Seed layer thickness measurements

Pre-coating the substrate with a film of ZnO seeds minimizes the crystal mismatch between the substrate and the nanostructures hence enabling the growth of vertically ordered ZnO nanorods. The ability to control the morphology of the grown nanorods by changing the seed layer thickness could enhance controllability of their properties. The ability to tune the properties of the grown nanostructures allows for their application in different opto-electronic devices.

The ZnO seed layer thicknesses were varied by spraying the precursor solutions on each glass substrate for 10 mins, 20 mins, 30 mins and 40 mins respectively. Literature indicates that shorter deposition times are preferred for the growth of vertical aligned nanorods with high aspect ratio [189]. Prolonged deposition times lead to nanorods with low aspect ratio. The film thickness of the samples was measured using KLA Tencor D-100 Surface profiler. The results show that as the spraying time was increased from 10 to 40 minutes, the film thickness also increased from 10 nm to 50 nm as shown in Figure 4.1. A seed layer thickness of 10 nm produced nanorods of high aspect ratio and better vertical arrangement hence was preferred for the growth.

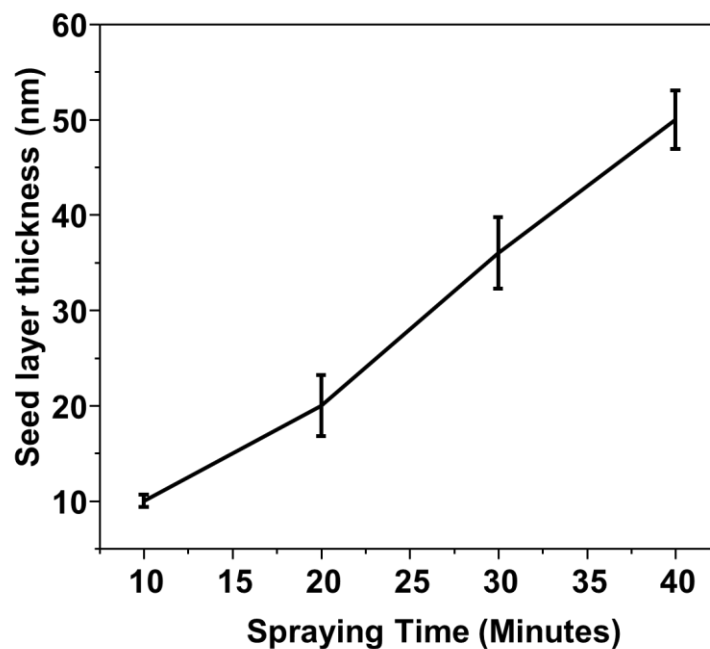


Figure 4.1: ZnO seed layer thicknesses from different deposition times.

4.2.2 Structural studies

Figure 4.2 shows XRD diffractograms of ZnO seed layers prepared by spray pyrolysis while varying the thickness by increasing the spraying time. The observed peaks indicate the presence of ZnO seed layers corroborating with the standard XRD signature of bulk ZnO (Crystallography Open Database, COD 10 11 258). All the samples show a dominant peak of 002 diffraction plane at 34.4° belonging to the wurtzite structured ZnO phase (Crystallography Open Database, COD 10 11 258).

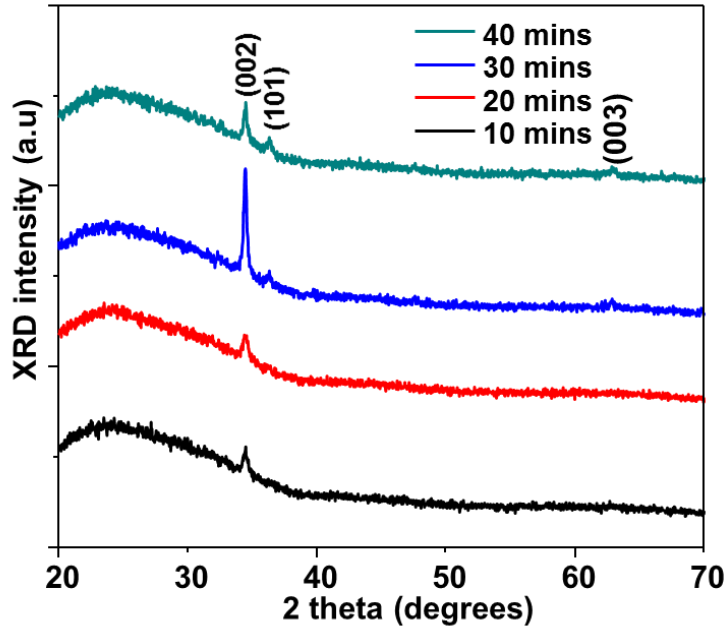


Figure 4.2: XRD of ZnO seed layers of different thicknesses.

The preferred 002-peak orientation intensity increased as the spraying time was increased indicating an improvement in the crystallinity of the seed layers [163, 190]. Additional weak peaks of 101 and 103 planes belonging to the hexagonal ZnO crystals were observed at 36.3° and 62.9° respectively as the thickness was increased from 36 nm to 50 nm [191]. The crystallite sizes were estimated from the 002 peaks using the Derby Scherrer's equation [192, 193]:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (4.1)$$

where D is the crystallite size, λ is the X-ray wavelength (1.5418 Å), β is full width at half maximum (FWHM) in radians and θ is Bragg's diffraction angle. The crystallite size was found to be increasing as the seed layer thickness increased indicating an improvement in the crystallinity as shown Figure 4.3. As the deposition period was increased, more of the ZnO precursors were deposited on the substrate resulting in a thicker seed layer and larger crystallite sizes [194].

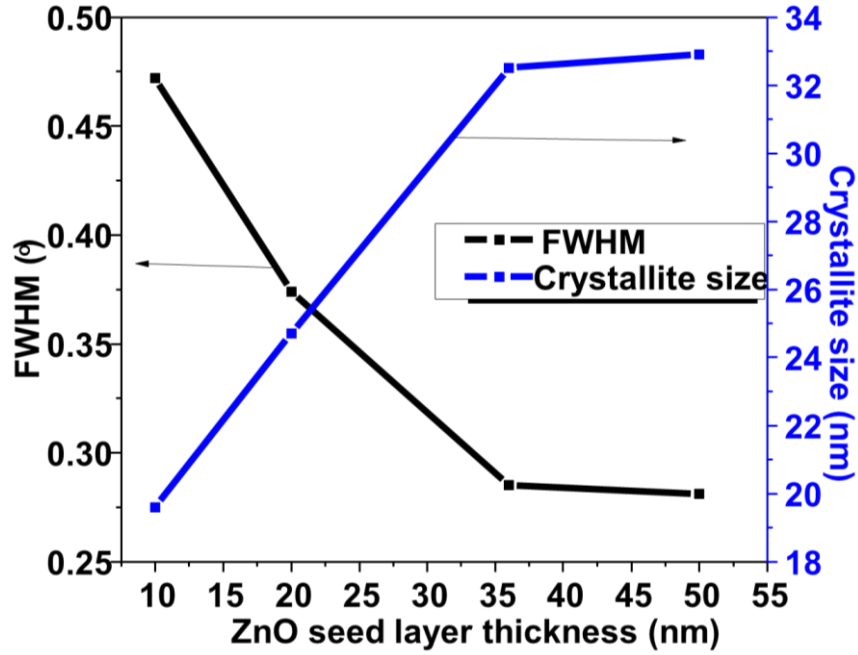


Figure 4.3: Plots of crystallite size and FWHM versus ZnO seed layer thickness.

The FWHM values were decreasing and this is attributed to the peaks narrowing as the thickness increased. According to the Derby Scherrer's equation, the narrowing of the peak indicates increase in the crystal sizes. Other structural properties belonging to ZnO seed layers were determined and recorded in Table 4.1.

Table 4.1: Structural properties of ZnO seeds with variation of thickness.

ZnO seed layer thickness (nm)	FWHM (°)	Crystallite size, D (nm)	Dislocation density, δ (line/m ²)	d-spacing (Å)- 002 peak	Lattice constant, c (Å)	Strain, ϵ (%) $\times 10^{-3}$	Stress, σ (GPa)
10	0.472	19.6	26.03	2.60257	5.2051	0.988	-0.230
20	0.374	24.7	16.39	2.60295	5.2059	1.135	-0.264
36	0.285	32.5	9.47	2.60516	5.2103	1.985	-0.462
50	0.281	32.9	9.24	2.60521	5.2104	2.004	-0.467

The dislocation density (δ), lattice constant or parameter (c), strain (ϵ) and stress (σ) of ZnO nanorods were calculated using the following formulas (4.2) - (4.5) [195, 196, 197, 198]:

$$\delta = \frac{1}{D^2} \quad (4.2)$$

$$\frac{1}{d_{(hkl)}^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \quad (4.3)$$

$$\varepsilon_{zz} = \frac{c - c_o}{c_o} \quad (4.4)$$

$$\sigma = -232.8 \frac{c - c_o}{c_o} \quad (4.5)$$

where D is the crystallite size, c denotes lattice parameter of the strained ZnO from the XRD, c_o is the lattice parameter of the unstrained bulk ZnO (COD 10 11 258), d denotes interplanar spacing (Å), a is the lattice parameter of ZnO from the XRD and hkl are miller indices.

The dislocation density, which is measured in line/m² is defined as dislocation lines per unit volume of a crystal. The calculated values of dislocation densities are listed in Table 4.1. The values were observed to be decreasing as the seed layer thickness increased signifying fewer crystal defects [106]. The lattice constant, c was deduced from equation (4.3) using the 002 plane where $h = 0$, $k = 0$ and $l = 2$ yielding equation (4.6):

$$c = 2d \quad (4.6)$$

The calculated values of the lattice parameter c were slightly higher than that of the pure bulk ZnO (COD 10 11 258) which has 5.2 Å. This may be attributed to tensile strain and compressive stress of the seed layers. The strain equation indicates that when the value of stress obtained is positive then the sample is under tensile stress, and when the stress is negative then the sample is under compressive stress [199]. The increase in the strain and stress values as the ZnO seed

layer thickness was increased may be due to the crystal defects and thermal expansion coefficient variance between the glass substrate and the sample [200].

Figure 4.4 shows XRD diffractograms of ZnO nanorods grown via CBD for 2 hrs at 90 °C on a seed layers deposited at different times using the USP method. It was observed from the patterns that the thickness of the seed layer affects the peaks intensity of the ZnO nanorods. A strong diffraction peak for the 002 plane at $2\theta = 34.4^\circ$ was observed from all the samples indicating the dominant orientation of the hexagonal wurtzite structured ZnO.

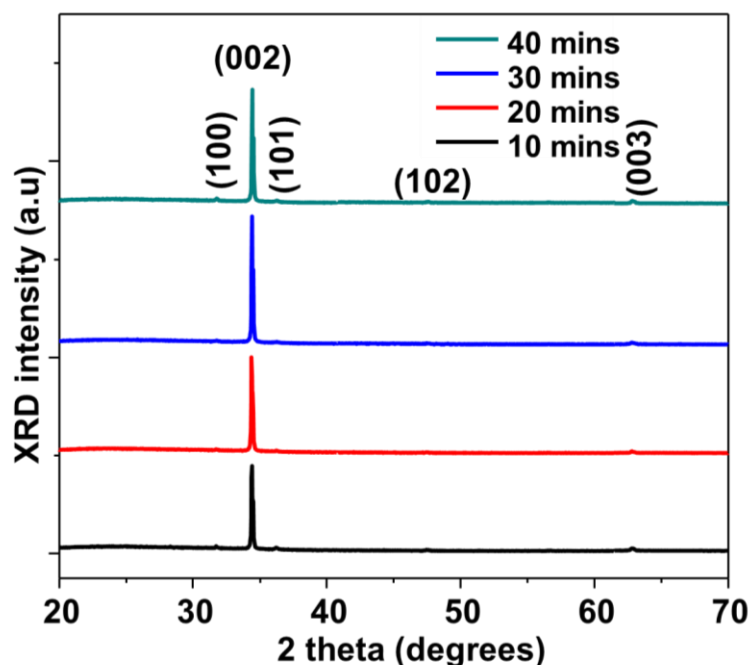


Figure 4.4: XRD diffractograms of ZnO nanorods fabricated from different seed layer thickness deposited at different times.

The 002 peak intensity increased as the seed layer thickness increased suggesting an improvement in crystallinity. Additional weak diffraction peaks for (100), (101), (102) and (003) were also observed at 31.7° , 36.3° , 47.6° and 62.9° corresponding to the hexagonal ZnO phase. No other peaks besides these were detected which indicates that there were no impurities in the samples. The crystallite sizes of ZnO nanorods were determined from FWHM of the 002 peaks using equation (4.1). Figure 4.5 illustrates a plot of the crystallite size of the nanorods increasing with decreasing FWHM as the seed layer thickness increased from 10 to 36 nm showing an

increment in the crystallinity. However, a decrease in the crystallite sizes was observed with further increase of seed layer thickness to 50 nm indicating a decline in the crystallinity. This can be attributed to the fact that a thicker seed layer consists of more than one monocrystal hence different orientation of the nanorods. Contrary to our results, the intensity of the 002-peak decreased as the number of sweeps of seed layers increased suggesting a decrease in the crystallinity [157].

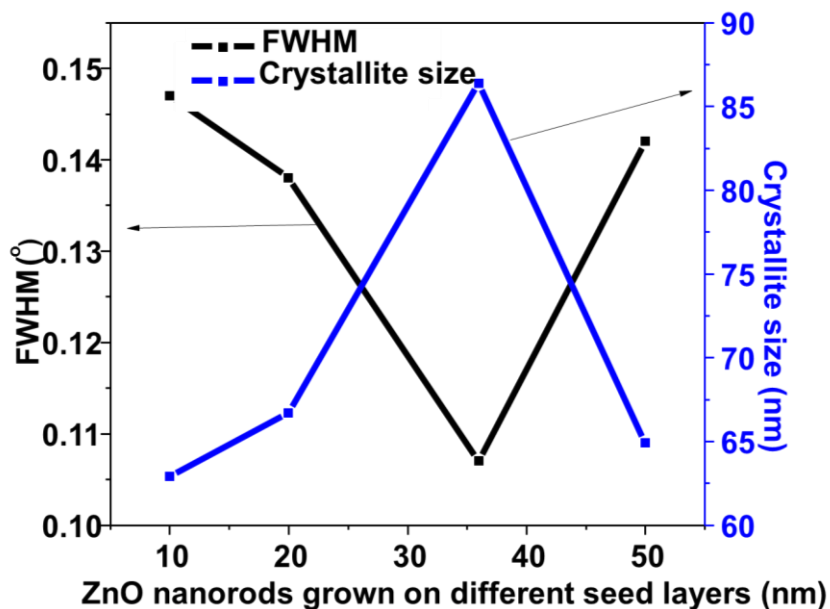


Figure 4.5: Crystallite size and FWHM plots of the ZnO nanorods grown on seed layers of different thicknesses.

Table 4.2 shows the structural information of the ZnO nanorods. The dislocation density was calculated using equation (4.2). The values obtained followed the same trend of the crystallite size values as the seed layer thickness was increasing as recorded in Table 4.2.

Table 4.2: Structural properties of ZnO nanorods grown on ZnO seed layers of different thicknesses.

ZnO seed layer thickness (nm)	FWHM (°)	Crystallite size (nm)	Dislocation density, δ (line/m ²)	d-spacing (Å)- 002 peak	Lattice constant, c (Å)	Strain, ϵ (%) x 10 ⁻³	Stress, σ (GPa)
10	0.147	62.9	2.53	2.60243	5.2049	0.935	-0.218
20	0.138	66.7	2.25	2.60344	5.2069	1.323	-0.308
36	0.107	86.4	1.34	2.60266	5.2053	1.023	-0.238
50	0.142	64.9	2.37	2.60009	5.2002	0.035	-0.008

The lattice constant, c values were found to be ranging from 5.2049 Å to 5.2002 Å. The values are higher than the 5.2 Å of the bulk ZnO (COD 10 11 258). The higher values of c might have been contributed by the positive strain and negative stress corresponding to tensile strain and compressive stress respectively.

4.2.3 Morphology studies

4.2.3.1 ZnO seed layer

SEM micrographs depicting the surface morphologies of ZnO seed layers deposited by USP at different times are presented in Figure 4.6. The deposition time was varied so as to study the influence of the seed layer thickness and uniformity on the growth of the ZnO nanorods. All the samples from the SEM images show spherically shaped particles varying in terms of their size, compactness and density. At a lower deposition time of 10 minutes, there was already a formation of ZnO nanoparticles uniformly covering the substrate as depicted in Figure 4.6. However, as the deposition time was increased the particles clustered together, became clearer and uniformly distributed suggesting that the nucleation was homogeneous during the seed layer deposition across the substrate.

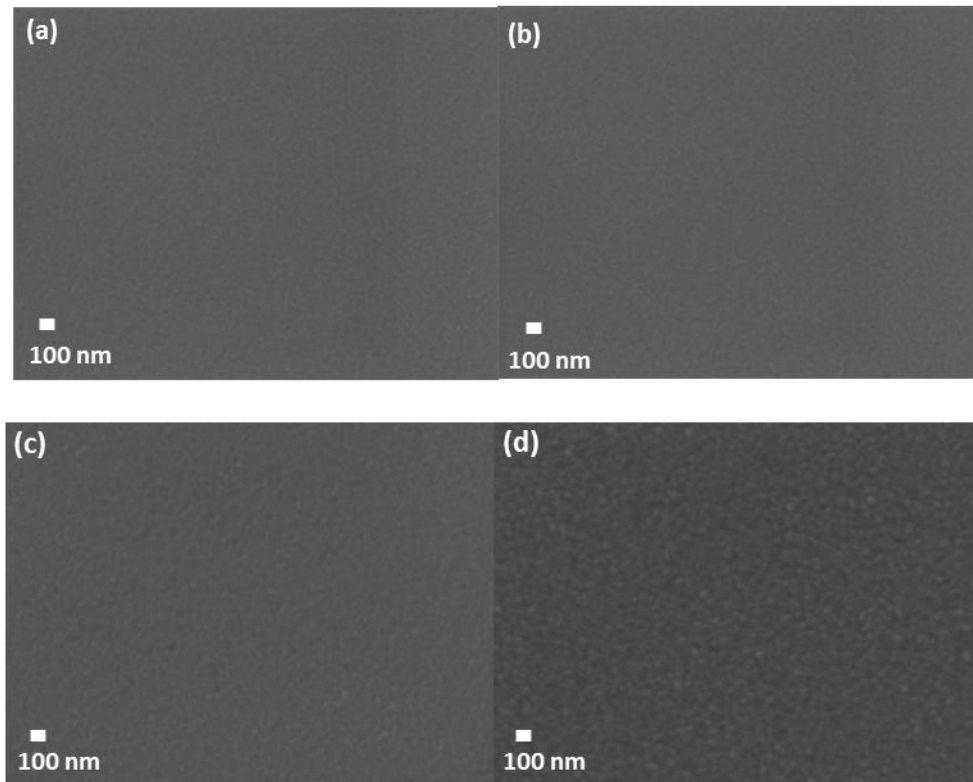


Figure 4.6: SEM images (x 30 000 magnification) of ZnO seed layers deposited by USP for (a) 10 mins, (b) 20 mins, (c) 30 mins and (d) 40 mins.

4.2.3.2 ZnO nanorods

Figure 4.7 shows the top and cross-sectional view of ZnO nanorods grown by CBD on seed layer of different thicknesses. The effects of ZnO seed layer thickness on the alignment, diameter, length and aspect ratio of the nanorods were noticed.

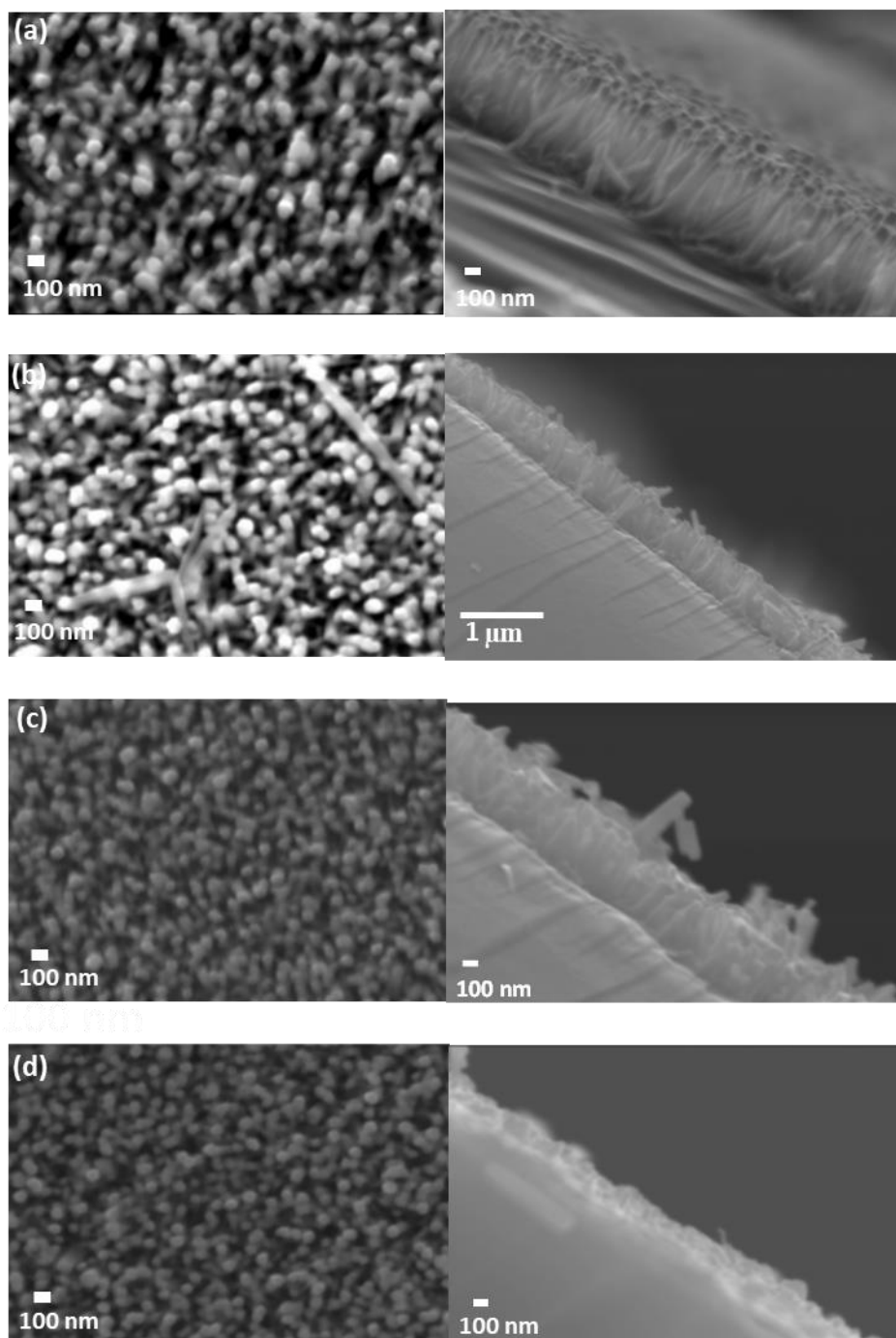


Figure 4.7: Top and cross-sectional view of ZnO nanorods grown on seed layers of different thicknesses (a) 10 nm, (b) 20 nm, (c) 36 nm and (d) 50 nm.

The nanorods appeared less vertically aligned when grown on thicker seed layers. In addition, the seed layer thickness has a definite effect on the growth of the ZnO nanorods. The nanorods length decreased from 790 nm to 250 nm while the diameter slightly increased from 62 nm to 83

nm as the thickness of the seed layer increased as indicated by the plot in Figure 4.8. The particle size of the seed layer strongly affects the diameter of the nanorods. As the seed layer thickness increased the particle sizes of the seed layer also increased, and since the seed layer plays a significant role on the growth of nanorods the diameter was found to be increasing. The length of the nanorods decreased due to the fact that the higher surface energy facets (0001) and (000 $\bar{1}$) attracts the opposite ions in the solution. Hence the axial growth is more preferred than the lateral growth. Similar results were observed in other studies [189, 190]. Contrary to the present work, both the length and diameter of the ZnO nanorods increased as the seed layer thickness increased because of the nanorod density and roughness of the ZnO seed layer [159].

Table 4.3: Lengths, diameters and aspect ratios of ZnO nanorods corresponding to different thicknesses.

ZnO seed layer thickness (nm)	Length of the nanorods (nm)	Diameter of the nanorods (nm)	Aspect ratio
10	790	62	12.7
20	500	70	7.1
36	430	75	5.7
50	250	83	3.0

A summary of the length, diameter and aspect ratio values is shown in Table 4.3. The aspect ratio which is defined as the fraction of the length to the diameter of the nanorods decreased from 12.7 to 3.0 as the seed layer thickness increased. The 10 nm seed layer was chosen as the optimum thickness as it yielded nanorods with high aspect ratio and better alignment. The same seed layer thickness was used for growing the nanorods in another work by other researchers [201, 202]. A combination of shorter USP process and longer CBD produced vertically arranged ZnO nanorods. In another study, longer USP process and CBD proved to be producing better structured ZnO nanorods [203]. It can be concluded that the seed layer is crucial on the growth of the desired orientation of the nanorods. It provides nucleation sites for the attachment and growth of the nanorods [177].

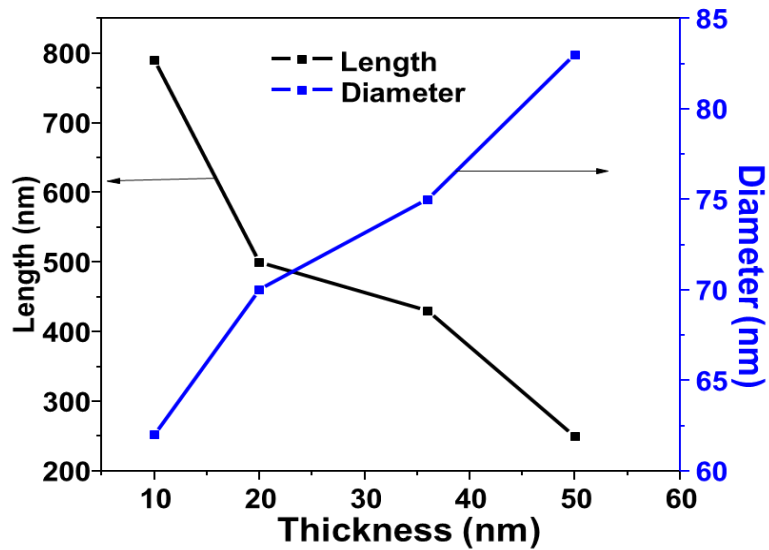


Figure 4.8: Plots of Length and diameter of ZnO nanorods with variation of seed layer thickness.

4.2.4 Elemental Analysis

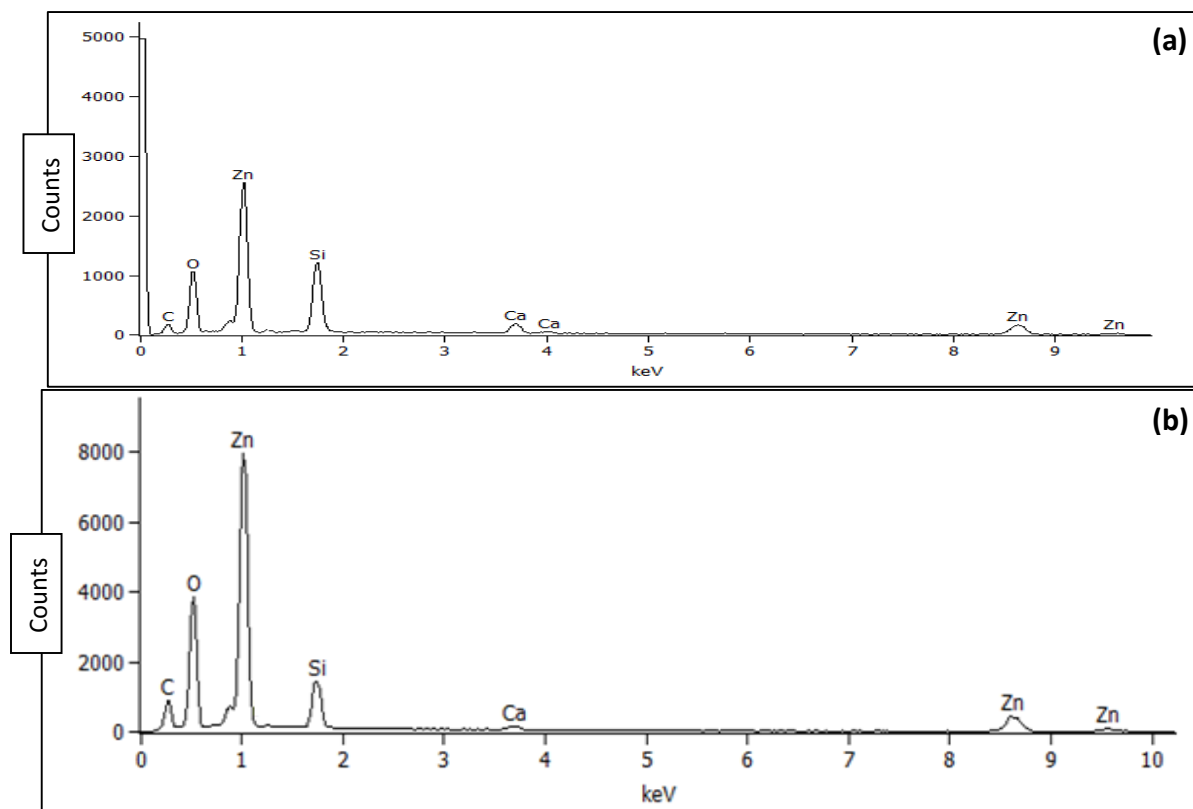


Figure 4.9: (a) EDS spectrum of ZnO seed layers, (b) EDS spectrum of ZnO nanorods.

Figure 4.9 (a) shows EDS spectrum of ZnO seed layers deposited by USP. The EDS spectrum of ZnO nanorods grown by CBD at 90 °C for 2 hrs is shown in

Figure 4.9 (b). The presence of Zn and O elements was confirmed by EDS in all the samples. However, there are other elements present which include Silicon (Si), Carbon (C) and Calcium (Ca). Si and Ca indicated by EDS are mainly due to the glass substrate. Ca might also be originating from USP process chamber [203]. Carbon was found to be present as the sample was coated with a carbon conductive layer to enable the imaging.

4.2.5 Optical properties

Figure 4.10 displays the optical transmittance spectra in the 300-800 nm range of ZnO nanorods grown by CBD on seed layers deposited by USP at different times. The transmittance spectra indicate that the nanorods had an average of 60-70 % optical transmittance in the visible region attributed to the random scattering of the incident light by the nanorods [76]. An absorption edge was noticed at around 378 nm - 380 nm for all the samples which is a common characteristic of ZnO. The absorption edge corresponds to the optical band gap where the incident photon possess energy that will result in excitations of the electrons from one band to another [204].

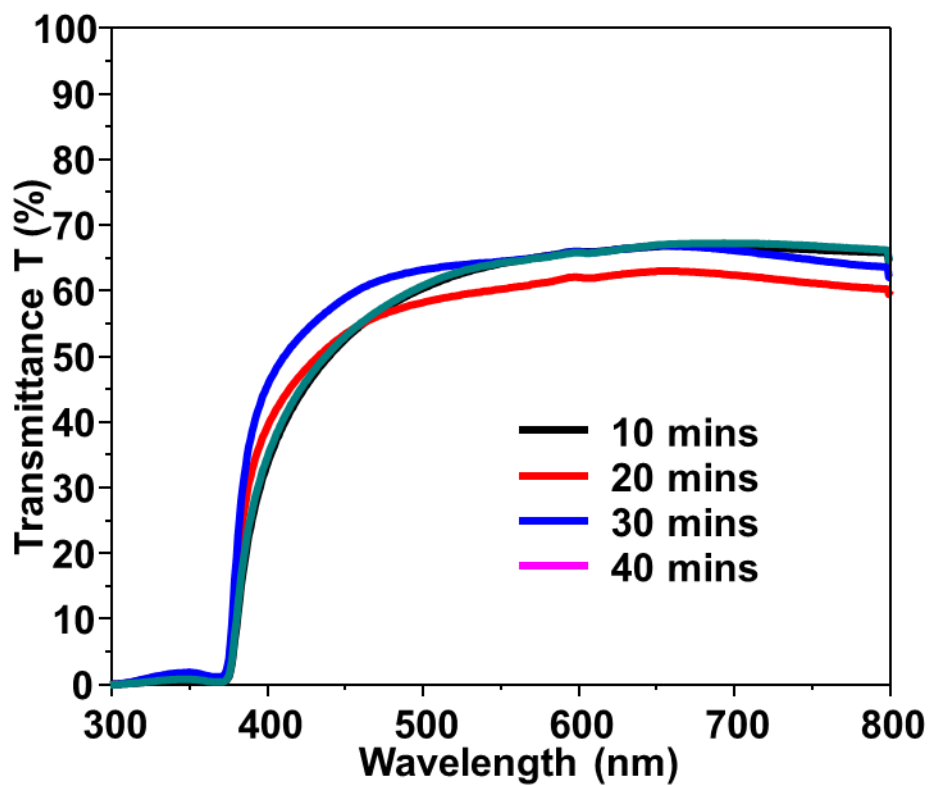


Figure 4.10: Transmittance spectra of ZnO nanorods grown on seed layers deposited by USP at different times.

Figure 4.11 shows a plot of the first derivative of optical transmittance versus wavelength resulting in a peak corresponding to the absorption band edge.

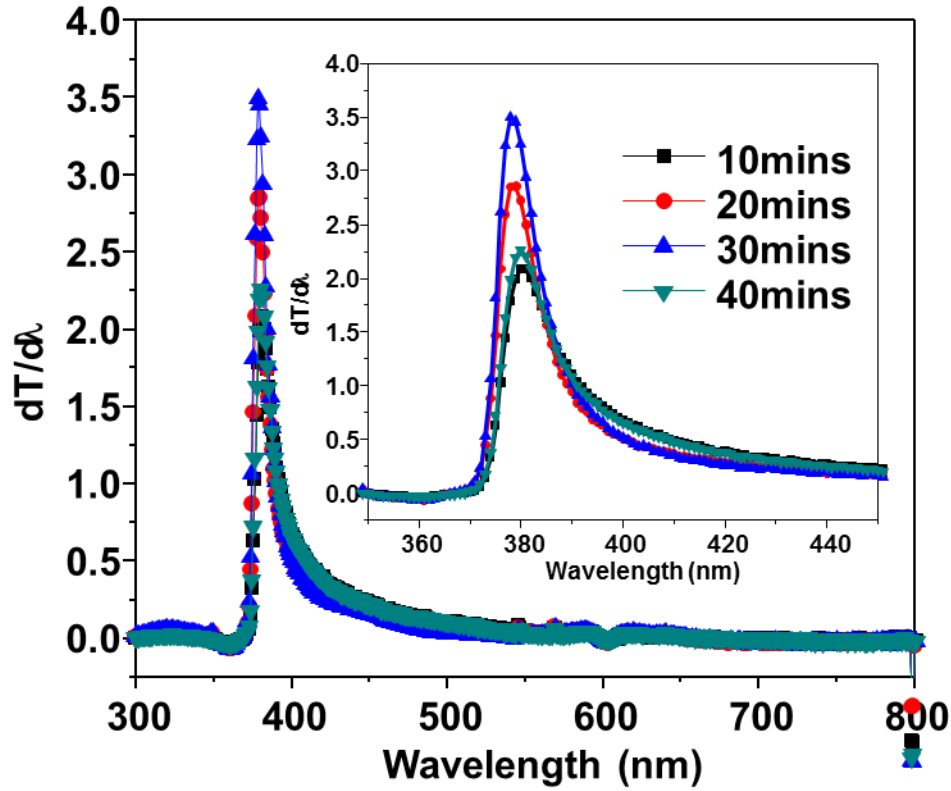


Figure 4.11: Plot of first derivative of transmittance of ZnO nanorods grown in different seed layers (insert shows the zoomed peaks).

The optical band gap calculations were done by using the wavelength of the peak corresponding to the absorption band edge obtained from the derivative plot using the equation [205]:

$$E_g = \frac{hc}{\lambda} \quad (4.7)$$

where E_g is the band gap energy, h is Planck's constant (6.626×10^{-34} Js), c is the speed of light (3.0×10^8 m/s) and λ is the wavelength corresponding to the absorption edge. The band gap energies of the ZnO nanorods as the seed layer thickness was varied are listed in Table 4.4.

Table 4.4: Band gap energies of ZnO nanorods grown on seed layers of different thicknesses.

ZnO seed layer thickness (nm)	Band gap energy (eV)
10	3.27
20	3.28
36	3.29
50	3.27

The values of the band gap are less than 3.37 eV of the single crystal ZnO, this may probably be as a result of formation of defects which includes oxygen vacancies, crystallite size and stress [205, 206, 207].

Optical parameters of ZnO nanorods which include extinction coefficient (k), refractive index (n), real (ϵ_1) and imaginary (ϵ_2) dielectric constants were derived from the transmittance spectra using the Opti layer thin film software. These parameters are vital in providing the optical properties of the nanorods.

The extinction coefficient which is directly linked to the absorption of light is defined using equation:

$$k = \frac{\alpha\lambda}{4\pi} \quad (4.8)$$

where α denotes the absorption coefficient and λ is the wavelength of the incident light.

Figure 4.12 (a) clearly shows the extinction coefficient rapidly reducing to lower values with increasing wavelength from 300 nm to 400 nm for all the samples. Lower values of k ranging from 0.010 to 0.025 were observed in the visible region. This means that the nanorods have low optical absorbance indicating their high transparency in the visible range [81, 106].

The refractive index of the nanorods which is the ratio of the phase velocity of the light in space to the phase velocity in a medium was also studied. It is defined by Cauchy law given by [208]:

$$n = n_o + \frac{A}{\lambda^2} + \frac{B}{\lambda^4} \quad (4.9)$$

where λ is the wavelength and A , B and n_o are the Cauchy's parameters.

The change in the refractive index with the wavelength for all the samples is shown in Figure 4.12 (b). The values of the refractive index ranged between 1.52 - 1.82 in the visible range. This suggests that the velocity of the light is 1.52 - 1.82 times slower in the nanorods as compared to its velocity in free space. The values of the refractive index are lower than the 2.0 of the standard ZnO. This suggest that the speed of light is slightly faster in the nanorods as compared to the standard ZnO due to less grain boundaries which contribute to the trapping of the photons resulting in internal reflections [80]. The lower values of the refractive index could also have resulted because of the presence of defects causing enhanced scattering of light [209].

The dielectric constant is another fundamental property belonging to materials. Normally low dielectric constant values of materials are imperative for several applications [210, 211]. The dielectric properties of a material are often characterized by the real and imaginary parts. In this study both parts of the dielectric constant belonging to ZnO nanorods were evaluated. Basically, the real part gives information on the energy absorbed by the dielectric material resulting from the applied electric field while the imaginary part is the quantity of the energy released by the dielectric material originating for the electric field created by the motion of the dipoles [81, 210]. The real part of the dielectric constant is also linked with expressing by how much the speed of light is slowed down by the material [81, 212]. Both parts of the dielectric constant were estimated by using the relations:

$$\varepsilon_1 = n^2 - k^2 \quad (4.10)$$

$$\varepsilon_2 = 2nk \quad (4.11)$$

The variation of ε_1 and ε_2 as a function of the wavelength of all the samples is illustrated in Figure 4.12 (c) and (d) respectively. The values of the ε_1 varied between 2.3 and 3.2 while ε_2 values ranged between 0.04 and 0.2 in the visible region.

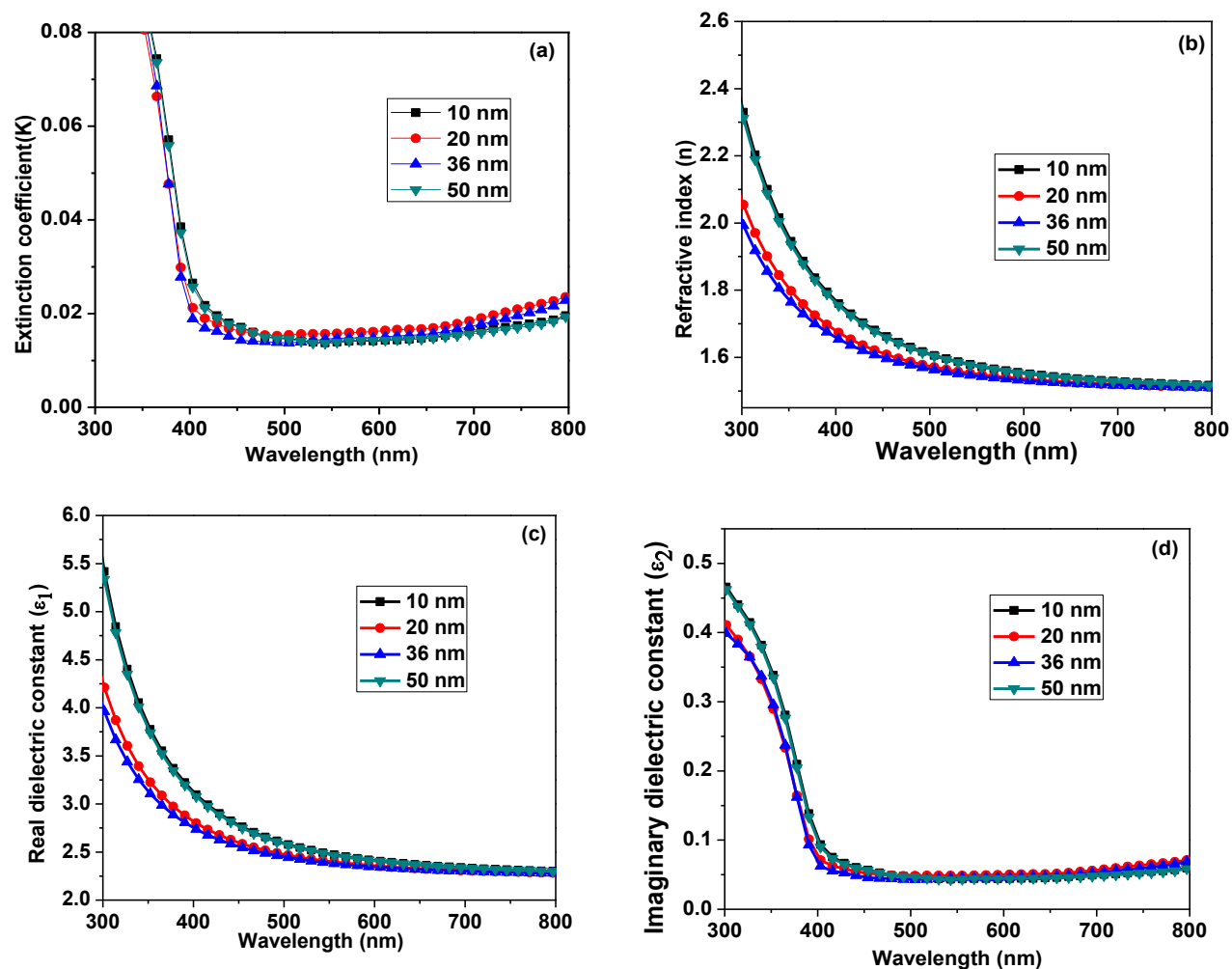


Figure 4.12: Plots of (a) extinction coefficient, (b) refractive index, (c) Real dielectric constant and (d) Imaginary dielectric constant vs wavelength with variation of the seed layer thickness from 10 nm - 50 nm.

4.2.6 Raman spectroscopy studies

Figure 4.13 displays the Raman spectra of the nanorods grown on ZnO seeds of different thickness obtained. All the ZnO nanorods show peaks at 96, 328, 377 and 435 cm^{-1} belonging to ZnO with hexagonal wurtzite structure. The dominant peaks revealed at 96 and 435 cm^{-1} corresponds to the Raman active E_2 (low) and E_2 (high) optical phonon modes respectively. The weak peaks at 328 and 377 cm^{-1} belong to the combined mode of E_2 (high)- E_2 (low) arising from the multiple phonon scattering process and A_1 (TO) respectively [213]. The intensity of the peaks

of the Raman active phonon modes of ZnO nanorods were observed to be increasing as the seed layer thickness increased suggesting an increase in the crystallinity of the nanorods corroborating with the XRD results [89, 189].

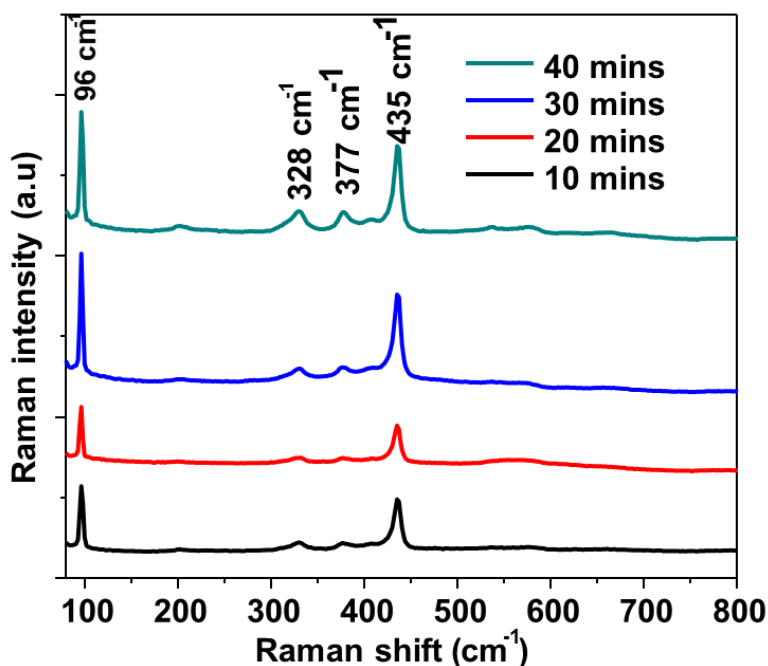


Figure 4.13: Raman spectra of ZnO nanorods grown on seed layers of different thickness.

All the peaks shifted by 3 cm^{-1} to lower frequencies when compared to the standard bulk ZnO. This process is known as Red shifting. The red shifting of the A_2 high peak is attributed by the strain variation [89, 189]. A shift of the A_2 high peak to lower frequencies suggest that the nanostructures are under tensile strain (red shifting) while a shift to higher frequencies denotes compressive strain (blue shifting) [84, 214]. The results obtained indicate that the nanostructures are under tensile strain in agreement with the XRD data studies where the value of the value of strain is positive.

4.2.7 Electrical properties

A four-point probe set up was used for the resistivity measurements of the samples. The sheet resistance (R_s) was calculated from the gradient of a respective IV plot. The resistivity of the nanorods was estimated using the following equation:

$$\rho = \left(\frac{\pi}{\ln 2} \right) \cdot R_s t \quad (4.12)$$

where R_s is the sheet resistance, t is the film thickness and $\frac{\pi}{\ln 2}$ is the correction factor. This correction factor is based on the geometry of sample such as the thickness of the sample. When the spacing of the probes is larger than the thickness of the sample, then the correction factor is included. The electrical resistivity of the nanorods was observed to be decreasing from $2.52 \times 10^2 \Omega\text{cm}$ to $0.39 \times 10^2 \Omega\text{cm}$ as the seed layer thickness increased as shown in Figure 4.14. The decrease in resistivity to lower values might have been caused by the increased crystallite size thereby minimizing the grain boundary scattering losses [94, 215].

The following equation by Haacke was used for the calculation of the figure of merit [216, 217]:

$$\varphi = \frac{T^{10}}{R_s} \quad (4.13)$$

where T is the optical average transmittance around 550 nm and R_s is the sheet resistance. The region around 550 nm in the visible range is known as the near solar spectrum maximum, where the maximum radiation intensity occurs [218]. The figure of merit values of the nanorods grown on seed layers of different thickness are illustrated in Figure 4.14. The values increased from $4.75 \times 10^{-5} \Omega^{-1}$ to $3.03 \times 10^{-4} \Omega^{-1}$ as the seed layer thickness was increased. The values obtained indicate the suitability of the nanorods to act as photoanodes in solar cell devices as there is consistency with other studies [106, 107].

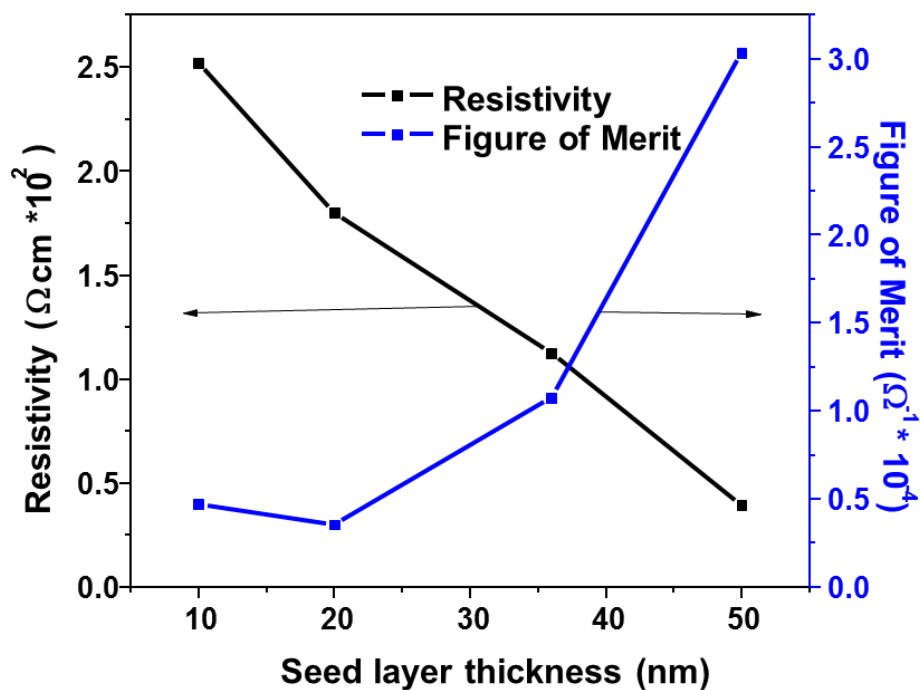


Figure 4.14: Variation of resistivity and figure of merit of ZnO nanorods grown on seed layers with different thickness.

4.3 Effect of the growth time of ZnO nanorods by chemical bath deposition

4.3.1 Structural properties

Figure 4.15 shows XRD patterns of ZnO nanorods grown by CBD for 1.5- 3 hrs on ZnO seed layer prepared by USP. The dominant 002 peak at $2\theta = 34.4^\circ$ revealed a hexagonal wurtzite structure of the grown ZnO nanorods. The 002-peak intensity increased as the growth time increased from 1.5 to 3 hrs suggesting an improvement in the crystal quality of the nanorods. Similarly, XRD diffractograms were observed from other studies showing increasing intensity of the 002 as the growth time increased [219, 220, 221].

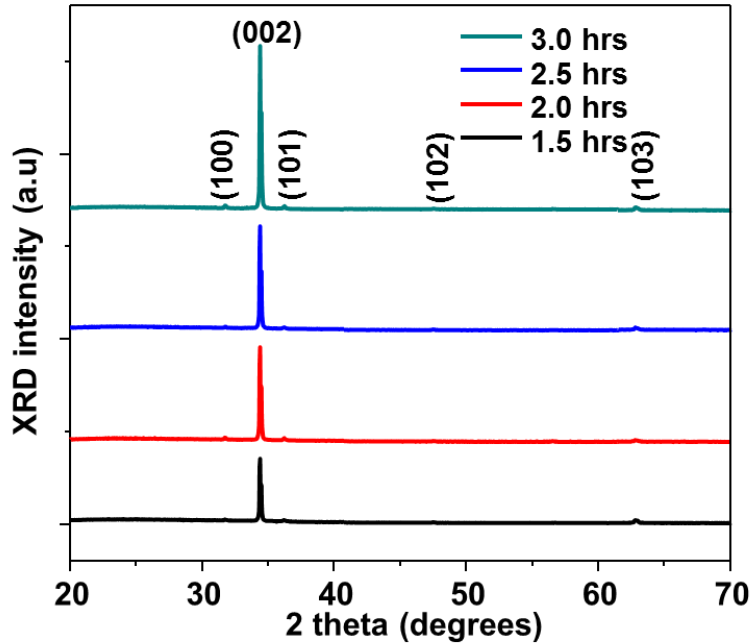


Figure 4.15: XRD patterns of ZnO nanorods grown for 1.5 to 3.0 hrs.

Additional weak diffraction peaks for (100), (101), (102) and (103) planes were observed at 31.7° , 36.3° , 47.6° and 62.9° corresponding to the hexagonal ZnO phase. The presence of the additional peaks indicates the presence of randomly oriented nanorods [222]. All the peaks detected are consistent with those of the standard bulk ZnO (COD 10 11 258) patterns. Table 4.5 shows the results of an analysis of the XRD diffractograms of ZnO nanorods grown at different times.

Table 4.5: Structural properties of ZnO nanorods from different growth times.

Growth time (hrs)	FWHM ($^\circ$)	Crystallite size (nm)	Dislocation density, δ (line/ m^2)	d- spacing ($\text{\AA}$)- 002 peak	Lattice constant, c ($\text{\AA}$)	Strain, ϵ (%) $\times 10^{-3}$	Stress, σ (GPa)
1.5	0.146	63.1	2.51	2.60254	5.2051	0.977	-0.228
2.0	0.145	63.7	2.46	2.60234	5.2047	0.900	-0.210
2.5	0.142	65.0	2.37	2.60231	5.2046	0.888	-0.207
3.0	0.133	69.3	2.08	2.60165	5.2033	0.635	-0.148

The crystallite sizes were calculated from Scherrer's formula (4.1) using the FWHM of the highest peak belonging to the 002-diffraction plane. The crystallite size and FWHM values are listed in Table 4.5. The FWHM values were observed to be decreasing from 0.146° to 0.133° while the

crystallite sizes increased from 63.1 nm to 69.3 nm as the growth time was increased from 1.5 hrs to 3.0 hrs, an indication of enhancement in the crystallinity. The trend of the FWHM and crystallite size values as the growth time increased is clearly shown in Figure 4.16.

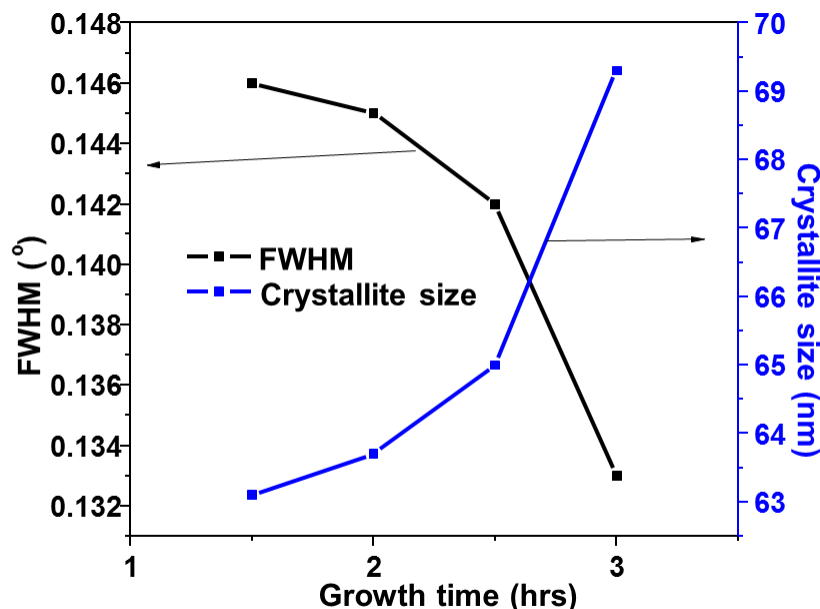


Figure 4.16: Crystallite size and FWHM against growth time plots.

The dislocation density, which represents the number of defects was calculated from the crystallite size using equation (4.2). The dislocation density decreased with an increase of the growth time as shown in Table 4.5. This is an indication of a decrease of lattice defects possessed by the nanorods with increased growth time [106]. The lattice constant (c) values were calculated from the d-spacing using equation (4.6). The obtained values of constant (c) are slightly higher than 5.2 Å of pure bulk ZnO (COD 10 11 258). This slight difference between the obtained results and the standard values might be originating from the tensile strain and compressive stress of the nanostructures [90, 223]. The strain of the grown ZnO nanorods on glass substrate was estimated using equation (4.4). Tensile strain of the nanorods gradually decreased with increased growth time from 1.5 hrs to 3.0 hrs. The ZnO nanorods also had compressive stresses reducing with growth time. Similar trends of stress and strain with growth duration were observed from other studies [90, 224].

4.3.2 Morphological studies

Figure 4.17 shows the histograms (inset), top and cross-sectional views of ZnO nanorods grown by CBD for 1.5 hrs- 3.0 hrs on a ZnO seed layer prepared by USP.

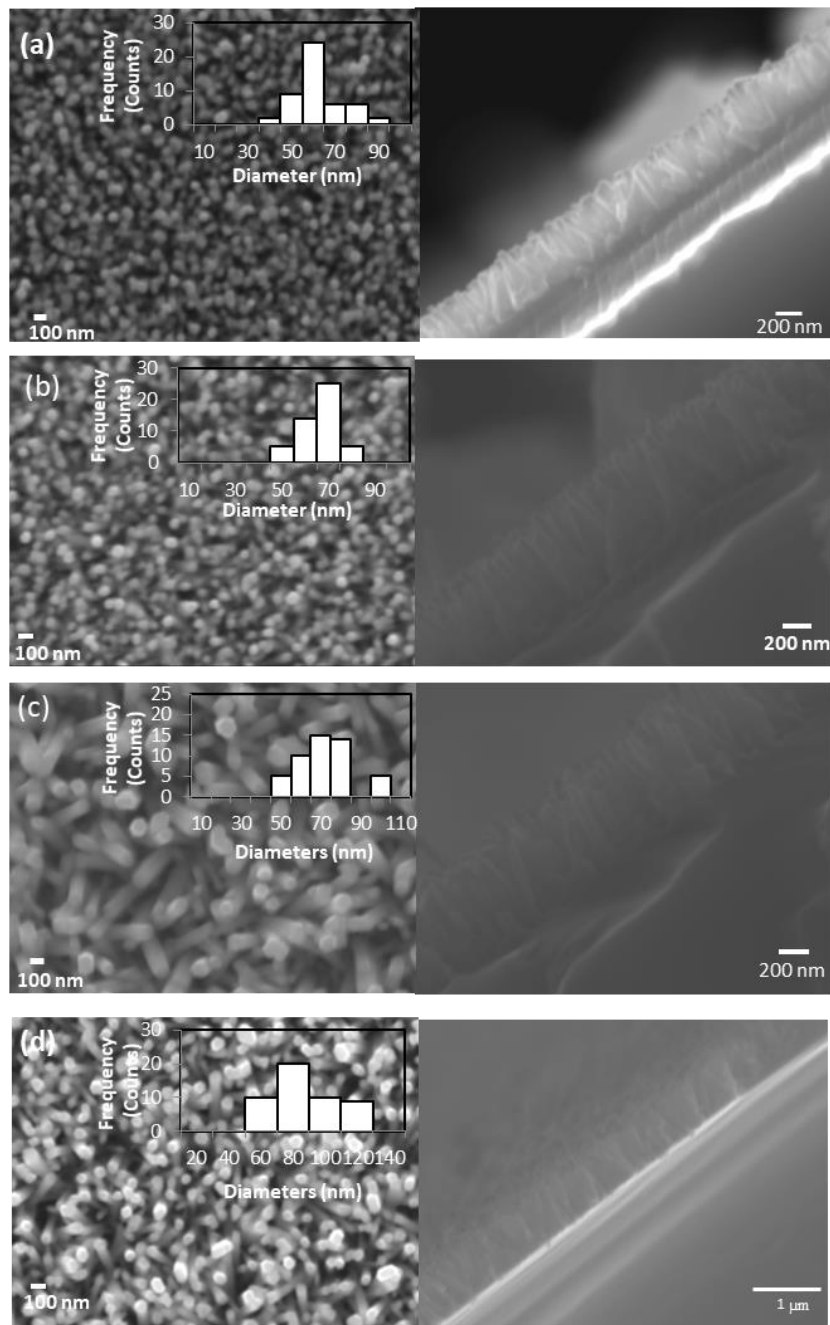


Figure 4.17: Top and cross-sectional view of ZnO nanorods grown for (a) 1.5 hrs, (b) 2 hrs, (c) 2.5 hrs and (d) 3 hrs. The insert of the histograms in each image correspond to the diameter distribution of the grown nanorods.

Histograms of nanorods diameter distribution with variation of growth time appear as insets in images. SEM images revealed that the shape, diameter and length of the nanorods depend on the growth time as observed in other studies [89]. The nanorods appear to be evenly and uniformly distributed on the substrate. A marginal increase of the average diameter of the nanorods was noted from the histograms ranging from 60 nm - 80 nm with variation of growth time. It was also seen that as the growth time increased from 1.5 hrs to 3.0 hrs, the average nanorods length increased from 500 nm for 1.5 hrs to 800 nm for 3 hrs. Similar observations were made in refs [225, 226, 227].

The trends of the change in length and diameter are indicated in the plots shown in Figure 4.18. The trend signifies that the axial growth rate was higher than the lateral growth. The aspect ratio which is defined as the fraction of the length to the diameter of the nanorods increased from 8.3 to 10.3 as the growth time increased from 1.5 hrs to 2.0 hrs. Further increase of growth time to 3.0 hrs leads to an aspect ratio decrease from 10.3 to 10.0. It was observed that the statistical distribution of the nanorods diameter is affected by the growth time. This is an indication of a rise in the length to diameter ratio of the nanorods. All in all the growth time contributes a lot in tailoring the morphology of the nanorods grown.

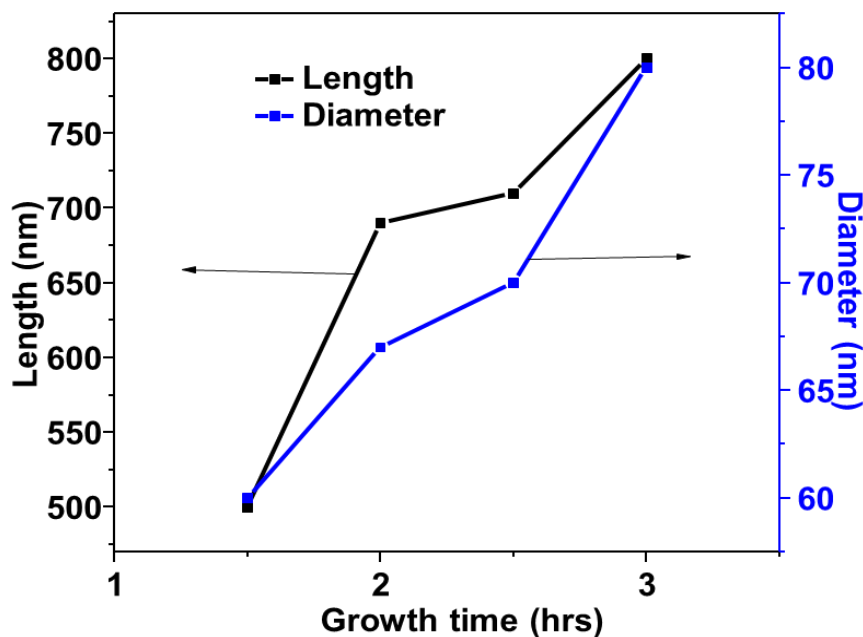


Figure 4.18: Length and diameter of ZnO nanorods with variation of growth time.

Table 4.6 gives a summary of the average length, diameter and aspect ratio with growth time. In general, most of the nanorods appear to be perpendicular to the substrate. However, some of the nanorods appear to be tilted as their lengths increased with growth time hence affecting the vertical arrangement. As such shorter growth times are preferred for ZnO nanorods growth. The best growth time was 2 hrs as most nanorods were still vertically arranged with high aspect ratio for this study. Longer growth periods of ZnO nanorods have been observed to cause predominant growth along the *c*-axis of the polar direction (001) as compared to the non-polar faces [174, 226].

Table 4.6: Lengths, diameters and aspect ratio of ZnO nanorods grown at different times.

Growth time (hrs)	Length of the nanorods (nm)	Diameter of the nanorods (nm)	Aspect ratio
1.5	500 ± 27	60 ± 12	8.3
2.0	690 ± 45	67 ± 10	10.3
2.5	710 ± 47	70 ± 11	10.1
3.0	800 ± 59	80 ± 23	10.0

4.3.3 Elemental analysis

Figure 4.19 shows the results of an EDS scan of ZnO nanorods grown by CBD at 90 °C for 2.0 hrs on a seed layer deposited by USP. The peaks of Zn and O elements belong to the nanorods grown. Other peaks belong to Silicon (Si), Carbon (C) and Calcium (Ca). Si and Ca peaks emanate from the glass substrate. The USP process chamber was also a possible source of Ca [203]. The C element can be attributed by the carbon coating paste applied on the sample to enable the imaging.

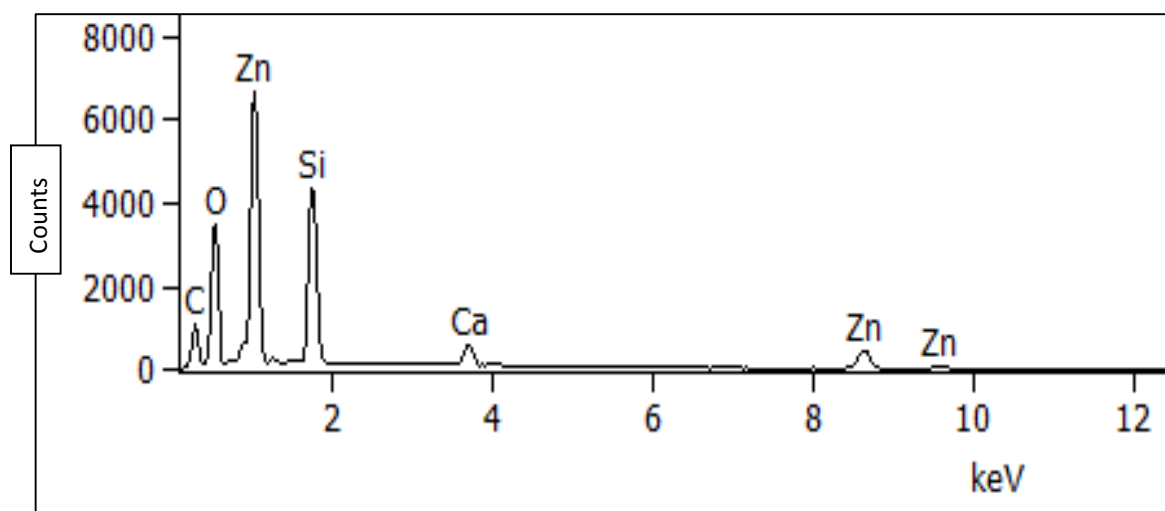


Figure 4.19: Elemental composition of ZnO nanorods grown at different times.

4.3.4 Optical properties

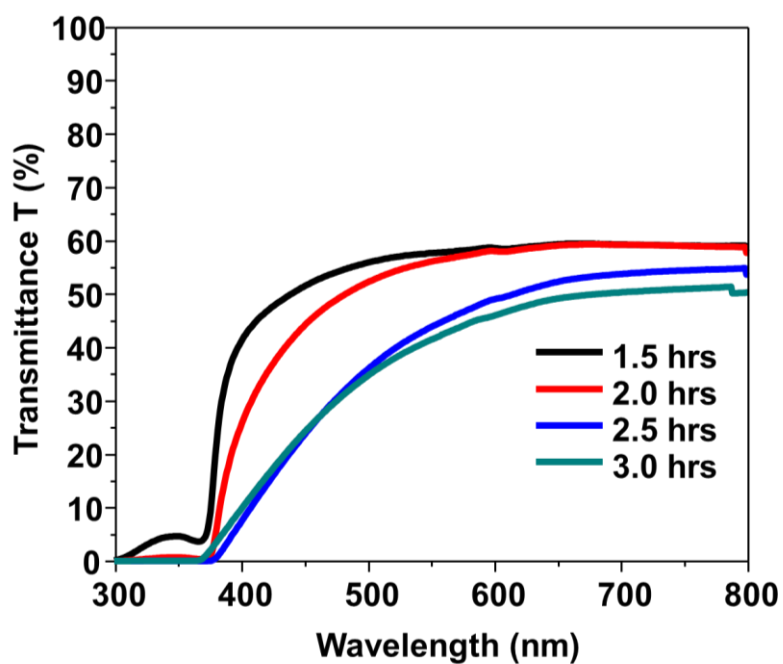


Figure 4.20: Transmittance spectra of ZnO nanorods for different growth times.

Figure 4.20 shows optical transmittance spectra of ZnO nanorods prepared by CBD while varying growth time in the wavelength range of 300- 800 nm. The nanorods had about 50-60 % light

transmittance in the visible region and lower transmittance in the UV region. The absorption edges were observed in the range 370-380 nm for all the samples. The absorption edge shifted to longer wavelength as the growth time increased from 1.5 hrs to 2.5 hrs. This may be due to the decrease of the band gap energy, defects, oxygen vacancies and the distribution of the nanorods [77, 228]. The transparency of the nanorods decreased as the growth time increased. Similar results were obtained in ref [89]. The decrease in the optical transmittance of the nanorods is due to the scattering of the light at the grain boundaries [229]. It was also noted that the transmittance decreases with an increase in the crystallite sizes causing increased light scattering [89]. The transmittance for wavelengths ranging between 300 and 380 nm for the 1.5 hrs run appears to suggest that nanorods grown for shorter times are very well networked.

The band gap energies of the nanorods were determined from a plot of first derivative of transmittance shown in Figure 4.21. The band gap energy values were calculated using equation (4.7) and are presented in Table 4.7. The values are lower than the 3.37 eV of the standard bulk ZnO as a result of the optical confinement effect of the nanorods [230]. The band gap energies decreased as the growth time increased from 1.5 to 3 hrs [89, 231]. Crystallite size, stress, strain, oxygen vacancies and carrier concentration are factors that affect the optical band gap energy [207]. The variation of the crystallite size, negative stress and positive strain of the nanorods as growth time increased might have contributed to the decrease of the band gap energy.

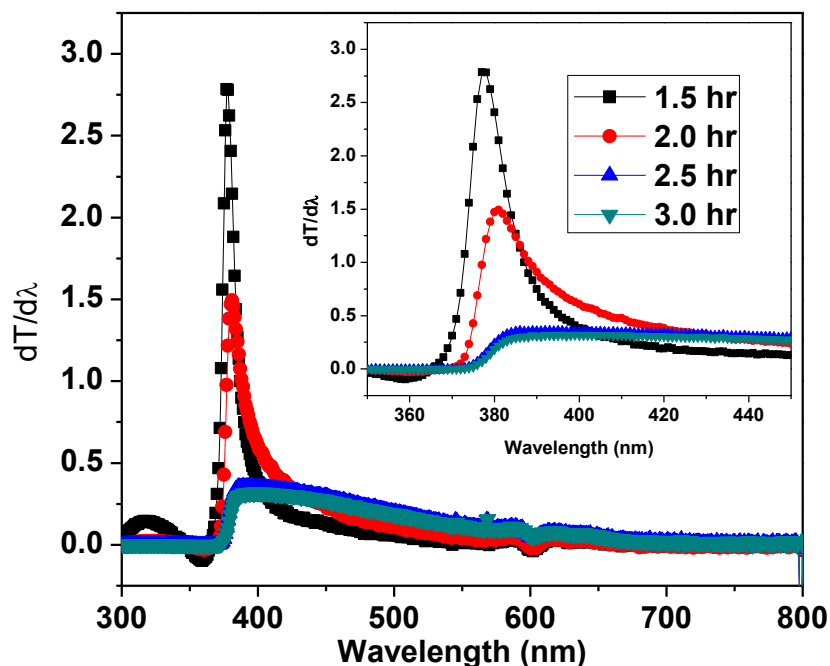


Figure 4.21: Plot of $dT/d\lambda$ vs wavelength for ZnO nanorods grown at varying times (insert shows zoomed peaks).

Table 4.7: Optical band gap energy values for ZnO nanorods grown at different times.

Growth time (hrs)	Band gap energy (eV)
1.5	3.30
2.0	3.28
2.5	3.25
3.0	3.25

The variation of the extinction coefficient (k) values with the wavelength is illustrated in Figure 4.22 (a). The values ranged between about 0.015 and 0.06 in the visible range for all the samples from the various growth times. A rapid decrease in the k values as the wavelength increased from 350 to 400 nm is directly related to the optical absorbance. The higher the value of k , the higher the absorption of light and vice versa. As such lower values of k shows that the grown nanorods are highly transparent.

Figure 4.22 (b) displays the refractive index of ZnO nanorods as the growth time was varied. The values of the refractive index were observed to be around 1.52 – 1.85 in the visible region slightly lower than 2.0, which is the refractive index of standard bulk ZnO. This suggests that speed of the light is 1.52- 1.85 times reduced when interacting with the nanorods. The lower values of n occur due to strong scattering of light by the nanorods. As the growth time was increased from 1.5 – 3.0 hrs the refractive index increased. The increase in the refractive index with growth time attributed to the increase in crystallinity and compactness of the nanorods corroborating with the XRD and SEM results. This was comparable with findings from other researchers [76, 232].

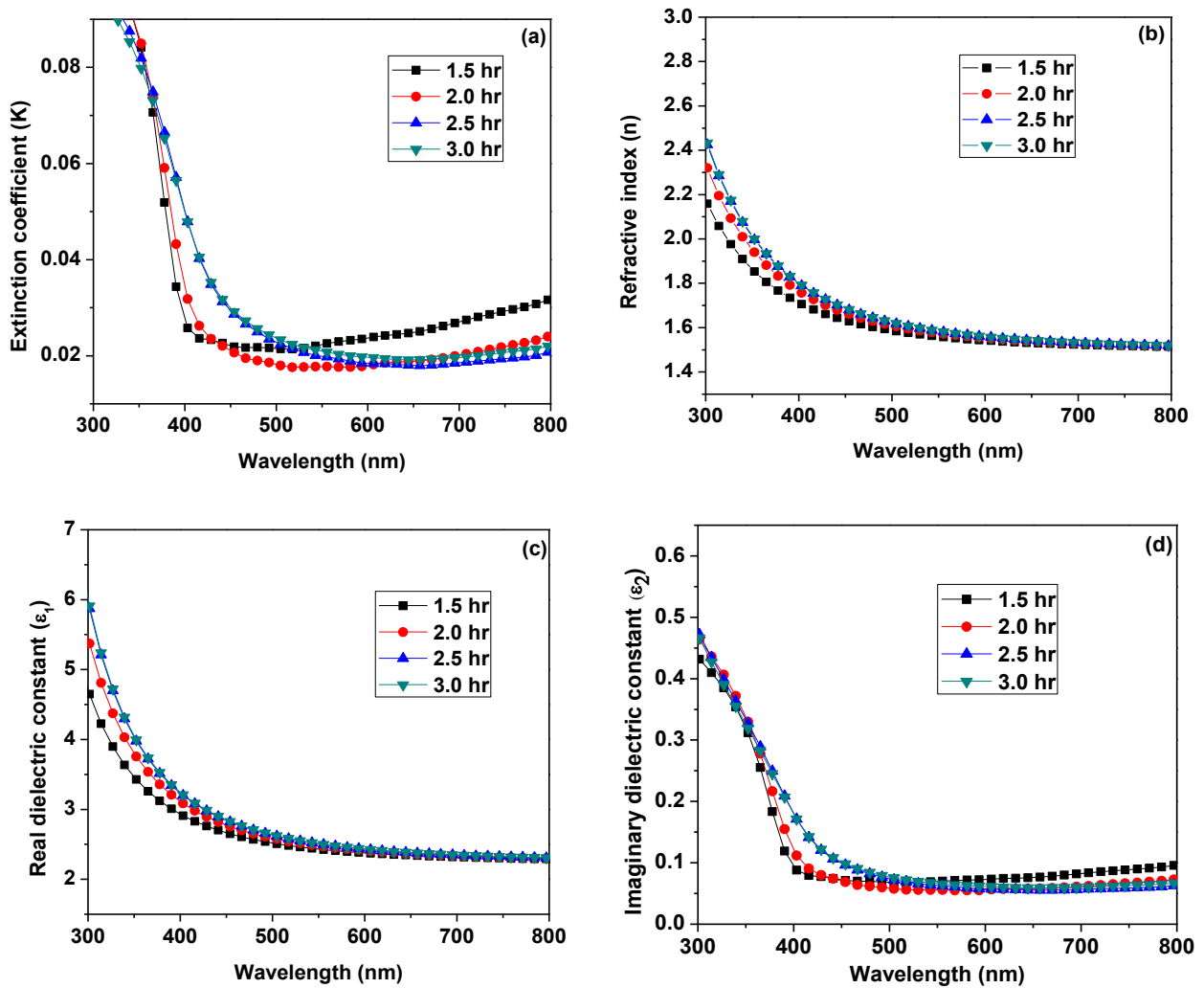


Figure 4.22: Plots of (a) extinction coefficient, (b) refractive index, (c) Real dielectric constant and (d) Imaginary dielectric constant vs wavelength of ZnO nanorods grown for 1.5 - 3.0 hrs.

The variation of the real and imaginary dielectric constants with wavelength for ZnO nanorods grown at different times is depicted in Figure 4.22 (c) and (d) respectively. As revealed by Figure 4.22 (c), the values of the real part ranged between 2.3 and 3.5 in the visible range. The lower values of 0.05- 0.25 of the imaginary part were observed in Figure 4.22 (d). A sharp decrease of both the real and imaginary part of the dielectric constant with increasing wavelength from 300 to 400 nm is contributed mainly by the polarization of space charge resulting from the presence of Zn interstitials and O vacancies in the nanorods which were also confirmed by Raman studies. Several dipole moments occur when the space charges are trapped by the defects under the influence of the electric field [233].

4.3.5 Raman studies

The Raman spectra of ZnO nanorods grown at varying times are shown in Figure 4.23. All the revealed phonon modes belong to the hexagonal wurtzite ZnO. No other peaks were noticed signifying the high purity state of the ZnO nanorods. The detectable dominant peaks at around 98 cm^{-1} and 437 cm^{-1} were assigned to the Raman active E_2 (low) and E_2 (high) optical phonon modes respectively. The dominant high intense peaks of these phonon modes indicate the good crystal quality of the grown ZnO nanorods [67, 234].

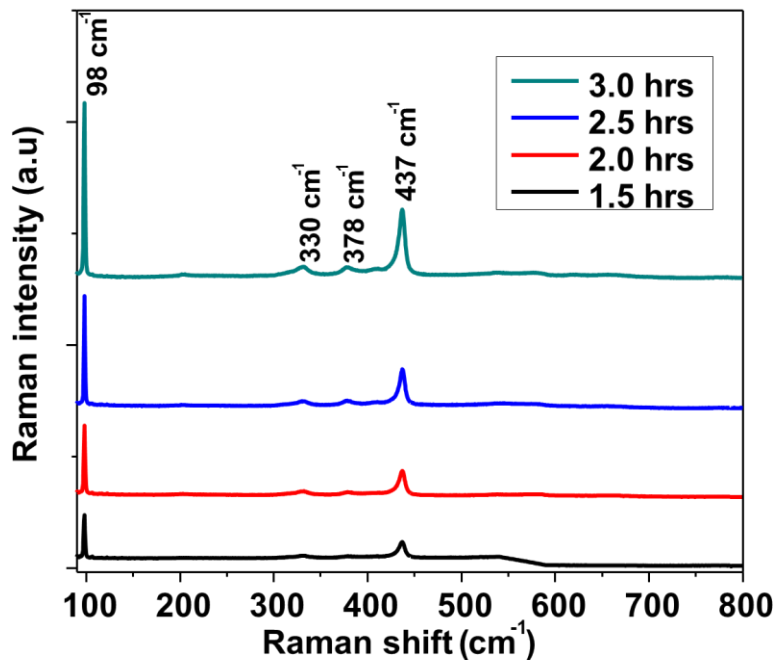


Figure 4.23: Raman patterns of ZnO nanorods grown for different durations.

Additional weak peaks at 330 cm^{-1} and 378 cm^{-1} correspond to combined mode of E_2 (high)- E_2 (low) arising from the multiple phonon scattering process and A_1 (TO) respectively. The intensity of the Raman peaks increased as the growth time increased indicating crystallinity improvement of the nanorods [89, 90, 235]. This was also revealed by the XRD results.

The peaks observed from all the samples shifted by 1 cm^{-1} to lower frequencies which is known as Red shifting. The high intensity peak of E_2 (high) is sensitive to the strain hence it is mostly used for analysis. The Raman shifting of the E_2 (high) suggests that the nanorods are under tensile strain concurring with the XRD analysis results.

4.3.6 Electrical properties

The effect of changing the growth time on the resistivity and figure of merit of the nanorods is indicated in Figure 4.24. The electrical resistivity ranges between about $1 \times 10^2\ \Omega\cdot\text{cm}$ and $5 \times 10^2\ \Omega\cdot\text{cm}$. Longer growth periods seem to lower electrical resistivity. This might have been caused by the improvement of the crystal quality as was observed in the XRD results. The variation of the

dislocation densities with growth time resulting from the crystallite size might be another factor affecting the trend of the resistivity. The presence of the Zn interstitials and O vacancies as revealed by the Raman studies may have led to the variation of the resistivity.

The figure of merit values ranged from $8.02 \times 10^{-6} \Omega^{-1}$ to $1.64 \times 10^{-6} \Omega^{-1}$ with variation of the growth time. The values obtained indicate the suitability of the nanorods to act as photoanodes in solar cell devices as there is consistency with other studies [106, 107]. According to the other study, a figure of merit value of the order $10^{-6} \Omega^{-1}$ was reported suitable for the nanostructures to be used as a photoanode in optoelectronic devices [107]. As such the grown nanorods are also appropriate for solar cell applications.

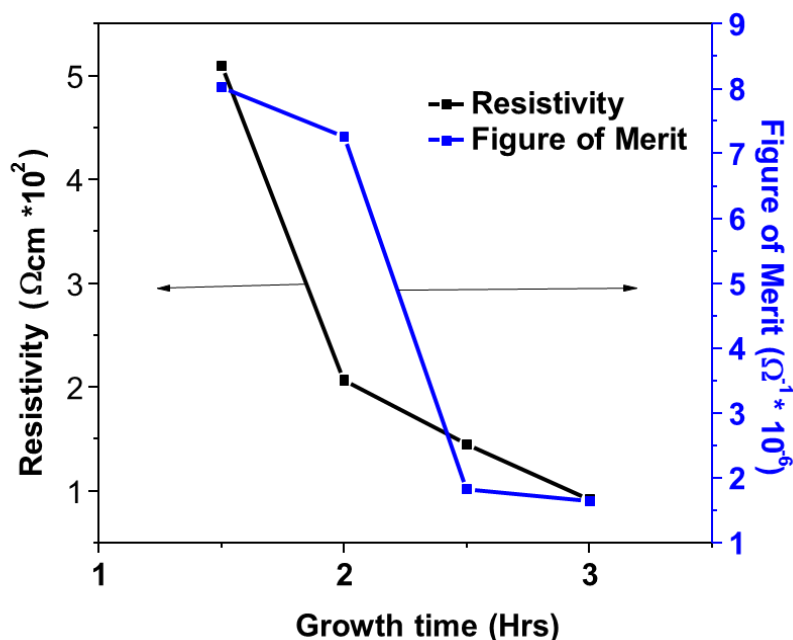


Figure 4.24: Variation of the electrical resistivity and figure of merit of ZnO nanorods grown at various times.

4.4 Effect of bath temperature on the growth of ZnO nanorods

4.4.1 Structural studies

Figure 4.25 shows XRD patterns of ZnO nanorods grown by CBD for 2hrs at different solution temperatures (60 °C - 90 °C). All the peaks revealed by the XRD are characteristic of the hexagonal wurtzite ZnO and are in agreement with pure bulk ZnO pattern (COD 10 11 258). A sharp dominant peak of the 002 plane at $2\theta = 34.4^\circ$ belonging to the hexagonal structured ZnO was detected from all the samples. It suggests that the grown ZnO nanorods are oriented along the c-axis vertical to the substrate [90]. The 002 peak intensity increased as the solution temperature was raised from 60 °C to 90 °C signifying an enhancement of the crystallinity of the grown ZnO nanorods [224, 236]. A weak peak of 103 planes at 62.9° belonging to ZnO was also observed as the temperature increased. No other peaks were detected, an indication that no detectable impurities were present in the samples.

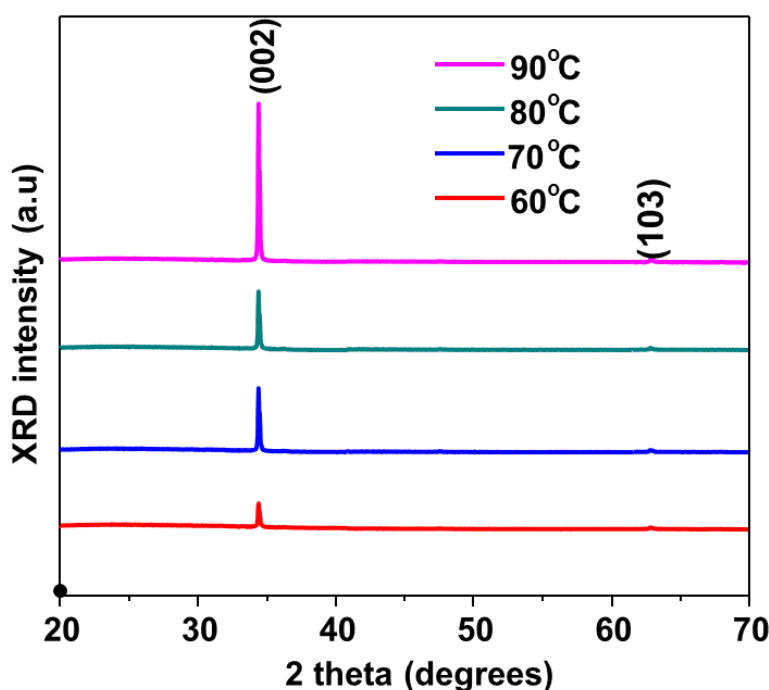


Figure 4.25: XRD patterns of ZnO nanorods grown under different solution temperatures.

The crystallite size, the FWHM, the dislocation density, the lattice constant c , the strain and stress of the ZnO nanorods are presented in Table 4.8. The Derby Scherrer's equation (4.1) was used to estimate the crystallite sizes of the nanorods using FWHM obtained from $2\theta = 34.4^\circ$. The crystallite sizes increased while the FWHM decreased as the bath temperature was raised from 60 °C to 90 °C showing an enhancement in the crystallinity of the nanorods [224, 236].

Table 4.8: Structural properties of ZnO nanorods grown at different solution temperatures.

Temperature (°C)	FWHM (°)	Crystallite size (nm)	Dislocation density, δ (line/m ²)	d- spacing (Å)- 002 peak	Lattice constant, c (Å)	Strain, ϵ (%) $\times 10^{-3}$	Stress, σ (GPa)
60	0.151	61.3	2.66	2.60381	5.2076	1.465	-0.341
70	0.142	65.3	2.35	2.60401	5.2080	1.542	-0.359
80	0.141	65.5	2.33	2.60409	5.2082	1.573	-0.366
90	0.137	67.5	2.19	2.60420	5.2084	1.615	-0.376

Figure 4.26 (b) also shows the trend of the crystallite size and FWHM value as the solution temperature raised from 60 °C to 90 °C. The crystallite size values were used in determination of the dislocation density using equation (4.2). The values of dislocation densities become lower as the temperature increased, suggesting improvement of the crystal quality of the nanorods. Equation (4.6) was used to calculate the lattice constant c . The values of the constant c obtained agree with the 5.2 Å of pure bulk ZnO (COD 10 11 258). However, a slight difference exists between the calculated and the standard values of lattice parameter c . This is attributed to the effect of the compressive stress and tensile strain on the nanorods. The strain on the nanorods was determined using equation (4.4). The positive values obtained suggest that the nanorods are under tensile strain. Equation (4.5) was used to determine the stress possessed by the nanorods. The nanorods were under compressive stress as the values found were negative. Both values of strain and stress along the c -axis increased with the temperature rise.

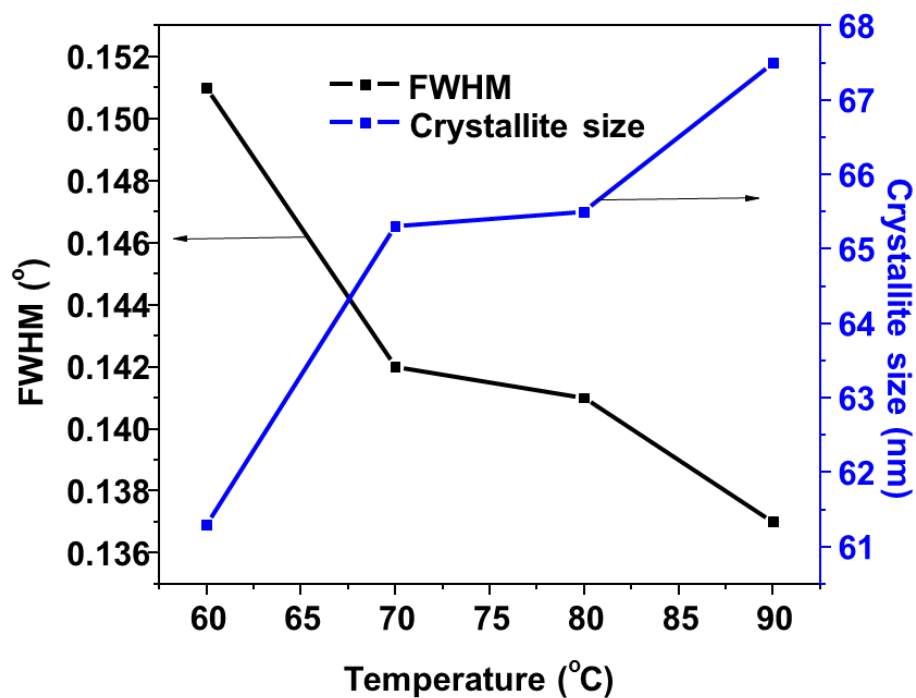


Figure 4.26: Crystallite size and FWHM plots of the ZnO nanorods grown under different bath temperatures.

4.4.2 Morphological studies

Figure 4.27 shows the top and cross-sectional views of ZnO nanorods prepared from equal precursor molarities of zinc nitrate hexahydrate and hexamethylenetetramine with variation of solution temperature from 60 °C to 90 °C for 2 hrs. An observation made from the SEM images is that growth of ZnO nanorods by CBD can occur at lower temperature of 60 °C.

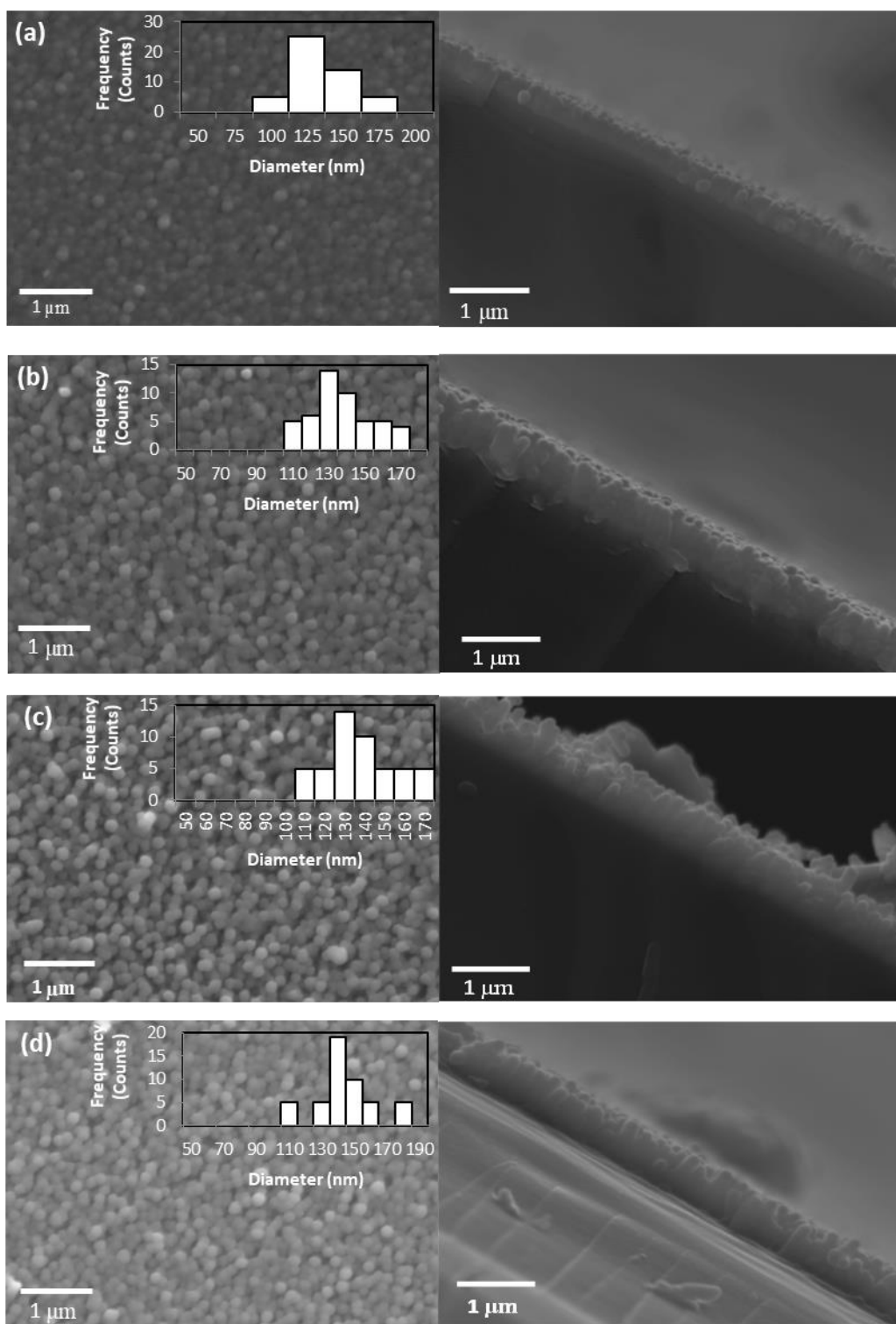


Figure 4.27: Top and cross-sectional view of ZnO nanorods grown at (a) 60 °C, (b) 70 °C, (c) 80 °C and (d) 90 °C. Histogram inserts in each SEM image represent nanorods diameter distribution.

It is also observed that the nanorods appear to be compact, vertically positioned and uniform on the substrate. However, the compactness, length and diameter of the nanorods tend to vary as the temperature was raised from 60 °C to 90 °C.

As the growth temperature increases the compactness of the nanorods decreases due to faster axial growth rate at higher temperatures. The histograms (insert) of nanorods diameter distribution are also shown in Figure 4.27. It was noted that the nanorods diameter distribution ranged between 100 nm and 190 nm with temperature variation. The average diameter of the grown nanorods increased from 129 nm to 143 nm as the temperature increased. On the other hand, the length increased from 400 nm to 700 nm as the temperature increased. The aspect ratio also increased as the temperature was raised due to improved reaction kinetics leading to a faster precipitation of ZnO [237].

Table 4.9 shows a list of the length, diameter and aspect ratio values of the nanorods as the temperature changed. The trend of the changes in the diameters and lengths of the nanorods is indicated in Figure 4.28. The optimum growth temperature characterized by longer and less compact ZnO nanorods was found to be 90 °C. This agrees with results of some previous similar studies [161, 238, 239].

Table 4.9: Lengths, diameters and aspect ratio of ZnO nanorods grown at different bath temperatures.

Temperature (°C)	Length of the nanorods (nm)	Diameter of the nanorods (nm)	Aspect ratio
60	400 ± 26	129 ± 17	3.1
70	657 ± 50	135 ± 20	4.8
80	671 ± 51	135 ± 20	5.0
90	700 ± 64	143 ± 25	5.0

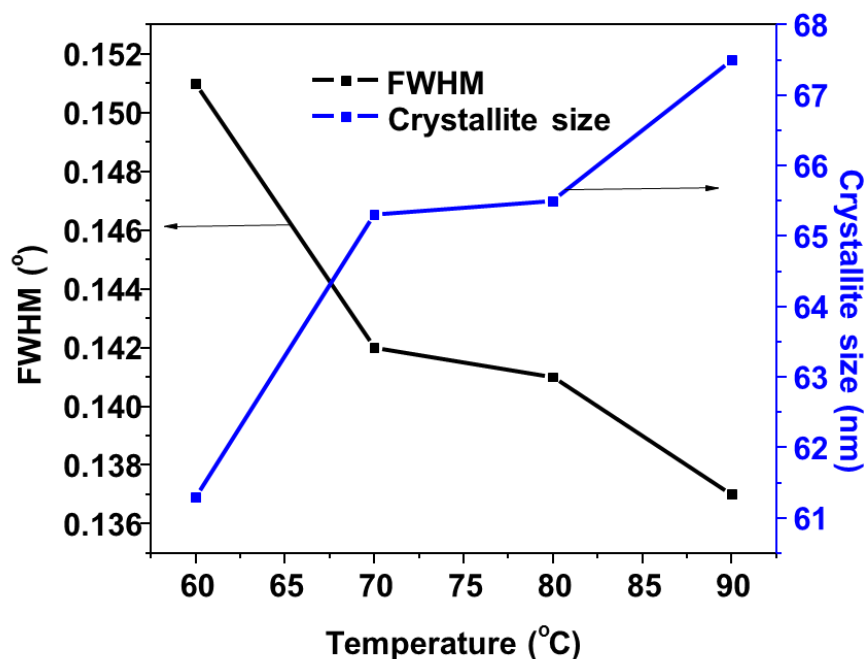


Figure 4.28: Lengths and diameters of ZnO nanorods with variation of temperature.

4.4.3 Elemental Analysis

Figure 4.29 shows an EDS spectrum of ZnO nanorods grown by CBD with variation of temperature for 2 hrs . The presence of Zn and O elements in all the samples was confirmed by EDS. However, there are other elements present which include Silicon (Si), Carbon (C) and Calcium (Ca). Si and Ca indicated by EDS are ascribed to the presence of glass substrate. Additionally, Ca may also be originating from Ultrasonic Spray Pyrolysis process chamber [203]. C element was present as the sample was coated with C to enable the imaging.

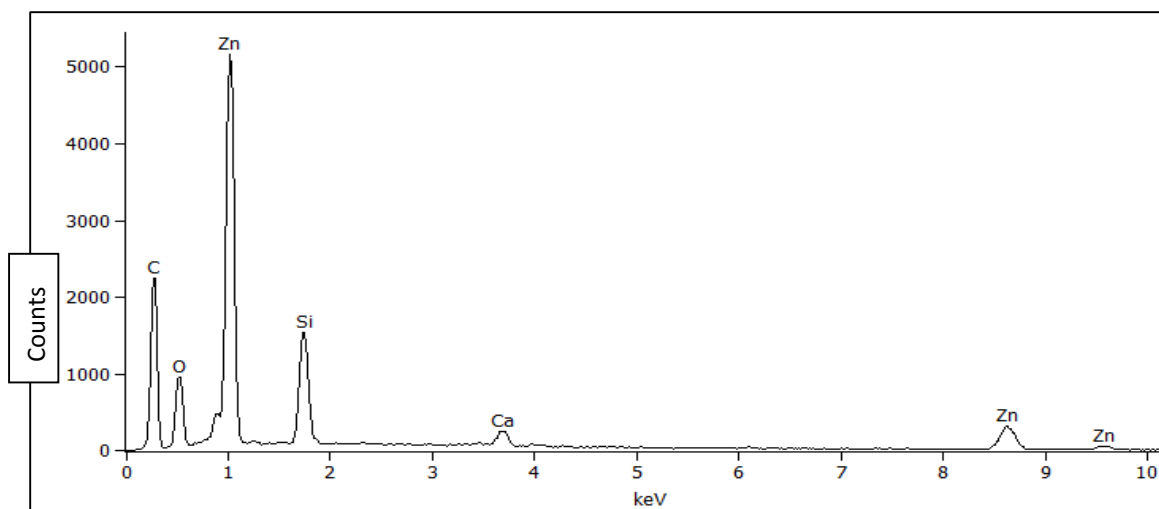


Figure 4.29: EDX spectrum of ZnO nanorods grown at different solution temperatures.

4.4.4 Optical Properties

Figure 4.30 illustrates optical transmittance of 300-800 nm wavelength region of ZnO nanorods prepared by CBD while varying growth temperature. The nanorods had an average optical transmittance 65-75 % in the visible region. The absorption edges were found at around 378 nm. Light transmittance by the nanorods decreased as the growth temperature increased.

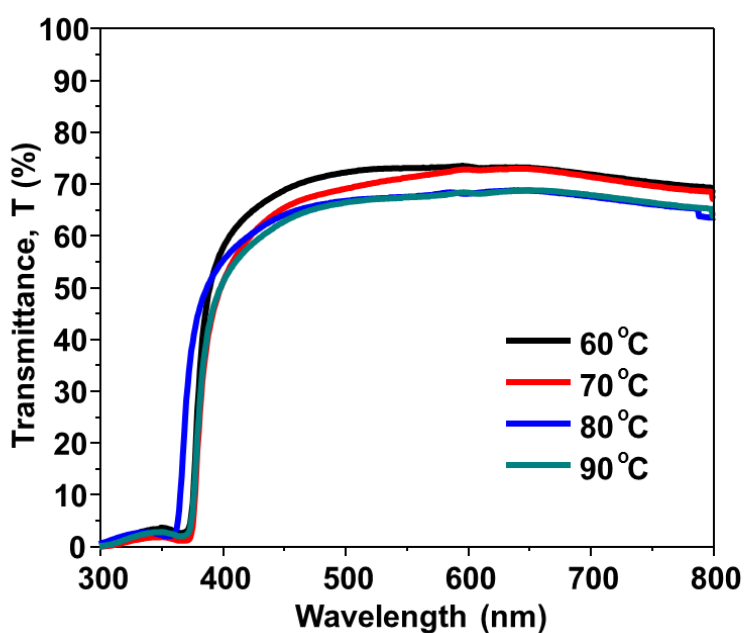


Figure 4.30: Optical transmittance of ZnO nanorods with variation of growth temperature.

The band gaps of the nanorods were calculated from a plot of first derivative of the optical transmittance as shown in Figure 4.31. The values of the band gaps were obtained using the maximum wavelength from the derivative plot and were presented in Table 4.10. The values slightly reduced from 3.30 eV to 3.29 eV as the temperature increased from 60 °C to 70 °C, and remained constant as temperature was increased to 90 °C. The results revealed that the decrease in the band gap energies was due to the increase in the diameter of the nanorods observed from the SEM results. This phenomenon is known as the quantum confinement effect which is observed when the nanostructure size is smaller than the electron wavelength.

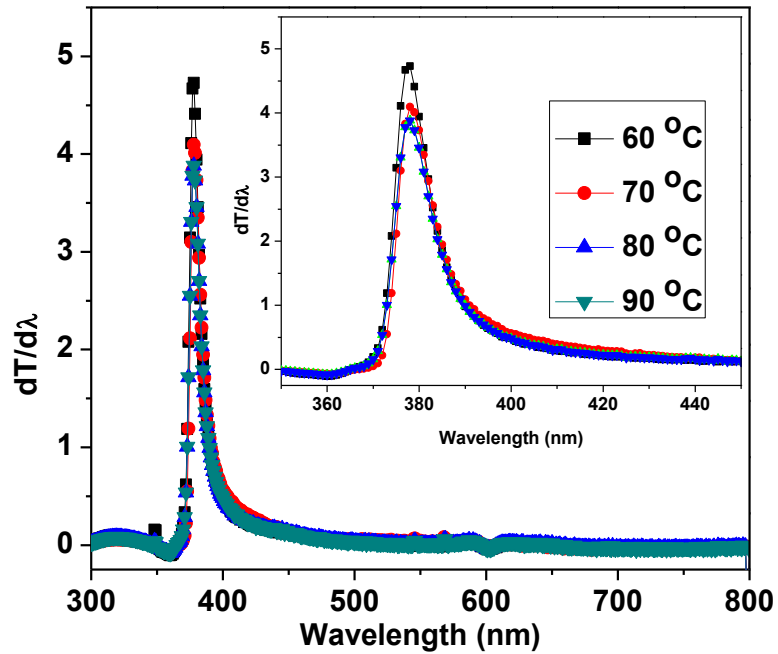


Figure 4.31: A plot of first derivative of optical transmittance of ZnO nanorods while varying growth temperature (insert showing zoomed peaks).

The band gap values exhibit a red shift relative to 3.37 eV of bulk ZnO related to the quantum confinement effect of the synthesized nanorods [230]. A similar trend was observed from other studies [240]. Contrary to our results, the band gap energy obtained from absorbance spectra increased when the temperature was raised from 70 °C to 90 °C due to quantum confinement effect [236].

Table 4.10: Band gap energies of ZnO nanorods with variation of temperature.

Growth temperature (°C)	Band gap energy (eV)
60	3.30
70	3.29
80	3.29
90	3.29

Fundamental intrinsic optical parameters of the ZnO nanorods are revealed in Figure 4.32 (a)-(d). The behavior of the extinction coefficient with the wavelength as the temperature increased is shown Figure 4.32 (a).

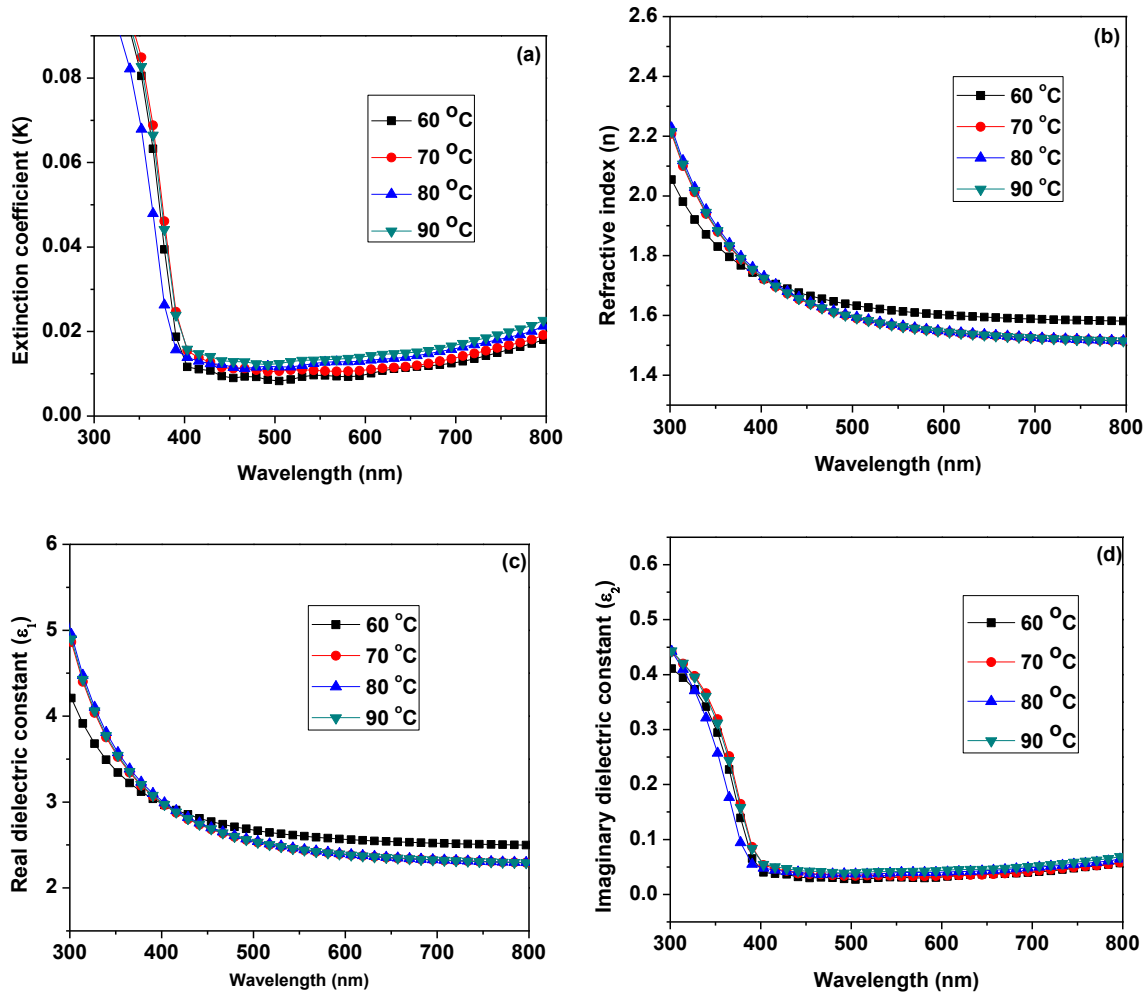


Figure 4.32: Plots of (a) extinction coefficient, (b) refractive index, (c) Real dielectric constant and (d) Imaginary dielectric constant wavelength of ZnO nanorods grown at different temperatures.

It was observed that the extinction coefficient rapidly decreases as the wavelength increased from 300 to 400 nm for all the samples. The values of the extinction coefficient reduce to around 0.01 which is an indication of low light absorption by the nanorods in the visible region [81]. It can therefore be concluded that the nanorods are highly transparent. However, the transparency of the nanorods is slightly reduced as the bath temperature increased. This is probably due to the enhanced scattering of light as the length and diameter of the nanorods is increased as revealed by the SEM investigations.

Figure 4.32 (b) shows the variation of refractive index with wavelength as the temperature increased for all the samples. The refractive indices of the ZnO nanorods were found to be ranging between 1.53 – 1.78 in the visible region. As such the speed of light in free space is 1.53 - 1.78 times faster than in the nanorods. The values of the refractive indices are relatively lower than that of bulk ZnO. This was attributed to the defects such as O vacancies and Zn interstitials [209].

The real and imaginary parts of the dielectric constant variation with respect to the wavelength for all the samples is illustrated in Figure 4.32 (a) and (b) respectively. The ZnO nanorods possess high values of the dielectric constant in short wavelength regions, which decreases rapidly as the wavelength increases and remains constant at longer wavelength. The values of the real part ranged between 2.3 and 3.1 higher than the imaginary part with a range of 0.01 – 0.1. The nanorods reveal polarization which can either be interfacial or space charge resulting from the structural defects [233].

4.4.5 Raman Studies

Raman spectra of ZnO nanorods grown at different temperatures is shown in Figure 4.33. The Raman peaks observed are characteristic to ZnO with hexagonal structure. No other peaks were noticed from the spectra, confirming the pure phase of the ZnO nanorods. Raman active E_2 (low), E_2 (high), E_2 (high)- E_2 (low) and A_1 (TO) optical phonon modes were observed.

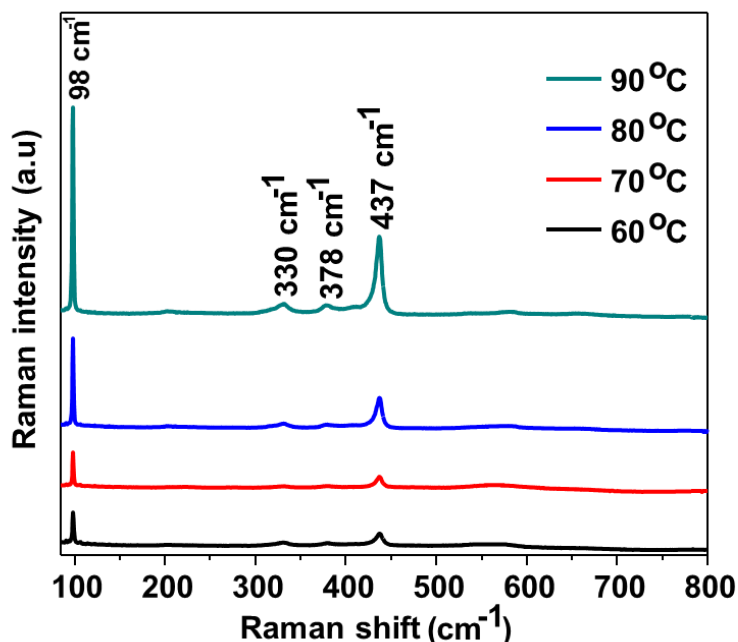


Figure 4.33: Raman spectra of ZnO nanorods grown at various temperatures for 2.0 hrs.

The E_2 (low) and E_2 (high) modes are associated with the dominant sharp peaks at around 98 cm^{-1} and 437 cm^{-1} respectively. The domination of these modes confirms the good crystallinity of the samples [89, 234, 67, 241]. The E_2 (low) modes are as a result of the sublattice of Zn while E_2 (high) are as a result of oxygen atoms vibration. Weak peaks of E_2 (high)- E_2 (low) and A_1 (TO) optical phonon modes also exist at around 330 cm^{-1} and 378 cm^{-1} . These weak peaks arise due to multiple photon scattering process. The A_1 (TO) and E_2 (high) Raman active modes present indicates that the inelastic scattering of light is normal to the c-axis of the nanorods [89, 242]. As the growth temperature increased from $60\text{ }^{\circ}\text{C}$ to $90\text{ }^{\circ}\text{C}$, the intensities of all the phonon modes increased suggesting that the crystal quality of the nanorods improved. On the other hand, it is also noted that the position of the peaks from all the samples shifted to lower frequency values when compared to the standard ZnO Raman spectrum. According to other studies, E_2 (high) peak shift arise due to strain [214, 243]. The red shifting of the Raman peaks suggests that the nanorods are under the tensile strain in agreement with the XRD data analysis.

4.4.6 Electrical properties

The influence of the solution temperature on the resistivity of the nanorods was studied. As revealed in the Figure 4.34, the resistivity of the nanorods lowered as the temperature of the growth solution increased from 60 °C to 90 °C. Similar trend was reported in other studies [94, 100]. The lowest resistivity value of $1.86 \times 10^2 \Omega \cdot \text{cm}$ was recorded at 90 °C. This low value resulted due to large grain sizes at higher solution temperatures which reduces the grain boundaries responsible for trapping charge carriers. The appropriateness of the ZnO nanorods for solar cell application was confirmed by the values of figure of merit ranging between $1.92 \times 10^{-4} \Omega^{-1}$ and $1.04 \times 10^{-4} \Omega^{-1}$ as illustrated in Figure 4.34. These values are slightly lower than $10^{-3} \Omega^{-1}$ recorded in a similar study [100]. However, in another study values of the order 10^{-6} for ZnO microstructures were obtained and recommended for optoelectronic devices [106, 107].

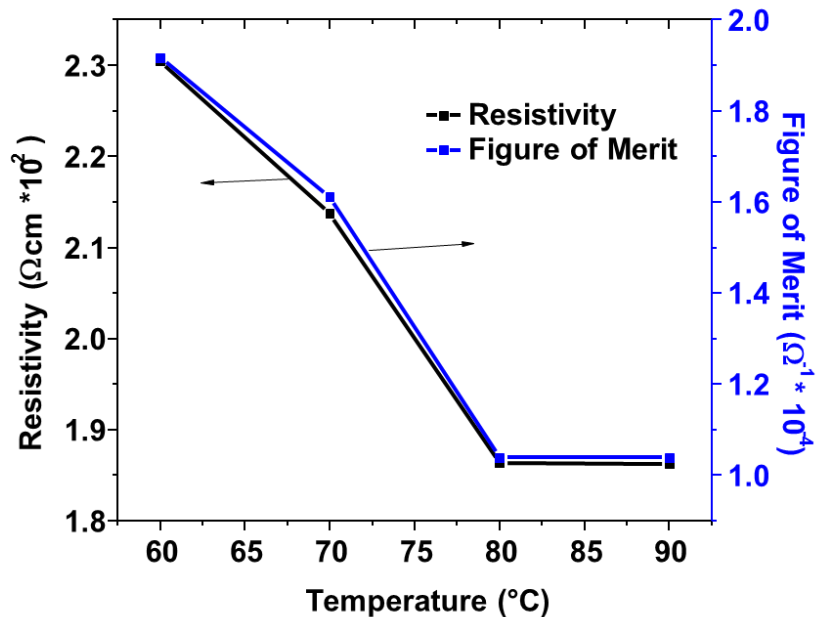


Figure 4.34: Variation of the electrical resistivity and figure of merit for ZnO nanorods grown from different solution temperatures for 2.0 hrs.

4.5 Effect of precursor concentration on the growth of ZnO nanorods by chemical bath deposition

4.5.1 Structural Properties

Figure 4.35 shows XRD diffractograms of ZnO nanorods prepared by CBD with different solution concentration for 2 hrs at 90 °C. The XRD reveal peaks belonging to the polycrystalline hexagonal wurtzite structured ZnO concurring with the standard pattern of bulk ZnO (COD 10 11 258). No other peaks belonging to impurity phases were observed. A dominant 002 peak at $2\theta = 34.4^\circ$ was observed from all the samples indicating the presence of wurtzite structured ZnO phase. The 002 peak also suggest that the nanorods are vertical to the substrate.

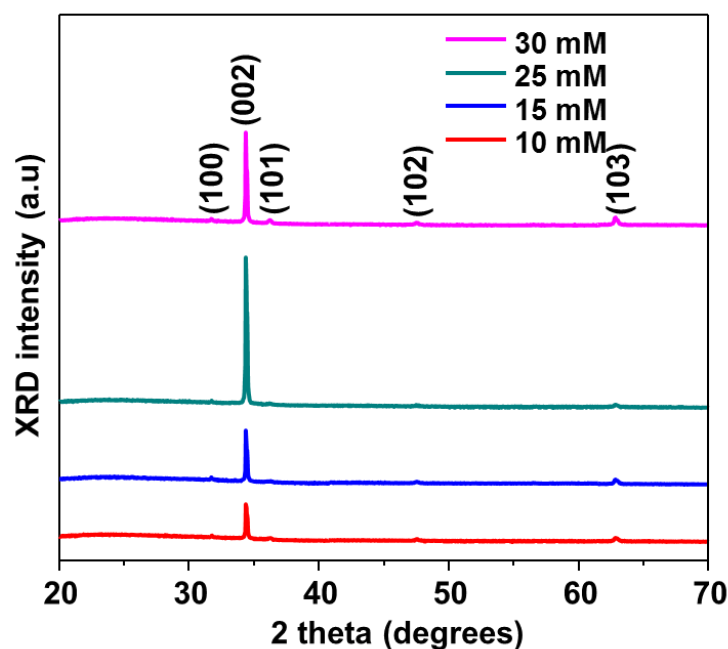


Figure 4.35: XRD diffractograms of ZnO nanorods grown from solutions of different concentrations for 2 hrs at 90 °C.

The peak intensified as the molarity increased from 10 mM to 25 mM signifying enhancement of the crystallinity and better alignment of the ZnO nanorods [91]. A slight decrease of the peak intensity was noticed with further increment of concentration to 30mM probably due to

nucleation and growth rate [244]. At higher concentrations the reaction proceeds faster than the regular nucleation and growth of the nanorods hence degrading the crystal quality. Additional weak peaks of the 100, 002, 101, 102 and 103 planes at 31.7°, 36.3°, 47.6° and 62.9° were also observed from the samples belonging to the ZnO.

Table 4.11 summaries the crystallite size, FWHM, dislocation density, c lattice parameter, stress and strain of the ZnO nanorods. The crystallite sizes of the nanorods were estimated using Derby Scherer's equation (4.1) with the FWHM of the 002 peak. The crystallite sizes increased with an increase in the concentration from 10 mM to 30 mM suggesting an improvement in crystallinity of the nanorods [91, 245]. The FWHM decreased as the 002-peak got narrower with increased concentration.

Table 4.11: Structural properties of ZnO nanorods grown from different concentrations.

Concent ration (mM)	FWHM (°)	Crystallite size (nm)	Dislocation density, δ (line/m ²)	d-spacing (Å)- 002 peak	Lattice constan t, c (Å)	Strain, ϵ (%) X 10 ⁻³	Stress, σ (GPa)
10	0.155	59.6	2.82	2.60265	5.2053	1.019	-0.237
15	0.150	61.5	2.64	2.60347	5.2069	1.335	-0.311
25	0.143	64.5	2.40	2.60367	5.2073	1.412	-0.329
30	0.142	65.2	2.35	2.60446	5.2089	1.715	-0.340

A clear indication of the increase in crystallite size and decrease in FWHM as the concentration increased is shown in Figure 4.36. The dislocation density was considered using equation (4.2). The increase in the concentration resulted in the decrease in the dislocation density values suggesting fewer defects and improved crystallinity of the nanorods.

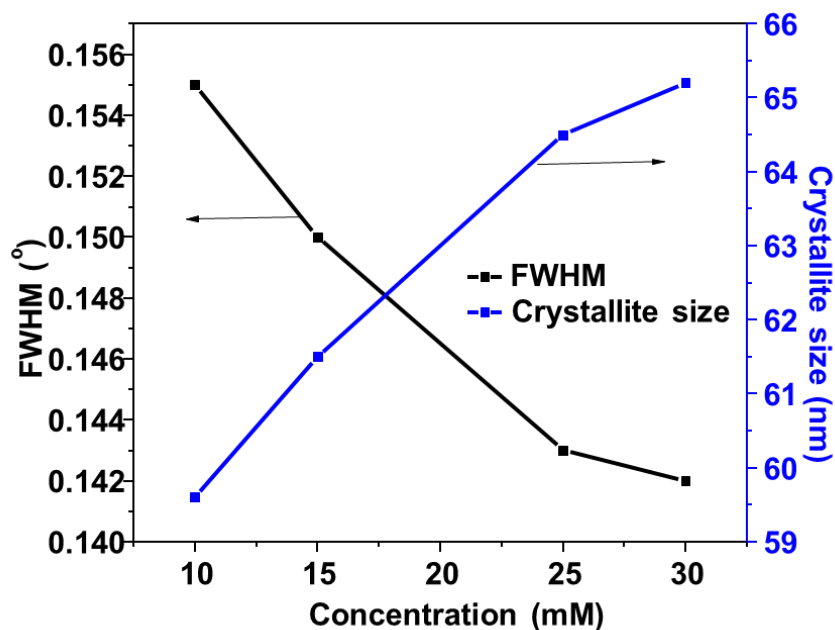


Figure 4.36: Crystallite size and FWHM plots of the ZnO nanorods grown from different concentration.

The lattice parameters c was estimated using equation (4.6). The lattice parameters were found to be slightly higher than the $c = 5.2 \text{ \AA}$ of the bulk ZnO (COD 10 11 258) because of tensile strain effects. The c constants increased with an increase in the concentration as shown in Table 4.11. The stress and strain in the nanorods along the c -axis were found using equations (4.4) and (4.5) respectively. The values obtained indicated that the nanorods are under tensile strain and compressive stress which may have caused relatively larger c lattice constants. As the concentration increased, both strain and stress of the grown nanorods increased.

4.5.2 Morphological properties

Figure 4.37 shows the top and cross-sectional SEM images of ZnO nanorods prepared by varying equal precursor concentrations of zinc nitrate hexahydrate and hexamethylenetetramine from 10 mM to 30 mM at 90°C for 2 hrs. It was observed that the length, diameter, distribution density and aspect ratios varied with increasing concentrations.

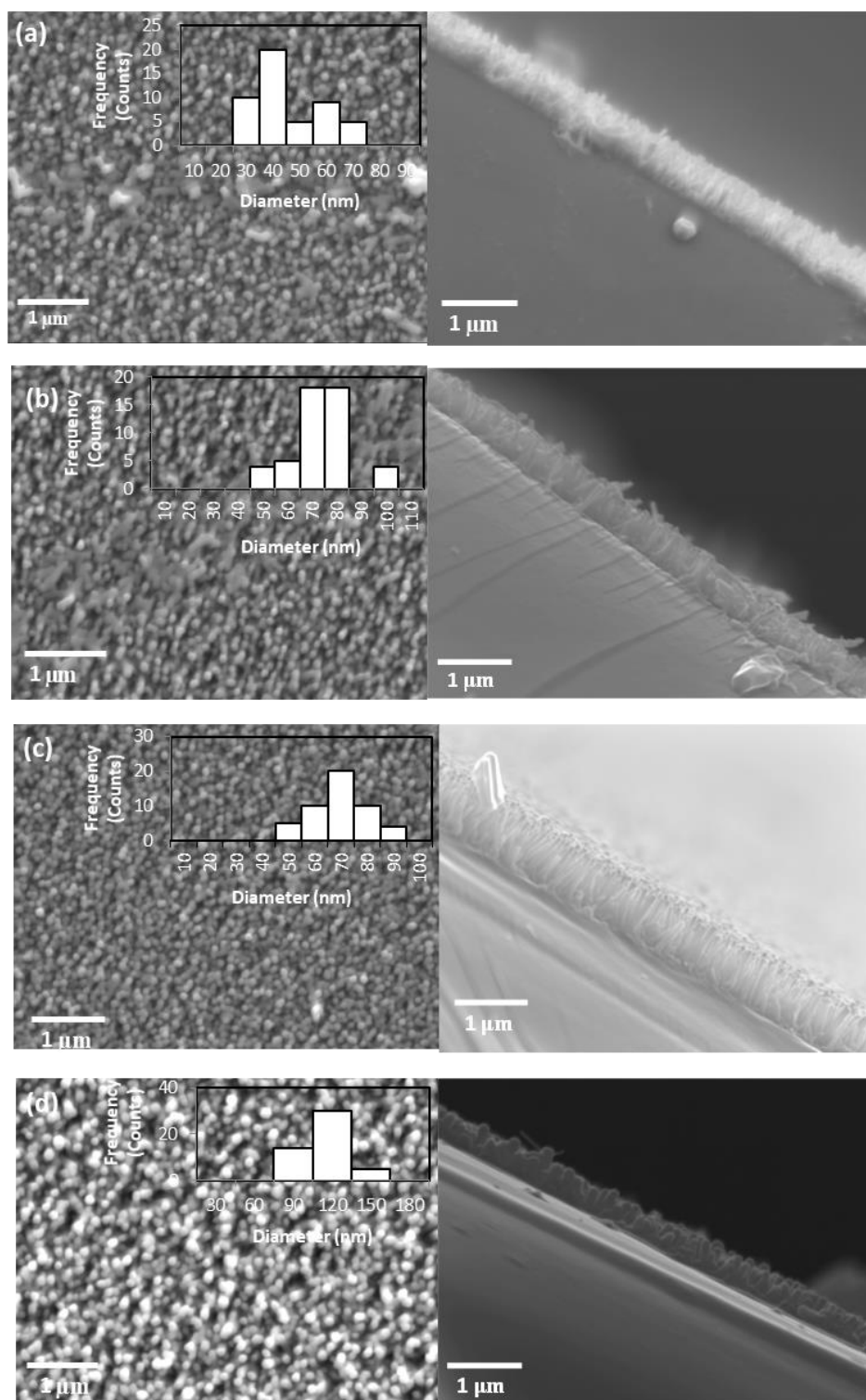


Figure 4.37: Top-view and cross-sectional view SEM images and diameter distribution histogram (insert) of ZnO nanorods fabricated from solutions of (a) 10 mM; (b) 15 mM; (c) 25 mM; (d) 30 mM of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and HMTA.

Statistical counting of the nanorods diameter distribution was performed from the images and histograms were plotted as shown in Figure 4.37. The nanorods diameter and distribution is dependent on the concentration as shown in the inserts. The diameter increased from 43 nm to 101 nm with an increase of the concentration from 10 mM to 30 mM due to higher degree of supersaturation [100]. The increase in the nanorods diameter attributed to the decrease in the density array of the nanorods [239]. Comparable observations were made in other studies [238, 246, 247].

On the other side the length of the nanorods increased from 519 nm to 609 nm when the concentration increased from 10 mM to 25 mM. Further increase of concentration to 30 mM lead to a decrease in the length of the nanorods to 435 nm. Similar observations were made by other researchers, that lower concentrations in the range of 10 mM- 25 mM yielded 1.2 μm long nanorods with the diameter less than 100 nm while further increase of concentration to higher values leads to formation polycrystalline films [248].

Based on the SEM micrographs the diameter, length and aspect ratios of the nanorods are presented in Table 4.12 and plotted in Figure 4.38 with respect to the solution concentrations. It was also observed that at lower concentration the nanorods were disorientated. It can be concluded that the solution concentration is key to tailoring the morphology of the nanorods. The optimum precursor concentration was found to be 25 mM associated with nanorods of high aspect ratio and vertical alignment.

Table 4.12: Length and diameter of ZnO nanorods fabricated from different concentrations.

Concentration (mM)	Length of the nanorods (nm)	Diameter of the nanorods (nm)	Aspect ratio
10	519 $\pm$ 46	43 $\pm$ 10	12.1
15	521 $\pm$ 47	70 $\pm$ 19	7.4
25	609 $\pm$ 51	72 $\pm$ 21	8.5
30	425 $\pm$ 25	101 $\pm$ 9	4.3

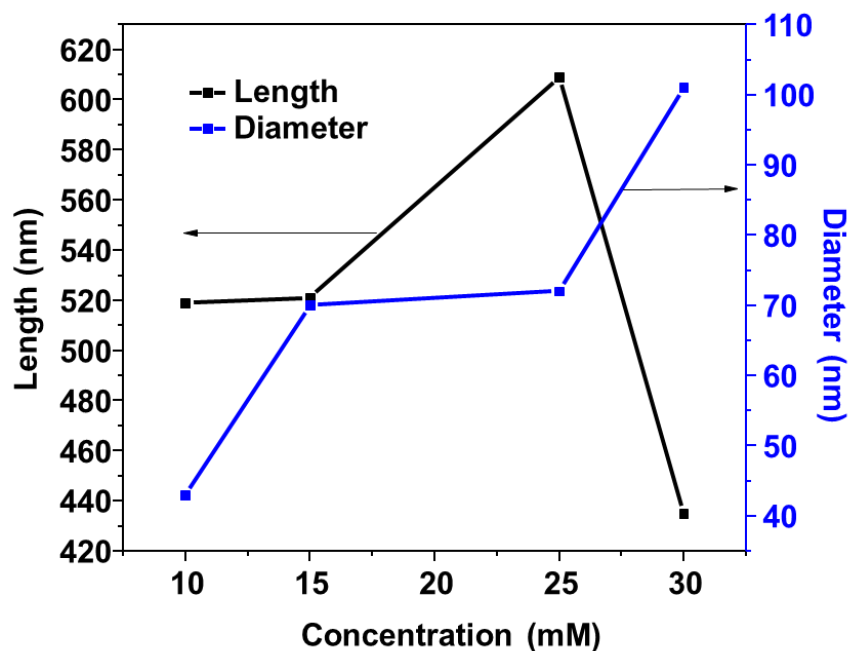


Figure 4.38: Lengths and diameters of ZnO nanorods with variation of precursor concentration.

4.5.3 Elemental composition

EDS spectrum of ZnO nanorods grown by CBD from different solution concentrations for 2 hrs is presented in Figure 4.39. Zn and O elements were detected by EDS from all the samples confirming the presence of ZnO nanorods. However, other peaks were observed belonging to other elements which includes Silicon (Si), Carbon (C) and Calcium (Ca). Si and Ca indicated by EDS may be due the glass substrate and the ultrasonic spray pyrolysis chamber [203]. C element originate from the carbon conductive coating on the sample that enable the imaging.

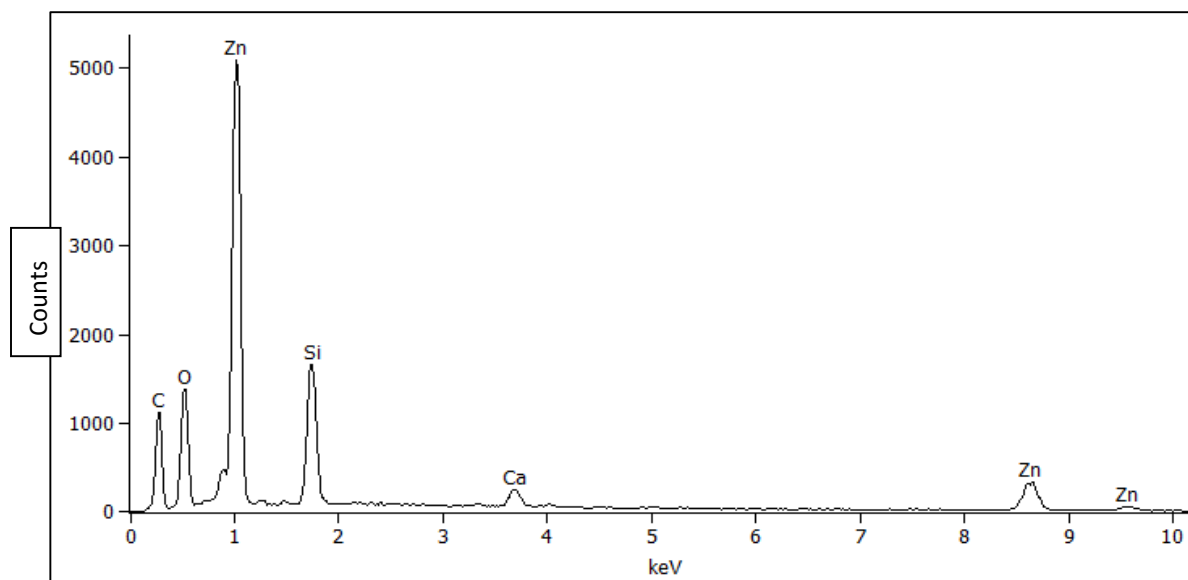


Figure 4.39: EDS spectrum of ZnO nanorods from different equal molar concentrations of zinc nitrate hexahydrate and hexamethylenetetramine.

4.5.4 Optical Properties

The optical transmittance spectra of ZnO nanorods grown by CBD while varying concentration ranging from 300 - 800 nm is shown in Figure 4.40. The spectra reveal high transparency of the nanorods in the visible and infra-red region and low transparency in the UV range. An average transmittance of 60 - 70 % by the nanorods within the visible region was observed. The transparency of the nanorods decreased as the solution concentration was increased from 10 mM to 30 mM. The transparency reduction was attributed by enhanced optical scattering by the increased diameters of the nanorods shown by SEM images. The sharp absorption edges were clearly observed at around 370 – 375 nm which corresponds to the optical band gap energy.

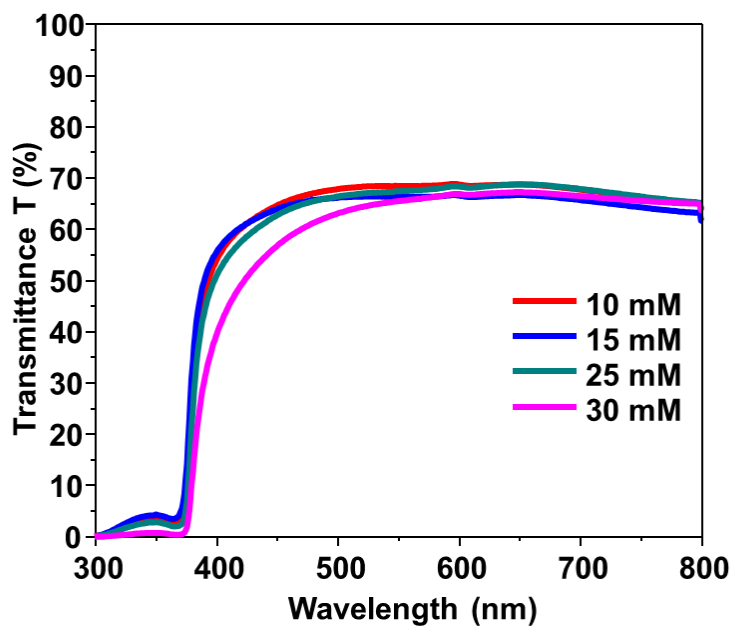


Figure 4.40: Transmittance spectra of ZnO nanorods with variation of solution concentration.

The energy band gap of the nanorods was estimated by equation (4.7) using the wavelength of the highest peak from the first derivative plot of transmittance shown in Figure 4.41. The band gap values are slightly lower than the 3.37 eV of the standard bulk ZnO.

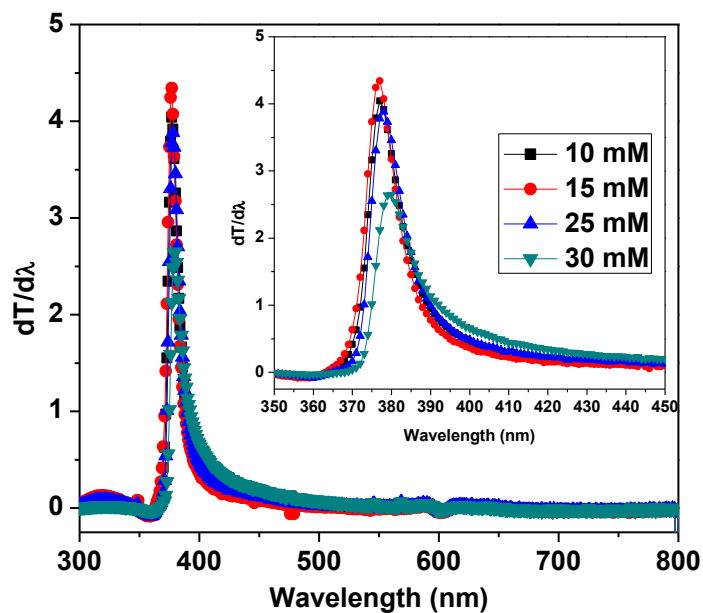


Figure 4.41: A plot of first derivative of optical transmittance of ZnO nanorods while varying concentration (insert shows zoomed peaks).

The band gap values decreased as the concentration was increased as shown in Table 4.13. The shift of the band gap values from 3.29 eV to 3.31 eV is attributed by stress, strain, oxygen vacancies and carrier concentration [207].

Table 4.13: Band gap energies of ZnO nanorods with variation of concentration.

Concentration (mM)	Band gap energy (eV)
10	3.31
15	3.31
25	3.30
30	3.29

The extinction coefficient behavior of the nanorods with respect to the wavelength as the solution concentration was varied is shown in Figure 4.42 (a). A sudden drop of the extinction coefficient between the 350 – 400 nm wavelength regions is observed in all the samples. It is evident that the nanorods are transparent as the values of the extinction coefficient are low in the visible region. It is also observed that the extinction coefficient slightly increased as the solution concentration increased from 10 mM to 30 mM.

Figure 4.42 (b) depicts the variance of the refractive index with wavelength in the range of 300 – 800 nm. The values of the refractive index obtained were between 1.52 and 1.75 in the visible region. This suggest that the nanorods reduces the speed of the light from free space 1.52-1.75 times. The variation of the real and imaginary part of the dielectric constant with wavelength for all the investigated samples is illustrated in Figure 4.42 (c) and (d). The values of 2.30 – 3.00 of the real part are higher than the values of the imaginary part with a range of 0.03 - 0.15. The values of the real part indicate how much speed of light is slowed down by the nanorods while the imaginary part reveals how much energy from an electric field is absorbed by the nanorods [81].

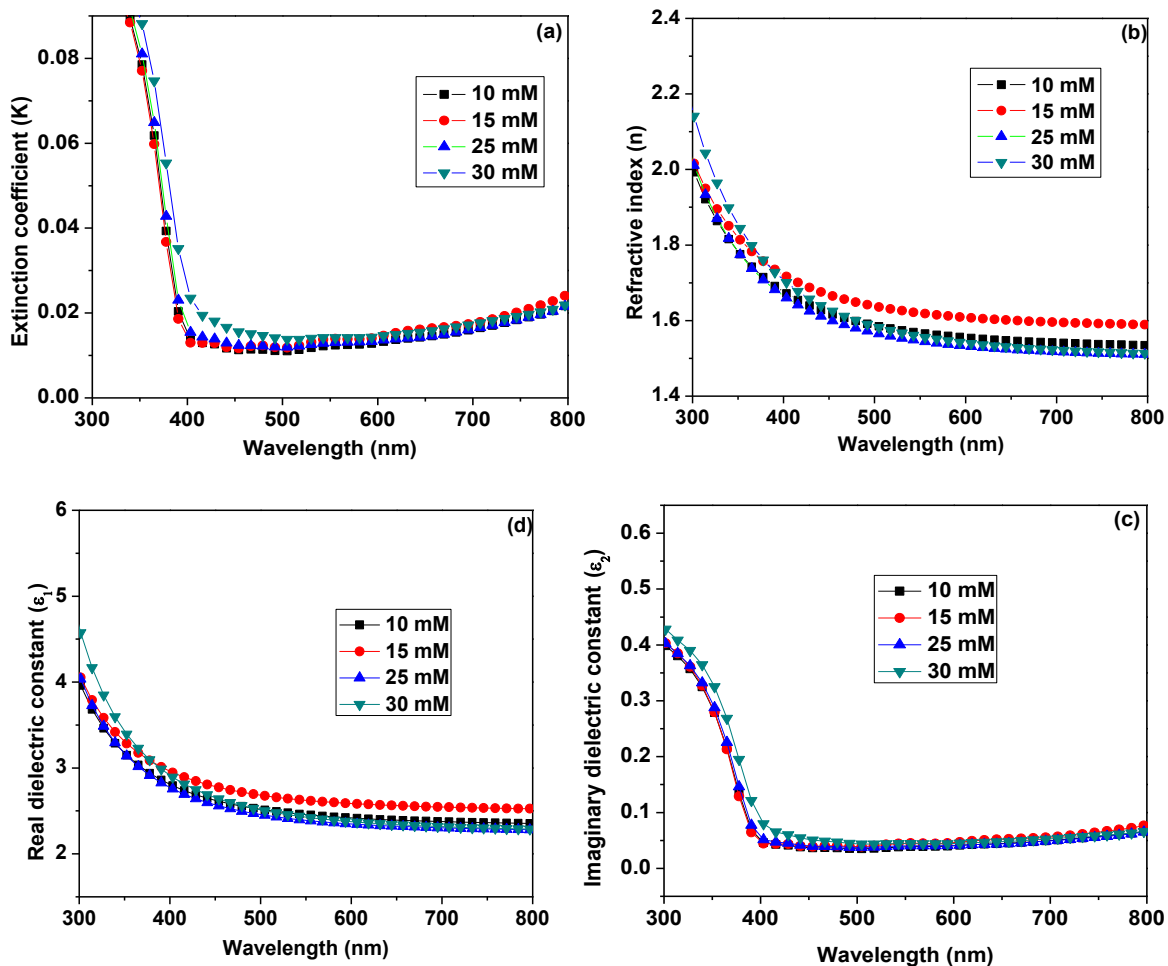


Figure 4.42: Plots of (a) extinction coefficient, (b) refractive index, (c) Real dielectric constant and (d) Imaginary dielectric constant vs wavelength of ZnO nanorods grown from different solution concentrations.

4.5.5 Raman Studies

Figure 4.43 shows the Raman spectra of ZnO nanorods grown using different solution concentration. All the ZnO nanorods grown show Raman peaks at 98 cm^{-1} , 331 cm^{-1} , 379 cm^{-1} and 438 cm^{-1} frequencies which are characteristic to hexagonal wurtzite ZnO. The observable intense peak at around 98 cm^{-1} correspond to the E_2 (low) Raman active mode related to the heavy Zn sublattice vibration. Another intense peak is detected at 438 cm^{-1} associated with the Raman

active E_2 (high) phonon modes which are due to the vibration of oxygen atoms. In addition, the E_2 (high) phonon mode emerges when the incident light is normal to the nanorods [83]. The weak peak at 331 cm^{-1} is assigned to the combined mode of E_2 (high)- E_2 (low) resulting from the multiple phonon scattering [213]. A_1 (TO) phonon mode observed at 379 cm^{-1} also arise from the multiple phonon scattering processes. The intensity of the ZnO nanorods Raman active peak increased as the solution concentration increased which denote the increase in crystallinity and coverage of the nanorods on the substrate. The position of the peaks red shifted slightly to lower frequencies indicating that the nanostructures are under tensile strain. The Raman results agree with the XRD and UV/Vis data analysis.

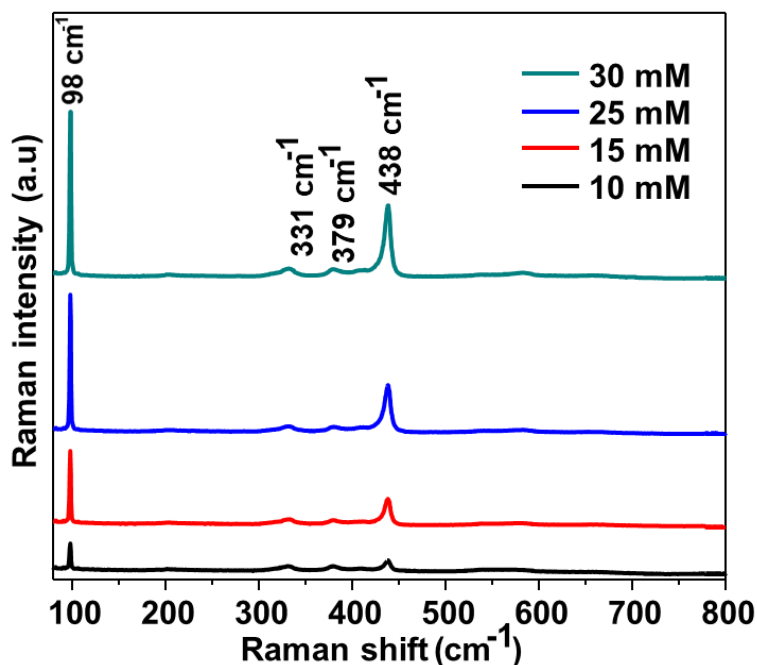


Figure 4.43: Raman spectra of ZnO nanorods grown with different solution concentration.

4.5.6 Electrical properties

Figure 4.44 represent plots of resistivity and figure of merit of ZnO nanorods grown from different solution concentrations. It is observed that the electrical resistivity decreased from a high value of $1.27 \times 10^2\ \Omega\cdot\text{cm}$ to a lower value of $0.41 \times 10^2\ \Omega\cdot\text{cm}$ with variation of concentration. As the precursor concentration increases, the number of Zn^{2+} ions also increase leading to decreased

resistivity and improved conductivity [96, 249]. On the one hand, the figure of merit of the nanorods reached a higher value of $3.54 \times 10^{-4} \Omega^{-1}$ as the concentration was increased to 30 mM.

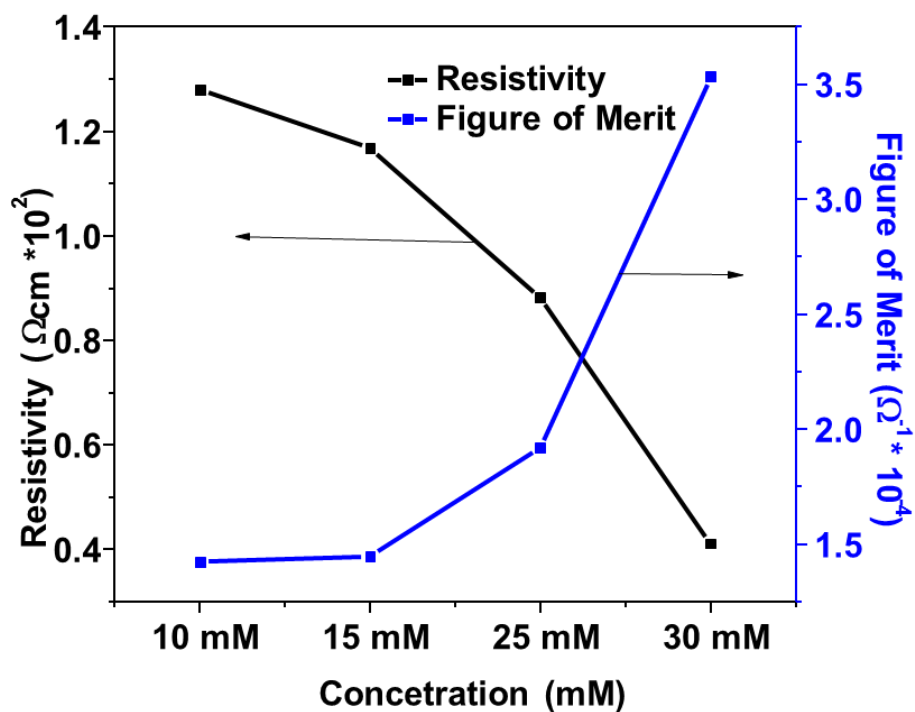


Figure 4.44: Variation of the electrical resistivity and figure of merit for ZnO nanorods grown from different equimolar mixture of Zinc nitrate hexahydrate and hexamethylenetetramine.

CHAPTER 5 : CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

ZnO nanorods were successfully fabricated by chemical bath deposition on glass substrates seeded with ZnO nanoparticles deposited by spray pyrolysis. The effects of seed layer thickness and chemical bath deposition growth parameters: growth time, temperature and precursor concentration on the nanorods morphology, structural, optical, vibrational and electrical properties were investigated.

The first stage involved synthesis of ZnO seed layers by spray pyrolysis. A short spraying time of 10 minutes resulted in an optimum seed layer thickness of 10 nm. ZnO nanorods grown on this seed layer exhibited a high aspect ratio and were well aligned. The sprayed ZnO seed layers exhibited a dominant peak of 002 diffraction plane at 34.4° belonging to the wurtzite structured ZnO phase. XRD was employed in studying the structural properties of ZnO seed layers. The observed XRD peaks indicating the presence of ZnO seeds corroborate with the standard pattern of bulk ZnO (Crystallography Open Database, COD 10 11 258). FESEM showed spherically shaped particles varying in terms of their size, compactness, distribution and density due to the rate of nucleation of the atoms during the seed layer deposition across the substrate. EDS confirmed the presence of Zn and O elements. Other elements detected in all the samples include Si, Ca and C thought to be originating from the glass substrate and carbon conductive layer respectively.

The second stage involved the fabrication of well aligned ZnO nanorods with high a aspect ratio by CBD. The synthesized ZnO nanorods revealed a wurtzite structure of ZnO with a dominant 002 peak from XRD analysis. Further analysis of the XRD data showed that the nanorods were under tensile strain and compressive stress attributed to crystal defects and thermal expansion coefficient difference between the glass substrate and the grown ZnO nanorods. The FESEM showed that the length and diameter of the nanorods increased as the growth time, temperature and precursor concentration were increased. The presence of Zn and O elements was confirmed by EDS. Dominant peaks were observed at 98 cm^{-1} and 438 cm^{-1} corresponding to the Raman

active $E_2(\text{low})$ and $E_2(\text{high})$ modes belonging to ZnO with a wurtzite structure respectively. The peaks were revealed using the Raman spectra technique.

An average optical transmittance range of 50-70 % with the band gap ranging between 3.25 eV and 3.31 eV within the visible spectra region was observed. The electrical resistivity of the nanorods was determined to be of the order of $10^2 \Omega\text{cm}$ while FOM ranged between $10^{-6} \Omega^{-1}$ and $10^{-4} \Omega^{-1}$. Optimum growth conditions found to be; a precursor concentration of 25 mM, bath temperature of 90 °C and growth time of 2 hrs yielded nanorods characterized by a high aspect ratio and vertically well aligned. The nanorods were characterized by an optical transmittance of around 70 %, band gap of 3.30 eV, electrical resistivity of $0.88 \times 10^2 \Omega\text{cm}$ and FOM of $1.92 \times 10^{-4} \Omega^{-1}$. The controllability of the properties of ZnO nanorods to the desired quality by variation of growth parameters allows for their application in photovoltaic cells as electron transporters. Furthermore, the ability to tune the properties of the nanorods using the growth parameters is a promising step towards attaining even better properties.

5.2 Recommendations for future work

The general aims or objectives of this study were successfully achieved; however, the following need to be implemented in future:

- Study the effects other chemical bath deposition parameters such as pH and annealing temperature on the growth of the nanorods.
- Fabrication and testing of solar cells using the synthesized ZnO nanorods with high aspect ratio and better alignment.

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