Defect characterization of low temperature solution grown ZnO

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2016

Liew, L. -L. (2016). Defect characterization of low temperature solution grown ZnO. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/66016>

<https://doi.org/10.32657/10356/66016>

**DEFECT CHARACTERIZATION OF LOW
TEMPERATURE SOLUTION GROWN ZINC OXIDE**

**LIEW LAURA-LYNN
SCHOOL OF MATERIALS SCIENCE AND ENGINEERING
2016**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2016

Acknowledgements

I would like to express my heartfelt gratitude to my supervisors, Dr. Gregory Goh from the Institute of Materials Research and Engineering (IMRE), A*STAR and Associate Professor Dong Zhili from the School of Materials Science and Engineering, NTU for their guidance and support. In addition, this thesis would not have been possible without the help of Professor Gopinathan Sankar from Department of Chemistry, University College London (UCL) with whom special thanks goes to, for the endless conversations and help in obtaining and analyzing synchrotron data, and for all the times spent at the beamlines. Thanks also to members of my thesis advisory committee, specifically, Associate Professor Su Haibin, from the School of Materials Science and Engineering, NTU for advice rendered.

I would also like to thank the following colleagues, past and present, from IMRE, A*STAR, who have helped me in obtaining data for this thesis - Lin Ming, Joyce, Hui Kim, Siew Lang, Sze Yu, Xue Qi, Doreen, and Poh Chong. Also, to Denny, Quang and Ajay for advice and help rendered with the various characterization equipment, growth techniques, data processing and writing; and all my lab-mates and students for their help. I would also like to thank Connie and Andrew for help with formatting and editing of this thesis.

Special thanks go to the beamline scientists, Dr. Giannantonio Cibin, from beamline B18 of Diamond Light Source, UK; Dr. Sergey Nikitenko, from beamline DUBBLE of the European Synchrotron Radiation Facilities (ESRF); Dr. Du Yonghua and Dr. Xi Shibo, from beamline XAFCA, Institute of Chemical Sciences and Engineering (ICES, A*STAR) and Singapore Synchrotron Light Source (SSLS); and Dr. Shinji Kohara from beamline BL04B2 of the Japan Synchrotron Radiation Research Institute (JASRI), SPring-8, Japan, for help with conducting the synchrotron experiments. Further thanks are extended to the past and present students from Department of Chemistry, UCL – Huw, for help with analyzing data, and to Andy, Gregory, Husna, Tom, Kerry and Jon, for being great company and help at the beamline experiments. Special mention goes to Dr. Jacob J. Richardson, University of California, Santa Barbara (UCSB) for collaboration on the ZnO film porosity work.

Thanks to my lunch '*kakis*' – Augustine, Khee Leong, Dennis, Shumei, Su Hui, Seok Hong, Connie, Weiyin, Jatin and Gen, for being a great source of company and support. And finally, I would like to thank my fiancé, Zi Xiang, for his love and patience.

This work is sponsored and supported by the Agency for Science, Technology and Research (A*STAR), Singapore under the Scientific Staff Development Award (SSDA). This research work has been partially funded by A*STAR IMRE core funded for projects IMRE/08-1P0603 and IMRE/10-1C0106.

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Summary

Zinc oxide (ZnO) is a wide bandgap semiconducting oxide with many potential applications in optoelectronic devices such as light emitting diodes (LEDs) and field effect transistors (FETs). Controlling the conductivity of ZnO is a foremost concern in the optoelectronic industry. Understanding the nature of ZnO native defects is vital for the application of ZnO in the semiconductor industry. Many electronic properties depend significantly on the intrinsic defect concentration as it affects the doping efficiency and the growth of the material. These properties also depend on the type and amount of impurities and degree of crystallinity. There is a need to understand the function of native point defects and the incorporation of impurities, with the intention for a better control of the conductivity of ZnO. However, one major issue in determining whether it is zinc or oxygen deficiency that provides ZnO its unique properties remains.

In this thesis, ZnO films and powders were synthesized via a low temperature aqueous solution chemical bath deposition route and its short to medium range structure order characterized. In addition, Ga-doped ZnO films and powders were also synthesized as Ga has been found to be an excellent donor, increasing the conductivity of ZnO films. All samples were post-growth thermally annealed in air in order to improve the electrical and optical properties, and correlate the annealing temperature with the defect structure.

The epitaxial nature of the ZnO films (undoped and Ga-doped) were determined via high resolution X-ray diffraction (HRXRD). The morphology of the films was studied via field emission gun scanning electron microscopy (FEGSEM) showed that the films were smooth and continuous on the plane-view. Cross-sectional images showed that the films were about 2 μm thick after a growth time of 4 hours at 90°C. Visible pores were also observed in the films after post-growth thermal annealing at temperatures of above 200°C. Electrical properties were obtained via Hall measurements showed characteristic *n*-type conductivity and a carrier concentration of the order of 10^{20} cm^{-3} after post-growth thermal annealing at 400°C in air for 1 h for the Ga-doped ZnO films.

For the ZnO powders, phase identification was determined by conventional powder XRD methods. The morphologies were obtained via FEGSEM and showed different nanorods morphologies for the different precursors used for the syntheses. Internal pores were observed in the ZnO nanorods upon thermal annealing at $>300\text{ }^{\circ}\text{C}$ and were examined using transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM). Three-dimensional electron tomography reconstruction shows that pores exist within the nanorods. These pores coalesce and also increase in size as the ZnO nanorods were annealed at higher temperatures or for extended periods of time, as observed by an *in situ* TEM study. As such, this pore formation phenomenon will significantly affect the utilisation of solution-synthesized ZnO for optoelectronic devices, but new application fronts such as gas sensors and photo/electro catalysis will benefit due to its high light absorption properties and high surface areas.

Further defect characterization was performed for the all the ZnO samples, largely using synchrotron-based characterization techniques, namely X-ray absorption spectroscopy (XAS) and X-ray pair distribution function (PDF) techniques. XAS is an ideal, atom specific characterization technique that is able to probe defect structure in many materials, including ZnO. Comparative studies of commercially available ZnO and aqueous solution grown ($\leq 90^{\circ}\text{C}$) ZnO powders using XAS and PDF has allowed for the study of short to medium range structure order. The ZnO films were studied via *ex situ* XAS and the ZnO powder samples were studied via *ex situ* and *in situ* XAS and *in situ* PDF experiments. The local structure order of the ZnO films and powders were determined. From XAS of the Ga-doped ZnO samples, it was evidently shown that Ga^{3+} resides tetrahedrally in the Zn^{2+} site within the ZnO lattice.

The understanding of the role of defects and the short to medium range order and structure within the ZnO system has provided useful insight for further exploitation of the material and is invaluable for the exploitation of ZnO for further development of optoelectronic device applications.

Chapter 1

Introduction and Literature Review

1.1 Background and Motivation

All good things must come to an end. Silicon (Si) integrated circuits that have spurred the advancement of technology since its discovery sixty years ago is nearing its fundamental physical limits. Gordon Moore predicted that over the history of computing hardware, the number of transistors incorporated on a chip doubles every two years or so.¹ However, Moore's prediction seems to have reached its limits due to the difficulties in dissipating heat from packing billions of transistors into a small footprint and also due to leakage issues because of the physical inadequacy of gate materials. Furthermore, recent demand for low-power electronic applications for popular handheld devices such as smart phones and tablets increases the demand for even smaller devices with greater computing power density and energy efficiency. The semiconductor industry today is in dire need for novel materials to break the barrier for greater development.

Our world today has become reliant on electronic devices. In particular, lighting has become an essential part of the sustainable first world nations we are currently living in. *Imagine a world without light!* Thus, we see an increase for the need of lighting, specifically *efficient* lighting. Solid state lighting, including light emitting diodes (LEDs) are the only type of lighting capable of delivering almost

15 times more lumens than conventional incandescent lamps.² Such technology is based on the material, gallium nitride (GaN), which forms the basis for LEDs. Since the first announcement of super high brightness Blue LED in 1993 by Nichia Corporation, Japan,³ worldwide revenue for GaN-based LEDs was \$12.4 billion in 2013, a 10.6% increase from 2012.⁴ Current state of the art LED technology comprises of CREE Inc.'s newly developed CXA2 LED arrays that enable system cost savings of up to 60%,⁵ making the use of such LEDs very favourable to replace conventional lighting technologies.

The price of such lighting is still considered expensive and there is a need to find cheaper and better ways of harvesting light for such solid state lighting applications. The manufacturing costs of GaN are very high as it is based upon an expensive and complex metal-organic chemical vapour deposition (MOCVD) technique. There is thus a significant research interest to develop new processes and new materials in place of MOCVD grown GaN. A new class of wide band gap materials that are cheaper, more readily available and easier to manipulate are now the prime subject in various research and development activities in search for GaN replacement for solid state lighting applications.

Our world today is increasingly reliant on electronic devices such as mobile phones, tablets and electronic displays (e.g. flat panel displays). There is a great concern with energy usage and conservation. Progressively, more interest is developed for materials to capture sunlight for use in buildings in order to reduce energy costs. Transparent conducting oxides (TCOs) form the basis of such application devices exhibiting both high optical transparency and good electrical conductivity. Some commonly used TCO materials include In_2O_3 and CdO . Due to the high costs of such materials, a new class of wide band gap materials that are cheaper and more readily available are currently needed for its replacement or substitution.

1.2 Introduction to Wide Band Gap Semiconductors

Wide band gap (WBG) semiconductors are poised to power the next generation of optoelectronic and power devices. These superior materials have emerged as the forerunners as the solution to the slow-down in using silicon in the high power, high temperature segments. They enable greater energy efficiency in industrial scale power electronics and clean energy technologies. They allow devices to be operated at higher voltages and frequencies. Exploiting the capabilities of such WBG semiconductors can potentially create huge energy and cost savings. They allow faster, smaller, more reliable and greater efficiency power electronic components to be used for device applications. Some of these materials include silicon carbon (SiC), gallium nitride (GaN) and zinc oxide (ZnO). These materials exhibit considerably superior voltage and power performance and demand less power than the more commonly used Si semiconductor devices.⁶ This positions WBG based semiconductors as key enablers for today's important emerging applications such as hybrid electric and electric vehicles and renewable energy generation and storage.

Some applications of WBG semiconductors include industrial motors, which enable higher efficiencies, and in electronics, for example, compact power supplies for consumer electronics. Other applications are grid integration, which exploit WBG-based inverters that convert DC into AC electricity or vice versa in electric vehicles. Most importantly, the use of WBG-based LEDs has been projected to conserve US\$250 billion in collective energy expenditure by 2030.⁷

However, there are various challenges faced in the manufacturing of WBG-based applications despite it quickly gaining acceptance. The main factor is the cost of manufacturing large and high quality substrates. This and other factors such as integration of systems and alternative packaging for higher temperatures,

limit the potential of WBG-based applications for commercialisation. In spite of all the challenges, there is still huge potential economic impact should WBG-based applications replace conventional Si-based devices.

Figure 1-1 shows the band gap distribution of various WBG semiconductors.⁸ Many of these materials are currently being exploited for semiconductor device applications.

Figure 1-1: Band gaps of several semiconductor materials.⁸ (Reprinted by permission from Macmillan Publishers Ltd: Nature Publishing Group, Grätzel, M., Nature 2001, 414, 338. Copyright © 2001)

GaN and SiC are at last beginning to be commercialised and are received for their exceptional high power, high temperature semiconductor characteristics. They have been used as switch technologies for automotive applications.⁹ As the markets for these devices become apparent, it is imperative to recognise what propels the commercial market to expend on WBG devices compared to other conventional materials such as silicon or gallium arsenide. Other materials being commercialised are GaN and ZnO, which are used in LED applications.¹⁰ In particular, ZnO has attracted greater attention in recent years for use in optical device applications as there are numerous possible benefits in contrast to GaN, for instance, the readily available bulk single crystals. ZnO also has a larger exciton

binding energy (~ 60 meV relative to ~ 25 meV for GaN).¹¹ Thus, we see much potential for ZnO based LEDs, ZnO-based TCOs and other device applications and want to further explore ways to take advantage of this superb material.

1.3 Introduction to Zinc Oxide

ZnO is a WBG II-VI semiconducting oxide that is of much significance of late due to its exceptional optical and electronic properties (exciton binding energy 60 meV, 3.37 eV band gap).¹²⁻¹⁴ ZnO demonstrates excellent electrical properties, with carrier concentrations of up to $10^{17} - 10^{19} \text{ cm}^{-3}$ as shown from Hall-effect measurements reported by a few research groups.¹⁵⁻¹⁷ It also has low resistivity and high mobilities. This material exists intrinsically as *n*-type and this conductivity is accredited to native defects.¹⁸ ZnO also exhibits superior optical properties, often presenting a high intensity and strong deep level (green) emission peak at $\lambda \approx 381 \text{ nm}$ (*ca.* 3.26 eV) in photoluminescence (PL) mapping.¹⁹ This has allowed its use in various devices such as for TCOs,²⁰⁻²² in light emitting diodes (LEDs)²³ and field effect transistors (FETs).²⁴ In addition, ZnO's WBG is exploited in a broad range of commodities such as anti-bacterial coatings,²⁵ in sunscreen as a UV blocker,²⁶ and in the area of catalysis.²⁷

ZnO has proven to be a potential alternative to GaN for light harvesting applications. In addition, the band gap of pristine ZnO is nearly identical to GaN and this gap can be modified without significant change in the crystal structure.²⁸ It has a close lattice mismatch to GaN (1.8%)²⁹ and has been proven useful in enhancing light extraction by the growth of ZnO nanowires on a p-GaN substrate.³⁰ In order to implement ZnO for LED applications, there are three main challenges that need to be addressed.

First, a *p-n* junction is required. Undoped ZnO without intentional doping is almost always an *n*-type semiconductor because the hydrogen is always present as a donor in ZnO.³¹ The carrier concentration of *n*-type carriers, and as a result, luminescence properties, can be enhanced by doping with group III dopants such as Ga^{32,33} and In.³⁴ However, *p*-type doping is at present a predicament due to stability issues. Second, low defect density in the film is required to increase the light output. Finally, to be suitable for LED applications, the ZnO needs to be grown epitaxially in order to harvest light efficiently. This is because like in GaN based LEDs, the electron-hole pair recombination must not happen in the intermediate states/recombination centres within the band gap. Such non-characteristic recombination would not produce a desirable light output for use in lighting applications. Defect sites, including grain boundaries and surfaces are the prime source of recombination centres in a crystal and is minimised by forming epitaxial film.

Epitaxial ZnO films have been synthesized through various different methods such as MOCVD,³⁵ molecular beam epitaxy (MBE),³⁶ laser ablation³⁷ and sputtering.³⁸ However these methods are costly, require expensive equipment and toxic precursors. Hydrothermal synthesis³⁹ on the other hand is a cheap and scalable method of synthesizing epitaxial films. Starting materials for ZnO growth, water and Zn salts are inexpensive and readily abundant. Growth temperatures and pressures are also low ($\leq 100^{\circ}\text{C}$) and there is minimum loss of dopants because of the closed system adopted and more relaxed growth requirements in view of the fact that only low pressure is necessary. For example, there is no need for a vacuum and since temperatures are $\leq 100^{\circ}\text{C}$, conventional ovens are sufficient to heat up the reaction vessel.

However, defects that are introduced during hydrothermal synthesis⁴⁰ have a different defect formation process as compared with other synthesis

techniques. The character and behaviour of the defects may be different. Defects such as point and lattice defects can act as recombination centres and reduce carrier concentration in the film.⁴¹ Therefore, there is an immediate urgency to understand the type of defects in hydrothermal ZnO and the defect behaviour (from annealing studies) to better understand the relation it has with the physical, and optoelectronic properties of hydrothermal ZnO films. Being able to control the electrical conductivity and nanostructure or morphology in ZnO thin films is vital measure for their relevance in electronics and optoelectronics. The key to realising ZnO for solid state lighting is therefore to gain definitive knowledge of intentional and unintentional defects and their related band gap states. Also, it is crucial to understand the given semiconductor and its defects and to tailor its properties by intentional doping.

1.4 Zinc Oxide: Crystal Structure and Nanostructures

ZnO crystal is a hexagonal wurtzite structure consisting of tetrahedrally coordinated cations that link together by sharing corners. The bases of each tetrahedron point in the same direction, namely the $[000\bar{1}]$, along the c-axis. The resulting plane perpendicular to this $[000\bar{1}]$ direction is called the oxygen-terminated plane. The apexes of each tetrahedron point in the opposite direction, namely the $[0001]$, whose terminating plane is called the zinc-terminated plane. This structure makes the material polar along the c-axis and due to the absence of inversion symmetry, gives it piezoelectric and pyroelectric properties. Its lattice parameters are $a = 3.296 \text{ \AA}$ and $c = 5.2065 \text{ \AA}$.⁴² Figure 1-2 shows a schematic representation of the wurtzite structure for ZnO.

Figure 1-2: Schematic representation of ZnO in the wurtzite structure form.

Because ZnO crystallizes preferentially grows and aligns in the c -axis direction, it often produces rod-like morphology.^{32,43-47} Much research has been done on ZnO nanorods for various applications. Sun *et al.* synthesized ZnO nanorods for use as a high performance thin-film field-effect transistor (TFT).²⁴ ZnO nanorods have also proven to be a good UV blocker,²⁶ and useful in solar cell applications.^{48,49} Wan *et al.* have used ZnO nanorods for gas sensor applications⁵⁰ and Huang *et al.* demonstrated that ZnO nanorods can be useful for nanolasers.⁵¹

There are also many other morphologies of ZnO such as nanotubes,⁵² nanoflowers,⁵³ flakes, columns, pyramids⁵⁴ and thin films,³⁹ etc. which have been synthesized commonly with the addition of surface active agents. Liu *et al.* used a wet direct method to synthesize single-crystal ZnO nanotubes and nanorods.⁵² This has previously only been done in an indirect approach. ZnO nanoflowers were synthesized by a hydrothermal method as a photoanode for dye-sensitized solar cell (DSSC) applications by Jiang *et al.*⁵³ The ZnO nanoflowers had increased dye-loading and light harvesting capabilities, providing much promise for potential applications of DSSCs, as compared to the nanorod morphology for this application. Han *et al.* controlled the morphology of ZnO and showed that three

different morphologies, namely, flakes, columns and pyramids, can be synthesized by means of different facile wet chemical routes.⁵⁴ They found that the different growth environments of the ZnO are responsible for the different morphologies obtained.⁵⁴

ZnO thin films are one of the most commonly used morphology for device applications. Typically, sodium citrate is added in aqueous solution growth routes to promote lateral growth.⁵⁵ These films have been demonstrated to have light emitting properties and are used for WBG semiconductors for device applications.²⁰

1.5 Properties and Applications of Zinc Oxide

1.5.1 Optical and Emission Properties and Applications

As a direct wide bandgap material, ZnO exhibits excellent electronic and optical properties. It is an extensively studied material for nanoelectronics. Electrical measurements have been performed on individual ZnO one-dimensional (1-D) nanostructures (e.g., nanorods, nanowires and nanobelts) measuring the electrical carrier transport through each nanowire or nanorod. These show *n*-type semiconductor behaviour and have potential applications as field effect transistors (FETs)⁵⁶⁻⁵⁸ and gas sensors.^{59,60}

Recently, it has been shown that ZnO is an ideal material as a TCO to prospectively take the place of indium-tin-oxide (ITO).⁶¹⁻⁶⁵ Device applications often require a layer of conducting oxide for carrier transport and in recent years, the demand for it to be transparent has become increasingly evident. Such TCOs are commonly found in devices with flat-panel displays such as in smart phones

and personal computers. It is also required for solar cells, touch panels, gas sensors, and anti-reflection coatings, etc.

Agrawal *et al.* deposited ZnO films by reactive DC magnetron sputtering using oxygen as the reactive gas. The samples were deposited on glass substrates by altering oxygen flow rates for the period of the deposition procedure. Subsequent to the deposition, the samples are heat treated at 300°C for 2 hours in a vacuum atmosphere. The samples showed very low resistivity of $1.5 \times 10^{-3} \Omega\text{-cm}$ and 80% transparency with no doping.⁶⁶ It was reported that these films, once improved with a small amount of aluminium doping could achieve higher conductivities with similar transparencies and may be used for TCO applications. The adaptability of ZnO deposited via a low pressure chemical vapour deposition (LPCVD) and its use in thin film Si solar cells was reported by Söderström *et al.*²² It was demonstrated that this technique of depositing ZnO thin films was able to achieve high transparency (>80%), with texture suitable for light trapping in prohibitive haze, and have elevated conductivity ($R_{sq} < 10 \Omega\text{-sq}$), making it a suitable technique for depositing ZnO for TCO applications.

Podlogar *et al.* grew ZnO layers on reasonably priced glass substrates by a low cost and simple low temperature hydrothermal method. The films obtained were smooth and dense (0 0 0 1) oriented polycrystalline ZnO films with outstanding optical properties. An optical transparency of 82% was achieved with exceptionally low sheet resistance for ZnO. This meets the high criterion for numerous photonic and electronic applications.⁶⁴ When ZnO thin films are further supplied with the doping of Group III metals, for example gallium, the optoelectronic properties are further enhanced, as demonstrated by Moe *et al.*⁶² In addition, Moe *et al.* deposited Ga-doped ZnO films at a low temperature on glass substrates by an aqueous solution means for use in dye-sensitized solar cells

(DSSCs). The transparency obtained was 85% with a low sheet resistance of up to $15 \Omega \text{ sq}^{-1}$.⁶¹⁻⁶³

ZnO nanowires were grown by Kushwaha *et al.* to investigate the defect states present using photoluminescence measurements.⁶⁷ Sim *et al.* grew epitaxial ZnO films and studied the photoluminescence.⁶⁸ The spectra revealed a strong near band-edge UV emission and deep level emission bands consisting of a green band ascribed to the existence of Zn vacancies and an orange-red band associated with the incidence of oxygen interstitials.⁶⁸ Park *et al.* showed that ZnO nanorods could be synthesized via a catalyst-free metallorganic vapour phase epitaxy route.⁶⁹ The nanorods exhibited excitonic emissions as seen from the photoluminescence spectra.⁶⁹ Gu *et al.* synthesized ZnO nanorods through a colloidal route and observed quantum confinement.⁷⁰ The exciton binding energy is therefore greatly enhanced due to the 1-D nature of the ZnO nanorods.⁷⁰

Thompson and co-workers exploited the superior optical property of ZnO and demonstrated that ZnO can be used as a transparent current spreading layer in light emitting diodes (LEDs).²⁰ Their results show an external quantum efficiency of 37.7% signifying an improvement of a factor 1.93 larger than the conventional LED with thin metal electrode.²⁰ Bao *et al.* fabricated the first ZnO single nanowire LED,⁷¹ dispersing the wires on a silicon substrate and thereafter spin-coating a thin layer of poly(methylmethacrylate), or PMMA onto the substrate. The device showed broad sub-band gap emission at room temperature,⁷¹ demonstrating the potential applications in LEDs and lasers.

1.5.2 Piezoelectric and Sensing Properties and Applications

ZnO is also widely used as a piezoelectric material^{72,73} due to its crystal structure in which is non-centrosymmetric, having oxygen atoms and zinc atoms

tetrahedrally bonded. Because of this, the centre of the charges can be re-located due to an induced lattice distortion caused by an external pressure. Thus, an electrical signal can be produced by a mechanical vibration and vice versa. This allows ZnO to be used in applications such as force sensing, as an acoustic wave resonator, and for microelectromechanical systems (MEMS) etc.⁷⁴⁻⁷⁸ Zhao *et al.* considered the effectual piezoelectric coefficient using piezoresponse force microscopy on discrete (0001) surface dominated ZnO nanobelts, situated on a conductive surface.⁷⁹ The results obtained were very favourable showing that ZnO nanobelts are frequency dependent and can potentially be used for nanoactuators and nanosensors.

ZnO has also proven to be an excellent material of choice for gas sensors. Various research groups have fabricated ZnO-based gas sensors for ethanol detection.⁸⁰⁻⁸³ Fan *et al.* fabricated a ZnO nanowire based field effect transistor.⁸⁴ Using it as a gas sensor, they exposed it to various gases such as oxygen, nitrogen dioxide and ammonia. Their results show that the conductance changes according to which gas it was exposed to, indicating that the gases affect the conductance of the nanowires, and is an effective gas sensor.⁸⁴ ZnO has also been used for various other types of sensors,⁸⁵ such as chemical sensors,⁸⁶⁻⁸⁸ biosensors,⁸⁹⁻⁹¹ UV sensors,⁹²⁻⁹⁵ and pH sensors,^{96,97} among others.

1.5.3 Catalytic and UV Blocking Properties and Applications

Cu/ZnO or Pd/ZnO-based catalysts are commonly used for the synthesis of methanol from CO/CO₂/H₂. This is an important industrial process and many studies have investigated the role of ZnO in this process.⁹⁸⁻¹⁰⁰ The photocatalytic property of ZnO is also extensively studied.¹⁰¹⁻¹⁰³ Kuriakose *et al.* used a wet chemical route to synthesize a flower-like ZnO nanostructure and studied its photocatalytic activity by quantifying the degradation of methylene-blue under

UV irradiation.¹⁰¹ These flower-like ZnO nanostructures demonstrated superior photocatalytic ability towards the degradation of methylene-blue under UV as compared to conventional nanorod morphology. These studies show that ZnO has exceptional photocatalytic properties, and can be used as a photocatalyst in the process of degradation of various substances.

ZnO is also commonly used as a UV blocker in sunscreens commercially.¹⁰⁴ ZnO has been found to be a safe and effective sunblock that provides broad spectrum UV protection including long wavelength UVA.¹⁰⁵ Many scientists have also been studying ZnO for use in self-cleaning, water repellent and UV-blocking textiles.^{26,106-109} It is bio-compatible and nanostructured ZnO are effective UV absorbers and blockers and are air-permeable, making it suitable for use in textiles. Du *et al.* also exploited the UV blocking property of ZnO and used it for anti-reflective coatings.¹¹⁰ Multilayer anti-reflection coatings using ZnO to provide UV blocking has also been developed.¹⁰⁹

Thus, we see that ZnO has many useful properties and applications. Apart from those aforementioned, ZnO is also commonly used for dye-sensitized solar cells and other photovoltaic applications,^{22,48,111-114} and as an anti-bacterial agent^{25,115-117} etc. This shows that nanostructured ZnO is a versatile material and high in demand for applications due to its outstanding properties.

1.6 General Synthesis Methods of ZnO

Zinc oxide can be synthesized through various techniques, broadly categorized as gas phase synthesis and solution phase synthesis. Physical methods typically employ gaseous atmosphere in enclosed chambers such as sputtering,¹¹⁸ metallorganic chemical vapour deposition (MOCVD),¹¹⁹ vapour phase transport (VPT),¹²⁰ molecular beam epitaxy (MBE),¹²¹ and pulsed-laser

deposition (PLD).¹²² Liu *et al.* grew ZnO thin films on several wafers such as GaAs and Al₂O₃ using radio frequency magnetron sputtering technique.¹¹⁸ ZnO has also been deposited on sapphire substrates via the MOCVD technique by Liu *et al.* for use as UV detectors.¹¹⁹ This technique produced epitaxial ZnO films. Bakin and co-workers developed a novel advanced VPT set-up for growing ZnO layers and nanostructures.¹²⁰ Ko *et al.* used a radio-frequency plasma assisted MBE technique to deposit high quality ZnO films.¹²¹ A PLD technique was used by Zeng *et al.* to deposit ZnO thin films, and these films are useful in potential applications such as direct current and medical applications.¹²²

Solution phase synthesis is however a cheaper and simpler way of producing ZnO. The growth procedure is done in a liquid environment using various precursors. Solution synthesis of ZnO can be done via a sol-gel route using zinc acetate hydrate;¹²³ a template assisted growth method, typically using porous alumina templates;¹²⁴ or the most common solution based method, by using a zinc precursor with sodium/potassium hydroxide or ammonium hydroxide in alcoholic or aqueous media. This method, commonly referred to as hydrothermal growth³⁹ or chemical bath deposition, allows for the growth of nanoparticles and various other nanostructures such as nanorods and nanowires. ZnO films are also commonly grown by this method. Although rod morphology is typical of ZnO growth, there are many factors which can influence the final crystallographic morphology obtained. The acidity or basicity of the reaction system, precursors, solvents, time and temperature are all experimental parameters that affect the resulting morphology.

Solution phase techniques are attractive methods to grow ZnO because of advantages such as uncomplicated equipment, low temperature which limits interdiffusion, ambient pressure, and locality to the thermodynamic equilibrium.⁴⁰ Notably, ZnO has been synthesized by various research groups

through hydrothermal means or chemical bath deposition.^{39,40,46,125} Chemical bath deposition is a cheap method and has great potential to scale up, making it favourable for ZnO growth. Furthermore, epitaxial ZnO has been synthesized through this method and high quality films have been shown to give extremely good optoelectronic properties.^{37,46,126,127} In addition, epitaxial films can be formed via templating on single crystal substrates. Moreover, by solution phase techniques, the morphology of ZnO nanostructures can be controlled with the use of different precursors or by the addition of surface active agents.

For solution based syntheses, ZnO typically crystallizes by the hydrolysis of Zn salts in a basic solution. Zn^{2+} is tetrahedrally coordinated and exists in a number of intermediates depending on the temperature and pH.¹²⁸ These Zn^{2+} intermediates ultimately dehydrate to form ZnO crystals. Chemical reactions in aqueous systems are typically in reverse equilibrium. The thrust is the minimization of free energy of the complete reaction system.¹²⁹

1.7 Chemical Bath Deposition of ZnO

Although rod morphology is typical of ZnO growth, there are many factors which can influence the final crystallographic morphology. The acidity or basicity of the reaction system, precursors, solvents, time and temperature are experimental parameters that affect the morphology. Typically, ZnO crystals are formed via the hydrolysis of Zn salts within a basic solution.¹³⁰ Zn^{2+} is tetrahedrally coordinated and exists in a number of intermediates depending on the temperature and pH.¹²⁸ These Zn^{2+} intermediates dehydrate to form ZnO crystals.

1.7.1 Ammonia Precursor Route

Andeen *et al.*³⁹ has reported epitaxial ZnO films deposited on <111> MgAl₂O₄ (spinel) substrates by a low temperature aqueous solution route via chemical bath deposition. The growth follows a nucleation and growth mechanism. The optimum growth condition is achieved in a solution of pH 10.9 at 90°C.³⁹ Material formation proceeds by hydrolysis of precursors (hydroxide) followed by dehydration to form the oxide material. The driving force (supersaturation/solubility) is affected by pH, precursor concentration, temperature, etc.

1.7.1.1 Nucleation

A reaction occurs when aqueous zinc nitrate hexahydrate is mixed with ammonia causing Zn complexes to form within the solution according to equation (1):¹³¹

In this aqueous solution route, $[\text{Zn}(\text{OH})_4]^{2-}$ ions are the species accountable for the nucleation of ZnO films. Li *et al.*⁴⁷ demonstrated a bonding of clusters due to supersaturation as the ions attach collectively, forming $[\text{Zn}_x\text{O}_y(\text{OH})_z]^{(z+2y-2x)-}$ clusters following the dehydration reaction (equation (2)):

Lastly, these clusters form ZnO grains when they attain a critical size as seen from reaction (3):⁴⁷

At the pH range of 10.5 – 11, the ZnO/substrate interface possesses a lower free energy comparative to the ZnO/solution boundary and this promotes nucleation on the substrate.³⁹

1.7.1.2 Growth

These nuclei will then proceed to grow into large ZnO islands that will cover the substrate via an island growth mechanism, resulting in the production of continuous ZnO films.

In the chemical bath deposition of ZnO, the resultant growth reaction equations are as follows for solutions having pH greater than 10:⁴⁴

From equation (4), when ammonia is added to aqueous Zn^{2+} it produces $Zn(NH_3)_4^{2+}$. Following that, the reaction between $Zn(NH_3)_4^{2+}$ and OH^- will then form ZnO (equation (5)).⁴⁷ If the concentration of OH^- is low level, ZnO nanorod growth will not proceed due to a deficiency of $Zn(NH_3)_4^{2+}$ species. Above the optimum pH of 10.9, further increases in the OH^- concentration will result in a reduction of the ZnO nanorod growth rate. This is due to the competing dissolution reaction(s) that may occur in the chemical bath deposition solution (equation (6)). Thus, the OH^- concentration or pH of the solution influences the growth rate of ZnO nanorods. There is competition between reaction rates involving ZnO

formation and dissolution. Ideally, the maximum rate of growth of ZnO nanorods is only attained at the optimum pH of 10.9.³⁹

1.7.2 Hexamethylenetetramine (HMT) Precursor Route

Many research groups have also synthesized nanostructures of ZnO in solution using the precursors of zinc acetate and zinc nitrate as precursors with HMT.¹³²⁻¹³⁷ The generally accepted mechanism is as follows:¹³⁴

(7)

(8)

(9)

(10)

(11)

(12)

Upon heating, HMT decomposes to produce formaldehyde and ammonia. Ammonia then reacts with water to form OH^- which impels the crystallization of ZnO.¹³⁶ The formation of ZnO nuclei is slow and is the limiting factor for the growth of ZnO films. The typical morphology obtained is that of nanorods where ZnO grow preferentially in the c-axis direction. This is because the (0001) basal plane of the hexagonal rod has an elevated surface energy and is polar. The relationship among the rates of growth (R) for the ZnO crystal planes has been

given by $R_{(0001)} > R_{(\bar{1}010)} > R_{(1000)}$.^{134,138} Figure 1-3 displays the field emission gun scanning electron microscope (FEGSEM) images of ZnO rods grown on Si wafer using this precursor chemistry route.

Figure 1-3: ZnO rods grown on Si wafer using equimolar zinc nitrate hexahydrate and hexamethylenetetramine precursors (a) plane-view, (b) cross-sectional view.

1.7.3 Role of Citrate Ions in the Growth of ZnO Films

Tian *et al.*⁴³ proposed a correlation between the aspect ratio of the ZnO nanorods and the citrate concentration. Citrate ions causes an inhibition of the crystal growth alongside the $\langle 001 \rangle$ orientation, producing plate-like crystals rather than rods. This provides a simple means of controlling the aspect ratio of the ZnO nanorods. Figure 1-4 below shows the chemical structure of a citrate ion.

Figure 1-4: Chemical structure of citrate 3⁻ ion.

Figure 1-5 shows that there is a strong relationship between crystal morphology and concentration of citrate ions inside the hydrothermal reactor.⁴³

Figure 1-5: Aspect ratios of ZnO versus citrate concentrations.⁴³ (Reprinted by permission from Macmillan Publishers Ltd: Nature Publishing Group, Tian, Z. R.; Voigt, J. A.; Liu, J.; McKenzie, B.; Mcdermott, M. J.; Rodriguez, M. A.; Konishi, H.; Xu, H., *Nat Mater* 2003, 2, 821. Copyright © 2003)

Andeen *et al.*⁵⁵ reported zeta potential measurements (Figure 1-6), which determines the sign and number density of surface charges on particles. This is a useful method of identifying the precise adsorption of citrate ions onto a specific material. Their results show the pH range with which citrate ions adsorb onto ZnO powder. It was found that increasing sodium citrate concentrations reduces the iso-electric point (IEP) of ZnO. For pH > 9.4 (IEP for ZnO), there occurs a slowing of the growth in the <0001> direction is reduced because citrate ions will adsorb onto the polar (0001) plane exclusively.

Figure 1-6: Graph showing the zeta-potential for ZnO powders as a range of sodium citrate added.⁵⁵ (From Lateral Epitaxial Overgrowth of ZnO in Water at 90°C, Andeen, D.; Kim, J. H.; Lange, F. F.; Goh, G. K. L.; Tripathy, S., *Advanced Functional Materials* 2006, 16, 799. Copyright © 2006 by John Wiley and Sons, Inc. Reprinted with permission of John Wiley and Sons, Inc.)

1.8 Point Defect Classification in ZnO

Controlling the conductivity of ZnO is a foremost concern in the optoelectronic industry. The understanding of the behaviour of native defects is vital for the application of ZnO in the semiconductor industry. Experimentally, there is little evidence of the role of native defects in as-grown ZnO, none of which are conclusive. Many electronic properties depend significantly on the intrinsic defect concentration as it affects the doping efficiency, and growth of the material. These properties also depend on the type and amount of impurities and degree of crystallinity. Oxygen vacancies, V_o , zinc interstitials, Zn_i , oxygen interstitials, O_i , and zinc vacancies, V_{zn} , are the primitive forms of native defects in ZnO. There is a need to understand the function of native point defects and the incorporation of impurities, with the intention for a better control of the conductivity of ZnO.

1.8.1 Native Defects

The persistent *n*-type nature of the conductivity of ZnO has traditionally been ascribed to native defects in the atomic level, for example oxygen vacancies (V_o) and zinc interstitials (Zn_i).¹⁸ Nonetheless, up to date density-functional calculations, substantiated by optically detected electron paramagnetic resonance measurements^{139,140} show that this is untrue and the cause of “native” *n*-type conductivity perhaps is due to the unintentional impurities instead.¹⁴¹⁻¹⁴⁴

1.8.1.1 Oxygen vacancies

Oxygen vacancies have been very widely discussed as a source of ZnO’s *n*-type conductivity as it has the least energy for formation as compared with the other defects that act as donors. However, density-functional theory (DFT)

calculations show it is a deep donor and therefore is not able to be a factor of ZnO's *n*-type conductivity.^{19,20,22}

Recent computational studies show that the calculated energies of formation suggests V_o has a high formation energy that prevents participation in a major function for *n*-type material, but rather acts like a compensating centre in *p*-type ZnO. First-principles calculations show that oxygen vacancy exists not as a shallow donor.¹⁴³ It is argued that V_o , at room temperature, does not supply electrons to the conduction band and that the energy for formation of V_o under *n*-type situations is especially elevated demonstrating improbability of formation in the course of growth.¹⁴³ Thus, oxygen vacancies are in reality deep donors and are not the reason for the *n*-type conductivity in ZnO.^{139,140,143}

1.8.1.2 Zinc interstitials

There are two main sites for zinc interstitials (Zn_i) in the wurtzite structure. It can in principle lie either in the octahedral site or the tetrahedral site. The Zn_i in the octahedral site is more stable than in the tetrahedral site as the geometrical constraints are less severe.^{142,145} It is also reported that Zn_i are not likely to be stable in pure ZnO at room temperature.¹⁴⁶ On the other hand, Zn_i is able to diffuse relatively easily due to its low barrier and may settle at other sites such as V_o to form antisite Zn_o . Another possibility is that the formation of a complex due to the Coulombic attraction of Zn_i with negatively charged impurities.¹⁴⁷ This interaction may offer a mechanism to participate in the inadvertent *n*-type conductivity of ZnO. Zn_i thus, behaves as shallow donors as it always donates electrons to the conduction band. It is also said to have formation energies that are high and are quick diffusers and so improbable to be stable as isolated point defects. Therefore, it is implausible to be accountable for the unintended *n*-type conductivity of ZnO under equilibrium conditions.¹⁴⁷

1.8.1.3 Oxygen interstitials

Oxygen interstitials (O_i) can also potentially occupy two sites in wurtzite ZnO structure; the tetrahedral site or the octahedral site, or form split interstitials. Calculations by Janotti *et al.* found that the O_i is unstable in the tetrahedral site.^{141,142} The deep acceptors of O_i at the octahedral site in *n*-type samples are electrically active.¹⁴² However, the formation energies are very high and this are not likely to be present in considerable concentrations.¹⁴⁵

1.8.1.4 Zinc vacancies

The electronic structure of zinc vacancies (V_{Zn}) is normally understood by an uncomplicated model in molecular orbital theory. For a V_{Zn} to form, a zinc atom will have to be removed from the lattice. Consequently, four oxygen dangling bonds and six electrons are formed. A doubly occupied symmetric a_1 state situated in the valence band and three practically degenerate states in the band gap, adjacent to the valence band maximum is formed from the combination of the four dangling bonds. Since the three almost degenerate states are only partly occupied by the four electrons, it can accept an additional two electrons. This causes V_{Zn} to be an acceptor in ZnO.

V_{Zn} have the least energy of formation compared with the other native point defects. It has been shown that V_{Zn} are also the prevailing compensating centre in *n*-type ZnO by positron annihilation spectroscopy measurements.¹⁴⁸ They are additionally favourable in environments which are abundant in oxygen.¹⁴⁵ Thus, V_{Zn} is a deep acceptor and possess minimal formation energies under *n*-type conditions and consequently exist as compensating defects in *n*-type materials.¹⁴⁵

1.8.1.5 Oxygen and zinc antisites

There are other native defects such as oxygen antisite (O_{Zn}) and zinc antisite (Zn_O) (i.e., a Zn atom lying at the oxygen site and an O lying at the zinc site). These possess superior energies of formation and as a result not likely to be a factor in ZnO formation when in equilibrium. The Zn_O antisite acts as a double donor in n -type ZnO and exists as a shallow donor, however its high formation energy prevents it from being the basis of the n -type conductivity of ZnO. The O_{Zn} is an acceptor-type defect with the highest formation energy among the acceptor-type native defects, even under O-rich conditions. Hence, it is unlikely that oxygen and zinc antisites are present in equilibrium. They are deep acceptors which exhibit considerable off-site displacements, whereby the O atom bonds chemically to just one of the O close by neighbours.

Despite all the native point defects present in the system, the calculations and little experimental evidence cannot fully elucidate the repeatedly observed intrinsic n -type conductivity of ZnO. This n -type conductivity is possibly a result of a variety of reasons, such as the incorporation of impurities during the growth or annealing process. Only a complete understanding and thereafter tailoring of properties of the intrinsic n -type conductivity of ZnO will allow it to be fully exploited as a semiconductor material for commercial device applications on the large scale.

1.8.2 Unintentional Hydrogen Impurity

It is known that manipulating of the defect states in the atomic scale can tailor the characteristics of ZnO from insulating¹⁴⁹ to semiconducting.^{65,67} Hydrogen, present in most growth and processing environments, can be incorporated into the ZnO lattice. It is debatable whether H is a plausible

candidate for the unintentional incorporation of impurities that behave as shallow donors.¹⁵⁰ Its stability is under much theoretical and experimental investigation.¹⁵⁰ Calculations based on DFT within the local density approximation (LDA) and the pseudopotential-plane-wave approach identified the unintentional impurities to be hydrogen. Interstitial hydrogen, which forms a robust bond with O in ZnO, is predicted to be present as a shallow donor,^{150,151} converse to the amphoteric behaviour of interstitial H in traditional semiconductors. This behaviour of hydrogen in ZnO is extremely atypical because interstitial H appears solely as a donor in positive charge state. Hydrogen doping is normally realized by the post-growth hydrogen gas or plasma treatment, or by H₂-based *in situ* growth.^{152,153} Spectroscopic evidence has been presented for hydrogen in the lattice,^{154,155} making hydrogen a probable candidate for the cause of the *n*-type conductivity of ZnO. However, the instability of H doping and the association involving hydrogenated defects and the electrical properties of ZnO remain unknown.

Kushwaha *et al.* reported a systematic doping with hydrogen of ZnO nanowire films by means of post-growth annealing treatment.¹⁵⁶ They established a connection between electrical conductivity and defect incorporation. It was postulated that there is a diffusion of hydrogen atoms in the direction of ZnO nanowire core during the annealing process.^{157,158} H diffuses into the ZnO lattice and bonds with the lattice oxygen. It is possibly located at the bond centres or at the anti-bonding sites. The oxygen vacancies additionally intermingle with H to form stable complexes.¹⁵⁹ Annealing of the H sample has been seen to cause a shift towards a lower 2θ value as seen from XRD measurements, representing a modest amplification of the lattice spacing. H₂ annealing may cause Zn-O lattice relaxation by incorporating H into the bond-centred position of the ZnO lattice.¹⁶⁰ It is suggested that the Zn atoms shift away from its ideal position by stretching of

the O–H bonds, in order to alleviate the hydrogen occupancy in the ZnO lattice. This eventually results in an enlargement in the lattice constant.¹⁵⁰

1.9 Scope and Objective

Experimentally, there has been no conclusive experimental evidence regarding a dominant role for native defects in as-grown ZnO. Understanding the behaviour of these native defects is critical in controlling the ZnO charge carrier type and conductivity to realize its full potential as a semiconducting material that can be used for device applications. As-grown ZnO appears to be primarily *n*-type and has limited its use as a semiconductor material for device applications.

This thesis seeks to grow ZnO films and powders via a low temperature solution route synthesis and to investigate the role of defects within the system. More specifically, it investigates the different intentional *n*-type donors, their possible sites and charge carrier generation mechanism and interaction with the ZnO lattice.

In addition, this project seeks to understand the defect structure present in the system when ZnO is grown using the low temperature aqueous solution route by understanding the as observed pore formation in the epitaxial ZnO films and powders after annealing.

This project will utilize synchrotron radiation (SR) techniques such as X-ray absorption (XAS) techniques, specifically X-ray near-edge absorption (XANES) and extended X-ray absorption fine structure (EXAFS) to obtain microstructure information. Synchrotron total scattering experiments will enable the understanding of bond pair disorders through pair distribution function (PDF) analysis. Additionally, transmission electron microscopy (TEM) will help in the

understanding of pore formation. Other characterizations techniques will also be employed to aid in this study.

1.10 Outline of Thesis

This thesis studies the defect structure of ZnO films and nanostructures synthesized by a low temperature aqueous solution route and comprises of 7 chapters. Chapter 1 gives an overall introduction of wide band gap semiconductors and zinc oxide (ZnO) – structure, properties and applications. In addition, general synthesis methods of ZnO are briefly mentioned, including some literature review. It also states the scope and objective, and the outline of this thesis. Chapter 2 gives details of the syntheses used in this thesis for the various different samples, as well as some background for all characterization methodologies. A brief description of synchrotron radiation techniques, a main characterization tool for structural defect study, is given. Chapter 3 studies the defect structure of epitaxial ZnO film synthesized by chemical bath deposition and post-growth thermally annealed to improve its electrical and optical properties. The films were characterized by various methods such as scanning electron microscopy (SEM), X-ray diffraction (XRD) and photoluminescence (PL) spectroscopy. Porosity was observed in the film's cross-section after annealing at temperatures above 200°C, similar to those observed by Richardson *et al.*¹⁵⁴ The local structure of the ZnO films was subsequently studied through the use of X-ray absorption spectroscopy (XAS). This enables a better understanding of the local defect structure of such epitaxial ZnO films, synthesized by an aqueous solution route. Chapter 4 investigates the short and medium range structural order of ZnO nanostructures in the form of powders that were synthesized by different precursors in solution. These powders are similarly post-growth thermally annealed, analogous to the films. The local defect structure was elucidated by *in*

situ and *ex situ* XAS and total scattering experiments, allowing the study of both short and medium range structural order. Chapter 5 examines the porosity that was observed in ZnO nanorods upon thermal annealing. Scanning transmission electron microscopy (STEM) and a 3-D electron tomography reconstruction was used to visualize the internal isolated pores within the ZnO nanorods. *In situ* TEM was used to observe the pores formed within the ZnO nanostructures when it was annealed up to temperatures of approximately 540°C. Chapter 6 specifically studies the local defect structure of Ga-doped ZnO. Ga-doping is a known technique used to improve the electrical properties of ZnO by enhancing the conductivity. Here, the position of Ga³⁺ in the ZnO lattice was experimentally shown in both Ga-doped ZnO films and powders. Finally, Chapter 7 gives a summary of the results and conclusions of this thesis and recommendations for future work.

Chapter 2

Methodology

2.1 Synthesis of Epitaxial ZnO Films on <111> MgAl₂O₄ Substrates

A two-step film growth method was employed as first reported by Andeen *et al.*³⁹ and subsequently other reports from the Lange group.^{20,32,39,55,154} For the first step, the precursor solution was prepared by mixing 0.028 M of zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) (98%, Sigma-Aldrich, St. Louis, USA) and 0.314 M ammonium nitrate (NH₄NO₃) (Sigma-Aldrich, St. Louis, USA) in deionised (DI) water (18.2 MΩ·cm, Millipore, Billerica, MA) and heated to 90°C. MgAl₂O₄ (spinel) substrates (MTI Corporation, Richmond, CA) were cleaned with organic solvents (acetone and isopropyl alcohol) and heat treated to 800°C in air for 8 h and maintained at 200°C then transferred into the precursor solution via a Teflon insert with polished side facing down. Ammonia solution (NH₃) (25%, J.T. Baker, Phillipsburg, NJ) was added to the solution to adjust the pH to ~7.6. The synthesis took place at a temperature of 90°C in a convection oven. Substrates were suspended in solution about 10 mm from the bottom of the vessel, ensuring that the entire substrate is submerged in the growth solution. After the growth time period of 4 h, samples were rinsed with DI water and dried gently with a nitrogen gas flow. A thin seed layer is formed on the substrate. Figure 2-1 shows the

FEGSEM images of the ZnO seed layer grown at pH 7.6 at magnifications of 20k, 50k and 100k.

Figure 2-1: FEGSEM images of ZnO seed layer grown at pH 7.6 at various magnifications.

For the second or growth step of the ZnO film, the precursor solution was prepared by mixing 0.028 M of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 7.08 mM of trisodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$) (Sigma-Aldrich, St. Louis, USA) in DI water and ammonia solution added to adjust the pH to 10.9. The seed layer obtained from the first-step of growth is then inserted gently faced-down into the solution at room temperature and placed in a convection oven at 90°C for 4 h. Figure 2-2 shows a schematic representation of the Teflon-lined stainless steel reactor used for growth.

Figure 2-2: Schematic representation of a stainless steel autoclave with PTFE inner lining for hydrothermal synthesis and general acid digestion purposes.

After a duration of 3 – 4 h, the substrates were removed and rinsed in DI water and lightly blown dry with a stream of nitrogen gas. Figure 2-3 shows a schematic representation of the ZnO film structure, showing the film on top of the seed layer on the substrate.

Figure 2-3: Schematic representation of ZnO film structure.

Ga-doped ZnO films were synthesized in the same manner with the addition of about 20 mg of gallium (III) nitrate hydrate ($\text{Ga}(\text{NO}_3)_3$) (99.9%, Sigma-Aldrich, St. Louis, MO) as a dopant into the precursor solution and stirred before growth. The same growth time and temperature was used for the Ga-doped ZnO film samples.

2.2 Synthesis of ZnO Powders

2.2.1 ZnO Powders Synthesized at pH 8.0

ZnO powder was synthesized using a hydrothermal route. In a typical synthesis, 0.028 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98%, Sigma-Aldrich, St. Louis, MO) was dissolved into DI water. Approximately 0.6 g of NH_4NO_3 was added as a buffer and NH_3 solution (25%, Honeywell, Morristown, NJ) was subsequently added to achieve a solution of about pH 8.0 to initiate precipitation. The solution was then transferred to a Teflon lined stainless steel reactor (Parr, Moline, IL) and placed in a convection oven at 90°C for 24 h. After growth, the powders were rinsed several times in DI water, centrifuged and dried overnight at 40°C and collected.

ZnO bulk powder (99.99%) was obtained from Aldrich (St. Louis, MO) and used as a comparison standard for the pH 8.0 as-synthesized powders.

2.2.2 ZnO Powders Synthesized at pH 10.9

Three powder samples (labelled S1, S2 and S3) with minor variations were prepared.

Table 2-1 shows a summary of the experimental conditions for samples S1, S2 and S3. For all the samples, 0.028 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98%, Sigma-Aldrich, St. Louis, MO) dissolved in DI water by stirring. NH_3 solution (25%, Honeywell, Morristown, NJ) was subsequently added to achieve a solution of pH 10.9. 7.08 mM of trisodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$) (Sigma-Aldrich, St. Louis, USA) was added to mimic the conditions for film formation. To initiate growth, ZnO seeds were required. For sample S1, about 5 mg of ZnO seed in the form of powder grown at pH 7.6. For sample S2, ZnO seed in the form of about 5 mg of National Institute of Standards and Technology (NIST) standard reference material (SRM) (674b-ZnO) was added to initiate precipitation. The solution was placed in either a Teflon-lined stainless steel reactor (Parr, Moline, IL) or in a PFA container (Saville, MN, USA), and placed in a convection oven at 90°C for growth times varying from 4 h – 24 h. After growth, the powders were rinsed several times in DI water, centrifuged and dried overnight at 40°C and collected. For sample S3, the synthesis was carried out in the same way as sample S2, with the addition of about 20mg of gallium (III) nitrate hydrate ($\text{Ga}(\text{NO}_3)_3$) (99.9%, Sigma-Aldrich, St. Louis, MO) as a dopant. X-ray fluorescence measurements confirmed the presence of Ga in the powder samples.

Table 2-1: Summary of experimental conditions.

Sample/ Growth conditions	S1	S2	S3
Growth precursors in DI water	0.028 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 7.08 mM $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ NH_3 (25%), added till pH 10.9	0.028 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 7.08 mM $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ NH_3 (25%), added till pH 10.9	0.028 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 7.08 mM $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ NH_3 (25%), added till pH 10.9 ~20mg $\text{Ga}(\text{NO}_3)_3$, as dopant
ZnO seed used	5mg of ZnO powder obtained at pH 7.6	5mg of NIST SRM 674b	5 mg of NIST SRM 674b
Growth temperature, time	90°C, 4 h	90°C, 24 h	90°C, 24 h

A ZnO standard reference material (SRM) was used as a reference material and compared with various samples that were synthesized. This was obtained from National Institute of Standards and Technology SRM 674b - X-Ray Powder Diffraction Intensity Set (Quantitative Powder Diffraction Standard) for zinc oxide. For convenience, this sample is labelled as S4.

Thermal annealing of the ZnO samples was performed in a Carbolite box furnace (air) for various temperatures ranging from 100°C – 600°C. Heating rates were kept at 5°C/min. Thermal annealing is known to improve the electrical and optical quality of ZnO and is a common process in the post-growth treatment of metal oxides such as ZnO. Several researchers have also employed this technique to enhance the properties of ZnO.^{46,161-165} Results clearly show that annealing ZnO has led to better optical quality with less nonradiative related defects.^{46,161} In addition, the electrical Hall measurements of ZnO films improve by two orders of magnitude, showing great improvement of the quality of such ZnO films.^{164,165}

2.3 Synthesis of ZnO Nanorods

ZnO nanorods were deposited on a silicon substrate using a two-step method. Si substrates were first cleaned with piranha solution (3:1 ratio of sulphuric acid (95 – 97%, semiconductor grade, Honeywell, Specialty Chemicals Seetze GmbH) and hydrogen peroxide (31%, electronics grade, MPCS Pure Chemicals Singapore)). The substrates were soaked in piranha solution for about 20 min and subsequently thoroughly washed with DI water and blown dry with a stream of nitrogen gas. A ZnO seed layer was then deposited using 0.005 M zinc acetate dihydrate (>98.0%, Fluka, Sigma-Aldrich Chemie GmbH) and ethanol (puriss. p.a., absolute, ≥99.8%, Sigma-Aldrich, St. Louis, USA) via a drop-wise method onto the Si substrate. Each drop was allowed to stand on the Si substrate for about 20-30 s, and then rinsed in ethanol before blow drying with nitrogen gas. This step was repeated 5 times. This was followed by thermal decomposition at 350°C in air for the zinc acetate seeds to form a ZnO seed layer. This whole cycle is repeated once to ensure a uniform coverage of the ZnO seed on the Si substrate. This method has previously been described by Greene *et al.*^{45,125}

The second growth step involves the growth of ZnO nanorods on the ZnO seed layer that has been deposited on the Si substrate. Equimolar $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and hexamethylenetetramine (HMT) (99+%, Alfa Aesar, Lancashire, UK) was dissolved in DI water. The ZnO seeded substrate was then placed face-down via a Teflon insert into the solution contained in either a Teflon-lined autoclave (Parr, Moline, IL, USA) or a PFA container (Saville, MN, USA), at about 10 mm above the bottom of the vessel. The solutions were then placed in a convection oven at 90°C for 3 – 6 h growth periods. After the growth period, the substrates were removed and rinsed in DI water and blown dry with a stream of nitrogen gas. This method has also been used by various research groups to synthesize ZnO nanorods.^{133,136} Figure 2-4 shows a schematic representation of the ZnO nanorods on Si substrate.

Thermal annealing of the ZnO nanorods was subsequently performed in a Carbolite box furnace (air) for various temperatures ranging from 100°C – 600°C. Heating rates were kept at 5°C/min.

Figure 2-4: Schematic representation of ZnO nanorods on Si substrate.

2.4 Materials Characterization

The following equipment were used for materials characterization of all the above mentioned samples:

2.4.1 X-ray Diffraction (XRD)

X-ray diffraction (XRD) is a central procedure in the area of materials characterization to attain atomic scale structural information from both crystalline and amorphous materials. XRD is non-destructive and can be useful for the determination of crystal structures of minerals, inorganic compounds, metals and alloys, and even organic materials and polymers. In addition, it has the capability to obtain information such as crystal orientation, chemical composition, crystallite size, lattice strain, and surface and interface roughness. Phase identification and orientation determination of the samples were performed by X-ray diffraction (XRD) with a General Area Detector Diffraction System (D8-Advance, Bruker AXS Inc, Madison, WI). The wavelength of the X-rays used in the XRD measurements was $\text{Cu-K}\alpha \approx 1.542 \text{ \AA}$.

High resolution X-ray diffraction (HRXRD) is an imperative method for investigating individual Bragg peaks of epitaxial materials and thin films. High

resolution and intensity is obtained by a combination of a very high quality mirror and monochromator. Crystal lattice information, such as strain, and the composition and thickness of films can be determined. The pole figure patterns and phi-scans were obtained with the Panalytical X'Pert Pro High Resolution XRD (voltage set at 40 kV and current at 40 mA). The rocking curve and Omega scan are obtained by fixing 2 theta to the plane of interest and scanning by rotating the substrate basal plane. The source and detector is fixed, while the sample is rocked around the Bragg peak slightly. Scanning Electron Microscopy (SEM)

The scanning electron microscope (SEM) is a useful characterization instrument for imaging of three-dimensional objects. It allows structural characterization by observing and imaging the morphology of materials. Morphological characterization of the samples was performed by JEOL-JSM6700F and JEOL-JSM7600F field emission gun scanning electron microscope (FEGSEM).

2.4.2 Hall Measurements

Electrical measurements (carrier concentration and Hall mobility) were made in van der Pauw geometry with four point leads on a Hall measurement system. The Hall Effect is typically used to study the physics of charge transport in metal and semiconductor samples. The Hall Effect results from the generation of a voltage difference, known as the Hall voltage, across an electrical conductor, transverse to an electric current in the conductor and a magnetic field perpendicular to the current. It is due to the nature of the current in a conductor and this migration of small charged carriers lead to the production of a perpendicular force, known as the Lorentz force, in the presence of a magnetic field. This causes the deflection towards one side and there is an accumulation of charges which creates a transverse electric field that counteracts the force of the

magnetic field. This allows for the measurement of various electrical properties such as the electron concentration and the electron mobility.¹⁶⁶

2.4.3 Photoluminescence (PL) Spectroscopy

Photoluminescence (PL) spectroscopy takes place when there is a spontaneous emission of light from a material under optical excitation. This optical characterization technique uses a laser source to excite the atoms in the sample. When this high energy light interacts with the sample, photons are absorbed and cause photo-excitation. When these excitations relax, they emit photons. The intensity versus wavelength of emitted photons is measured which represents the rate of radiative recombination. The PL spectra can reveal transition energies which represent various defect states in the material.

PL mapping measurements were performed at room temperature using a rapid photoluminescence mapping setup (Accent, RPM2000), using a CCD detector and He–Cd laser source with wavelength set at 325 nm. The PL spectra of zinc oxide (ZnO) typically show a near band edge (NBE) transition at about 3.25 eV, originating from exciton radiative recombination. The PL spectra of ZnO also show broad defect peak or deep-level emission (DLE) peak at lower energies (higher wavelengths) due to impurities or structural defects. This DLE is normally de-convoluted by Gaussian-fitting into three colour bands (red, yellow, green) for further analysis. TGA-MS

Thermo-gravimetric analysis coupled with a mass spectrometer (TGA-MS) was carried out using Netzsch Thermal Gravimetric Mass Spectrometer, TGMS (TG209F1 & QMS403C). The parameters for the TGA experiments was kept at a heating rate of 20°C/min from room temperature to 900°C in N₂ ambient (purge of 20 mL/min). There was a correction run done prior to the sample run. Sample compartment is vacuumed and purged with N₂ 3 times prior to start of the run.

The MS used was a Quadrupole Mass Spectrometer (QMS) with electron impact ionization in MID (multi-ion detection) mode. The specific mass of 18 and 44 were monitored for a dwell time of 1 s and resolution of 50. The transfer line between TG and MS is set at 200°C.

2.4.4 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) is a characterization tool for imaging one-dimensional, two-dimensional and three-dimensional materials in the nanoscale.¹⁶⁷ It exploits the concept of wave-particle duality. Typically, there is a transmission of a beam of electrons through an ultra-thin specimen (sample preparation required), and the electrons interact with the specimen as it passes through. In general, in a TEM, a monochromatic beam of electrons in the electron gun is accelerated to an energy range of 20 – 1000 keV. The electron beam subsequently passes through a set of condenser lenses to yield a beam of electrons with a required diameter. There are two principal modes which the illumination system operates on, namely, the parallel beam and the convergent beam. The former is primarily used for TEM imaging and selected area diffraction (SAD), while the latter is used for scanning (STEM) imaging and analysis via X-ray and electron spectroscopy. The interactions between the electron beam and the specimen takes place after the objective lens on the specimen stage creating images and diffraction patterns. The image is subsequently magnified and focused onto an imaging device. The resolution of a modern TEM is about 0.2 nm. The capability to establish the position of atoms within a material has made the high resolution TEM (HRTEM) a key instrument for nanotechnology research.

To obtain powder samples for TEM analysis, the ZnO nanorods grown on Si substrates were mechanically scrapped off using a small cutter blade into ethanol solution and dispersed by sonication. One drop of solution containing ZnO

nanorods was dropped onto a TEM grid coated with a layer of carbon film. *Ex situ* TEM imaging was performed on the JEOL JEM-2100 with an accelerating voltage of 200 kV.

For electron tomography analysis, the sample was analyzed using an FEI Titan 80-300 S/TEM (Scanning/Transmission Electron Microscope), which was operated at 200 kV. A total of 75 HAADF-STEM images were collected over a tilt range of -74° to 74° with 2° tilt step for electron tomographic reconstruction. Stage tilting and image acquisition were performed automatically by the FEI Xplore-3D tomography program, while tracking and refocusing of the specimen were carried out manually in order to shorten the total acquisition time. The images were acquired with a magnification of 44,000, corresponding to 3.09 nm per pixel. Acquisition time for one 1024×1024 sized image was 20 s. The final tilt series was aligned using a cross-correlation method and reconstructed by the simultaneous iterative reconstruction technique (SIRT, 40 iterations) using Inspect3D and the reconstructed 3D volume was visualized with Amira 4.1.

The porous ZnO nanorods were recorded by bright field TEM and HAADF-STEM images. Compared to bright field TEM images, HAADF-STEM images are dominated by mass-thickness contrast and the image intensity is approximately proportional to $Z^{1.7}$ of the elements in the samples. HAADF-STEM images are also much less sensitive to the complexity associated with diffractions and Fresnel fringes.

Thermal annealing of ZnO nanorods was carried out in an *in situ* JEOL 2000V TEM with a miniature molecular beam epitaxy chamber which forms the objective lens of the instrument. ZnO nanorods were placed on Mo grids coated with a layer of silicon oxide membrane in order to avoid a chemical reaction between ZnO and the supporting film during heating process. The sample TEM

grid is heated via resistive heating of a silicon heating substrate. The structural and morphological evolution of one single ZnO nanorod was tracked during the annealing process. A series of images were taken at different temperatures and periods. To minimize the damage of high energy electron to ZnO nanorods, the electron beam was only focused on samples during image acquisition and moved away immediately.

2.4.5 X-ray Absorption Spectroscopy (XAS)

XAS is a synchrotron radiation technique based on the photoelectric effect. It signifies modulations in X-ray absorption coefficient about an X-ray absorption edge. The X-ray absorption spectrum is typically divided into two parts: X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS). The former provides information on the chemical states and local electronic structure of the incorporated atoms in the material under study. Specifically, the absolute energy position of the edge spectra contains information about the valence state of the absorbing elements. The latter gives local structural information about disorder and coordination. XAS also gives information on how X-rays are absorbed by an atom at energies close to and above the core-level binding energies of that specific atom. The XAS spectra are highly correlated to the oxidation state, coordination chemistry, and the distances, coordination number and species of the atoms directly surrounding the specific element. This makes XAS a useful tool for the study of the local structure of a material around selected elements, for observing its short range order, determining the chemical state and the local atomic structure for a specific atomic species. XAS can be used for crystals as well as materials that have no long-range orders, such as amorphous materials and glasses.

The fundamental physical quantity that is determined in this X-ray spectroscopy is the X-ray absorption coefficient, $\mu(E)$. This quantity is related to how X-rays are absorbed as a function of the X-ray energy, E . The absorption coefficient, μ provides the likelihood that X-rays will be absorbed according to Beer's Law: $I = I_0 e^{-\mu t}$ where I_0 is the X-ray intensity incident on the sample, t is the sample thickness, and I is the intensity transmitted through the sample. Thus the energy dependence of the absorption coefficient $\mu(E)$ in transmission mode as $\mu(E) = \log\left(\frac{I_0}{I}\right)$, and in fluorescence mode as $\mu(E) \propto \frac{I_f}{I_0}$, where I_f is the measured intensity of a fluorescence line associated with the absorption process.¹⁶⁸

Figure 2-5: Schematic representation of the EXAFS process showing the interaction of the photo-electron and the back-scattered wave.

EXAFS is often described by the wave-behaviour of the photoelectron as shown in Figure 2-5. The main concern is the oscillations well above the absorption edge which gives information on the correlations between elements surrounding the selected element. The standard EXAFS equation is:¹⁶⁸

$$\chi(E) = \sum_j \frac{N_j f_j(k) e^{-2k^2 \sigma_j^2}}{k R_j^2} \sin[2k R_j + \delta_j(k)]$$

where $f(k)$ and $\delta(k)$ are the scattering properties of the atoms neighbouring the excited atom, N is the number of neighbouring atoms, R is the distance to the neighbouring atom, and σ^2 is the disorder in the neighbour distance.¹⁶⁸

EXAFS has proven to be a useful characterization technique to determine the local structure of materials, especially the coordination and disorder between atoms.¹⁶⁹ Several researchers have exploited its use in the field of catalysis.¹⁷⁰⁻¹⁷³ In addition, it allows for the study of materials *ex situ* as well as *in situ* studies which enable the user to study materials in its native environment during formation or annealing.¹⁷⁴⁻¹⁷⁷

Bhachu *et al.* reported the presence of Zn vacancies in aerosol assisted chemical vapour deposition (AACVD) of ZnO films. Characterization to elucidate the existence of unintentionally doped H⁺ was performed using XAS measurements at the Zn K-edge.¹⁷⁸ McPeak *et al.* showed the earliest work of *in situ* XANES to study ZnO nanowire growth during chemical bath deposition.¹³⁷ The speciation chemistry of zinc nitrate/HMT was thoroughly investigated to illustrate that ZnO crystallizes unequivocally from $[Zn(H_2O)_6]^{2+}$ with no prolonged intermediates. This evidently shows the supremacy of XANES as a superb instrument for such characterization.

The following beamlines were used for characterization of the samples.

1. Zn K-edge and Ga K-edge *ex situ* XAS experiments were carried at XAFCA beamline (with an energy range of 1.2 – 12.8 keV) at Singapore Synchrotron Light Source (SSLS), Singapore. In a typical experiment, the ZnO films are mounted onto a sample holder and XAS data were collected using fluorescence mode using a high rate fluorescence silicon drift detector.
2. Zn K-edge *ex situ* XAS experiments were also carried out at the European Synchrotron Radiation Facilities (ESRF), Beamline BM26A. The samples were probed at the Zn K-edge with absorption energy just above 9600 eV, in transmission mode. This beam line is equipped with Si (111)

monochromator and ion-chambers for measuring incident and transmitted beam intensities.

3. For the powder samples synthesized at pH 10.9, EXAFS experiments were performed at Singapore Synchrotron Light Source (SSLS), beamline XAFCA. About 5 – 8 mg of sample (ZnO powder) is mixed with about 70 – 80 mg of Boron nitride, BN (99.5%, Alfa Aesar, MA) and pressed into a pellet. The pellets are mounted on a sample holder. All measurements were performed at the Zn k-edge with energy about 9650 eV. An ion chamber is used for transmission measurements.

Typically, samples were investigated at the Zn *K*-edge with absorption energy about 9.6 keV in transmission mode for powders and fluorescence mode for films. Ga-doped ZnO samples were also investigated at the Ga *K*-edge with absorption energy about 10.37 keV. All beamlines used were equipped with Si (111) monochromators and ion-chambers for measuring incident and transmitted beam intensities. Detectors were also installed for fluorescence mode measurements. EXAFS data were processed using Visual Processing in EXAFS Researches (VIPER)¹⁷⁹ and ATHENA software package^{180,181} for normalisation and background subtraction. Detailed analysis of the EXAFS data were then achieved using the ARTEMIS software package^{180,181} and EXCURVE software (EXCURV98)¹⁸² to fit and study the changes in the disorder in the sample.

Overall, the fit methodology developed follows a simple alternation strategy. Initial values of fit were obtained by first creating scattering paths of all atoms present, i.e., Zn and O, in relation to the Zn atom at the origin, also known as the central Zn atom. Once all the parameters for all paths were defined, a fit for the room temperature data were first processed to obtain the amplitude reduction factor, S_0^2 , which is does not depend on the structure of the material and it is mainly due to other effects. The amplitude reduction factor value that is

obtained is then fixed for further refinement of structural parameters. For the first fit of each subsequent data set, the occupancy of each Zn-O and Zn-Zn correlation is initially fixed at 1. The remaining parameters are refined to obtain initial σ^2 values. σ^2 is often referred to as the Debye-Waller factor which is a measure of the disorder of the distances between atoms. For the following fit step, the σ^2 values are then fixed, releasing the occupancies and all other refinement parameters. The main reason for not refining the coordination number, N and σ^2 together is that they are highly correlated and this refinement needs to be carefully done to avoid this correlation, as followed in this work. This process of alternating between fixing the occupancies and the Debye-Waller factors and releasing the other to be refined was repeated several times (iteration), noting the changes in the values till they remained relatively unchanged, seen from a reasonably constant R -factor value. Errors were also noted to remain small in all refined parameters. Once a consistent set of values are obtained, all structural parameters are refined together several times to obtain the final values which are relatively stable, with minimal changes in value and error.

2.4.6 Pair Distribution Function (PDF)

Pair Distribution Function (PDF) represented by the function $G(r)$ is a total scattering approach that describes the probability of finding two atoms at a given inter-atomic distance r . It can be used to study short, medium and long range order of crystalline and amorphous materials, in addition to liquids. It is commonly used complementary to Rietveld refinement, which is obtained from the intensities of Bragg reflections from a diffraction pattern and modelled to attain the average crystal structure of a specific material, as the PDF calculation is based on both the Bragg and diffuse scattering intensities.

The PDF method is a characterization technique for nanomaterials^{183,184} as it observes systematic deviations from an ideal crystal structure. It uses high energy X-ray or hot neutrons for measurement and the use of Fourier Transform is then applied to the data to obtain the real space analysis. The basis of the PDF method is the following equation:

$$I_N \propto S(Q) = 1 + \frac{1}{N} \sum_{i,j \neq i}^N f_i f_j \frac{\sin(Qr_{ij})}{Qr_{ij}}$$

$S(Q)$ is the measured intensity corrected for background, Compton and multiple scattering, absorption, geometric and other factors, and is known as the structure factor with $Q = \frac{4\pi \sin(\theta)}{\lambda}$, where θ is the diffraction angle and λ is the wavelength of the incident radiation. A Fourier transform from reciprocal space to real space gives the equation below:

$$g(r) - 1 = \frac{1}{2\pi^2 r \rho_0} \int_0^\infty Q[S(Q) - 1] \sin(Qr) dr$$

The PDF has proven to be a useful technique for determining nanomaterial structure as it is not centred on any specific atom. It gives a structural description of local ordering around any atom in a specific structure, making it a versatile characterization technique for nanomaterials.¹⁸⁵⁻¹⁸⁸

There are very few reports of utilizing PDF analysis for ZnO.^{189,190} Kim *et al.* studied a $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ alloy system and determined through synchrotron X-ray PDF that the Mg atoms have a smaller parameter to some extent and greater periodic tetrahedral bond distances.¹⁹⁰ Rosenthal *et al.* studied the structural role of ZnO in silica and soda-silica glasses.¹⁸⁹ It was reported that the coordination numbers and bond lengths for each atomic species has a good fit for the series of data for instance, the number of crystalline and glassy silicates.¹⁸⁹

There are however, other reports of using PDF as a characterization tool for other related materials.^{191,192} Wang *et al.* exploited the use of PDF to characterize SnO₂ nanocrystals and studied its structure.¹⁹² PDF has also been used by Masadeh *et al.* to characterize CdSe nanoparticles.¹⁹¹ This exhibits the robustness of the PDF characterization technique.

High energy X-ray diffraction (HEXRD) experiments were carried out on the horizontal two-axis diffractometer built at the BL04B2¹⁹³ high-energy X-ray diffraction beamline of the Japan Synchrotron Radiation Research Institute (JASRI), SPring-8. The incident photon has wavelength of 0.2 Å. The diffraction patterns were measured in a transmission geometry from $Q_{\min} = 0.03 \text{ Å}^{-1}$ to $Q_{\max} = 23 \text{ Å}^{-1}$.

The data reduction, data corrections (background, polarization and absorption corrections, the combination of separate runs, data normalization to the structure factor and Fourier transformation was carried out using the in-house data analysis software developed using IGOR (WaveMetrics, Inc., Lake Oswego, OR, USA).¹⁹³ The PDF data were then inputted into the PDFgui software with the structure of ZnO. Refinement was carried out by first refining the scale factor and the lattice parameters. Once a reasonable fit was obtained, the coordinates were then refined. Care was taken not to refine the occupancy and the temperature factor together. Instead, the occupancy and the temperature factor were refined alternately to achieve the best result. The total PDF, $G(r)$, of the ZnO samples at room temperature essentially contain structural information in real-space and are the Fourier Transforms of the reduced structure factor $Q[S(Q)-1]$. It uses similar parameters, e.g. lattice parameters, atomic displacement parameters, occupancies etc. to those used in a Rietveld Refinement but performs it on the real space ($G(r)$) data.

Chapter 3

Local Structure Investigation of Epitaxial ZnO Films Grown on <111> MgAl₂O₄ Substrates

3.1 Summary of Chapter 3

In this chapter, epitaxial ZnO films with high crystallinity are grown on MgAl₂O₄ substrates through a low temperature solution synthesis route and post-growth thermally annealed to improve the electrical and optical properties of ZnO films with the intention of exploiting it for device applications.^{46,161} The electrical properties of these ZnO films were characterized using Hall measurements. The ZnO films obtained are characteristically *n*-type with carrier concentration of the order of 10¹⁹ cm⁻³ after annealing in air at 400°C for 1 h in a box furnace. The source of the intrinsic *n*-type conductivity in ZnO is a controversial topic as previously discussed in Section 1.8. Defect characterization studying the local structure of the synthesized ZnO films was investigated using X-ray absorption spectroscopy (XAS). It was found that zinc vacancies are predominantly present in the as-synthesized ZnO films. Upon annealing at higher temperatures (300°C – 400°C), there is a reduction in the concentration of zinc and oxygen vacancies.

The optical properties of the ZnO films were also determined by room temperature photoluminescence (PL) mapping spectroscopy. It was found that upon annealing the film, there is a red-shift, suggesting the presence of oxygen

interstitials. The results of this study provide a better understanding of the local defect structure of epitaxial ZnO films grown by a low temperature aqueous solution chemical bath deposition route and may potentially aid in the realization of such films for optoelectronic device applications.

3.2 Characterization of ZnO Films Grown on <111> MgAl₂O₄ Substrates

ZnO films were synthesized on <111> MgAl₂O₄ substrates using an aqueous solution route. The synthesis was carried out at 90°C in a convection oven, as described in Section 2.1.

3.2.1 Crystallinity of ZnO Films

Phase identification of the ZnO films and the epitaxial relationship between the film and the substrate was established by high resolution XRD (HRXRD). Figure 3-1 shows the gonio-scan of the as-synthesized undoped ZnO film on <111> MgAl₂O₄ substrate. All the annealed samples also show the presence of the same peaks. In the $\theta/2\theta$ gonio-scan, only diffraction peaks of ZnO (002) and (004) index planes appear showing that the film is *c*-oriented implying that ZnO film has a preferred orientation in the *c*-axis direction; this is typical of ZnO which adopts the wurtzite structure.¹⁹⁴ The lattice constant, *c* of ZnO film is 5.1932 Å, calculated from the peak position of (002) plane using Bragg's law and is close to bulk ZnO (5.2065 Å).¹⁹⁵ Note that the small peak in Figure 3-1 at about $2\theta \approx 25^\circ$ is due to the scattering from the sample holder and can be ignored.

Figure 3-1: HRXRD goni-scan of the as-synthesized undoped ZnO film on <111> MgAl₂O₄ substrate.

Figure 3-2: Omega (ω) scan or rocking curves of the (002) peak of the as-synthesized ZnO film and those annealed at 100°C, 200°C, 300°C and 400°C.

Figure 3-2 shows the omega (ω) scan or rocking curves of the (002) peak of the as-synthesized ZnO film and those annealed (HT) at 100°C, 200°C, 300°C and 400°C. The omega scan gives information on the material crystalline quality. The full width half maximum (FWHM) of the (002) peaks are calculated and the results shown in Table 3-1.

Table 3-1: FWHM of ZnO (002) rocking curves.

	FWHM (°)
As-synthesized	1.189
HT 100°C	1.367
HT 200°C	1.142
HT 300°C	1.361
HT 400°C	1.159

Calibration was done using the Si (111) wafer standard and the accuracy of the FWHM is 0.0053°. From the table, it is observed that the FWHM of ZnO (002) plane rocking curves increases from 1.189° to 1.367° when the film is annealed at 100°C. This peak broadening indicated that the alignment of the film has worsened after annealing, possibly as trapped hydroxyl groups are removed from the film. After annealing at 200°C, the FWHM reduced from 1.367° to 1.142° indicating a peak narrowing and an improvement in the film alignment. However, as the film is annealed at 300°C, there is an increase in the FWHM, from 1.142° to 1.361°, again showing peak broadening which may be due to the emergence of pores in the film as shown in Figure 3-4 (h). When the film is further annealed at 400°C, there is a peak narrowing which may indicate that thermal annealing removes defects in the ZnO film and improves the crystallinity.

Figure 3-3: XRD pole figures for ZnO films (101) and corresponding MgAl_2O_4 substrate (400) for (a) as-synthesized ZnO film, (c) after annealing at 400°C , and (b, d) the corresponding ϕ -scans.

Figure 3-3 shows the pole figures and the corresponding ϕ -scan for the as-synthesized and annealed at 400°C ZnO film and the corresponding MgAl₂O₄ substrate. It is seen that the films grew with a *c*-axis orientation on the <111> MgAl₂O₄ substrates. The respective peaks of the films and the substrate in the ϕ -scan spectra are separated by 30° along the ϕ -axis (Figure 3-3 (b) and (d)), indicating the in-plane orientation given by ZnO [11 $\bar{2}$ 0]||MgAl₂O₄ [$\bar{1}$ $\bar{1}$ 2] and ZnO [01 $\bar{1}$ 0]||MgAl₂O₄ [$\bar{1}$ 10]. This in-plane alignment of the ZnO film and the substrate was obtained by the off-axis ϕ -scan of the ZnO (101) and MgAl₂O₄ (400). The films display the expected six-fold rotational symmetry of an epitaxial hexagonal layer. These results are comparable to other reports.^{32,68,196} These results demonstrate that an aqueous solution synthesis route can be used to achieve highly epitaxial ZnO films on <111> MgAl₂O₄ substrates.

3.2.2 Morphology of ZnO Films

Morphological characterization was carried out using field emission gun scanning electron microscopy (FEGSEM). The images of the as-synthesized ZnO film (Figure 3-4 (a)) and its corresponding cross-section (Figure 3-4 (b)) are shown in Figure 3-4. It was observed that the films are continuous and smooth on the surface. Figure 3-4 (c-j) shows the plane-view of the films and their corresponding cross-sections after annealing in air for 1 h at temperatures of 100°C – 400°C.

Figure 3-4: FEGSEM images of the plane-view and cross-section of the ZnO films (a, b) as-synthesized, and after annealing in air for 1 h at (c, d) 100°C, (e, f) 200°C, (g, h) 300°C, and (i, j) 400°C.

It was observed that pores form when the ZnO films were annealed at temperatures above 200°C (Figure 3-4 (h) and Figure 3-4 (j)). The formation of pores in the ZnO films has previously been observed by Richardson *et al.*¹⁵⁴ where films grown by the same low temperature aqueous solution route were annealed at temperatures above 200°C. Our as-synthesized film and the film annealed at 100°C and 200°C in Figure 3-4 (b), Figure 3-4 (d), and Figure 3-4 (f) show no sign of pore formation. However, annealing at temperatures above 200°C clearly display signs of pore formation, as expected. As the temperature increases, the pores also get bigger and there are also more pores observed. Although the pores appear larger after annealing at higher temperatures, there is also a large amount of small pores present. Pore size and density is random and there is no systematic pattern to the process of pore formation. An estimated count of the number of visible pores was made from a selected area of 4500 by 1500 nm (as marked by the yellow rectangular boxes in Figure 3-4 (h) and Figure 3-4 (j)), with the former having approximately 110 pores, while the latter has about 91 pores. This decrease may be due to smaller pores coalescing together to form larger pores. There are an estimated 24 large pores (with diameters larger than or equal to 50 nm) in Figure 3-4 (h), while Figure 3-4 (j) has an estimated 37 large pores, but the former has approximately 86 small pores (with diameters less than 50 nm) as observed, while the latter has an estimated 54 small pores.

Pores are thought to have evolved from the lattice hydroxide. A similar observation of BaTiO₃ powders produced by hydrothermal method was reported by Hennings *et al.*¹⁹⁷ and Nakano *et al.*¹⁹⁸ The BaTiO₃ powders synthesized showed intragranular pores after heating above 400°C believed to be caused by the dehydration of the BaTiO₃ powder. It is alleged that a whole host of hydroxide ions are substituted on the oxygen site and are incorporated into the powder during the synthesis. In order to ensure charge balance, there is a compensation

of cation vacancies which are incorporated into the BaTiO₃ crystals. As the annealing proceeds, oxygen is eliminated via the removal of water. As a result, oxygen vacancies come together and merge with the existing cation vacancies thereby forming void space, or a pore.

For ZnO systems, Richardson *et al.*¹⁵⁴ proposed that pore formation can be associated to a decrease in hydrogen impurities and the removal of water vapour from ZnO. It is believed that the formation of the pores is a result of a vacancy coalescence mechanism, analogous to that seen in hydrothermally synthesized perovskite materials which have a large amount of hydroxide ions substituting for oxygen in the lattice.¹⁹⁷ It is suggested that a similar mechanism happens when ZnO is synthesized from aqueous solution. Figure 3-5 below shows a schematic of the proposed mechanism.

Figure 3-5: Schematic diagram of pore formation via the coalescence of vacancies as water is removed. (a) Zn vacancies are formed to compensate for hydroxide substituting for O (hydrogen interstitial), (b) Oxygen vacancies form when hydrogen is removed from the lattice in the form of water vapour, (c) Oxygen vacancies then react with Zn vacancies to form vacancy pairs, which cluster into pore nuclei.¹⁵⁴ (Reprinted with permission from Richardson, J. J.; Goh, G. K. L.; Le, H. Q.; Liew, L. L.; Lange, F. F.; DenBaars, S. P. *Crystal Growth & Design* 2011, 11, 3558. Copyright © 2011 American Chemical Society.)

A hydrogen interstitial, which results from a hydroxide substitution on the oxygen site, has low formation energy.¹⁵⁰ There are plenty of hydroxide ions

during the aqueous synthesis process and hydrogen, being the main external impurity in this process, compensates to maintain charge neutrality. This process can be rationalized and shown by the Kröger-Vink notation as

$$[OH_O] + \frac{1}{2}[V_O] + [V_O] = \frac{1}{2}[V_{Zn}'''] + [V_{Zn}'] + n \quad (1)$$

where n is the free electron concentration.¹⁵⁴

Hydrogen is the said cause of doping in ZnO as it is envisaged to play a role as a shallow donor in ZnO.¹⁵⁰ Hydrogen incorporation is thus correlated to the n -type conductivity in such ZnO films synthesized via a low temperature aqueous solution route.¹⁵⁵ Richardson *et al.*¹⁵⁴ further conducted a depth profile using secondary ion mass spectroscopy (SIMS) on deuterated ZnO films before and after annealing at 600°C. Hydrogen in the ZnO films is seen to be removed as water vapour. A quasi-chemical reaction showing the expulsion of water from the hydroxide in the ZnO lattice is anticipated to follow the equation

This results in oxygen vacancies combining with existing zinc vacancies forming voids.

Thus, the overall reaction would be

In conclusion, there is a huge amount of hydrogen incorporated as water into the ZnO films during the synthesis process using a low temperature aqueous synthesis route. Pore formation occurs when hydrogen is removed as water vapour. Pores are formed as a result of the coalescence of zinc vacancies and oxygen vacancies.

This phenomenon may have a large consequence on the transparency and electrical conductivity of the ZnO films. This may be vital in the optoelectronic application of such ZnO films produced by a low temperature aqueous synthesis route. On the contrary, the formation of the pores could plausibly be beneficial for applications such as light scattering or for the creation of high surface area mesoporous films for use in applications such as gas sensors.¹⁹⁹ This understanding of pore formation is significant in the exploitation of solution synthesized ZnO films in order to control the prevention or formation to tailor to specific applications.

3.2.3 Hall Measurements of ZnO Films

It has been shown previously that the thermal annealing of ZnO films enhances its electrical and optical properties.^{32,46,161} Thus, the ZnO films were annealed at various temperatures (100 – 400°C) to improve its electrical and optical properties, in order to further study the correlation between annealing and the defect structure.

The electrical properties of ZnO films as-synthesized and after thermal annealing were determined using the Hall measurement technique in the van der Pauw geometry with indium as contacts. The results obtained are shown in Table 3-2.

Table 3-2: Hall mobility and carrier concentration of ZnO films obtained from Hall measurements.

	Resistivity (Ω -cm)	Hall mobility ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	Carrier concentration (cm^{-3})
As-synthesized	0.173	7.83	4.60×10^{18}
HT 100°C	0.037	7.67	2.24×10^{19}
HT 200°C	0.005	37.47	3.22×10^{19}
HT 300°C	0.004	42.93	3.77×10^{19}
HT 400°C	0.008	22.93	3.45×10^{19}

Hall mobility is generally increased as the films are annealed, reaching the highest value of $42.93 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ when annealed at 300°C . The carrier concentration increases one order of magnitude from 10^{18} cm^{-3} in the as-synthesized film, to 10^{19} cm^{-3} when annealed at temperatures of 100°C and above. There is an enhanced electrical property and increased n -type nature of the annealed ZnO films. This value of carrier concentration is similar to that reported by Zhang *et al.*¹⁵⁵ The large increase in carrier concentration after annealing at 100°C and above may be due to existing compensators, e.g. zinc vacancies, being removed by reacting with existing oxygen vacancies (as shown by PL spectroscopy in Section 3.4). The increase in the mobility and carrier concentration could also be due to the annealing process which restructures and recrystallizes the grains within the film indicating less grain boundaries for trapped carriers as the grain size increases due to the annealing process.³²

3.3 X-ray Absorption Spectroscopy (XAS) Analysis of Epitaxial ZnO Films

The ZnO films grown on MgAl_2O_4 (spinel) substrates were characterized using X-ray absorption spectroscopy (XAS). XAS is a useful characterization tool that provides element specific information about the local atomic geometry and about the chemical state of the absorbing atom. The technique can be used for crystalline phase materials, and highly disordered amorphous, liquid and gaseous samples. XAS can be broadly divided into two parts, namely the X-ray absorption near edge spectroscopy (XANES) and the extended X-ray absorption fine structure (EXAFS). The former provides information on the chemical states and local electronic structure of the incorporated atoms in the material under study. Specifically, the absolute energy position of the edge spectra contains information about the valence state of the absorbing elements. The latter gives local structural

information about disorder and coordination. More information about this technique has been given in Section 2.4.5. Bhachu *et al.* performed similar measurements on ZnO films grown using aerosol-assisted chemical vapour deposition (AACVD) and found zinc vacancies present.¹⁷⁸ Therefore, a detailed investigation into its defect structure will aid in the further understanding of the material so as to fully exploit it for optoelectronic applications, etc. This provides a platform of knowledge in the field and is useful for further development of ZnO as a wide band gap semiconductor.

Here, *ex situ* annealing XAS measurements were performed on the epitaxial ZnO films. The samples were annealed separately in a box furnace at temperatures of 100°C, 200°C, 300°C and 400°C for 1 h in air. XAS data obtained was then fitted using a starting model which is assumed to be ideal to obtain the short range structural information of the ZnO film.

The Zn *K*-edge X-ray absorption near edge spectroscopy (XANES) spectrum for the ZnO film as-synthesized and when the film was annealed *ex situ* at temperatures of 100°C, 200°C, 300°C and 400°C is shown in Figure 3-6.

Figure 3-6: Zn *K*-edge XANES spectra of epitaxial ZnO films as-synthesized and after annealing *ex situ* at temperatures from 100°C to 400°C.

The absorption edge is observed at 9658.9 eV, corresponding closely to the Zn *K*-edge binding energy. XANES is typically used to study the variation of core electron configuration and can give information about the valency changes of atoms in a matrix. For example, if there is a decrease in the valency, the XANES absorption structure will tend to move to lower energies.²⁰⁰ From Figure 3-6, it is observed that there are no shifts in the XANES edge position indicating that the electronic configuration for the Zn central atom was unchanged and is stable at various temperatures for annealing. There are no changes in the valence of Zn in the system even as the sample is annealed up to 400°C.

Raw XAS data were first processed by subtracting the background and normalizing using the ATHENA software.¹⁸⁰ The extracted data were then analyzed by using ARTEMIS software.^{180,181} Figure 3-7 shows the Zn *K*-edge extended X-ray absorption fine structure (EXAFS) spectra in $\chi(k)$ of the epitaxial ZnO films (a) as-synthesized, and after annealing *ex situ* at (c) 100°C, (e) 200°C, (g) 300°C, and (i) 400°C. The Fourier Transform and its imaginary part are correspondingly shown beside the EXAFS spectra. The first two prominent peaks in the Fourier Transform are assigned to the first two coordination shells of ZnO at *ca.* 1.9 Å (Zn-O) and 3.2 Å (Zn-Zn), respectively. Refinement was performed using a k^3 weighting. The $k^3\chi(k)$ for the ZnO films as a function of the photoelectron wave vector k , gives information about the mean immediate atomic environment of the specified lattice site.²⁰¹ All the EXAFS of the ZnO films measured fit well with the corresponding ZnO crystallographic information file (CIF)²⁰² used for the analysis, with minimal error. For a quantitative analysis of the local structural properties, the Fourier Transformed data in R-space was studied. To minimize errors, only data in the k -range of 2.54 – 11.0 Å⁻¹ was used for further analysis. Details of the fit methodology have been given in Section 2.4.5. The refinement of the amplitude reduction factor, S_0^2 yielded a value of 0.72

for the Zn-O correlation and 0.71 for the Zn-Zn correlation. This value was fixed for further refinement of the other structural parameters.

Figure 3-7: Zn K-edge EXAFS spectra in $\chi(k)$ of epitaxial ZnO films (a) as-synthesized, and after annealing *ex situ* at (c) 100°C, (e) 200°C, (g) 300°C, and (i) 400°C. The Fourier Transform and its imaginary part are shown for epitaxial ZnO films (b) as-synthesized, and after annealing *ex situ* at (d) 100°C, (f) 200°C, (h) 300°C, and (j) 400°C.

From the fitting analysis, it was found that the coordination number varies and is not close to the expected value of for the crystalline material (4 for Zn-O and 12 for Zn-Zn shells). This could be due to (a) defects or, (b) due to self absorption; note that the measurements were carried out using fluorescence mode and this method is usually used for dilute systems. These films are not dilute and it has to be measured by this fluorescence method, which when used for concentrated samples, the amplitude tends to decrease due to the self absorption process. This could be the main reason the coordination number estimated from the analysis is not completely reliable. Therefore, to estimate the defects based on the coordination number, we adopted a new strategy by taking the ratios of the coordination numbers of Zn-O and Zn-Zn correlations. The final values obtained from the fit of the ZnO film as-synthesized and after annealing *ex situ* are shown in Table 3-4. The fit of the NIST standard was also performed and used as a standard comparison. The values obtained from the NIST standard EXAFS analysis are shown in Table 3-3 for the as-synthesized, and that annealed *ex situ* at 200°C and 400°C.

Table 3-3: Structural parameters obtained from the EXAFS analysis of Zn *K*-edge data on NIST standard annealed *ex situ*.

	Zn-O			Zn-Zn			R-factor	Ratio of Zn-O to Zn-Zn
	N-1	R-1 (Å)	σ^2 -1 (Å ²)	N-2	R-2 (Å)	σ^2 -2 (Å ²)		
NIST standard	3.9 (0.2)	1.97 (0.02)	0.005 (0.004)	11.9 (0.2)	3.22 (0.01)	0.007 (0.002)	0.016	0.328
HT 200°C	4.2 (0.3)	1.98 (0.02)	0.005 (0.004)	13.1 (0.3)	3.22 (0.02)	0.008 (0.002)	0.021	0.321
HT 400°C	4.0 (0.3)	1.98 (0.02)	0.004 (0.004)	13.1 (0.3)	3.22 (0.02)	0.008 (0.002)	0.023	0.305

Table 3-4: Structural parameters obtained from the EXAFS analysis of Zn *K*-edge data on ZnO films annealed *ex situ*.

	Zn-O			Zn-Zn			R-factor	Ratio of Zn-O to Zn-Zn
	N-1	R-1 (Å)	σ^2 -1 (Å ²)	N-2	R-2 (Å)	σ^2 -2 (Å ²)		
As-synthesized	3.1 (0.1)	1.96 (0.01)	0.002 (0.003)	7.5 (0.3)	3.24 (0.01)	0.011 (0.005)	0.064	0.413
HT 100°C	3.2 (0.1)	1.97 (0.01)	0.002 (0.003)	11.7 (0.5)	3.25 (0.01)	0.013 (0.005)	0.057	0.274
HT 200°C	3.5 (0.1)	1.98 (0.02)	0.003 (0.003)	7.1 (0.3)	3.25 (0.01)	0.008 (0.003)	0.049	0.493
HT 300°C	2.9 (0.1)	1.97 (0.02)	0.002 (0.003)	9.8 (0.4)	3.25 (0.01)	0.011 (0.004)	0.085	0.296
HT 400°C	3.2 (0.1)	1.98 (0.02)	0.004 (0.003)	10.4 (0.4)	3.25 (0.01)	0.012 (0.004)	0.052	0.308

From the tables, N corresponds to the coordination number of the Zn-O and Zn-Zn correlations (first and second neighbours around Zn atom). This coordination number (N) is determined by multiplying the ideal coordination of Zn-O and Zn-Zn correlation (i.e., 4 and 12, respectively) by the occupancies obtained from the EXAFS fit. $R-1$ is the average atomic distance between the central Zn atom and the first nearest neighbour, i.e., oxygen (O), while $R-2$ is the average atomic distance between the central Zn atom and the next nearest neighbour, i.e., zinc atom in the next shell. The values are obtained by fitting the singly scattered paths which are calculated for the EXAFS of ZnO, and taking the average. σ^2 is the Debye-Waller factor, which is a function of disorder and temperature. The temperature dependence provides information about the stiffness of the bonds and the mass of the atoms.¹⁶⁸

As shown in Table 3-4, the refinement revealed that the nearest neighbour distance obtained for the as-synthesized film was 1.96 Å (Zn-O) and the next nearest neighbour distance was 3.24 Å, which corresponds within the error limits of those reported by similar studies.^{201,203,204} The Debye-Waller factor (σ^2) of the Zn-O pair was 0.002 Å² and 0.011 Å² for the Zn-Zn pair of the as-synthesized ZnO films. These values remained relatively constant even after annealing the film *ex situ* at temperatures up to 400°C. These values obtained are also close to those of previous reports.^{201,205,206}

The aim of the study was to observe defect structures, however, due to the limitations of the fitting model, defects were not clearly observed as the coordination number is not accurately obtained because it depends on various factors including the correlation with the Debye-Waller factor, etc. Thus, it is best to describe the defects as ratios of the coordination numbers which were taken as a means to quantify the defects, within error limits. For example, for bulk and

complete stoichiometry, the coordination of an ideal ZnO system will have 4 nearest neighbours of Zn-O coordination and 12 next nearest Zn atoms with reference to the central Zn atom at the origin. Thus, the ratio of Zn-O/Zn-Zn should be 4/12 or 0.333. Any deviation with more than 10% (including error) can be interpreted as Zn or O vacancy, respectively. Thus, the ratio would give an idea of how the coordination of the structure varies as compared to that of ideal stoichiometric ZnO.

From Table 3-4, the ratio of Zn-O to Zn-Zn coordination for the as-synthesized film is 0.413. This value is higher than 0.333 suggesting that zinc vacancies are present in the as-synthesized ZnO film. The ratios of the annealed samples were similarly taken and given in Table 3-4. At 100°C, there seems to be oxygen vacancies as the ratio obtained is lower than 0.333. However, at 100°C, there are many dynamic changes that may occur such as water/hydroxyl adsorption/desorption and therefore the result is unreliable and thus inconclusive. For the film annealed at 200°C, the ratio of the coordination gives a value of 0.493 indicating that more Zn vacancies are forming. This supports the Hall measurement results in Section 3.2.3 as the carrier concentration also increases by one order of magnitude when the film is annealed at 200°C. For the film annealed at 300°C and 400°C, the ratio obtained is 0.296 and 0.308, respectively. These values are lower than 0.333 indicating oxygen vacancies within the film. Oxygen vacancies can be formed when hydrogen is removed from the lattice during the annealing.¹⁵⁴ 300°C is also the temperature that pores start to form within the ZnO film as seen from the FEGSEM image (Figure 3-4 (h)). These pores are initially composed of zinc and oxygen vacancies which annihilate to form pores as explained in Section 3.2.2 and by Richardson *et al.*¹⁵⁴ Thus, there is a net reduction of zinc vacancies as pores are formed but there may be additional oxygen vacancies forming at the same time due to removal of hydroxyl

groups from the annealing. However, it is noted that the ratios for the coordination of Zn-O and Zn-Zn are 0.296 and 0.308, at 300°C and 400°C, respectively, are close to the ideal ratio of 0.333. This suggests that at higher annealing temperatures, there is a reduction in the concentration of zinc and oxygen vacancies.

3.4 Photoluminescence Spectroscopy of ZnO Films

The room temperature photoluminescence (PL) spectra of the ZnO film – as-synthesized and after annealing at temperatures 100°C – 400°C are shown in Figure 3-8.

Figure 3-8: Room temperature PL spectra of ZnO films as-synthesized, and after annealing (HT) at 100°C, 200°C, 300°C and 400°C.

The PL spectra of ZnO show a near band edge (NBE) transition at about 3.25 eV, originating from exciton radiative recombination.²⁰⁷ In the as-synthesized film, this PL NBE transition is weak, but upon annealing the peak is sharp and especially apparent after annealing at 300°C and 400°C. This NBE peak originates from radiative recombinations. The as-synthesized ZnO usually consists of excess Zn atoms and oxygen vacancies, leading to many lattice and surface defects acting as non-radiative centres and thus reducing the light emission from the ZnO film.¹⁶¹ After annealing, these non-radiative defects are reduced and restructured,

greatly enhancing the crystal structure leading to a reduction in the non-radiative recombination, and hence, an increase in the luminescence efficiency,¹⁶¹ shown by the sharp peak observed in the film annealed at 300°C and 400°C.

The PL spectra also show broad defect peak or deep-level emission (DLE) peak at lower energies (higher wavelengths) due to impurities or structural defects. This DLE is normally de-convoluted by Gaussian-fitting into three colour bands (red, yellow, green) for further analysis. There are various literature explaining the associated defects with the peaks present, although this is still a divisive topic.²⁰⁸⁻²¹¹ At *ca.* 2.25 – 2.58 eV (480 – 550 nm), the defect band is green; at *ca.* 2.03 – 2.25 eV (550 – 610 nm), the defect band is yellow; and, at *ca.* 1.65 – 2.03 eV (610 – 750 nm), it is red.²⁰⁸ The origin of the green band has been attributed to the presence of zinc vacancies.^{68,212} The yellow band has been attributed to the doubly charged oxygen vacancy.^{213,214} The red band edge is attributed to the presence of oxygen interstitials.^{213,215}

Figure 3-9: De-convoluted defect level emission for PL spectra of epitaxial ZnO film (a) as-synthesized, and after annealing at (b) 100°C, (c) 200°C, (d) 300°C, and (e) 400°C.

Figure 3-10: Correlation of the total integrated intensity of the PL spectra at each annealing temperature with the ratio of the integrated intensity of the NBE to DLE peak.

The DLE of the epitaxial ZnO films were de-convoluted by Gaussian-fitting analysis and shown in Figure 3-9. The as-synthesized ZnO films (Figure 3-9 (a)) showed a high degree of green and yellow bands centred at approximately 2.4 eV (510 nm) and 2.0 eV (610 nm), respectively. This is due to zinc vacancies and the doubly charged oxygen vacancies (V_o^{2+}), respectively.²¹²⁻²¹⁴

From Figure 3-9, it is seen that as the film is annealed at higher temperatures, the green luminescence band is reduced and eventually becomes much less when the film was annealed at 400°C. Concurrently, the appearance of the red luminescence band becomes evidently more prominent when the film was annealed at 400°C.

Figure 3-10 shows the correlation of the total integrated intensity of the PL spectra at each annealing temperature with the ratio of the integrated intensity of the NBE to DLE peak. As annealing temperature is increased, the total integrated intensity increases, and the ratio of the NBE to DLE peak also increases, reaching a peak at 300°C. This represents a better crystalline quality of the ZnO film at 300°C. This is a possible reason for the increase in mobility as seen from

the Hall measurements in Section 3.2.3, indicating fewer defects within the ZnO film after annealing at 300°C.

Figure 3-11: Integrated intensity variation of DLE of the epitaxial ZnO film with annealing temperature and the respective peak position at each annealing temperature.

Figure 3-11 shows the integrated intensity variation of each of the deconvoluted bands as a function of annealing temperature and the peak positions of the DLE at each annealing temperature. It is seen that the DLE peak shifts to higher wavelength or to lower energy levels (i.e., red-shift) with increasing annealing temperature. Concurrently, the green band is reduced. This suggests that zinc vacancies are reduced upon annealing while the red band, attributed to defects associated with oxygen interstitials^{209,215} increases. The red band has previously been attributed to defects associated with oxygen interstitials.^{209,215} Annealing in air leads to an increase in the amount of adsorbed oxygen at the surface.⁶⁷ Oxygen atoms are diffused into the bulk and fill the oxygen vacancies or occupy the interstitial sites to form oxygen interstitials. This results in a reduction of singly charged oxygen vacancies as O-H groups and O⁻ are removed from the material and an increase in oxygen interstitials as oxygen is adsorbed. The results

observed are consistent with several other experimental and theoretical reports.^{67,140,216-218}

3.5 Discussion

XAS results obtained showed that zinc vacancies are predominantly present in the as-synthesized ZnO film. As the film is annealed at 200°C, there is an increase in zinc vacancy concentration. Further annealing the film at 300°C and 400°C seems to cause the appearance of oxygen vacancies. However, as the ratio of the coordination numbers of Zn-O and Zn-Zn correlations are close to ideal, it can be said that there are about the same concentration of zinc and oxygen vacancies in the lattice. A possible reason for this could be the appearance of pores, formed by annihilation of cation and anion vacancies, which is observed at temperatures above 200°C.

Figure 3-12: Correlation between the integrated intensity of the respective de-convoluted DLE bands and the ratio of the refined coordination numbers of Zn-O to Zn-Zn.

Figure 3-12 shows the correlation between the integrated intensity of the respective de-convoluted DLE bands and the ratio of the refined coordination

numbers of Zn-O to Zn-Zn. From the PL results, it is seen that as the as-synthesized ZnO film does not have a prominent NBE peak but has a DLE peak centred at about 2.25 eV. As the sample is annealed to higher temperatures (i.e., 200°C, 300°C and 400°C), the sharp NBE peak becomes apparent, with the film annealed at 400°C displaying the greatest intensity. Broad DLE peaks are also observed for the films and these are attributed to defects in the system. Deconvolution of the PL defect spectra clearly shows a shift from green to yellow and red as the sample is annealed at higher temperatures. Red band is attributed to oxygen interstitials. From the XAS results, because the Zn central atom was probed, no information can be obtained about oxygen interstitials. However, the presence of zinc vacancies in the as-synthesized film has been shown by both XAS and PL mapping. Note that the zinc vacancy increase seen by XAS is more reflective of the bulk while the zinc vacancy decrease as indicated by PL is more indicative of the surface.

3.6 Conclusion of Chapter 3

Epitaxial ZnO films have been successfully synthesized on MgAl_2O_4 substrates by a low temperature chemical bath deposition route. XRD confirmed that ZnO was produced in the synthesis and shows the highly crystalline epitaxial nature of the films. From FEGSEM images, the morphology of the top surface of the films is smooth and continuous. However, upon a closer investigation of the cross-section, visible pores are observed within the films after annealing at temperatures above 200°C. A vacancy coalescence mechanism has been proposed for the formation of such pores, due to the coalescence of zinc and oxygen vacancies.¹⁵⁴ As the film is annealing at a higher temperature of 400°C, there is an increase in the number of pores and it is observed that pore size increases. The epitaxial ZnO films also exhibit excellent optical and electrical properties as

shown from room temperature PL mapping measurements and Hall measurements, respectively. It has been shown that upon annealing in air at temperatures from 200°C – 400°C, the electrical and optical properties are enhanced, possibly due to an increase in grain size, thus removing grain boundary trapped carrier states.

The local structural defects were investigated using XAS. This analysis strategy involves the alternation of the refinement of occupancies and the Debye-Waller factor during fitting. Zinc vacancies are predominantly present in the as-synthesized ZnO film. As the film is annealed at 200°C, there is an increase in zinc vacancy concentration. Further annealing the film at 300°C and 400°C seems to cause the appearance of oxygen vacancies. However, as the ratio of the coordination numbers of Zn-O and Zn-Zn correlations are close to ideal, it can be said that there are about the same concentration of zinc and oxygen vacancies in the lattice. A possible reason for this could be the appearance of pores, formed by annihilation of cation and anion vacancies, which is observed at temperatures above 200°C.

Thus, it has been shown that XAS has served to be a very useful and applicable characterization tool to measure the local defect structure in thin films, as well as the defect structural changes within the ZnO film system as annealing proceeds. This enhances the knowledge of the defect structure of ZnO thin films grown by an aqueous solution chemical bath deposition method and will narrow the gap in realizing these ZnO films for device applications such as TCOs and other applications in the optoelectronics field.

Chapter 4

Defect Structure Investigation of Low Temperature Solution Grown ZnO Powders

4.1 Summary of Chapter 4

This chapter reports a structure order investigation of low temperature solution grown zinc oxide (ZnO) nanostructures synthesized in the form of powders by various different precursor routes. The main characterization tools employed are X-ray absorption spectroscopy (XAS) and X-ray total scattering using synchrotron radiation (SR).

ZnO exhibits intrinsic *n*-type conductivity which has conventionally been accredited to native defects, such as oxygen vacancies or zinc interstitials.¹⁸ First principal studies by Kohan *et al.* attributes the source of “native” *n*-type conductivity to unintentional impurities instead.¹⁴⁴ Subsequently, calculations based on density functional theory (DFT) within the local density approximation (LDA) and the pseudopotential-plane-wave method pinpointed the unintentional impurities to be hydrogen (H).¹⁵⁰

For solution grown ZnO, there has been spectroscopic evidence presented for H in the lattice.^{154,155} H incorporation necessitates zinc vacancies for partial charge balance, however, no structural evidence has been presented. Results obtained from X-ray absorption spectroscopy (XAS), and total scattering experiments (using high-energy X-ray diffraction (HEXRD)) are reported here.

XAS is an atom specific technique, which gives valuable information on the local environment, as it is very sensitive to changes in the local structure. Total scattering experiments using HEXRD will yield the pair distribution function (PDF) and this technique will give information on the short and medium range order. More information about these techniques have been given in Section 2.4.6.

In the first part of this chapter, a study of ZnO powders grown at moderate pH ($\sim$ pH 8.0) is studied. This growth condition is usually used to obtain the seed layer for the growth of ZnO films (Chapter 3) using a two-step solution synthesis method (Section 2.1). The powders synthesized at pH 8.0 are then compared to commercially available ZnO powder. It was found that the Zn-Zn correlations in the commercially obtained sample are higher than in the ZnO powders synthesized in solution at pH 8.0, suggesting a zinc deficient system for the as-synthesized powders. Total scattering experiments yielding the PDF, confirmed the results that zinc deficiency exists in the system, as the Zn-Zn correlation intensities are less than that of the commercial ZnO.

Subsequently, ZnO nanostructures in powder form were synthesized in a similar manner to that of a film at a pH of 10.9 using different seeds. The synthesis details have been given in Section 2.2. These powders allow the further characterization using techniques such as powder X-ray diffraction (XRD) and total scattering experiments generating PDFs, in addition to XAS. Typically, a post-growth thermal annealing process of ZnO is used to improve its optical and electrical properties as seen in the ZnO films as reported in Chapter 3. These powders were similarly annealed and studied. From transmission electron microscopy (TEM), it is observed that pores are present in the powders after annealing, similar to those obtained in the film after annealing as shown in Chapter 3. Photoluminescence (PL) mapping showed a red-shift as the powders

are annealed, suggesting a reduction in zinc vacancies and the emergence of oxygen interstitials. Further defect characterization using *ex situ* and *in situ* XAS and *in situ* PDF showed that the as-synthesized ZnO powders generally have a predominantly zinc deficient system with less Zn-Zn correlations than that of ZnO, notwithstanding which seed was used for the synthesis. From the *in situ* XAS and PDF analysis, zinc vacancies are also found to be present in the ZnO powders when annealed.

This defect characterization of ZnO powders has enabled the understanding of the short and medium range structure order of ZnO and may potentially aid in the development and use of ZnO powders in catalysis or gas sensing applications.

4.2 Characterization of Solution Grown Zinc Oxide Powders Synthesized at pH 8.0

As presented in Chapter 3, for ZnO film growth, a seed layer is usually required for growth on a substrate to nucleate further growth of a thicker film. Conventionally, for solution based methods such as hydrothermal synthesis or chemical bath deposition, a seed layer is deposited on a substrate before subsequent growth of the film occurs. This seed layer can be grown at a low pH 7.6 – 8.0 as shown by several research groups.^{32,39,55} In this part of the chapter,¹⁸⁸ the growth of the seed (synthesized at pH 8.0) was replicated but without adding a substrate into the precursor solution, allowing powders to form within the solution during growth. The powders are then collected by centrifugation and rinsed and dried to obtain enough powder for characterization. The details of the synthesis have been given in Section 2.2.1. These powders were then structurally

compared to the commercially available ZnO powder purchased from Sigma-Aldrich, which is assumed to be defect-free.

4.2.1 Crystallinity of ZnO Powders Grown at pH 8.0

X-ray diffraction (XRD) results show that both the commercially obtained ZnO powders (Figure 4-1 (a)) and solution grown ZnO powders at pH 8.0 (Figure 4-1 (b)) are highly crystalline ZnO residing in the wurtzite structure,²¹⁹ with no impurity peaks observed.

Figure 4-1: XRD patterns of ZnO powders (a) commercial and (b) produced in solution at pH 8.0.¹⁸⁸ (Reprinted from *Journal of Solid State Chemistry*, 189, Liew, L.-L.; Sankar, G.; Handoko, A. D.; Goh, G. K. L.; Kohara, S., Understanding the defect structure of solution grown zinc oxide, 63 – 67, Copyright © 2012, with permission from Elsevier.)

4.2.2 Morphology of ZnO Powders Grown at pH 8.0

Observations of the morphology were made using field emission gun scanning electron microscopy (FEGSEM) which shows that commercial ZnO powders consist of small, irregular particles and the solution grown powders at pH 8.0, on the other hand consist of noticeably longer and pointed rods with aspect ratio greater than 10. The rods are about 1.0 – 1.4 μm in length and have diameters of 100 – 150 nm (Figure 4-2).

Figure 4-2: FESEM image of ZnO powders (a) commercially obtained and (b) synthesized in solution at pH 8.0.¹⁸⁸ (Reprinted from Journal of Solid State Chemistry, 189, Liew, L.-L.; Sankar, G.; Handoko, A. D.; Goh, G. K. L.; Kohara, S., Understanding the defect structure of solution grown zinc oxide, 63 – 67, Copyright © 2012, with permission from Elsevier.)

4.3 Defect Structure of ZnO Powders Grown at pH 8.0

The XRD pattern shown in Figure 4-1 does not give information about local structural changes and thus, X-ray absorption spectroscopy (XAS) and high energy X-ray diffraction (HEXRD) was used to further characterize the samples. A comparison of the commercial ZnO powder (99.99%, purchased from Aldrich, St. Louis, MO) and the ZnO powders synthesized in solution at pH 8.0 was then made. The commercial ZnO powder was used as a standard for the analysis.

4.3.1 X-ray Absorption Spectroscopy (XAS) of ZnO Powders Grown at pH 8.0

Using XAS technique, a central Zn atom was probed at the Zn *K*-edge. Figure 4-3 shows the comparison of Zn *K*-edge extended X-ray absorption fine structure (EXAFS) and the corresponding Fourier Transforms (FT) of the EXAFS data of the ZnO obtained commercially and the one synthesized at pH 8.0. The FT ((Figure 4-3 (b)) shows 2 distinct peaks; the first dominant peak reveals information about the bond distance between the central Zn atom and the nearest

neighbouring oxygen, i.e., the Zn-O correlation, and the second dominant peak manifests the Zn-Zn correlations.

It is clear from both the FTs that all the intensities of the peaks related to Zn-Zn correlations are noticeably reduced compared to that of Zn-O. Such reduction in the intensities of the Zn-Zn correlations could be due to the absence of some zinc ions or an increase in static disorder. Static disorder represents the deviation from the average distance that EXAFS measurements give since there are multiple distances present. Dynamic disorder is due to thermal effects and this has been excluded since both the measurements were performed at the same temperature. Static disorder effects are seen in many poorly defined systems but the XRD data (shown in Figure 4-1) shows that the ZnO powders synthesized at pH 8.0 are highly crystalline. In addition, it is noted that the FT magnitude can decrease rapidly at higher shells for small particles below 5 – 10 nm. However, the ZnO powders synthesized at pH 8.0 are much larger, about 1.0 – 1.4 μm in length and diameters of 100 – 150, and are large well-defined material as shown in the FEGSEM image (Figure 4-2 (b)), therefore it is not anticipated that any reduction in FT magnitude is due to particle size effects. Thus, the reduction in intensity of the Zn-Zn FT peak is neither due to particle size effects or static disorder. Most likely, the reduction in intensity with respect to the Zn-Zn correlations arises from the defects created by absence of Zn ions in the system.

Figure 4-3: Comparison of Zn K-edge (a) EXAFS and (b) Fourier transform of commercial ZnO and ZnO powders synthesized in solution.¹⁸⁸ (Reprinted from *Journal of Solid State Chemistry*, 189, Liew, L.-L.; Sankar, G.; Handoko, A. D.; Goh, G. K. L.; Kohara, S., Understanding the defect structure of solution grown zinc oxide, 63 – 67, Copyright © 2012, with permission from Elsevier.)

In order to substantiate this finding, a detailed analysis of the Zn *K*-edge EXAFS for both the materials were carried out. The best fit between the experimental and computed EXAFS and the respective FTs are shown in Figure 4-4. The experimental EXAFS *K*-edge data of the commercial ZnO and the ZnO powders produced in solution are shown with the best fit after refining the coordination number (*N*), inter-atomic distances (*R*) and the Debye-Waller factor (σ^2). The refinements of the various parameters are found in Table 4-1.

Figure 4-4: Best fit between experimental EXAFS spectra and computed EXAFS (first two shells) of (a) commercial ZnO powder and (b) pH 8.0 powders that were synthesized in solution. The respective FT's are given at the bottom.¹⁸⁸ (Reprinted from *Journal of Solid State Chemistry*, 189, Liew, L.-L.; Sankar, G.; Handoko, A. D.; Goh, G. K. L.; Kohara, S., Understanding the defect structure of solution grown zinc oxide, 63 – 67, Copyright © 2012, with permission from Elsevier.)

Table 4-1: Structural parameters obtained at Zn K-edge. (Reprinted from *Journal of Solid State Chemistry*, 189, Liew, L.-L.; Sankar, G.; Handoko, A. D.; Goh, G. K. L.; Kohara, S., Understanding the defect structure of solution grown zinc oxide, 63 – 67, Copyright © 2012, with permission from Elsevier.)

	Atom pair	Coordination number, N	Inter-atomic distance, R ($\text{\AA}$)	Debye-Waller factor, σ^2 ($\text{\AA}^2$)	Fit index
ZnO commercial	Zn-O	4.0	1.97 (0.02)	0.0054 (0.0004)	36.34
	Zn-Zn	12.0	3.23 (0.02)	0.0098 (0.0004)	
ZnO pH 8.0 powders	Zn-O	3.72 (0.4)	1.97 (0.02)	0.0050 (0.0004)	34.27
	Zn-Zn	10.9 (1.1)	3.23 (0.02)	0.105 (0.0004)	

The first 2 shells of the ZnO structure were used for the analysis, since data range (in k -space) is limited due to the increased noise at the higher k values, leading to a poor reliability in the data. Analysis of the Zn K-edge EXAFS show that the coordination numbers are lower for the Zn-Zn correlation of the ZnO pH 8.0 powders as compared to the commercially obtained ZnO powder. There is a larger

decrease in coordination number of the Zn-Zn correlations (from 12.0 to 10.9) as compared to the Zn-O correlations (from 4.0 to 3.72) suggesting zinc vacancies present in the system. However, it is noted that the decrease for both the coordination numbers of Zn-Zn and Zn-O correlations are close to the error limit, but from Figure 4-3, it is noted that the FT magnitude for the Zn-Zn peak of the EXAFS FT of the ZnO powders produced in solution are much lower in intensity as compared to that of the commercially obtained ZnO.

4.3.2 High Energy X-ray Diffraction (HEXRD) and Pair Distribution Function (PDF) of ZnO Powders Grown at pH 8.0

To further confirm the findings from the EXAFS data, total scattering experiments were performed.¹⁸⁸ Total scattering is not atom specific and gives information on longer range order. A Fourier Transform of the scattering data gives the PDF, which is shown in Figure 4-5.

Figure 4-5: PDF of ZnO commercial (blue trace) as compared to ZnO pH 8.0 powders synthesized in solution (red trace).¹⁸⁸ (Reprinted from *Journal of Solid State Chemistry*, 189, Liew, L.-L.; Sankar, G.; Handoko, A. D.; Goh, G. K. L.; Kohara, S., Understanding the defect structure of solution grown zinc oxide, 63 – 67, Copyright © 2012, with permission from Elsevier.)

From the PDF analysis (Figure 4-5), it is seen that all the peaks corresponding to the Zn-Zn correlations are lower in intensity for the ZnO

powders produced in solution as compared to the commercial ZnO. This indicates the presence of Zn deficiency in the system.

To determine whether such differences in intensity can be explained based on Zn deficiency, PDF data were simulated by altering the Zn occupancy in the system. This is achieved using the PDFGUI program.²²⁰

Figure 4-6: Simulated PDF data showing a ZnO with stoichiometry and with various reductions in Zn occupancy factor.

Figure 4-7: Simulated PDF data showing a ZnO with stoichiometry and with a 20% reduction in Zn occupancy factor.¹⁸⁸ (Reprinted from *Journal of Solid State Chemistry*, 189, Liew, L.-L.; Sankar, G.; Handoko, A. D.; Goh, G. K. L.; Kohara, S., Understanding the defect structure of solution grown zinc oxide, 63 – 67, Copyright © 2012, with permission from Elsevier.)

Figure 4-6 shows the simulated results obtained for a various reductions in Zn occupancy factors. All the peaks corresponding to the Zn-Zn correlations are lower in intensity when the Zn occupancies are reduced. Figure 4-7 shows the simulated result for only a 20% reduction in Zn occupancy factor, giving a clearer picture of the simulation of the result of a 20% reduction in Zn occupancy showing that Zn-Zn correlations are much lower in intensity and indicating that zinc vacancies are present in the system. This is in good agreement with the EXAFS results which show that there are indeed zinc vacancies present in the system. As mentioned earlier, from the FEGSEM image shown in Figure 4-2 (b), it is clear that the particles are not small enough to contribute to the reduction in the intensities in the Fourier Transforms. Thus, it is likely that the ZnO grown by aqueous solution is predominantly zinc deficient, with the presence of zinc vacancies, as compared to the commercial ZnO sample.

In summary, the defect structure of ZnO powders synthesized through an aqueous solution method at low temperature has been studied using X-ray

absorption spectroscopy and pair distribution function analysis. By comparing the powders produced and the commercial ZnO sample, it is shown that Zn-Zn correlations appear to be less in the ZnO powders synthesized in solution and thus, zinc vacancies are present in the ZnO powders synthesized at pH 8.0.

4.4 Characterization of Solution Grown Zinc Oxide Powders Synthesized at pH 10.9

ZnO films are requisite for device applications such as transparent conducting oxides (TCOs) and light emitting diodes (LEDs), etc.^{20,66,178,221,222} However, due to the limitations of fully characterizing the defect structure of ZnO films using EXAFS (Chapter 3), powders are needed for further characterization using methods such as powder X-ray diffraction (XRD) and pair distribution function analysis. Characterization of ZnO powders can provide additional insight into the ZnO defect structure, as various techniques are inaccessible to the ZnO films such as high energy X-ray diffraction and subsequent quantitative analysis and pair distribution function. Thus, ZnO powders were synthesized in a way that mimics that of the ZnO films, using a low pH seed, followed by growth at higher pH of 10.9, analogous to the synthesis of ZnO films (Chapter 3). Another sample of ZnO powder was also synthesized using a different seed, the ZnO NIST standard powder (SRM 674b), to further understand the properties and defects present in solution grown ZnO.

The syntheses of these samples have already been given in Section 2.2.2. In summary, two different ZnO powders were synthesized and characterized. Sample S1 was synthesized in the same way as that of the ZnO films, i.e., by using a low pH seed ($\sim 7.6 - 8.0$) and subsequently growing the ZnO powder at pH 10.9 with the addition of sodium citrate as a surface active agent. The difference

between the film growth and the powder growth lies in that the powder growth had no substrate added into the precursor solution during growth. ZnO powders grown were allowed to only attach to the seed powders that were added in to allow for nucleation and grow from there. All precursors remained the same as the ZnO film growth process. For Sample S2, the growth process was the same as the ZnO film, i.e., at pH 10.9 with the addition of sodium citrate. However, instead of using the low pH seed, ZnO powder SRM 674b (purchased from NIST) was used as a seed and added to the precursor solution for nucleation and growth. Both powders obtained were white in colour and several syntheses were needed to obtain sufficient powder for characterization. These two powder samples and the NIST ZnO standard powder (labelled sample S4) used as a reference were characterized and compared.

4.4.1 Crystallinity of ZnO Powders Grown at pH 10.9

Figure 4-8 (a) and (b) shows the XRD pattern obtained for samples S1 and S2 as-synthesized and that after annealing in air for 1 h at 600°C, respectively. Figure 4-8 (c) shows the XRD pattern for the sample S4, NIST standard (SRM 674b) and that after annealing in air for 1 h at 600°C, respectively. Sharp peaks are observed from all the X-ray diffraction (XRD) patterns indicating a crystalline material.

Figure 4-8: GADDS XRD pattern for samples (a) S1 as-synthesized (black trace) and after annealing at 600°C (red trace), (b) S2 as-synthesized and after annealing at 600°C and (c) S4 (ZnO NIST standard SRM 674b) and after annealing at 600°C.

All the reflections correspond closely to those from JCPDS 36-1451.¹⁹⁴ The XRD pattern obtained for samples S1 and S2 (Figure 4-8 (a) and (b)) indicate that the phase obtained from the synthesis of the ZnO powder is consistent with the hexagonal wurtzite ZnO structure with lattice constants $a = 3.24982 \text{ \AA}$ and $c = 5.20661 \text{ \AA}$.²²³ Diffraction peaks associated with impurities were not observed in the XRD pattern, indicating a high purity of the ZnO powders synthesized. There

were no shifts in any of the peak positions or any changes in the FWHM of the peaks after annealing at 600°C, thus no compromise in the crystal structure was observed.

4.4.2 Morphology of ZnO Powders Grown at pH 10.9

The morphology of the ZnO powders was investigated using field emission gun scanning electron microscopy (FEGSEM). The morphology of the two ZnO powder samples (labelled S1 and S2) are shown in Figure 4-9 and Figure 4-10, respectively. Figure 4-11 shows the FEGSEM image of sample S4 – the ZnO SRM 674b purchased from NIST that was used as a comparison for the XAS analysis.

Figure 4-9: FEGSEM image showing the morphology of sample S1 (a) 15k magnification and (b) 30k magnification.

Figure 4-10: FEGSEM image showing the morphology of sample S2 (a) 10k magnification and (b) 20k magnification.

Figure 4-11: FEGSEM image showing the morphology of sample S4 – the SRM 674b obtained from NIST (a) 30k magnification and (b) 50k magnification.

From Figure 4-9, it is seen that sample S1, synthesized via using a low pH seed ($\sim$ pH 8) and grown at pH 10.9, yielded ZnO powder that is generally rod-like. These rods are short and thick with lengths of about 1 μ m and thickness range from 300 – 500 nm. Sample S2 (Figure 4-10), synthesized using the NIST standard (sample S4) as a seed and grown at pH 10.9, yielded ZnO rods which have much larger aspect ratios. These rods are about 1.5 – 2 μ m in length and their diameters are about 200 – 500 nm. From Figure 4-11, the ZnO powder purchased from NIST (used as a standard) is irregularly shaped with a wide size distribution ranging from about 100 nm to several hundred nanometres.

4.4.3 Transmission Electron Microscopy Observations of ZnO Powders Grown at pH 10.9

High resolution transmission electron microscopy (HRTEM) was carried out on the ZnO powders. An annealing at 600°C in air for 1 h was performed on the same samples and also investigated with HRTEM.

Figure 4-12: TEM images (low magnification, HRTEM higher magnification image and corresponding SAED pattern, with zone axis $[\bar{1}2\bar{1}0]$) of sample (a) S1 as-synthesized, and (b) S1 after annealing at 600°C for 1 h in air. Dotted circle shows pores are formed within the ZnO upon annealing at 600°C for 1 h in air.

Figure 4-13: TEM images (low magnification, HRTEM higher magnification image and corresponding SAED pattern, with zone axis $[\bar{1}2\bar{1}0]$) of sample (a) S2 as-synthesized, and (b) S2 after annealing at 600°C for 1 h in air. Dotted circle shows pores are formed within the ZnO upon annealing at 600°C for 1 h in air.

Figure 4-14: TEM images (low magnification, HRTEM higher magnification image and corresponding SAED pattern, with zone axis $[\bar{1}2\bar{1}0]$) of sample (a) S4 (NIST SRM 674b – ZnO), and (b) S4 after annealing at 600°C for 1 h in air.

Figure 4-12 shows the HRTEM images (including higher magnification showing lattice fringes and SAED pattern) of sample S1 and Figure 4-13 shows the HRTEM images (including higher magnification showing lattice fringes and SAED pattern) of sample S2, (a) as-synthesized and (b) after annealing at 600°C for 1 h in air, respectively. From the low magnification images, it is evident that pores are formed within the ZnO upon annealing at 600°C for 1 h in air for both sample S1 and S2. This is highlighted by the white dotted circles in the figures above. This is analogous to the porosity observations of the epitaxial ZnO films observed by Richardson *et al.*¹⁵⁴ and also in the ZnO films synthesized in Section 3.2.2. Figure 4-14 (a) shows the HRTEM images of the ZnO NIST standard (SRM 674b), and after annealing (Figure 4-14 (b)). The sample is a single crystal ZnO as seen from

the selected area electron diffraction (SAED) pattern. Annealing the sample led to rounded edges as sintering has probably already started but there are no pores observed.

4.4.4 Thermal Analysis and Mass Spectrometry of ZnO Powders Grown at pH 10.9

Thermogravimetric analysis-mass spectrometry (TGA-MS) was performed to investigate the effect of annealing temperature on the extent of dehydration in the ZnO powders. Figure 4-15 and Figure 4-16 shows the TGA-MS results of sample S1 and S2, respectively.

Figure 4-15: TGA (black trace) and evolved gas mass spectrometry ($m/z = 18$, blue trace) results from sample S1.

Figure 4-16: TGA (black trace) and evolved gas mass spectrometry (blue trace) results from sample S2.

As seen from Figure 4-15 and Figure 4-16, the evolved gas mass spectrometry (blue trace) show that there are three distinct maxima of H_2O ($m/z = 18$) mass spectrum signals seen at 268.8°C, 317.5°C and approximately 600°C, for sample S1 (Figure 4-15) and at 272.6°C, 359°C and approximately 600°C, for sample S2 (Figure 4-16). Each peak generally corresponds to an increase in the rate of mass loss due to the removal of hydroxyl groups at the specific temperatures. Note that the syntheses were carried out with an aqueous solution (DI water) at low temperature of 90°C (below the boiling point of water). The multiple H_2O evolution events may be an indication that various hydrogen-related defects with different stabilities are present within the ZnO powder samples. This is accompanied by a mass loss of 2.02% for sample S1 and a mass loss of 1.24% for sample S2, as hydroxyl groups are expelled from the system. The higher mass loss in sample S1 is probably due to the higher content of hydroxyl groups in the sample as compared to sample S2, as the seed used for sample S1 was synthesized by a low temperature aqueous solution route while the seed used for sample S2 was purchased from NIST and the synthesis conditions are unknown, though it was probably not solution synthesized and may contain less hydroxyl groups.

However, it is noted that to acquire acceptable signal-to-noise ratio for the H_2O mass spectrum signal, it was essential to use a lot of sample and a high heating rate, both of which reduce the accuracy of the measurement with respect to the actual sample temperature.¹⁵⁴

4.5 *Ex Situ* XAS of ZnO Powders Grown at pH 10.9

Ex situ XAS measurements were performed on the two ZnO powder samples labelled as S1 and S2. XAS measurements were also performed on the ZnO NIST standard SRM 674b labelled as S4, used as a reference. All samples were annealed separately at temperatures of 200°C, 400°C, and 600°C for 1 h in air in a box furnace. XAS is a useful characterization tool that provides element specific information about the local atomic geometry and about the chemical state of the absorbing atom.

Zn *K*-edge XANES spectrum for ZnO samples S1 and S2 at room temperature (RT) and when the powders were annealed *ex situ* at temperatures 200°C, 400°C, and 600°C are shown in Figure 4-17 and Figure 4-18, respectively.

Figure 4-17: Zn *K*-edge XANES spectra of sample S1 as-synthesized and annealed *ex situ* at 200°C, 400°C, and 600°C for 1 h in air.

Figure 4-18: Zn K-edge XANES spectra of sample S2 as-synthesized and annealed *ex situ* at 200°C, 400°C, and 600°C for 1 h in air.

The absorption edge is observed at approximately 9658.96 eV, corresponding closely to the Zn K-edge binding energy. XANES is typically used to study the variation of core electron configuration and can give information about the valency changes of atoms in a matrix. For example, if there is a decrease in the valency, the XANES absorption structure will tend to move to lower energies.²⁰⁰ From Figure 4-17 and Figure 4-18, it is observed that there are no shifts in the XANES edge position indicating that the electronic configuration for the Zn central atom was unchanged and is stable. There are no changes in the valence of Zn in the system even as the samples are annealed up to 600°C.

Similar to the ZnO films XAS data shown in Section 3.3, the raw XAS data of the ZnO powders were first processed by subtracting the background and normalizing using the ATHENA software.¹⁸⁰ The extracted data were then analyzed by using ARTEMIS software.^{180,181} Figure 4-19, Figure 4-20, and Figure 4-21 shows the Zn K-edge EXAFS spectra in $\chi(k)$ of the ZnO powders samples S1, S2 and S4 (a) as-synthesized, and after annealing *ex situ* at (c) 200°C, (e) 400°C, and (g) 600°C, respectively. The Fourier Transform and its imaginary part are correspondingly shown beside the EXAFS spectra.

The first two prominent peaks in the Fourier Transform are assigned to the first two coordination shells of ZnO at *ca.* 1.9 Å (Zn-O) and 3.2 Å (Zn-Zn), respectively. Refinement was performed using a k^3 weighting. The $k^3\chi(k)$ for the ZnO powders as a function of the photoelectron wave vector k , gives information about the mean immediate atomic environment of the specified lattice site.²⁰¹ The EXAFS of the ZnO powders measured fit well with the corresponding ZnO crystallographic information file (*CIF*)²⁰² used for the analysis, with minimal error. For a quantitative analysis of the local structural properties, the Fourier Transformed data in R-space was studied. To minimize errors, only data in the k -range of 2.0 – 11.0 Å⁻¹ was used for further analysis.

Figure 4-19: Zn *K*-edge EXAFS spectra in $\chi(k)$ of sample S1 ZnO powder (a) as-synthesized, and annealed *ex situ* at (c) 200°C, (e) 400°C, and (g) 600°C. The Fourier Transform and its imaginary part is shown for sample S1 ZnO powder (b) as-synthesized, and annealed *ex situ* at (d) 200°C, (f) 400°C, and (h) 600°C.

Figure 4-20: Zn *K*-edge EXAFS spectra in $\chi(k)$ of sample S2 ZnO powder (a) as-synthesized, and annealed *ex situ* at (c) 200°C, (e) 400°C, and (g) 600°C. The Fourier Transform and its imaginary part is shown for sample S2 ZnO powder (b) as-synthesized, and annealed *ex situ* at (d) 200°C, (f) 400°C, and (h) 600°C.

Figure 4-21: Zn *K*-edge EXAFS spectra in $\chi(k)$ of sample S4 NIST ZnO powder (a) as-synthesized, and annealed *ex situ* at (c) 200°C, (e) 400°C, and (g) 600°C. The Fourier Transform and its imaginary part is shown for sample S4 NIST ZnO powder (b) as-synthesized, and annealed *ex situ* at (d) 200°C, (f) 400°C, and (h) 600°C.

The fit methodology developed here follows a simple alternation strategy, same as that used for the analysis of the ZnO films presented in Section 3.3. Details about the fitting procedure have been given in Section 2.4.5. The refinement of the amplitude reduction factor, S_0^2 , yielded a value of 0.84 for the Zn-O correlation and 0.92 for the Zn-Zn correlation. This value was fixed for further refinement of the structural parameters.

The final values obtained from the fit of the ZnO powder samples (sample S1 and S2) as-synthesized and after annealing *ex situ* are shown in Table 4-2 and Table 4-3, respectively. The ZnO NIST standard was similarly analyzed and shown in Table 4-4. The coordination number (N) of Zn-O and Zn-Zn correlations are determined by multiplying the ideal coordination (i.e., 4 and 12, respectively) by the occupancies obtained from the EXAFS fit. The average atomic distance, r , between the central zinc (Zn) atom and the first nearest neighbour, i.e., oxygen (O) is obtained by fitting the singly scattered paths which are calculated for the EXAFS of ZnO, and taking the average. The Debye-Waller factor, σ^2 , is a function of disorder and temperature provides information about the stiffness of the bonds and the mass of the atoms.¹⁶⁸

Table 4-2: Structural parameters obtained from the EXAFS analysis of Zn *K*-edge data on ZnO powders (sample S1) annealed *ex situ*.

S1	Zn-O			Zn-Zn			R-factor	Ratio of Zn-O to NIST standard	Ratio of Zn-Zn to NIST standard
	N-1	R-1 (Å)	σ^2 -1 (Å ²)	N-2	R-2 (Å)	σ^2 -2 (Å ²)			
As-synthesized	3.7 (0.2)	1.98 (0.02)	0.005 (0.003)	10.3 (0.2)	3.22 (0.01)	0.008 (0.002)	0.015	0.937	0.866
HT 200°C	3.7 (0.2)	1.97 (0.02)	0.005 (0.004)	11.9 (0.3)	3.22 (0.02)	0.008 (0.002)	0.021	0.879	0.910
HT 400°C	3.6 (0.2)	1.98 (0.02)	0.005 (0.004)	11.5 (0.3)	3.22 (0.02)	0.008 (0.002)	0.022	0.902	0.881
HT 600°C	3.7 (0.2)	1.97 (0.02)	0.005 (0.004)	10.6 (0.2)	3.22 (0.01)	0.007 (0.002)	0.014	0.922	0.882

Table 4-3: Structural parameters obtained from the EXAFS analysis of Zn *K*-edge data on ZnO powders (sample S2) annealed *ex situ*.

S2	Zn-O			Zn-Zn			R-factor	Ratio of Zn-O to NIST standard	Ratio of Zn-Zn to NIST standard
	N-1	R-1 (Å)	σ^2 -1 (Å ²)	N-2	R-2 (Å)	σ^2 -2 (Å ²)			
As-synthesized	3.3 (0.1)	1.97 (0.02)	0.005 (0.003)	9.6 (0.2)	3.22 (0.01)	0.007 (0.002)	0.015	0.845	0.803
HT 200°C	3.5 (0.2)	1.98 (0.02)	0.005 (0.004)	10.8 (0.2)	3.22 (0.02)	0.008 (0.002)	0.020	0.833	0.828
HT 400°C	3.3 (0.2)	1.98 (0.02)	0.005 (0.004)	10.1 (0.2)	3.22 (0.02)	0.007 (0.002)	0.020	0.827	0.776
HT 600°C	3.5 (0.2)	1.97 (0.02)	0.005 (0.004)	10.2 (0.2)	3.22 (0.01)	0.007 (0.002)	0.015	0.880	0.851

Table 4-4: Structural parameters obtained from the EXAFS analysis of Zn *K*-edge data on ZnO NIST standard (sample S4) annealed *ex situ*.

S4	Zn-O			Zn-Zn			R-factor
	N-1	R-1 (Å)	σ^2 -1 (Å ²)	N-2	R-2 (Å)	σ^2 -2 (Å ²)	
NIST standard	3.9 (0.2)	1.97 (0.02)	0.005 (0.004)	11.9 (0.2)	3.22 (0.01)	0.007 (0.002)	0.016
HT 200°C	4.2 (0.3)	1.98 (0.02)	0.005 (0.004)	13.1 (0.3)	3.22 (0.02)	0.008 (0.002)	0.021
HT 400°C	4.0 (0.3)	1.98 (0.02)	0.004 (0.004)	13.1 (0.3)	3.22 (0.02)	0.008 (0.002)	0.023
HT 600°C	4.0 (0.2)	1.97 (0.02)	0.005 (0.004)	12.0 (0.2)	3.22 (0.01)	0.007 (0.002)	0.015

For sample S1, the refinement revealed that the nearest neighbour distance obtained for the as-synthesized powders was 1.98 Å for the Zn-O bond and next nearest neighbour distance was 3.22 Å for the Zn-Zn bond. The Debye-Waller factor (σ^2) of the Zn-O pair was given as 0.005 Å², and 0.008 Å² for the Zn-Zn pair. For sample S2, the refinement revealed that the nearest neighbour distance obtained for the as-synthesized powders was 1.97 Å for the Zn-O bond and next nearest neighbour distance was 3.22 Å for the Zn-Zn bond. The σ^2 of the Zn-O pair was 0.005 Å², and 0.007 Å² for the Zn-Zn pair. All the values obtained for the distances between neighbours and the Debye-Waller factors corresponds within error limits of those reported by similar studies.^{201,203-206} These values remained relatively constant even after annealing the powders at temperatures up to 600°C, showing little change at temperatures up to 600°C.

To determine the local structure order defects, the coordination numbers of the Zn-O and Zn-Zn correlations are considered. Annealing conditions were kept invariable for all the samples for direct comparison. For sample S1, a coordination number of 3.7 is obtained for the Zn-O correlation and a coordination number of 10.3 for the Zn-Zn correlation, for the as-synthesized sample. These values were then compared to the coordination numbers for Zn-O and Zn-Zn correlations obtained from the refinement of the NIST standard (sample S4). As shown in Table 4-2 for sample S1, the as-synthesized sample has a lower coordination number ratio indicating a *ca.* 13.4% decrease in coordination of Zn-Zn correlations. This suggests that zinc vacancies are present in the as-synthesized S1 sample. The coordination of Zn-O are within the 10% error limit and no conclusive finding can be made about the presence of oxygen vacancies in the system. The coordination numbers obtained at each annealing temperature are similarly compared with the coordination numbers of the NIST standard (sample S4). At 200°C, there seems to be a predominance of oxygen vacancies. At

400°C and 600°C, the ratios suggest the presence of zinc vacancies in the system. There is a 10% error limit and ratios obtained that fall within the error limit are not able to provide any conclusive findings.

Similarly, for sample S2, a coordination number of 3.3 is obtained for the Zn-O correlation and a coordination number of 9.6 for the Zn-Zn correlation, for the as-synthesized sample. This indicates a *ca.* 19.7% decrease in coordination of Zn-Zn correlations and that there is a larger concentration of zinc vacancies as compared to oxygen vacancies (*ca.* 15.5%) in the as-synthesized sample S2. The coordination numbers obtained at each annealing temperature are similarly compared with the ideal coordination numbers. At 200°C, 400°C and 600°C, the values of the coordination numbers suggest that there are both oxygen vacancies and zinc vacancies present in the system, but a slightly larger concentration of zinc vacancies are present as the ratio as compared to the NIST standard (sample S4) are much less for the Zn-Zn correlations.

However, a more detailed look at the coordination numbers of sample S1 and sample S2 show that the coordination numbers of the Zn-O correlations remains relatively constant (3.6 – 3.7 for sample S1 and 3.3 – 3.5 for sample S2) at different annealing temperatures, while the coordination numbers of the Zn-Zn correlations have a greater variation (10.3 – 11.9 for sample S1 and 9.9 – 10.8 for sample S2) at different annealing temperatures. Note that the ideal coordination number for Zn-O correlation is 4 and for Zn-Zn correlation is 12. This could suggest the presence of zinc vacancies in both sample S1 and S2. However, further investigation and analysis of the samples are required to make a conclusive finding.

4.6 *In Situ* XAS of ZnO Powders Grown at pH 10.9

In situ XAS measurements were attempted with the ZnO powders (sample S1 and S2), pressed into a pellet diluted with boron nitride (BN), and placed into the specimen chamber with measurements taken at the Zn *K*-edge. This was done at room temperature before heating the chamber to an elevated temperature of 200°C. For the collection of subsequent spectra, the chamber was maintained at this temperature and measurements were performed. The chamber was then heated to temperatures of 400°C, and 600°C, with measurements performed while the chamber was maintained at the respective temperatures. The chamber was subsequently allowed to cool to room temperature before another measurement was performed at room temperature. The ZnO NIST standard powder (sample S4) was similarly measured as a reference.

Figure 4-22, Figure 4-23, and Figure 4-24 shows the Zn *K*-edge XANES spectra of the ZnO powders, sample S1, S2 and S4, respectively, at room temperature (RT) and when annealed *in situ* at temperatures of 200°C, 400°C and 600°C, and after cooling back to room temperature. The absorption edge is observed at approximately 9658.9 eV, corresponding to the Zn *K*-edge binding energy. Similar to the *ex situ* measurements shown in Section 4.5, there are no shifts in the XANES edge position indicating that the electronic configuration is unchanged and stable. There is no change in the valance of Zn in the system even as the samples are annealed up to 600°C and cooled back to room temperature.

Figure 4-22: Zn *K*-edge XANES spectra of sample S1 annealed *in situ* at temperatures from room temperature (RT) to 600°C and after cooling to RT.

Figure 4-23: Zn *K*-edge XANES spectra of sample S2 annealed *in situ* at temperatures from room temperature (RT) to 600°C and after cooling to RT.

Figure 4-24: Zn K-edge XANES spectra of sample S4 (ZnO NIST - SRM 674b) annealed *in situ* at temperatures from room temperature (RT) to 600°C and after cooling to RT.

Similar to the *ex situ* XAS data processing done in Section 4.5, the raw XAS data of the ZnO powders were first processed by subtracting the background and normalizing using the ATHENA software.¹⁸⁰ The extracted data were then analyzed by using ARTEMIS software.^{180,181} Figure 4-25, Figure 4-26 and Figure 4-27 shows the Zn K-edge EXAFS spectra and fit in $\chi(k)$ of ZnO powders, sample S1, S2 and S4, respectively, annealed *in situ* at (a) room temperature (RT), (c) 200°C, (e) 400°C, (g) 600°C, and, (i) after cooling back to RT. The Fourier Transform and its imaginary part are correspondingly shown beside the EXAFS spectra.

The first two prominent peaks in the Fourier Transform are assigned to the first two coordination shells of ZnO at *ca.* 1.9 Å (Zn-O) and 3.2 Å (Zn-Zn), respectively. Refinement was performed using a k^3 weighting. The $k^3\chi(k)$ for the ZnO films as a function of the photoelectron wave vector k , gives information about the mean immediate atomic environment of the specified lattice site.²⁰¹ All the EXAFS of the ZnO films measured fit well with the corresponding ZnO crystallographic information file (CIF)²⁰² used for the analysis, with minimal error.

For a quantitative analysis of the local structural properties, we studied the Fourier Transformed data in R-space. To minimize errors, only data in the k -range of $2.0 - 11.0 \text{ \AA}^{-1}$ was used for further analysis.

Figure 4-25: Zn K-edge EXAFS spectra in $\chi(k)$ of sample S1 ZnO powder (a) as-synthesized, annealed *in situ* at (c) 200°C, (e) 400°C, (g) 600°C, and (i) after cooling down to room temperature. The Fourier Transform and its imaginary part is shown for sample S1 ZnO powder (b) as-synthesized, annealed *in situ* at (d) 200°C, (f) 400°C, (h) 600°C, and (j) after cooling down to room temperature.

Figure 4-26: Zn K-edge EXAFS spectra in $\chi(k)$ of sample S2 ZnO powder (a) as-synthesized, annealed *in situ* at (c) 200°C, (e) 400°C, (g) 600°C, and (i) after cooling down to room temperature. The Fourier Transform and its imaginary part is shown for sample S2 ZnO powder (b) as-synthesized, annealed *in situ* at (d) 200°C, (f) 400°C, (h) 600°C, and (j) after cooling down to room temperature.

Figure 4-27: Zn K-edge EXAFS spectra in $\chi(k)$ of sample S4 (a) ZnO NIST (SRM 674b) powder, and annealed *in situ* at (c) 200°C, (e) 400°C, (g) 600°C, and (i) after cooling down to room temperature. The Fourier Transform and its imaginary part is shown for sample S4 (b) ZnO NIST (SRM 674b), and annealed *in situ* at (d) 200°C, (f) 400°C, (h) 600°C, and (j) after cooling down to room temperature.

The fit methodology developed here follows a simple alternation strategy, same as that used for the analysis of the ZnO films presented in Section 3.3 and those shown in Section 4.5. Details about the fitting procedure have been given in Section 2.4.5. The refinement of the amplitude reduction factor, S_0^2 , yielded a value of 0.95 for the Zn-O correlation and 1.17 for the Zn-Zn correlation. This value was fixed for further refinement of the structural parameters.

The final values obtained from the fit of the ZnO powder samples (sample S1 and S2) as-synthesized and after annealing *in situ* are shown in Table 4-5 and Table 4-6, respectively. The ZnO NIST standard (sample S4) was similarly analyzed and shown in Table 4-7. The coordination number (N) of Zn-O and Zn-Zn correlations are determined by multiplying the ideal coordination (i.e., 4 and 12, respectively) by the occupancies obtained from the EXAFS fit. The average atomic distance, r , between the central Zn atom and the first nearest neighbour, i.e., oxygen (O) is obtained by fitting the singly scattered paths which are calculated for the EXAFS of ZnO, and taking the average. The Debye-Waller factor, σ^2 , is a function of disorder and temperature provides information about the stiffness of the bonds and the mass of the atoms.¹⁶⁸

Table 4-5: Structural parameters obtained from the EXAFS analysis of Zn *K*-edge data on ZnO powders (sample S1) annealed *in situ*.

S1	Zn-O			Zn-Zn			R-factor	Ratio of Zn-O to NIST standard	Ratio of Zn-Zn to NIST standard
	N-1	R-1 (Å)	σ^2 -1 (Å ²)	N-2	R-2 (Å)	σ^2 -2 (Å ²)			
As-synthesized	3.6 (0.1)	1.97 (0.02)	0.005 (0.004)	9.4 (0.2)	3.21 (0.01)	0.008 (0.003)	0.014	0.878	0.994
HT 200°C	3.4 (0.1)	1.97 (0.02)	0.005 (0.003)	9.0 (0.2)	3.21 (0.02)	0.010 (0.003)	0.016	0.790	0.774
HT 400°C	3.3 (0.1)	1.97 (0.02)	0.006 (0.003)	8.8 (0.2)	3.21 (0.02)	0.013 (0.004)	0.013	0.828	0.900
HT 600°C	3.3 (0.1)	1.97 (0.02)	0.007 (0.003)	8.5 (0.2)	3.21 (0.02)	0.016 (0.006)	0.011	0.833	0.900
Cooled to RT	3.4 (0.2)	1.97 (0.02)	0.005 (0.004)	9.9 (0.2)	3.22 (0.01)	0.007 (0.002)	0.014	0.853	0.841

Table 4-6: Structural parameters obtained from the EXAFS analysis of Zn *K*-edge data on ZnO powders (sample S2) annealed *in situ*.

S2	Zn-O			Zn-Zn			R-factor	Ratio of Zn-O to NIST standard	Ratio of Zn-Zn to NIST standard
	N-1	R-1 (Å)	σ^2 -1 (Å ²)	N-2	R-2 (Å)	σ^2 -2 (Å ²)			
As-synthesized	3.4 (0.2)	1.97 (0.02)	0.005 (0.004)	9.5 (0.2)	3.22 (0.01)	0.007 (0.002)	0.014	0.787	0.763
HT 200°C	3.4 (0.1)	1.97 (0.02)	0.005 (0.003)	9.1 (0.2)	3.21 (0.02)	0.010 (0.003)	0.015	0.786	0.784
HT 400°C	3.3 (0.1)	1.97 (0.02)	0.006 (0.003)	8.5 (0.2)	3.21 (0.02)	0.012 (0.004)	0.014	0.816	0.867
HT 600°C	3.2 (0.1)	1.97 (0.02)	0.007 (0.003)	8.2 (0.2)	3.21 (0.02)	0.016 (0.006)	0.011	0.824	0.872
Cooled to RT	3.3 (0.2)	1.97 (0.02)	0.005 (0.004)	9.6 (0.2)	3.22 (0.02)	0.007 (0.003)	0.019	0.830	0.818

Table 4-7: Structural parameters obtained from the EXAFS analysis of Zn *K*-edge data on ZnO NIST standard (sample S4) annealed *in situ*.

S4	Zn-O			Zn-Zn			R-factor
	N-1	R-1 (Å)	σ^2 -1 (Å ²)	N-2	R-2 (Å)	σ^2 -2 (Å ²)	
NIST standard	4.0 (0.2)	1.98 (0.02)	0.005 (0.004)	12.5 (0.3)	3.22 (0.02)	0.007 (0.002)	0.018
HT 200°C	4.4 (0.2)	1.97 (0.02)	0.005 (0.004)	11.7 (0.2)	3.22 (0.02)	0.008 (0.003)	0.018
HT 400°C	4.2 (0.2)	1.97 (0.02)	0.006 (0.004)	9.8 (0.2)	3.22 (0.02)	0.010 (0.003)	0.015
HT 600°C	4.1 (0.1)	1.97 (0.02)	0.007 (0.003)	9.4 (0.2)	3.21 (0.02)	0.015 (0.006)	0.012
Cooled to RT	4.0 (0.2)	1.98 (0.02)	0.004 (0.004)	11.8 (0.3)	3.22 (0.02)	0.007 (0.002)	0.020

For sample S1, the refinement revealed that the nearest neighbour distance obtained for the as-synthesized powders was 1.97 Å for the Zn-O bond and next nearest neighbour distance was 3.21 Å for the Zn-Zn bond. The Debye-Waller factor (σ^2) of the Zn-O pair was given as 0.005 Å² and 0.008 Å² for the Zn-Zn pair. For sample S2, the refinement revealed that the nearest neighbour distance obtained for the as-synthesized powders was 1.97 Å for the Zn-O bond and next nearest neighbour distance was 3.22 Å for the Zn-Zn bond. The σ^2 of the Zn-O pair was 0.005 Å² and 0.007 Å² for the Zn-Zn pair. All the values obtained for the distances between neighbours and the Debye-Waller factors corresponds within error limits of those reported by similar studies.^{201,203-206}

As shown in Table 4-5 and Table 4-6, the Debye-Waller factor, σ^2 , is generally increased when the annealing proceeds, increasing with an increase in temperature. When the samples are cooled back to room temperature, the σ^2 value is typically changed back to its original room temperature value. This is expected of the temperature dependent factor, σ^2 , which is correlated to the thermal disorder of the system.

Similar to the study on the *ex situ* XAS of the ZnO powders shown in Section 4.5, the coordination numbers of the Zn-O and Zn-Zn correlations are considered in order to determine the local structure order defects. The coordination number (N) represents the number of nearest neighbour atoms surrounding the central Zn atom. For sample S1, a coordination number of 3.6 is obtained for the Zn-O correlation and a coordination number of 9.4 for the Zn-Zn correlation, for the as-synthesized sample. These values were then compared to the coordination numbers for Zn-O and Zn-Zn correlations of the NIST standard (sample S4). The as-synthesized sample S1 seem to contain oxygen vacancies, however, it is noted that the refinement for the *ex situ* experiments showed zinc

vacancies. Thus, total scattering experiments yielding pair distribution function (PDF) was used to establish the defects present in the samples. This is presented in Section 4.8. The coordination numbers obtained at each annealing temperature and after cooling back to room temperature are similarly compared with the ideal coordination numbers. Similarly for sample S2, the coordination numbers of the Zn-O and Zn-Zn correlations are considered in order to determine the local structure order defects. For both sample S1 and S2, there is a large variation in the coordination numbers and this is due to the thermal factors which are greatly influencing the values obtained, as this was an *in situ* experiment. Further investigation is necessary for a conclusive finding. Total scattering experiments yielding pair distribution function (PDF) was used to establish the defects present in the samples and is presented in Section 4.8.

As the powders are produced in aqueous solution using a chemical bath deposition route, there is the presence of hydroxyl groups within the sample. This is seen clearly from the TGA-MS results shown in Section 4.4.4 where there is the evolution of hydroxyl groups from the samples as the samples are heated up. The predominant zinc vacancy seen could be due to the annealing process where more oxygen is annealed and forced out of the system at higher annealing temperatures. This can be correlated to the TGA-MS results which showed a mass spectrum maxima for H₂O ($m/z = 18$) at 268.8°C, 317.5°C and approximately 600°C, for sample S1 (Figure 4-15) and at 272.6°C, 359.0°C and approximately 600°C, for sample S2 (Figure 4-16). This resulted in a mass loss of 2.02% for sample S1 and a mass loss of 1.24% for sample S2. The higher mass loss in sample S1 is due to the higher content of hydroxyl groups in the sample as compared to sample S2, as the seed used for sample S1 was synthesized by a low temperature aqueous solution route while the seed used for sample S2 was purchased from

NIST and was probably not solution synthesized and so does not contain significant amount of hydroxyl groups.

4.7 Photoluminescence Spectroscopy of ZnO Powders Grown at pH 10.9

The room temperature photoluminescence (PL) spectra of the ZnO powders, sample S1 and S2 – as-synthesized and after annealing *ex situ* at temperatures 200°C – 600°C are shown in Figure 4-28 and Figure 4-30, respectively. The corresponding de-convoluted defect level emissions of sample S1 and S2 are shown in Figure 4-29 and Figure 4-31, respectively.

Figure 4-28: Room temperature PL spectra of sample S1 as-synthesized and after annealing at 200°C, 400°C and 600°C for 1 h in air.

Figure 4-29: De-convoluted defect level emission for sample S1 (a) as-synthesized, and after annealing at (b) 200°C, (c) 400°C, and (d) 600°C for 1 h in air.

Figure 4-30: Room temperature PL spectra of sample S2 as-synthesized and after annealing at 200°C, 400°C and 600°C for 1 h in air.

Figure 4-31: De-convoluted defect level emission for sample S2 (a) as-synthesized, and after annealing at (b) 200°C, (c) 400°C, and (d) 600°C for 1 h in air.

The PL spectra of ZnO show a near band edge (NBE) transition at about 3.25 eV, originating from exciton radiative recombination.²⁰⁷ In the as-synthesized samples, this PL NBE transition is weak and not noticeable, especially for sample S1, but upon annealing at 400°C, the peak becomes relatively sharper. The as-synthesized ZnO usually consists of many lattice and surface defects acting as non-radiative centres and thus reducing the light emission from the ZnO samples.¹⁶¹ After annealing, these non-radiative defects are reduced and restructured, greatly enhancing the crystal structure leading to a reduction in the non-radiative recombination, and hence, an increase in the luminescence efficiency,¹⁶¹ shown by the sharp peak observed in the film annealed at 400°C. A broad deep level emission (DLE) is also observed at lower energies (higher wavelengths) due to impurities or structural defects. As compared to the ZnO film shown in Section 3.4, the ratio of the intensity of the NBE to the DLE is much lower. This is possibly due to surface effects as powders have much more surfaces exposed as compared to the film during the measurement. A de-convolution of the DLE was done by Gaussian fitting analysis, as shown in Figure 4-29 and Figure 4-31 for sample S1 and S2, respectively.

The de-convoluted DLE for both sample S1 and S2 appear similar. For the as-synthesized ZnO powders, a mixture of green, yellow and red bands are observed centred at approximately 2.3 eV (540 nm), 2.0 eV (610 nm) and 1.8 eV (690 nm), respectively. The origin of the green band has been attributed to the presence of zinc vacancies.^{68,212} The yellow band has been attributed to the doubly charged oxygen vacancy.^{213,214} The red band edge is attributed to the presence of oxygen interstitials.^{213,215}

As the powders are annealed at higher temperatures, the green luminescence band is reduced and eventually becomes insignificant and nonexistent when the powders were annealed at 600°C. Concurrently, with the increase in annealing temperature to 600°C, there is the emergence of the red luminescence band which becomes evidently more prominent, centred at about 1.8 eV.

Figure 4-32: Correlation of the total integrated intensity of the PL spectra at each annealing temperature with the ratio of the integrated intensity of the NBE to DLE peak for sample S1.

Figure 4-33: Correlation of the total integrated intensity of the PL spectra at each annealing temperature with the ratio of the integrated intensity of the NBE to DLE peak for sample S2.

Figure 4-32 and Figure 4-33 shows the correlation of the total integrated intensity of the PL spectra at each annealing temperature with the ratio of the integrated intensity of the NBE to DLE peak for sample S1 and sample S2, respectively. As the annealing temperature is increases, the total integrated intensity increases, and the ratio of the NBE to DLE peak also increases, reaching a peak at 400°C. This represents a better crystalline quality of the ZnO samples at 400°C. At 600°C, there is an obvious decrease in the ratio of NBE to DLE for both sample S1 and sample S2. This could be due to the presence of a large number of pores within the ZnO samples which could be an indication of a large amount of defects within the ZnO powder samples.

Figure 4-34: Correlation of the integrated intensity variation of DLE of sample S1 with annealing temperature and the respective peak position at each annealing temperature.

Figure 4-35: Correlation of the integrated intensity variation of DLE of sample S2 with annealing temperature and the respective peak position at each annealing temperature.

Figure 4-34 and Figure 4-35 shows correlation of the integrated intensity variation of each of the de-convoluted bands with annealing temperature and the peak positions of the DLE at each annealing temperature, for sample S1 and S2 respectively. It is seen that the DLE peak shifts to higher wavelength or to lower energy levels (i.e., red-shift) with increasing annealing temperature.⁶⁷ The red band is attributed to defects associated with oxygen interstitials.^{209,215} The green

band is attributed to zinc vacancies, and is reduced as annealing temperature increases. This corresponds to the XAS results in Section 4.5. Annealing in air leads to an increase in the amount of adsorbed oxygen at the surface.⁶⁷ Oxygen atoms are diffused into the bulk and fill the oxygen vacancies or occupy the interstitial sites to form oxygen interstitials. This results in a reduction of singly charged oxygen vacancies as O-H groups and O⁻ are removed from the material and an increase in oxygen interstitials as oxygen is adsorbed. This is consistent with several other experimental and theoretical reports.^{67,140,216-218}

4.8 *In Situ* Pair Distribution Function Analysis of ZnO Powders Grown at pH 10.9

In situ total scattering experiments were carried out on the ZnO powder samples S1 and S2 to complement the EXAFS data. Unlike EXAFS, this high energy X-ray diffraction technique is not atom specific but it can provide valuable information about the structure on a much longer range. The Fourier Transform of the measured data gives the pair distribution function (PDF). More details of this technique have been given in Section 2.4.6. The plot of the total scattering data of sample S4 (ZnO NIST standard SRM 674b) obtained at room temperature by high energy X-ray diffraction (HEXRD) measurements is shown in Figure 4-36. $S(Q)$ of all the other samples are closely similar to that of the NIST standard.

Figure 4-36: Total scattering data for sample S4 (ZnO NIST standard SRM 674b) obtained at room temperature by HEXRD measurements.

Figure 4-37: Fourier Transformed $S(Q)$, generating *in situ* PDFs of sample S1 from measurements at room temperature (RT), 200°C, 400°C and 600°C; and after cooling back to room temperature.

Figure 4-38: Fourier Transformed $S(Q)$, generating *in situ* PDFs of sample S2 from measurements at room temperature (RT), 200°C, 400°C and 600°C; and after cooling back to room temperature.

Figure 4-39: Fourier Transformed $S(Q)$, generating *in situ* PDFs of sample S4 (ZnO NIST standard SRM 674b) from measurements at room temperature (RT) and 600°C.

Figure 4-37, Figure 4-38 and Figure 4-39 shows the Fourier Transformed $S(Q)$ which generates the PDF of the ZnO samples S1, S2 and S4 (NIST standard)

from *in situ* measurements at room temperature and at 200°C, 400°C and 600°C and after it is cooled to room temperature. From the graphs, the intensities of all the correlations decrease as temperature increases. This intensity difference is related to the temperature factor. When the samples S1 and S2 are cooled back to room temperature, the intensities of the peaks are slightly higher than those obtained before it was heated i.e., at room temperature (more apparent in sample S1 (Figure 4-38)). This indicates that the powders are more structured after annealing.

A comparison of the room temperature data of samples S1 and S2 was made against the NIST standard (sample S4). Figure 4-40 shows the comparison of the Fourier transformed $S(Q)$, or PDFs of sample S1 and sample S2 with the ZnO NIST standard (S4) at room temperature (RT).

Figure 4-40: Comparison of the Fourier transformed $S(Q)$, or PDFs of sample S1 and sample S2, with ZnO NIST standard (S4) at room temperature (RT). The inset shows the enlarged area from 1.5 – 4.0 Å.

As seen from Figure 4-40, the intensities of the Zn-Zn correlation peaks are lower than the ZnO NIST standard (sample S4) for both sample S1 and sample S2, while the Zn-O correlation peaks have no change in intensity (specifically shown in the inset – red circle). Assuming that the ZnO NIST standard (SRM 674b) (sample S4) has the ideal stoichiometry of ZnO, the results obtained suggests that zinc vacancies are present in the as-synthesized ZnO powder sample S1 and sample S2 at room temperature.

Further analysis of the powders was attempted using PDFgui.²²⁰ Data were first inputted into the programme PDFFit2 and PDFgui. The PDF function, $G(r)$ data were then studied. The total PDF, $G(r)$, of the ZnO samples at room temperature essentially contain structural information in real-space and are the

Fourier Transforms of the reduced structure factor $Q[S(Q)-1]$. It uses similar parameters, e.g. lattice parameters, atomic displacement parameters, occupancies etc. to those used in a Rietveld refinement of powder diffraction data but performs it on the real space $G(r)$ data. More details of the fitting analysis have been given in Section 2.4.6. Table 4-8, Table 4-9 and Table 4-10 show the refined structural parameters from *in situ* PDF fitting of X-ray total scattering data for sample S1, sample S2 and sample S4, respectively.

Table 4-8: Refined structural parameters from *in situ* PDF fitting of X-ray total scattering data for sample S1.

S1	a = b (Å)	c (Å)	Vol. (Å ³)	Zn			O			Occupancy		Red. chi ²	Rw
				u11 = u22	u33	u12	u11 = u22	u33	u12	Zn	O		
RT	3.2502 (0.0013)	5.2246 (0.0040)	47.796	0.0055 (0.00013)	0.0064 (0.00046)	0.0027	0.0084 (0.00072)	0.0051	0.0042	1.0195 (0.013)	0.8570 (0.030)	0.16	0.14
200°C	3.2551 (0.0015)	5.2255 (0.0047)	47.948	0.0108 (0.00027)	0.0121 (0.00095)	0.0054	0.0159 (0.0015)	0.0069	0.0080	1.0202 (0.014)	0.8439 (0.032)	0.15	0.14
400°C	3.2598 (0.0018)	5.2279 (0.0057)	48.110	0.0143 (0.00036)	0.0155 (0.0013)	0.0072	0.0219 (0.0022)	0.0118	0.0110	1.0169 (0.014)	0.8648 (0.036)	0.14	0.15
600°C	3.2646 (0.0021)	5.2262 (0.0065)	48.237	0.0200 (0.00052)	0.0202 (0.0017)	0.0100	0.0296 (0.0032)	0.0344	0.0148	1.0064 (0.015)	0.9455 (0.041)	0.12	0.15
Cooled to RT	3.2486 (0.0011)	5.2171 (0.0035)	47.681	0.0080 (0.00018)	0.0091 (0.00061)	0.0040	0.0114 (0.00095)	0.0058	0.0057	1.0254 (0.012)	0.8121 (0.027)	0.15	0.12

Table 4-9: Refined structural parameters from *in situ* PDF fitting of X-ray total scattering data for sample S2.

S2	a = b (Å)	c (Å)	Vol. (Å ³)	Zn			O			Occupancy		Red. chi ²	Rw
				u11 = u22	u33	u12	u11 = u22	u33	u12	Zn	O		
RT	3.2500 (0.0013)	5.2246 (0.0040)	47.792	0.0055 (0.00013)	0.0064 (0.00046)	0.0027	0.0087 (0.00074)	0.0059 (0.003)	0.0043	1.0190 (0.013)	0.8676 (0.030)	0.16	0.14
200°C	3.2552 (0.0015)	5.2279 (0.0049)	47.974	0.0077 (0.0002)	0.0089 (0.00069)	0.0039	0.0109 (0.0011)	0.0068 (0.0042)	0.0055	1.0248 (0.014)	0.8167 (0.032)	0.14	0.13
400°C	3.2606 (0.0018)	5.2297 (0.0059)	48.150	0.0113 (0.0003)	0.0124 (0.001)	0.0057	0.0181 (0.0018)	0.0102 (0.0061)	0.0090	1.0199 (0.015)	0.8490 (0.037)	0.12	0.14
600°C	3.2657 (0.0022)	5.2307 (0.0067)	48.311	0.0161 (0.00043)	0.0157 (0.0014)	0.0080	0.0224 (0.0026)	0.0270 (0.0098)	0.0112	1.0109 (0.016)	0.9169 (0.042)	0.10	0.14
Cooled to RT	3.2493 (0.0011)	5.2193 (0.0036)	47.722	0.0047 (0.00011)	0.0052 (0.00036)	0.0023	0.0062 (0.00058)	0.0046 (0.0024)	0.0031	1.0278 (0.012)	0.7961 (0.027)	0.15	0.12

Table 4-10: Refined structural parameters from *in situ* PDF fitting of X-ray total scattering data for sample S4 (ZnO NIST standard SRM 674b).

S4	a = b (Å)	c (Å)	Vol. (Å ³)	Zn			O			Occupancy		Red. chi ²	Rw
				u11 = u22	u33	u12	u11 = u22	u33	u12	Zn	O		
RT	3.2479 (0.0011)	5.2149 (0.0034)	47.641	0.0115 (0.00027)	0.0127 (0.00087)	0.0057	0.0157 (0.0014)	0.0071 (0.0049)	0.0079	1.0489 (0.012)	0.8176 (0.027)	0.14	0.12
600°C	3.2657 (0.0022)	5.2298 (0.065)	48.303	0.0163 (0.00043)	0.0154 (0.0014)	0.0081	0.0275 (0.0028)	0.0239 (0.0092)	0.0138	1.0061 (0.016)	0.9506 (0.043)	0.11	0.14

From the refinement, it was found that the lattice parameters of sample S1 increases upon annealing *in situ* from $a = 3.2502 \text{ \AA}$ for the as-synthesized sample to $a = 3.2646 \text{ \AA}$ at 600°C , and $c = 5.2246 \text{ \AA}$ for the as-synthesized sample to $c = 5.2262 \text{ \AA}$ at 600°C . This also leads to an increase in cell volume from $47.796 \text{ \AA}^3$ for the as-synthesized sample to $48.237 \text{ \AA}^3$ at 600°C . The lattice parameters of sample S2 also similarly increases upon annealing *in situ* from $a = 3.2500 \text{ \AA}$ for the as-synthesized sample to $a = 3.2657 \text{ \AA}$ at 600°C , and $c = 5.2246 \text{ \AA}$ for the as-synthesized sample to $c = 5.2307 \text{ \AA}$ at 600°C . This similarly leads to an increase in cell volume from $47.792 \text{ \AA}^3$ for the as-synthesized sample to $48.311 \text{ \AA}^3$ at 600°C . This expansion in the lattice may be due to the increase in thermal vibrations at high temperatures. Upon cooling the sample back to room temperature, the cell volume returns to a value close to that of the as-synthesized sample, with a slight reduction of 0.241% for sample S1 and 0.146% for sample S2.

U parameters are related to the thermal disorder of the system and these values increases as temperature increases, and decreases again when the samples are cooled back to room temperature.

Attempt was made to refine the occupancies of Zn and O. First we analysed the ZnO NIST standard. From this best fit, the refinement yielded predominantly oxygen vacancies even at room temperature, which is difficult to rationalize. Ideally, the ratio of O to Zn should equate to 1, however the refinement revealed that this value deviates from 1 and yielded a ratio of 0.78. Therefore, it is not clear if the NIST standard contains oxygen vacancies in the system. This analysis procedure contains errors; however, in order to rationalize the remaining results, this value of 0.78 was taken as a base standard. Thus, comparing the occupancies of sample S1 and S2 with sample S4 (ZnO NIST standard SRM 674b), the ratios of O to Zn obtained for sample S1 was 0.84 and

0.85 for sample S2. These higher values as compared to sample S4 indicate more zinc vacancies in the real systems as compared with the NIST standard. After annealing and cooling down to room temperature, the values become closer to that of the ZnO NIST standard. There is a possibility that zinc vacancies were annihilated during the annealing process. Furthermore, there is a high correlation between temperature factor and occupancy which may lead to an underestimate in the refined parameters of the PDF analysis. Thus, the values obtained for the occupancies of Zn and O may not be real and varies with the R-range of about a 10 Å distance. The reliability of the results obtained for the occupancies of Zn and O is greatly reduced. It is difficult to accurately model the structure without the information on the stoichiometry of the NIST standard.

Nonetheless, this high energy X-ray diffraction technique has enabled the study of defects within the lattice at the atomic scale as compared to observing only the microstructure from microscopy, and thus proves to be a useful technique in complementing the results obtained from X-ray absorption spectroscopy, which is a more reliable characterization technique.

4.9 Discussion

Ex situ XAS measurements found that the as-synthesized ZnO powder samples contain predominantly zinc vacancies. *In situ* PDF analysis similarly found zinc vacancies present in the ZnO powder samples. Room temperature PL mapping studies showed the presence of a green and yellow band in the as-synthesized ZnO samples, indicating the presence of zinc vacancies and the doubly charged oxygen vacancy, respectively. When the ZnO powders were annealed in air at temperatures from 200°C – 600°C, there was a red-shift suggesting the presence of oxygen interstitials. From the PL results, as annealing temperature increases, there is a shift from green to yellow to red, suggesting that

the net zinc vacancies reduces and oxygen interstitials become more prominent in the ZnO powder system. From XAS results, because the Zn central atom was probed, no information can be obtained about oxygen interstitials. Nonetheless, the presence of zinc vacancies is confirmed by XAS and PL mapping. Furthermore, an *in situ* total scattering experiment was carried out with PDF analysis done and it was found that in the short to medium range structure order, zinc vacancies are present. This is shown by a reduction in the Zn-Zn peak intensities when compared with a ZnO standard (sample S4) (purchased from NIST, SRM 674b). However, further investigation is needed to substantiate the results.

4.10 Conclusion of Chapter 4

This chapter investigated the local structure of ZnO powders grown by various chemical precursor routes and at different pHs. In the first part of the chapter, a study of moderate pH (~ 8.0) grown ZnO powders were studied. This low pH grown ZnO synthesis step is typically used for growing a seed layer when high quality epitaxial films are grown using a two-step solution synthesis method. X-ray absorption spectroscopy (XAS) and pair distribution function (PDF) analysis found that zinc vacancies are predominant in the system of solution synthesized ZnO grown at moderate pH (pH ~ 8.0) that is typically used as a seed layer for subsequent film growth.

In the next part of the chapter, ZnO powder (sample S1) was synthesized to mimic the ZnO film and studied using XAS and X-ray total scattering. In addition, another sample of ZnO powder (sample S2) was synthesized using a ZnO standard (purchased from NIST) as a seed, and similarly studied. *Ex situ* XAS measurements found that the ZnO powders predominantly contain zinc vacancies. From the *in situ* pair distribution function (PDF) experiment, it was found that in the short to medium range structure order, zinc vacancies are present. This is

shown by a reduction in the Zn-Zn peak intensities when compared with a ZnO standard (purchased from NIST, SRM 674b).

In conclusion, an elucidation of the local atomic structure of ZnO grown by low temperature aqueous solution route has been presented in this chapter and results generally show a predominance of zinc vacancies in the ZnO powder system albeit the seed used for the powder synthesis. These results will potentially be useful in the aid for the further development of ZnO for applications in catalysis and gas sensing, etc.

Chapter 5

Growth and Characterization of ZnO Nanorods

5.1 Summary of Chapter 5

Zinc oxide (ZnO) nanorods, which is the most commonly observed morphology of ZnO was synthesized using a very well-known method of solution synthesis, i.e., through the use of a zinc precursor and hexamethylenetetramine (HMT/HMTA). The nanorods were then post-growth annealed to enhance the optical properties of the ZnO nanorods and also to determine if induced thermal porosity is a common occurrence in solution synthesized ZnO. It was found that these ZnO nanorods exhibited porosity formation similar to that observed in the ZnO films (Chapter 3). A detailed study of the synthesized ZnO nanorods was then carried out using transmission electron microscopy (TEM). A three-dimensional electron tomography reconstruction was done to show that the pores exist within the nanorod. Upon increasing the annealing temperature or annealing for extended periods of time, these pores then strived to reduce the total surface energy of the system by coalescing and were subsequently forced out of the morphology, as observed by an *in situ* TEM study. Further defect characterization was also performed using extended X-ray absorption fine structure (EXAFS) spectroscopy and it was found that zinc vacancies are predominantly present in the as-synthesized ZnO nanorods synthesized using this chemical precursor route. The understanding of this pore formation will aid in the exploitation of ZnO

nanorods for use in device applications such as dye-sensitized solar cells, catalysis systems and sensors.

5.2 Characterization of ZnO Nanorods

The synthesis of ZnO nanorods via a zinc precursor and hexamethylenetetramine (HMT/HMTA) route has been described in Section 2.3.

5.2.1 Crystallinity of ZnO Nanorods

The crystallinity of the obtained ZnO nanorods was investigated using X-ray diffraction (XRD). The XRD pattern showed that the ZnO nanorods were highly crystalline with a prominent *c*-axis peak given by a strong (002) reflection at about $2\theta = 34.5^\circ$. All other peaks obtained matched closely with the ZnO database JCPDS 36-1451.¹⁹⁴ The XRD pattern is given in Figure 5-1.

Figure 5-1: XRD pattern of ZnO nanorods grown on Si wafer wafer using equimolar zinc nitrate hexahydrate and hexamethylenetetramine precursors.

5.2.2 Morphology of ZnO Nanorods

ZnO obtained from the synthesis via a zinc nitrate and HMT precursor route yielded nanorod morphology, as expected from this synthesis route. Figure 5-2 shows the field emission gun scanning electron microscope (FEGSEM) image obtained in plane-view (Figure 5-2 (a)) and the cross-sectional view (Figure 5-2 (b)). The ZnO nanorods obtained are about 1 – 1.5 μm in length with a diameter of about 50 – 80 nm.

Figure 5-2: FEGSEM images of ZnO nanorods grown on Si wafer using equimolar zinc nitrate hexahydrate and hexamethylenetetramine precursors; (a) plane-view, (b) cross-sectional view.

5.3 Detailed Investigation of Thermally Induced Porosity in ZnO Nanorods Using TEM

As shown in Chapter 3, the post-growth annealing of ZnO films improves its optical and electrical properties. However, the post-growth annealing of ZnO films led to induced thermal porosity.¹⁵⁴ Annealing of ZnO powders grown at pH 10.9 also showed the presence of pores within the nanostructure, as seen from TEM images in Section 4.4.3 (Figure 4-12 and Figure 4-13). Annealing is an important process in the fabrication of devices in order to improve the opto-electrical properties of ZnO. From the porosity observed in the ZnO powders, it is seen that by inducing porosity, the surface area to volume ratio of the ZnO powders can be increased and this may potentially be useful for energy

conversion and storage, photonics, catalytic or gas sensor applications. Few research groups have reported the presence of porous ZnO nanorods.²²⁴⁻²²⁶

In this chapter, ZnO nanorods were synthesized via a very common precursor route (i.e., through the use of a zinc precursor and HMT) and post-growth thermal annealed in order to determine if induced thermal porosity is a common occurrence in solution synthesized ZnO. The use of transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM) and electron tomography has allowed the imaging and analysis of three-dimensional structure of ZnO nanowires and nanobelts.²²⁷ This technique is thus exploited to investigate the pores formed within the ZnO nanorod when annealed.

5.3.1 Characterization of ZnO Nanorods by HRTEM

Typical TEM and high resolution TEM (HRTEM) imaging was carried out on the ZnO nanorods synthesized and its annealed (at 600°C) counterpart. The ZnO nanorods are about 1 – 1.5 μm in length with a diameter of about 50 – 80 nm. It has been observed that pore formation occurs in ZnO nanorods after heat treatment of the ZnO. Analogous to the thermal porosity observed in ZnO films, thermal annealing has caused the formation of pores through the desorption of hydroxyl groups from the nanorods leaving anion vacancies to combine with cation vacancies to form pores.¹⁵⁴ Figure 5-3 shows the bright field TEM and HRTEM images of as-synthesized ZnO nanorods at magnifications of (a) 15k, (b) 50k, and (c) 300k, and (d) the corresponding selected area electron diffraction (SAED) pattern. The nanorods are single crystalline with a *c*-axis growth direction. Figure 5-4 shows the shows the bright field TEM and HRTEM images of ZnO nanorods after annealing at 600°C at magnifications of (a) 15k, (b) 25k, (c) 50k, (d) 150k, and (e) 300k, and (f) the corresponding selected area electron diffraction (SAED) pattern.

Figure 5-3: TEM and HRTEM images of as-synthesized ZnO nanorods at magnifications of (a) 15k, (b) 50k, and (c) 300k, and (d) the corresponding SAED pattern, with zone axis $[12\bar{1}0]$.

Figure 5-4: TEM and HRTEM images of ZnO nanorods after annealing at 600°C at magnifications of (a) 15k, (b) 25k, (c) 50k, (d) 150k, and (e) 300k, and (f) the corresponding SAED pattern, with zone axis $[12\bar{1}0]$.

Pores formed are not aligned in any order and are random. Further *in situ* TEM studies were then carried out to prolong annealing time and observe *in situ* the changes that occur in the formation of such pores (Section 5.3.4).

5.3.2 Characterization of ZnO Nanorods by STEM

High angle annular dark field-scanning transmission electron microscope (HAADF-STEM) images are dominated by mass-thickness contrast and are much less sensitive to the complexity associated with diffractions and Fresnel fringes. As a result, nanosized pores were clearly visualized in the ZnO nanorods, even

when they were as small as 1 nm. Several STEM studies were previously similarly carried out on CeO₂ nanoparticles.^{228,229}

STEM images show that clearly visible pores are present in the ZnO nanorods annealed at a temperature of 500°C as seen in Figure 5-5 (b). The as-synthesized ZnO nanorod is shown in Figure 5-5 (a). From Figure 5-5 (b), pores are visibly randomly distributed and have a vast distribution in size from as small as visibly possible, i.e., about 5 nm to as large as 50 nm. It is noted that STEM imaging can image up to a resolution of 1 nm as shown from the imaging of CeO₂ nanoparticles.²²⁸

Figure 5-5: STEM images of ZnO rods (a) as-synthesized, and (b) after annealing at 500°C for 1 h in air.

Figure 5-6: EELS spectra obtained from ZnO nanorods.

Richardson *et al.*¹⁵⁴ postulated the pore formation mechanism in ZnO films. A similar mechanism is expected for ZnO nanorods. An electron energy loss spectroscopy (EELS) analysis was carried out and the presence of O *K*-edge and Zn *L*-edge is evident from the peaks at 532 eV and 1020 eV respectively. It is observed that nitrogen (N) *K*-edge ionization edge peak is absent in the spectrum at 401.6 eV of energy loss (shown in Figure 5-6), indicating that NH₃ gas had not evolved. Thus, the pore formation is attributed to the coalescence of cation and anion vacancies in the system, similar to the mechanism proposed by Richardson *et al.*¹⁵⁴ and as outlined in Section 3.2.2 for the induced thermal porosity of the ZnO film.

5.3.3 Electron Tomography of ZnO Nanorod

Imaging and visualization of three-dimensional structures of materials at the nanometer scale can provide imperative information on the performance of their applications and offer insight into the growth and behavioural mechanisms. Conventional TEM images only show two-dimensional projections of three-dimensional particles. This makes it tricky to recognize the crystallographic orientation and location of pores from a single TEM image. Electron tomography allows a three-dimensional reconstruction of two-dimensional images, permitting to resolve complex morphologies and geometries to characterize internal crystal structures of materials at the nanometer scale. Thus, a detailed analysis of the three-dimensional shape and morphology of porous ZnO nanorods was done using electron tomography.

Figure 5-7 shows microscope images of the ZnO nanorods after annealing at 600°C in air for 1 h. Figure 5-7 (a) shows the FEGSEM image showing pores in the ZnO nanorods. It seems that the pores are seen in the fractured surface of the rods of the image, shown by the black circles on the image. Figure 5-7 (b) and (c) shows the slice-view in the xy-direction and the xz-direction of the ZnO nanorod STEM image, respectively, showing the cross-sections whereby isolated pores are visibly present.

Figure 5-7: (a) FEGSEM image showing pores in the ZnO nanorods after annealing at 600°C, (black circles indicate pores present) (b) slice-view in the xy-direction of ZnO nanorod STEM image showing the cross-section whereby pores are visibly present after annealing at 600°C, (c) slice-view in the xz-direction of ZnO nanorod STEM image showing isolated pores after annealing at 600°C.

Figure 5-8: 3-D reconstructed tomography images, showing the isolated pores present within the nanorod at different angles.

Figure 5-8 shows a three-dimensional reconstruction of the tip of one single-crystalline ZnO nanorod. Segmentation was used to identify the surface of the particle and the outline of individual pores by automatic selection of the threshold values of the crystal and the pores, and the subsequent manual touch-up was applied to remove as much as possible the missing wedge artefacts. The

reconstruction has enabled the observation that isolated pores are present within the ZnO nanorods and are not merely on the surface.

5.3.4 Characterization of ZnO Nanorods by *In situ* TEM

Because of the distinct pore formation observed after annealing at varying temperatures, an *in situ* TEM study was performed to monitor the pore formation and its subsequent behaviour. Initial TEM images of the as-synthesized nanorods at room temperature do not show the presence of pores but as the temperature of the TEM hot stage increases, the pores become more prominent and enlarge in size. Figure 5-9 shows the *in situ* TEM images of the same ZnO nanorods (a) at about 320°C, (b) as the temperature is increased to 469°C, (c) as the temperature is increased to 553°C, and (d) finally when the TEM hot stage is at 638.8°C. These images were taken after maintaining the temperature for at least 1 hour to ensure that it is stable before imaging.

Figure 5-9: *In situ* TEM images of the same ZnO nanorod (a) at about 320°C, (b) as the temperature is increased to 469°C, (c) as the temperature is increased to 553°C, and (d) finally when the TEM hot stage is at 638.8°C. Dotted circles showing pores coming together or the coalescence of small pores to form bigger pores as the temperatures further increases.

Figure 5-10: Enlarged *in situ* TEM images of the tip of the same ZnO nanorod in Figure 5-9. Black arrows indicate pores coming together. The black circles indicate a pore after the coming together of two pores as the temperatures further increases.

As observed, prominent pores form when the temperature of the hot stage is above 300°C. This can be correlated to the pore formation observed in the ZnO films as reported by Richardson *et al.*¹⁵⁴ These pores appear relatively small in size initially and when the temperature is further increased, there is an increase in the number of pores as well as pore size. This is observed in Figure 5-9 (b) and (c). There seems to be a coming together or coalescence of small pores to form

bigger pores as the temperatures further increases. This can be seen when comparing Figure 5-9 (c) and (d) as the temperature increases from 553°C to 638.8°C, as shown by the black dotted circles. This is attributed to a need for the minimization of surface energy of the entire system.

Figure 5-10 shows the enlarged *in situ* TEM images of the tip of the same ZnO nanorods as in Figure 5-9. The white arrows indicate the pores coming together. The white circles show a pore after the coming together of two pores as the temperatures further increases. In Figure 5-10 (b), it is seen that 2 small pores of diameters about 50 nm and 85 nm move towards each other and join together to form one pore of diameter about 65 nm as seen in the black circle in Figure 5-10 (c). A similar occurrence is observed in Figure 5-10 (c) to Figure 5-10 (d), as the temperature further increases.

Subsequently, another experiment was carried out to verify the pore formation and coalescence behaviour as observed earlier. The temperature of the system is slowly increased and allowed to stabilize at a temperature of 540°C before imaging. No initial pores were observed before the temperature was increased. Figure 5-11 and Figure 5-12 shows the pore formation and coalescence in the ZnO nanorods. Images were taken at intervals of 10 min for the first hour (Figure 5-11) and subsequently at regular intervals of about 30 min (Figure 5-12). We track the formation and coalescence of pores over a total 5 h time period. It was observed that initially there are a small number of pores, a few large observable ones while more small pores form. These pores then seem to come together as time progresses and become larger in size as they coalesce together. Finally, as pores coalesce together, there is a decrease in the number of pores as time proceeds.

In addition, another phenomenon visibly present is the distortion and change of the shape and size of the ZnO nanorod. It is observed that the final ZnO

nanorod after cooling to room temperature, Figure 5-12 (h), is significantly smaller and varies distinctly different from its initial shape as seen in Figure 5-11 (a). Pores seemed to have escaped from the surface of the ZnO nanorod and have caused this distortion and decrease in area and consequent reduction in volume of the ZnO nanorod. This is observed strongly after the 180th min (Figure 5-12 (c)) of the experiment where there is a change of shape and the size of the nanorod and is most significantly decreasing. This is also attributed for the need to minimize the surface energy of the entire system.

Figure 5-11: *In situ* TEM images of the same ZnO nanorod at 540°C tracked over the 1st hour.

Figure 5-12: *In situ* TEM images of the same ZnO nanorod at 540°C tracked over (a-g) the next 4 hours and (h) after cooling back to room temperature.

A portion of the nanorods were taken for further examination. This was set at an area of 250 nm by 120 nm towards the right end of the rod. Imaging processing was first done to enhance the visual for clearer observation of the pores. An example of how the images were processed is shown. First, the colours

of the image were inverted to allow for a clearer observation of the pores. This is shown in Figure 5-13 for the TEM image taken at 0 min, where Figure 5-13 (a) is the original TEM image, and Figure 5-13 (b) shows the image when the colours were inverted.

Figure 5-13: TEM image processing procedure showing (a) the original image, and (b) the image with the colours inverted.

Figure 5-13 (b) was then used for further inspection. A specific area of the rod is selected for further inspection (set at 250 nm by 120 nm) towards the right end of the rod, as shown in Figure 5-14 (a). Figure 5-14 (b) shows the enlarged selected area used for selecting the pores.

Figure 5-14: (a) Selected area of nanorods used for further image inspection (set at 250 nm by 120 nm), and (b) the enlarged selected area.

This was done for all the images at each respective time. Figure 5-15 shows the enlarged selected areas of the ZnO nanorods corresponding to Figure

5-11 and Figure 5-12. It is observed that there is a general increase in the trend of the total area of pores as time proceeds, with some pores getting larger over time. In addition, there is the formation of new pores as time proceeds.

From Figure 5-15, it is observed that there is a coalescence of pores. In addition, it is also observed that some pores get larger over time. Generally, the former is likened to an Ostwald ripening process.²³⁰ Larger pores grow at the expense of smaller ones. The size of the smaller pores will be reduced or may even disappear owing to the net atomic transport to the larger pore. The latter seems to be caused by smaller pores joining to that pore from the top or bottom which cannot be seen in the two-dimensional TEM image. Alternatively, the increase in size of the pore may be due to the same mechanism as the formation of pores as reported by Richardson *et al.*,¹⁵⁴ whereby cation and anion vacancies come together to form a pore. The pores may possibly get larger by having vacancies added to it. Although this cannot be observed from the TEM images directly as it is only a two-dimensional representation, it seems to be a plausible cause for the increase in size of the pore.

Figure 5-15: Enlarged selected areas of the ZnO nanorods corresponding to Figure 5-11 and Figure 5-12, showing the increase in area of the pores with time.

Three pores were then separately tracked over time. Firstly, the large pore on the left side of the images (pore 1, shown in the red circle of Figure 5-15 (a)) was used for tracking from 0 min to 300 min. Another pore (pore 2, shown in the blue circle of Figure 5-15 (a)) was similarly tracked from 0 min to 150 min, as beyond that time it is not quite noticeable anymore. Also, another pore (pore 3, shown in the green circle of Figure 5-15 (a)) was similarly tracked from 0 min to 50 min, as beyond that time it is not quite noticeable anymore. Figure 5-16 shows the linear fit of the projected pore radius cubed, r^3 plotted against time, for 3 different pores as labelled in Figure 5-15 (a); (a) for pore 1, (b) for pore 2, and (c) for pore 3. It is seen that the radius cubed generally increases linearly with time. All linear fits obtained have an R-squared value or goodness of fit of at least 0.92. This is attributed to an Ostwald²³⁰ ripening process.²³¹ This unstructured process happens due to larger pores being favoured over smaller pores. This formation of a larger pore is thermodynamically favoured. Larger pores have a smaller surface area to volume ratio and are stable in a lower energy state. The rate law can be derived from the Gibbs-Thomson equation and Fick's Law.²³¹ Also, Lifshitz and Slyozov²³² and later Wagner,²³³ developed a theory known as the LSW theory. In both cases, the equation given is $\bar{r}^3 = Kt$, where $\bar{r}$ is the average pore radius and K is a temperature and material dependence constant.^{231,234}

Figure 5-16: Fit of the projected pore radius cubed, r^3 plotted against time, for 3 different pores as labelled in Figure 5-15 (a); (a) for pore 1, (b) for pore 2, and (c) for pore 3.

In addition, there is the coalescence of pores as indicated by the black arrows in Figure 5-15 (b) to (e) for 2 pores which seem to come together from 10

min to 40 min. In Figure 5-15 (f), i.e., at 50 min, it is observed that the two pores have now merged to become one pore, as indicated by the black circle. Furthermore, as indicated by the white arrows in Figure 5-15 (g) to (n), i.e., from 60 min to 300 min, it is observed that there is the escape of pores to the surface of the material, governed by the reduction in surface energy given by the area of the pore multiplied by the surface energy of ZnO nanorods, γ . This causes the surface to become rough. Shrinkage of the total material is observed. These mechanisms strive to reduce the total energy of the system by minimizing surfaces. It is noted that these mechanisms may occur simultaneously within the ZnO nanorod during the annealing process.

5.4 XAS Analysis of ZnO Nanorods Synthesized Via the HMT Route

XAS measurements were conducted on the ZnO nanorods grown via a HMT route. Figure 5-17 shows the Zn *K*-edge XANES spectrum for ZnO nanorods synthesized via the HMT route as-synthesized and after annealing in air at temperatures from 200°C – 600°C.

Figure 5-17: Zn K-edge XANES spectra for ZnO nanorods synthesized via the HMT route (as-synthesized and after annealing at temperatures from 200°C – 600°C).

The absorption edge is observed at 9658.97 eV, corresponding to the Zn *K*-edge binding energy. XANES is typically used to study the variation of core electron configuration and can give information about the valency changes of atoms in a matrix. From Figure 5-17, it is observed that there are no shifts in the XANES edge position indicating that the electronic configuration for the Zn central atom was unchanged and is stable. There are no changes in the valence of Zn in the system even as the sample is annealed up to 600°C.

Figure 5-18 shows the Zn *K*-edge extended X-ray absorption fine structure (EXAFS) spectra in $\chi(k)$ of the ZnO nanorods (a) as-synthesized, and after annealing at (c) 200°C, (e) 400°C, and (g) 600°C. The Fourier Transform and its imaginary part are correspondingly shown beside the EXAFS spectra. The first two prominent peaks in the Fourier Transform are assigned to the first two coordination shells of ZnO at *ca.* 1.9 Å (Zn-O) and 3.2 Å (Zn-Zn), respectively. Refinement was performed using a k^3 weighting. The $k^3\chi(k)$ for the ZnO nanorods as a function of the photoelectron wave vector k , gives information about the mean immediate atomic environment of the specified lattice site.²⁰¹ The

measurements were fitted using a starting model which is assumed to be ideal. The fit methodology followed the same procedure as reported in Section 3.3 for ZnO films and in Section 4.5 for ZnO powders, with details given in Section 2.4.5. The EXAFS of the ZnO nanorods measured fit well with the corresponding ZnO crystallographic information file (*CIF*)²⁰² used for the analysis, with minimal error. For a quantitative analysis of the local structural properties, we studied the Fourier Transformed data in R-space. To minimize errors, only data in the *k*-range 2.54 – 11.0 Å⁻¹ was used for further analysis.

Figure 5-18: *Ex situ* Zn K-edge EXAFS spectra in $\chi(k)$ of ZnO nanorods synthesized via the HMT route (a) as-synthesized, and after annealing at (c) 200°C, (e) 400°C, and (g) 600°C. The corresponding imaginary part and Fourier Transform is shown for ZnO nanorods (b) as-synthesized, (d) 200°C, (f) 400°C, and (h) 600°C.

The final values obtained from the fit of the ZnO nanorods as-synthesized and after annealing at temperatures of 200°C – 600°C for 1 h in air are shown in Table 5-1. The ZnO NIST standard was similarly analyzed and shown in Table 5-2. The coordination number (N) of Zn-O and Zn-Zn correlations are determined by multiplying the ideal coordination (i.e., 4 and 12, respectively) by the occupancies obtained from the EXAFS fit. The average atomic distance, r , between the central Zn atom and the first nearest neighbour, i.e., oxygen (O) is obtained by fitting the singly scattered paths which are calculated for the EXAFS of ZnO, and taking the average. The Debye-Waller factor, σ^2 , is a function of disorder and temperature provides information about the stiffness of the bonds and the mass of the atoms.¹⁶⁸

The analysis revealed that the next nearest neighbour distance obtained for the as-synthesized nanorods was 1.97 Å for the Zn-O correlation and next nearest neighbour distance was 3.25 Å for the Zn-Zn correlation. These values remained relatively constant even after annealing at temperatures up to 600°C. The Debye-Waller factor (σ^2) of the Zn-O pair was 0.001 Å² and 0.010 Å² for the Zn-Zn pair of the ZnO films. All values obtained correspond within the error limits of those reported by similar studies.^{201,203-206}

Table 5-1: Structural parameters obtained from the EXAFS analysis of Zn K-edge data on ZnO nanorods annealed *ex situ*.

	Zn-O			Zn-Zn			R-factor	Ratio of Zn-O to Zn-Zn
	N-1	R-1 (Å)	σ^2 -1 (Å ²)	N-2	R-2 (Å)	σ^2 -2 (Å ²)		
As-synthesized	3.8 (0.1)	1.97 (0.01)	0.001 (0.003)	11.0 (0.4)	3.25 (0.01)	0.010 (0.004)	0.044	0.345
HT 200°C	4.1 (0.2)	1.98 (0.02)	0.004 (0.003)	11.6 (0.4)	3.24 (0.01)	0.010 (0.003)	0.045	0.353
HT 400°C	3.9 (0.2)	1.98 (0.02)	0.003 (0.003)	14.2 (0.5)	3.25 (0.01)	0.011 (0.004)	0.055	0.275
HT 600°C	3.9 (0.1)	1.98 (0.01)	0.003 (0.003)	9.4 (0.3)	3.24 (0.01)	0.008 (0.003)	0.035	0.415

Table 5-2: Structural parameters obtained from the EXAFS analysis of Zn K-edge data on ZnO NIST standard (sample S4) annealed *ex situ*.

S4	Zn-O			Zn-Zn			R-factor	Ratio of Zn-O to Zn-Zn
	N-1	R-1 (Å)	σ^2 -1 (Å ²)	N-2	R-2 (Å)	σ^2 -2 (Å ²)		
NIST standard	3.9 (0.2)	1.97 (0.02)	0.005 (0.004)	11.9 (0.2)	3.22 (0.01)	0.007 (0.002)	0.016	0.328
HT 200°C	4.2 (0.3)	1.98 (0.02)	0.005 (0.004)	13.1 (0.3)	3.22 (0.02)	0.008 (0.002)	0.021	0.321
HT 400°C	4.0 (0.3)	1.98 (0.02)	0.004 (0.004)	13.1 (0.3)	3.22 (0.02)	0.008 (0.002)	0.023	0.305
HT 600°C	4.0 (0.2)	1.97 (0.02)	0.005 (0.004)	12.0 (0.2)	3.22 (0.01)	0.007 (0.002)	0.015	0.333

To determine the local structure order defects, the coordination numbers of the Zn-O and Zn-Zn correlations are considered. Annealing conditions were kept invariable for all the samples for direct comparison. The coordination number (N) represents the number of nearest neighbour atoms surrounding the central Zn atom. A study of the coordination numbers was performed, analogous to that performed for the ZnO films in Section 3.3, as the measurements were also performed in fluorescence mode and the sample may have self absorption issues. In general, the coordination of an ideal ZnO system will have 4 nearest neighbours of Zn-O coordination and 12 next nearest Zn atoms with reference to the central Zn atom at the origin. This gives a ratio of 0.333 for Zn-O to Zn-Zn coordination.

From Table 5-1, the as-synthesized nanorods have a coordination number of 3.8 for the Zn-O correlation and a coordination number of 11.0 for the Zn-Zn correlation. Taking the ratio of Zn-O to Zn-ZnO coordination numbers yields a value of 0.345, which is greater than 0.333, indicating a system with zinc vacancies, analogous to the results obtained from Section 3.3 for ZnO films. As the ZnO nanorods are further annealed at 200°C, there is a slight increase of zinc vacancies as the ratio of the coordination numbers of Zn-O to Zn-Zn increases. However, after annealing at 400°C, there seems to be oxygen vacancies present in the system as the ratio obtained (0.275) is lower than the ideal ZnO coordination ratio of 0.333. When the ZnO nanorods are further annealed to 600°C, there is however, a large increase in zinc vacancies as the ratio obtained (0.415) for the Zn-O to Zn-Zn coordination is much higher than 0.333.

5.5 Photoluminescence Spectroscopy of ZnO Nanorods

Photoluminescence (PL) mapping was carried out to determine the optical properties of ZnO nanorods synthesized by a zinc nitrate precursor and HMT route. Post-growth annealing of ZnO films have been demonstrated by Le *et al.*^{46,161} Thermal annealing is said to improve the optical quality of ZnO nanorods particularly when oxygen is used.²³⁵ Thus, ZnO nanorods were subsequently annealed in air and its optical properties studied via room temperature PL mapping.

Figure 5-19: Room temperature PL spectra of ZnO nanorods as-synthesized and after annealing at temperatures from 200°C - 600°C.

Figure 5-19 shows the PL spectra of ZnO nanorods as-synthesized and after annealing at temperatures from 200°C - 600°C. The PL spectra of ZnO nanorods show a near band edge (NBE) transition at about 3.25 eV, originating from exciton radiative recombination.²⁰⁷ The as-synthesized ZnO usually consists of many lattice and surface defects acting as non-radiative centres and thus reducing the light emission from the ZnO samples.¹⁶¹ After annealing, these non-radiative defects are reduced and restructured, greatly enhancing the crystal

structure leading to a reduction in the non-radiative recombination, and hence, an increase in the luminescence efficiency,¹⁶¹ shown by the sharp peak observed in the nanorods annealed at 400°C. A broad deep level emission (DLE) is also observed at lower energies (higher wavelengths) due to impurities or structural defects. This DLE is normally de-convoluted by Gaussian-fitting into three colour bands (red, yellow, green) for further analysis. There are various literature explaining the associated defects with the peaks present, although this is still a divisive topic.²⁰⁸⁻²¹¹ At *ca.* 2.25 – 2.58 eV (480 – 550 nm), the defect band is green; at *ca.* 2.03 – 2.25 eV (550 – 610 nm), the defect band is yellow; and, at *ca.* 1.65 – 2.03 eV (610 – 750 nm), it is red.²⁰⁸ The origin of the green band has been attributed to the presence of zinc vacancies.^{68,212} The yellow band has been attributed to the doubly charged oxygen vacancy.^{213,214} The red band edge is attributed to the presence of oxygen interstitials.^{213,215}

Figure 5-20: De-convoluted defect level emission for PL spectra of ZnO nanorods (a) as-synthesized, and annealed at (b) 200°C, (c) 400°C and (d) 600°C.

The defect level emission curves were de-convoluted by Gaussian-fitting analysis and presented in Figure 5-20. The as-synthesized sample consists of a large yellow and green band, a high degree of green and yellow bands centred at approximately 2.4 eV (510 nm) and 2.0 eV (610 nm), respectively. This is due to

zinc vacancies and the doubly charged oxygen vacancies (V_o^{2+}), respectively.²¹²⁻²¹⁴

As the annealing temperature increases to 400°C and 600°C, there is an obvious red-shift. The green luminescence band is reduced when the nanorods were annealed at 600°C. Concurrently, the appearance of the red luminescence band becomes evidently more prominent when the nanorods were annealed at 600°C.

Figure 5-21: Correlation of the total integrated intensity of the PL spectra at each annealing temperature with the ratio of the integrated intensity of the NBE to DLE peak.

Figure 5-21 shows the correlation of the total integrated intensity of the PL spectra at each annealing temperature with the ratio of the integrated intensity of the NBE to DLE peak. As annealing temperature increases, the total integrated intensity decreases while the ratio of the NBE to DLE peak increases, reaching a peak at 400°C. The increase in the ratio of NBE to DLE represents a better crystalline quality of the ZnO nanorods at 400°C. At 600°C, there is an obvious decrease in the ratio of NBE to DLE possibly due to the presence of a large number of pores within the ZnO nanorods which indicates lots of defects.

Figure 5-22: Correlation of the integrated intensity variation of DLE of the ZnO nanorods with annealing temperature and the respective peak position at each annealing temperature.

Figure 5-22 shows correlation of the integrated intensity variation of each of the de-convoluted bands with annealing temperature and the peak positions of the DLE at each annealing temperature, for the ZnO nanorods. It is seen that the DLE peak shifts to higher wavelength or to lower energy levels (i.e., red-shift) with increasing annealing temperature.⁶⁷ The red band has been attributed to defects associated with oxygen interstitials.^{209,215} The green band has been attributed to zinc vacancies, which shows an overall reduction as temperature increases. This corresponds to the XAS results in Section 5.4.

5.6 Discussion

XAS results of the fit analysis of the as-synthesized ZnO nanorods showed a predominantly Zn deficient system. Figure 5-23 shows the correlation between the integrated intensity of the respective PL de-convoluted DLE bands and the ratio of the refined coordination numbers of Zn-O to Zn-Zn.

Figure 5-23: Correlation between the integrated intensity of the respective deconvoluted DLE bands and the ratio of the refined coordination numbers of Zn-O to Zn-Zn for the ZnO nanorods.

There is a shift in the PL DLE band from green to yellow and red as the sample is annealed at higher temperatures. The red band is attributed to oxygen interstitials. From the XAS results, because the Zn central atom was probed, no information can be obtained about oxygen interstitials. However, the presence of zinc vacancies in the as-synthesized ZnO nanorods has been confirmed by both XAS and PL mapping. It is noted that at 400°C, there is a decrease in the PL DLE green band, attributed to zinc vacancies. Simultaneously, there is a decrease in the Zn-O to Zn-Zn ratio of coordination numbers, indicating the presence of oxygen vacancies. This seems to correlate to show the decrease of zinc vacancies in the system. At 600°C, both the green band (attributed to zinc vacancies) and the ratio of Zn-O to Zn-Zn coordination similarly increases. However, it is noted that XAS is a bulk technique while PL is a surface technique and caution must be exercised when using the absolute correlations.

5.7 Conclusion of Chapter 5

ZnO nanorods were successfully synthesized by a low temperature aqueous solution route with Zn precursors and hexamethylenetetramine (HMT). The nanorods were successfully characterized by SEM, XRD and room temperature PL mapping. Post-growth annealing was carried out to liken the process to the films whereby optical properties were enhanced upon annealing. PL spectroscopy revealed an enhanced UV peak when the nanorods were annealed at 400°C.

TEM studies show that the annealing the ZnO nanorods at temperatures above 300°C, induces pores within the nanorods system. The formation of pores is attributed to the desorption of hydroxyl groups from the nanorods leaving anion vacancies to combined with cation vacancies forming a pore. Electron tomography has allowed a 3-D reconstruction of the 2-D image of the pores within the nanorods taken with STEM, clearly showing pores within the nanorods and not merely on the surface. *In situ* TEM studies clearly show the emergence of pores and subsequently, the coalescence of pores which strives to reduce the total energy of the system, analogous to an Ostwald ripening process. Pores also move towards the surface of the nanorods in order to minimize the total energy of the system. Further defect characterization was carried out using XAS found zinc vacancies to be present in the as-synthesized ZnO nanorods. As the ZnO nanorods are further annealed at 200°C, there is a slight increase of zinc vacancies as the ratio of the coordination numbers of Zn-O to Zn-Zn increases. However, after annealing at 400°C, there seems to be oxygen vacancies present in the system. When the ZnO nanorods are further annealed to 600°C, there is however, a large increase in zinc vacancies.

Thus, since ZnO nanorods are very commonly grown using a chemical solution route, careful consideration of the results obtained should be taken into account when using such nanorods for device applications. The results obtained will potentially aid in the further development of gas sensors or catalysis systems, where large internal surface areas are beneficial.

Chapter 6

Defect Structure Investigation of Low Temperature Solution Grown Ga-doped ZnO Film and Powders

6.1 Summary of Chapter 6

In this chapter, zinc oxide (ZnO) films and powders which have been doped with gallium (Ga) were investigated. The doping of ZnO with a group III element has long been studied, however, the local structure of Ga-doped ZnO is rarely reported. Common extrinsic dopants include Al, In and Ga.²³⁶ Most commonly, Ga³⁺ is doped into ZnO to enhance its optoelectronic properties. The doping of Ga³⁺ into ZnO has several advantages as the atomic radii of Ga³⁺ is similar to that of Zn²⁺, making Ga³⁺ highly soluble in ZnO.²³⁷ Ga³⁺ acts as a donor in ZnO and reduces the electrical resistivity, in turn increasing its electrical conductivity. Ga-doped ZnO (GZO) films are also said to be more stable with respect to oxidation due to Ga³⁺'s greater electronegativity as compared with Al³⁺.²³⁸ This makes GZO an appealing candidate as a transparent conducting oxide (TCO)²³⁹ for applications including solar cells, flat and flexible displays and light emitting diodes (LEDs).²⁴⁰ Traditionally, indium tin oxide (ITO) is used as a TCO but due to its scarcity and high cost, GZO is a favourable alternative due to its comparatively lower cost.²⁴¹

In this chapter, GZO films and powders have been synthesized and characterized in a similar way as the undoped ZnO films in Chapter 3 and undoped ZnO powders studied in Chapter 4, to study its local structure. Using XAS technique, experimental proof is given for the substitution of Ga^{3+} into the tetrahedral Zn^{2+} site in the lattice. This shows that Ga^{3+} is acting as a donor, generating one free carrier and increasing the carrier concentration of the GZO film.

6.2 Characterization of Epitaxial Ga-doped ZnO Films Grown on $\langle 111 \rangle$ MgAl_2O_4 Substrates

Epitaxial Ga-doped ZnO (GZO) films were grown on MgAl_2O_4 substrates in the same way to the undoped ZnO films presented in Chapter 3, except with the addition of a small amount of gallium (III) nitrate hydrate as a dopant. Synthesis details have been given in Section 2.1. The GZO films were post-growth thermally annealed at temperatures of 200°C, 400°C and 600° for 1 h in air, analogous to the undoped ZnO films in Chapter 3.

6.2.1 Crystallinity of Ga-doped ZnO Film

The epitaxial relationship between the GZO films and the substrate was established by high resolution X-ray diffraction (HRXRD). Figure 6-1 shows the gonio-scan of the as-synthesized GZO film on $\langle 111 \rangle$ MgAl_2O_4 substrate. All the annealed samples showed a similar pattern. In the $\theta/2\theta$ gonio-scan, only diffraction peaks originating from ZnO (002) and (004) planes appeared, showing that the film is *c*-oriented. Note that the small peak in Figure 6-1 at about $2\theta \approx 25^\circ$ is due to the scattering from the sample holder and can be ignored.

Figure 6-1: HRXRD $\theta/2\theta$ gonio-scan of as-synthesized GZO film on $\langle 111 \rangle$ MgAl_2O_4 substrate.

Figure 6-2: Omega (ω) scan or rocking curves of the (002) reflection of the as-synthesized GZO film and those annealed at 200°C, 400°C and 600°C.

Figure 6-2 shows the omega (ω) scan or rocking curves of the (002) reflection of the GZO film and those annealed at 200°C, 400°C and 600°C. The full width half maximum (FWHM) of the peaks are calculated and the results shown in Table 6-1.

Table 6-1: FWHM of GZO (002) rocking curves.

	FWHM (°)
As-synthesized	1.374
HT 200°C	1.425
HT 400°C	1.797
HT 600°C	2.233

It is observed that the FWHM of ZnO (002) plane rocking curves increases gradually from 1.374° to 2.233° when the film is annealed at 200°C, 400°C and 600°C. This peak broadening may indicate changes in the film alignment due to the restructuring of grains and addition of the Ga³⁺ dopant. Furthermore, there is the formation of pores clearly, visible at 600°C, as shown in Section 6.2.2 (Figure 6-4). It is noted that the FWHM values are larger than the undoped ZnO film (Chapter 3) and the scanning electron microscopy images shows this to be the case especially in the as-grown film with lots of non-aligned facets sticking out, as seen in Figure 6-4 (a).

Figure 6-3: XRD pole figures for GZO films (1 0 1) and corresponding MgAl₂O₄ substrate (4 0 0), for (a) as-synthesized, (c) after annealing at 400°C, and (b, d) corresponding ϕ -scan.

The pole figures for the as-synthesized GZO film and the corresponding MgAl₂O₄ substrate, and the corresponding ϕ -scan, are shown in Figure 6-3 (a) and

(b). It is seen that the films grew with a c -axis orientation on the $\langle 111 \rangle$ MgAl_2O_4 substrates. The respective peaks of the films and the substrate in the ϕ -scan spectra are separated by 30° along the ϕ -axis, indicating the in-plane orientation given by ZnO $[11\bar{2}0]||\text{MgAl}_2\text{O}_4$ $[\bar{1}\bar{1}2]$ and ZnO $[01\bar{1}0]||\text{MgAl}_2\text{O}_4$ $[\bar{1}10]$. These in-plane alignment of the GZO film and the substrate was obtained by the off-axis ϕ -scan of the ZnO (101) and MgAl_2O_4 (400). The films display the expected six-fold rotational symmetry of an epitaxial hexagonal layer. These results are consistent with other reports.^{32,68,196} The pole figures for the GZO film after annealing at 400°C and the MgAl_2O_4 substrate are given in Figure 6-3 (c) and the ϕ -scan is shown in Figure 6-3 (d). These results demonstrate that an aqueous solution synthesis route can be used to achieve epitaxial GZO films on $\langle 111 \rangle$ MgAl_2O_4 substrates.

6.2.2 Morphology of Ga-doped ZnO Film

Morphological characterization was carried out using field emission gun scanning electron microscopy (FEGSEM) and the images of the as-synthesized GZO film and its corresponding cross-section are shown in Figure 6-4. It was observed that the films are continuous and smooth on the surface. Figure 6-4 (c – f) shows the plane-view of the films and their corresponding cross-sections after annealing at temperatures of 200°C , 400°C and 600°C for 1 h in air. All films obtained are about $1.8 - 2.5 \mu\text{m}$ in thickness. Similar to the undoped ZnO films in Chapter 3, pores are observed when the film was annealed, especially evident when annealed at 400°C and 600°C as seen in Figure 6-4 (f) and Figure 6-4 (h), respectively. The formation of pores in ZnO films has previously been observed by Richardson *et al.*¹⁵⁴ when the films grown by the same low temperature aqueous solution route were annealed at temperatures above 200°C . The as-synthesized film and the film annealed at 200°C in Figure 6-4 (b) and Figure 6-4 (d),

respectively, showed no sign of pore formation. However, annealing at a temperature of 400°C and 600°C clearly show the presence of pores within the GZO films. As the temperature increases, the pores also get bigger and there are also more pores observed. Although the pores appear larger after annealing at higher temperatures, there is also a large amount of small pores present. Pore size and density is random and there is no systematic pattern to the process of pore formation. An estimated count of the number of visible pores was made from a selected area of 4500 by 1500 nm (as marked by the yellow rectangular boxes in Figure 6-4 (h) and Figure 6-4 (j)), with the former having approximately 162 pores, while the latter has about 142 pores. This decrease may be due to smaller pores coalescing together to form larger pores. There are an estimated 35 large pores (with diameters larger than or equal to 50 nm) in Figure 6-4 (h), while Figure 6-4 (j) has an estimated 46 large pores, but the former has approximately 127 small pores (with diameters less than 50 nm) as observed, while the latter has an estimated 96 small pores.

Figure 6-4: FEGSEM images of the plane-view and cross-section of the epitaxial GZO films on MgAl_2O_4 substrate (a, b) as-deposited, and after annealing in air for 1 h at (c, d) 200°C, (e, f) 400°C, and (g, h) 600°C.

The presence of gallium in the film was confirmed by energy dispersive X-ray spectroscopy (EDX) using a detector coupled with the FEGSEM. It was found

that between 2.31 – 2.78 at.% of Ga was present in the GZO films. Figure 6-5 shows the spectra obtained from the EDX measurements of the as-synthesized GZO film showing 2.33 at.% of Ga present. It is expected that gallium is in the +3 state, acting as an *n*-type donor, analogous to that reported by Le *et al.*³²

Figure 6-5: FEGSEM image and EDX spectrum showing the presence of 2.33 at.% Ga in the as-synthesized GZO film.

6.2.3 Hall Measurements of Ga-doped ZnO Film

It has been shown previously (Section 3.2.3) that the thermal annealing of ZnO films further enhances its electrical properties.³² Thus, the GZO films were annealed at temperatures of 200°C, 400°C and 600° for 1 h in air in order to improve its electrical properties and correlate the annealing temperature with the defect structure.

The electrical properties of GZO films as-synthesized and after thermal annealing were determined using the Hall measurement technique in the van der Pauw geometry. The results obtained are shown in Table 6-2. Hall mobility is

increased as the films are annealed, reaching the highest value of $18.87 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ when the film was annealed at 400°C . The carrier concentration obtained is of the order of 10^{20} cm^{-3} in the films annealed at 200°C and 400°C . This is one order of magnitude higher than as-synthesized GZO film (10^{19} cm^{-3}) and around two orders of magnitude higher than the as-synthesized undoped ZnO film (10^{18} cm^{-3}) shown in Section 3.2.3 (Table 3-2). This shows an increased *n*-type nature of the annealed GZO films, as Ga^{3+} acts as an effective donor after the annealing treatment.³² The higher conductivity is expected to be because of the effect of Ga^{3+} sitting on the substitutional site of Zn^{2+} and acting as a donor, generating one free carrier. In addition, there is a large increase in carrier concentration after annealing at 200°C and above which may be due to existing compensators, e.g. zinc vacancies, being removed by reacting with existing oxygen vacancies (as shown by photoluminescence spectroscopy in Section 6.4). The increase in the mobility and carrier concentration could also be due to the annealing process which restructures and recrystallizes the grains within the film indicating less grain boundaries for trapped carriers as the grain size increases due to the annealing process.³²

Table 6-2: Electrical properties of GZO films obtained from Hall measurements.

	Resistivity ($\Omega\text{-cm}$)	Hall mobility ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	Carrier concentration (cm^{-3})
As-synthesized	0.1666	1.14	3.76×10^{19}
HT 200°C	0.0031	11.27	1.81×10^{20}
HT 400°C	0.0015	18.87	2.28×10^{20}
HT 600°C	21.3514	4.71	6.23×10^{16}

6.3 XAS analysis of Ga-doped ZnO Films

Similar to studies in the earlier chapters, the GZO films were investigated using XAS both at the Ga *K*-edge and the Zn *K*-edge. The samples were similarly post-growth thermal annealed in a box furnace at temperatures of 200°C , 400°C

and 600°C for 1 h in air. The Ga *K*-edge and Zn *K*-edge X-ray absorption near edge spectroscopy (XANES) spectra for GZO film as-synthesized and when the film was annealed *ex situ* at temperatures of 200°C, 400°C and 600°C are shown in Figure 6-6 and Figure 6-7, respectively.

Figure 6-6: Ga *K*-edge XANES spectra of epitaxial GZO films as-synthesized and after annealing *ex situ* at temperatures from 200°C to 600°C.

Figure 6-7: Zn *K*-edge XANES spectra of epitaxial GZO films as-synthesized and after annealing *ex situ* at temperatures from 200°C to 600°C.

The XANES spectra at the Ga-edge (~ 10366 eV) and the Zn-edge (~ 9659 eV) were compared to that of Ga_2O_3 powder (used as a Ga^{3+} reference). Figure 6-8

shows the comparison of the XANES spectra of the as-synthesized GZO film at the Ga-edge and the Zn-edge and that of Ga_2O_3 powder.

Figure 6-8: XANES spectra of epitaxial GZO films as-synthesized at the Ga-edge and Zn-edge, compared to that of Ga_2O_3 .

As observed from Figure 6-8, the XANES spectrum of the GZO film at the Ga-edge is very similar to that of the GZO film at the Zn-edge and not that of Ga_2O_3 . Therefore, it can be concluded that the local structure around Ga^{3+} is closer to Zn^{2+} compared with Ga_2O_3 . This shows that the Ga^{3+} dopant is sitting in the tetrahedral Zn site and is being substituted in the lattice. If the Ga^{3+} dopant were to be in the octahedral site (akin to Ga_2O_3), it will be expected that the XANES spectrum of the GZO film will be similar to that of Ga_2O_3 instead.

The EXAFS in $\chi(k)$ of the GZO film is shown in Figure 6-9 at the Ga *K*-edge and in Figure 6-10 at the Zn *K*-edge. Similarly, the EXAFS spectra of the as-synthesized film were compared with that of Ga_2O_3 (Figure 6-11).

Figure 6-9: Ga K -edge EXAFS spectra in $\chi(k)$ of epitaxial GZO films as-synthesized and after annealing *ex situ* at 200°C, 400°C, and 600°C.

Figure 6-10: Zn K -edge EXAFS spectra in $\chi(k)$ of epitaxial GZO films as-synthesized and after annealing *ex situ* at 200°C, 400°C, and 600°C.

Figure 6-11: EXAFS spectra in $\chi(k)$ of epitaxial GZO films as-synthesized at the Ga-edge and Zn-edge, compared to that of Ga_2O_3 .

As observed from Figure 6-11, the EXAFS spectra of the GZO film at the Ga-edge is very much different to that of Ga_2O_3 but similar to that of the GZO film at the Zn-edge. This is in agreement with the XANES spectra showing that the structure of the GZO film is similar to that of the undoped ZnO film with the Ga^{3+} dopant sitting in the substitutional Zn^{2+} site.

However, EXAFS data obtained at the Ga K -edge was not of sufficient quality for a thorough analysis. Information about the coordination numbers are not able to be extracted and therefore only the fit distance of the first shell (i.e., nearest neighbour) was performed. The distances of the first neighbour were determined from the fit and the results are shown in Table 6-3.

Table 6-3: Bond distances obtained from the fit analysis of the first neighbour for the GZO film as-synthesized and after annealing *ex situ* at 200°C, 400°C and 600°C.

	Bond distance of first neighbour (Å)
As-synthesized	1.820
HT 200°C	1.830
HT 400°C	1.845
HT 600°C	1.830

Table 6-4: Table showing the crystal radius and ionic radius for Ga^{3+} , Zn^{2+} and O^{2-} .²⁴²

<i>Ion</i>	<i>Charge</i>	<i>Coordination</i>	<i>Crystal Radius</i>
<i>Ga</i>	<i>+3</i>	<i>IV</i>	<i>0.61</i>
		<i>V</i>	<i>0.69</i>
		<i>VI</i>	<i>0.76</i>
<i>Ion</i>	<i>Charge</i>	<i>Coordination</i>	<i>Crystal Radius</i>
<i>Zn</i>	<i>+2</i>	<i>IV</i>	<i>0.74</i>
		<i>V</i>	<i>0.82</i>
		<i>VI</i>	<i>0.88</i>
		<i>VIII</i>	<i>1.04</i>
<i>Ion</i>	<i>Charge</i>	<i>Coordination</i>	<i>Crystal Radius</i>
<i>O</i>	<i>-2</i>	<i>II</i>	<i>1.21</i>
		<i>III</i>	<i>1.22</i>
		<i>IV</i>	<i>1.24</i>
		<i>VI</i>	<i>1.26</i>
		<i>VIII</i>	<i>1.28</i>

Table 6-4 shows the crystal radii of Ga^{3+} , Zn^{2+} , and O^{2-} taken from the database of the Atomistic Simulation Group in the Materials Department of Imperial College.²⁴² Taking the summation of the radii of Ga^{3+} and O^{2-} in the tetrahedral coordination yields a value of $0.61 + 1.24 = 1.85 \text{ \AA}$. Thus, the distances obtained from the fit analysis is similar to that of Ga-O. This further confirms the presence of Ga^{3+} substituted in the Zn^{2+} site of the lattice. The results are in good agreement with the Hall measurement results shown above in Section 6.2.3, where there is an increase in the carrier density after doping with Ga^{3+} as compared with the undoped film mentioned in Section 3.2.3 (Table 3-2). This increased *n*-type nature of the annealed GZO films show that Ga^{3+} acts as an effective donor.³²

6.4 Photoluminescence Spectroscopy of Ga-doped ZnO Films

The optical properties of the GZO film were characterized by using room temperature photoluminescence (PL) spectroscopy. The spectra of the GZO film – as-synthesized and after annealing at temperatures 200 – 600°C are shown in Figure 6-12. The PL spectra obtained distinctively showed two peaks – a near band edge (NBE) transition or UV peak at *ca.* 3.25 eV, originating from exciton radiative recombination,²⁰⁷ followed by a broad defect peak or defect level emission (DLE) in the region of higher wavelengths.

Figure 6-12: Room temperature PL spectra of GZO films as-synthesized, and after annealing at 200°C, 400°C, and 600°C.

Figure 6-12 shows the PL spectra of the solution grown GZO film as-synthesized, and after annealing at 200°C, 400°C, and 600°C. In the as-synthesized film, this PL NBE transition is weak, but upon annealing at 400°C, this UV peak is sharp, indicating an intense light emission. After annealing, the non-radiative defects are reduced and restructured, greatly enhancing the crystal structure leading to a reduction in the non-radiative recombination, and hence, an increase in the luminescence efficiency,¹⁶¹ shown by the sharp peak at *ca.* 3.25 eV observed

in the film annealed at 400°C. The NBE is not visible for the film annealed at 600°C, possibly due to structural defects and impurities. Note that the Hall measurements did not yield as high a carrier concentration for the film annealed at 600°C.

The PL spectra also consist of a broad defect peak or deep-level emission (DLE) peak at lower energies (higher wavelengths) due to impurities or structural defects. This DLE is normally de-convoluted by Gaussian-fitting into three colour bands (red, yellow, green) for further analysis. There are various literature explaining the associated defects with the peaks present, although this is still a divisive topic.²⁰⁸⁻²¹¹ At *ca.* 2.25 – 2.58 eV (480 – 550 nm), the defect band is green; at *ca.* 2.03 – 2.25 eV (550 – 610 nm), the defect band is yellow; and, at *ca.* 1.65 – 2.03 eV (610 – 750 nm), it is red.²⁰⁸ The origin of the green band has been attributed to the presence of zinc vacancies.^{68,212} The yellow band has been attributed to the doubly charged oxygen vacancy.^{213,214} The red band is attributed to the presence of oxygen interstitials.^{213,215}

Figure 6-13: De-convoluted defect level emission for PL spectra of epitaxial GZO film (a) as-synthesized, and after annealing at (b) 200°C, (c) 400°C, and (d) 600°C.

The DLE of the epitaxial ZnO films were de-convoluted by Gaussian-fitting analysis and shown in Figure 6-13. The as-synthesized GZO film (Figure 6-13 (a)) showed a high degree of green and yellow bands centred at approximately 2.4 eV (510 nm) and 2.0 eV (610 nm), respectively. These are due to zinc vacancies and the doubly charged oxygen vacancies (V_o^{2+}), respectively.²¹²⁻²¹⁴ From Figure 6-13, it is seen that as the film is annealed at higher temperatures, the green luminescence band is reduced and eventually becomes much less when the film was annealed at 600°C. Concurrently, the appearance of the red luminescence band becomes evidently more prominent when the film was annealed at 600°C.

Figure 6-14: Correlation of the total integrated intensity of the PL spectra at each annealing temperature with the ratio of the integrated intensity of the NBE to DLE peak.

Figure 6-14 shows the correlation of the total integrated intensity of the PL spectra at each annealing temperature with the ratio of the integrated intensity of the NBE to DLE peak. As annealing temperature is increases, the total integrated intensity increases, and the ratio of the NBE to DLE peak also increases, reaching a peak at 400°C. This represents a better crystalline quality of the GZO film at 400°C. This is a possible reason for the increase in mobility as seen from the Hall measurements in Section 6.2.3, indicating fewer defects within the GZO film after annealing at 400°C.

Figure 6-15: Integrated intensity variation of DLE with annealing temperature and the respective peak position at each annealing temperature for the GZO film.

Figure 6-15 shows the integrated intensity variation of each of the deconvoluted bands with annealing temperature and the peak positions of the DLE at each annealing temperature. It is seen that the DLE peak shifts to higher wavelength or to lower energy levels (i.e., red-shift) with annealing temperature. Concurrently, the green band is reduced. This suggests that zinc vacancies are reduced upon annealing while the red band, attributed to defects associated with oxygen interstitials,^{209,215} increases.

6.5 Characterization of Ga-doped ZnO Powders Grown at pH 10.9

The defect structure order of solution grown GZO films have been shown in Section 6.3. Powders will enable the further understanding of such a structure through various other characterization methods such as powder XRD and total scattering experiments yielding the pair distribution function (PDF), in addition to X-ray absorption spectroscopy (XAS). Thus, GZO powders were produced in a similar way to that of the GZO films. The synthesis remains relatively identical to

the films but without the addition of a substrate and instead, with the addition of a small amount of ZnO NIST powder used as a seed for nucleation and growth of the powders. Detailed synthesis method of GZO powders has been given in Section 2.2.2. This sample is labelled S3.

6.5.1 Crystallinity of Ga-doped ZnO Powders

Figure 6-16: GADDS XRD pattern for the as-synthesized GZO powders and after annealing (HT) at 600°C.

Sharp peaks are observed from the X-ray diffraction (XRD) patterns indicating a highly crystalline material. The XRD pattern (Figure 6-16) obtained indicate that the phase obtained from the synthesis of the GZO powder is wurtzite. These patterns can be indexed closely with JCPDS 36-1451.¹⁹⁴ There are no shifts in any of the peak positions after annealing at 600°C thus no change in the crystal structure is observed. This shows that the crystal structure of the low temperature synthesized GZO powders are stable even after annealing at 600°C.

6.5.2 Morphology of Ga-doped ZnO Powders

Figure 6-17: FEGSEM images of GZO powders at different magnifications.

The morphology of the obtained GZO powders (sample S3) was investigated using field emission gun scanning electron microscopy (FEGSEM). Figure 6-17 shows the FEGSEM images of the GZO powder at different magnifications. This synthesis used the ZnO powder obtained from NIST as a seed (Chapter 4 (Figure 4-11)). The growth process yielded ZnO that is generally rod-like. These rods are short with lengths of about 0.2 – 0.5 μm and thickness of about 100 – 300 nm.

6.5.3 Transmission Electron Microscopy of Ga-doped ZnO Powders

High resolution transmission electron microscopy (HRTEM) was carried out on the GZO powders (sample S3). An annealing at 600°C in air for 1 h was performed on the same sample and also investigated with HRTEM. Figure 6-18 shows the TEM images for sample S3.

Figure 6-18: TEM images (low magnification, HRTEM higher magnification image and corresponding SAED pattern, with zone axis $[\bar{1}2\bar{1}0]$) of sample (a) S3 as-synthesized, and (b) S3 after annealing at 600°C for 1 h in air.

The selected area electron diffraction (SAED) pattern obtained from the TEM shows a single crystal GZO powder obtained from the synthesis. Annealing the sample seems to have caused the edges of the nanorods to become rougher as seen in Figure 6-18 (b). However, there are no pores observed within the nanorods after annealing. One possibility is that the pores have been annealed out of the sample which causes the rougher surfaces. Also, additional pores may be too small for visual observation. There are no changes to the crystal structure of the sample as seen from the (SAED) pattern.

6.6 *Ex Situ* XAS analysis of Ga-doped ZnO Powders at the Zn K-Edge

X-ray absorption (XAS) measurements were performed on the GZO powders grown at pH 10.9 at the Zn K-edge as well as the Ga K-edge. Ga K-edge and Zn K-edge XANES spectra for GZO sample S3 at room temperature (RT) and when the powders were annealed *ex situ* at temperatures 200°C, 400°C, and 600°C are shown in Figure 6-19 and Figure 6-20, respectively. XANES is typically used to study the variation of core electron configuration and can give information about the valency changes of atoms in a matrix. For example, if there is a decrease in the valency, the XANES absorption structure will tend to move to lower energies.²⁰⁰ From Figure 6-19 and Figure 6-20, it is observed that there are no shifts in the XANES edge position indicating that the electronic configuration for the Zn central atom was unchanged and is stable. There are no changes in the valance of Zn²⁺ even though Ga³⁺ was doped into the system and annealed up to 600°C.

Figure 6-19: Ga K-edge XANES spectra of GZO powder (sample S3) as-synthesized and after annealing *ex situ* at temperatures from 200°C to 600°C.

Figure 6-20: Zn K-edge XANES spectra of GZO powder (sample S3) as-synthesized and after annealing *ex situ* at temperatures from 200°C to 600°C.

The XANES spectra at the Ga-edge and the Zn-edge were compared to that of Ga_2O_3 powder (used as a reference). Figure 6-21 shows the comparison of the XANES spectra of the as-synthesized GZO powder (sample S3) at the Ga-edge and the Zn-edge and that of Ga_2O_3 powder.

Figure 6-21: XANES spectra of epitaxial GZO powders as-synthesized at the Ga-edge and Zn-edge, compared to that of Ga_2O_3 .

As observed, the XANES spectrum of the GZO powders at the Ga-edge is very similar to that of the GZO powders at the Zn-edge and not that of Ga_2O_3 .

Therefore, it is deduced that the structure of the GZO powders is similar to ZnO and not Ga₂O₃. It can be concluded that the Ga³⁺ dopant is sitting in the tetrahedral Zn site and is being substituted in the lattice. If the Ga³⁺ dopant were to be in the octahedral site, it will be expected that the XANES spectrum will be similar to that of Ga₂O₃ instead. The results obtained are similar to the GZO film shown in Section 6.3.

However, EXAFS data obtained at the Ga *K*-edge was not of sufficient quality for a thorough analysis. Information about the coordination numbers are not able to be extracted and therefore only the fits of the bond distances was performed and are shown in Table 6-5.

Table 6-5: Bond distances obtained from the fit analysis for the GZO powder (sample S3) as-synthesized and after annealing *ex situ* at 200°C, 400°C and 600°C.

	Bond distance of first neighbour (Å)	Bond distance of second neighbour (Å)
As-synthesized	1.84	3.24
HT 200°C	1.85	3.24
HT 400°C	1.84	3.22
HT 600°C	1.82	3.19

Taking the summation of the radii of Ga³⁺ and O²⁻ in the tetrahedral coordination (from Table 6-4 – the crystal radii of Ga³⁺, Zn²⁺, and O²⁻)²⁴² yields a value of 0.61 + 1.24 = 1.85 Å. Thus, the distances obtained from the fit analysis is similar to that of Ga-O. This confirms the presence of Ga³⁺ substituting in the Zn²⁺ site of the lattice. This is analogous to the GZO film shown in Section 6.3.

The EXAFS data obtained at the Zn *K*-edge EXAFS was of sufficient quality for further analysis. Figure 6-22 shows the Zn *K*-edge EXAFS spectra in $\chi(k)$ of the GZO powder (sample S3) (a) as-synthesized, and after annealing *ex situ* at (c) 200°C, (e) 400°C, and (g) 600°C, respectively. The Fourier Transform and its imaginary part are correspondingly shown beside the EXAFS spectra. The $k^3\chi(k)$ for the ZnO powders as a function of the photoelectron wave vector k , gives information about the mean immediate atomic environment of the specified

lattice site.²⁰¹ All the EXAFS of the GZO powders measured fit well with the correspondingly ZnO crystallographic information file (CIF)²⁰² used for the analysis, with minimal error. For a quantitative analysis of the local structural properties, we studied the Fourier Transformed data in R-space. To minimize errors, only data in the k -range 2.0 – 11.0 Å⁻¹ was used for further analysis.

Figure 6-22: Zn *K*-edge EXAFS spectra in $\chi(k)$ of sample S3 GZO powder (a) as-synthesized, and annealed *ex situ* at (c) 200°C, (e) 400°C, and (g) 600°C. The Fourier Transform and its imaginary part is shown for sample S3 GZO powder (b) as-synthesized, and annealed *ex situ* at (d) 200°C, (f) 400°C, and (h) 600°C.

The fit methodology developed here follows a simple alternation strategy, same as that used for the analysis of the ZnO powders presented in Section 4.5. Details about the fitting procedure have been given in Section 2.4.5. The refinement of the amplitude reduction factor, S_0^2 yielded a value of 0.84 for the Zn-O correlation and 0.92 for the Zn-Zn correlation. This value was fixed for further refinement of the structural parameters.

The final values obtained from the fit of the GZO powder (sample S3) as-synthesized and after annealing *ex situ* are shown in Table 6-6. The ZnO NIST standard was similarly analyzed and shown in Table 6-7. The coordination numbers (N) of Zn-O and Zn-Zn correlations were determined by multiplying the ideal coordination (i.e., 4 and 12, respectively) by the occupancies obtained from the EXAFS fit. The average atomic distance, r , between the central Zn atom and the first nearest neighbour, i.e., oxygen (O) is obtained by fitting the singly scattered paths which are calculated for the EXAFS of ZnO, and taking the average. The Debye-Waller factor, σ^2 , is a function of disorder and temperature provides information about the stiffness of the bonds and the mass of the atoms.¹⁶⁸

The refinement revealed that the nearest neighbour distance obtained for the as-synthesized powders was 1.96 Å for the Zn-O bond and next nearest neighbour distance was 3.21 Å for the Zn-Zn bond. The Debye-Waller factor (σ^2) of the Zn-O pair was given as 0.005 Å² and 0.008 Å² for the Zn-Zn pair of the ZnO films. All the values obtained for the distances and the σ^2 correspond within error limits of those reported by similar studies.^{201,203-206} These values remained relatively constant even after annealing the powders at temperatures up to 600°C.

Table 6-6: Structural parameters obtained from the EXAFS analysis of Zn *K*-edge data on GZO powders (sample S3) annealed *ex situ*.

S3	Zn-O			Zn-Zn			R-factor	Ratio of Zn-O to NIST standard	Ratio of Zn-Zn to NIST standard
	N-1	R-1 (Å)	σ^2 -1 (Å ²)	N-2	R-2 (Å)	σ^2 -2 (Å ²)			
As-synthesized	2.9 (0.1)	1.96 (0.02)	0.005 (0.003)	8.7 (0.2)	3.21 (0.01)	0.008 (0.003)	0.013	0.744	0.731
HT 200°C	3.5 (0.2)	1.97 (0.02)	0.005 (0.004)	11.1 (0.2)	3.22 (0.02)	0.008 (0.003)	0.019	0.833	0.847
HT 400°C	3.4 (0.2)	1.97 (0.02)	0.005 (0.004)	10.8 (0.2)	3.22 (0.02)	0.008 (0.002)	0.019	0.850	0.824
HT 600°C	3.4 (0.2)	1.97 (0.02)	0.005 (0.004)	9.9 (0.2)	3.22 (0.01)	0.007 (0.002)	0.014	0.850	0.825

Table 6-7: Structural parameters obtained from the EXAFS analysis of Zn *K*-edge data on ZnO NIST standard (sample S4) annealed *ex situ*.

S4	Zn-O			Zn-Zn			R-factor
	N-1	R-1 (Å)	σ^2 -1 (Å ²)	N-2	R-2 (Å)	σ^2 -2 (Å ²)	
NIST standard	3.9 (0.2)	1.97 (0.02)	0.005 (0.004)	11.9 (0.2)	3.22 (0.01)	0.007 (0.002)	0.016
HT 200°C	4.2 (0.3)	1.98 (0.02)	0.005 (0.004)	13.1 (0.3)	3.22 (0.02)	0.008 (0.002)	0.021
HT 400°C	4.0 (0.3)	1.98 (0.02)	0.004 (0.004)	13.1 (0.3)	3.22 (0.02)	0.008 (0.002)	0.023
HT 600°C	4.0 (0.2)	1.97 (0.02)	0.005 (0.004)	12.0 (0.2)	3.22 (0.01)	0.007 (0.002)	0.015

To determine the local structure order defects, the coordination numbers of the Zn-O and Zn-Zn correlations are considered. Annealing conditions were kept invariable for all the samples for direct comparison. For the as-synthesized powder, the coordination number obtained from the fitting analysis is 2.9 for the Zn-O correlation and a coordination number of 8.7 for the Zn-Zn correlation. These values were then compared to the coordination numbers for Zn-O and Zn-Zn correlations obtained from the refinement of the NIST standard. As shown in Table 6-6, the as-synthesized sample has a lower coordination number ratio of Zn-Zn correlations as compared to Zn-O and the NIST standard, indicating a *ca.* 26.9% decrease in coordination of Zn-Zn correlations. This suggests that zinc vacancies are present in the as-synthesized sample. The coordination numbers obtained at each annealing temperature are similarly compared with the coordination numbers of the NIST standard. At 200°C, there seems to be a predominance of oxygen vacancies. At 400°C and 600°C, the ratios suggest the presence of zinc vacancies in the system.

6.7 *In Situ* XAS analysis of Ga-doped ZnO Powders at the Zn *K*-Edge

In situ XAS measurements were similarly attempted with the GZO powders analogous to the undoped ZnO powder presented in Section 4.6. The powders were pressed into a pellet diluted with BN, placed into the specimen chamber and measurements taken at the Zn *K*-edge was performed at room temperature before heating the chamber to an elevated temperature of 200°C. The chamber was maintained at this temperature and measurements were performed. The chamber was subsequently heated to temperatures of 400°C, and 600°C, with measurements performed while the chamber was maintained at the

respective temperatures. The chamber was subsequently allowed to cool to room temperature before another measurement was performed at room temperature.

Figure 6-23 shows the Zn *K*-edge XANES spectra for the GZO powder (sample S3) at room temperature (RT)/as-synthesized and when annealed *in situ* at temperatures of 200°C, 400°C and 600°C, and after cooling back to room temperature. The absorption edge is observed at *ca.* 9658.9 eV, corresponding to the Zn *K*-edge binding energy. Similar to the *ex situ* measurements, there are no shifts in the XANES edge position indicating that the electronic configuration is unchanged and is stable. There is no change in the valance of Zn in the system even as the samples are annealed up to 600°C and cooled back to room temperature.

Figure 6-23: Zn *K*-edge XANES spectra of GZO powder (sample S3) annealed *in situ* at temperatures from room temperature (RT) to 600°C and after cooling to RT.

Figure 6-24 shows the Zn *K*-edge EXAFS spectra and fit in $\chi(k)$ of the GZO powders (sample S3) annealed *in situ* at (a) room temperature (RT), (c) 200°C, (e) 400°C, (g) 600°C, and, (i) after cooling back to RT. The Fourier Transform and its imaginary part are correspondingly shown beside the EXAFS spectra. The first two prominent peaks in the Fourier Transform are assigned to the first two coordination shells of ZnO at *ca.* 1.9 Å (Zn-O) and 3.2 Å (Zn-Zn), respectively.

Refinement was performed using a k^3 weighting. The $k^3\chi(k)$ as a function of the photoelectron wave vector k , gives information about the mean immediate atomic environment of the specified lattice site.²⁰¹

The EXAFS measured correspondingly fit well with the ZnO crystallographic information file (*CIF*)²⁰² used for the analysis, with minimal error. For a quantitative analysis of the local structural properties, we study the Fourier Transformed data in R-space. To minimize errors, only data in the k -range of 2.0 – 11.0 Å⁻¹ was used for further analysis. The fitting procedure followed that of the *in situ* analysis of the undoped ZnO powders presented previously in Section 4.6 with details given in Section 2.4.5.

Figure 6-24: Zn K-edge EXAFS spectra in $\chi(k)$ of GZO powder (sample S3) (a) as-synthesized, annealed *in situ* at (c) 200°C, (e) 400°C, (g) 600°C, and (i) after cooling down to room temperature. The Fourier Transform and its imaginary part is shown for sample S3 GZO powder (b) as-synthesized, annealed *in situ* at (d) 200°C, (f) 400°C, (h) 600°C, and (j) after cooling down to room temperature.

The fit methodology performed follows a simple alternation strategy, same as that used for the analysis of the ZnO powders presented in Section 4.5 as well as for the GZO powders annealed *ex situ* shown in Section 6.6. The refinement of the amplitude reduction factor, S_0^2 , yielded a value of 0.95 for the Zn-O correlation and 1.17 for the Zn-Zn correlation. This value was fixed for further refinement of the structural parameters.

The final values obtained from the fit of the GZO powder sample as-synthesized and after annealing *in situ* are shown in Table 6-8. The ZnO NIST standard was similarly analyzed and shown in Table 6-9. The coordination number (N) of Zn-O and Zn-Zn correlations are determined by multiplying the ideal coordination (i.e., 4 and 12, respectively) by the occupancies obtained from the EXAFS fit. The average atomic distance, r , between the central Zn atom and the first nearest neighbour, i.e., oxygen (O) is obtained by fitting the singly scattered paths which are calculated for the EXAFS of ZnO, and taking the average. The Debye-Waller factor, σ^2 , is a function of disorder and temperature provides information about the stiffness of the bonds and the mass of the atoms.¹⁶⁸

From Table 6-8, the nearest neighbour distance obtained for the as-synthesized powder was 1.97 Å and next nearest neighbour distance was 3.22 Å. The Debye-Waller factor (σ^2) for the first shell analysis is given as 0.005 Å² and 0.007 Å² for the next nearest shell. These values obtained are close to those of previous reports.^{201,205,206} As σ^2 is a temperature dependent factor, it is generally increased when the annealing proceeds, increasing with an increase in temperature. When the samples are cooled back to room temperature, the σ^2 value returns back to its original room temperature value. This is expected of the temperature dependent factor, σ^2 , which is correlated to the thermal disorder of the system.

Table 6-8: Structural parameters obtained from the EXAFS analysis of Zn *K*-edge data on GZO powders (sample S3) annealed *in situ*.

S1	Zn-O			Zn-Zn			R-factor	Ratio of Zn-O to NIST standard	Ratio of Zn-Zn to NIST standard
	N-1	R-1 (Å)	σ^2 -1 (Å ²)	N-2	R-2 (Å)	σ^2 -2 (Å ²)			
As-synthesized	3.4 (0.2)	1.97 (0.02)	0.005 (0.004)	9.3 (0.2)	3.22 (0.02)	0.007 (0.002)	0.016	0.781	0.741
HT 200°C	3.2 (0.1)	1.97 (0.02)	0.006 (0.003)	8.5 (0.2)	3.22 (0.02)	0.010 (0.003)	0.013	0.752	0.725
HT 400°C	3.2 (0.1)	1.97 (0.02)	0.006 (0.003)	7.7 (0.2)	3.21 (0.02)	0.011 (0.004)	0.013	0.794	0.791
HT 600°C	3.1 (0.1)	1.97 (0.02)	0.007 (0.003)	7.5 (0.2)	3.21 (0.02)	0.016 (0.006)	0.010	0.797	0.800
Cooled to RT	3.3 (0.1)	1.97 (0.02)	0.005 (0.003)	9.1 (0.2)	3.22 (0.01)	0.007 (0.002)	0.014	0.809	0.774

Table 6-9: Structural parameters obtained from the EXAFS analysis of Zn *K*-edge data on ZnO NIST standard (sample S4) annealed *in situ*.

S4	Zn-O			Zn-Zn			R-factor
	N-1	R-1 (Å)	σ^2 -1 (Å ²)	N-2	R-2 (Å)	σ^2 -2 (Å ²)	
NIST standard	4.0 (0.2)	1.98 (0.02)	0.005 (0.004)	12.5 (0.3)	3.22 (0.02)	0.007 (0.002)	0.018
HT 200°C	4.4 (0.2)	1.97 (0.02)	0.005 (0.004)	11.7 (0.2)	3.22 (0.02)	0.008 (0.003)	0.018
HT 400°C	4.2 (0.2)	1.97 (0.02)	0.006 (0.004)	9.8 (0.2)	3.22 (0.02)	0.010 (0.003)	0.015
HT 600°C	4.1 (0.1)	1.97 (0.02)	0.007 (0.003)	9.4 (0.2)	3.21 (0.02)	0.015 (0.006)	0.012
Cooled to RT	4.0 (0.2)	1.98 (0.02)	0.004 (0.004)	11.8 (0.3)	3.22 (0.02)	0.007 (0.002)	0.020

Similar to the study on the *in situ* XAS of the ZnO powders shown in Section 4.6, and the *ex situ* XAS of the GZO powders shown in Section 6.6, the coordination numbers of the Zn-O and Zn-Zn correlations are considered in order to determine the local structure order defects. The coordination number (N) represents the number of nearest neighbour atoms surrounding the central Zn atom. In general, the coordination of an ideal ZnO system will have 4 nearest neighbours of Zn-O coordination and 12 next nearest Zn atoms with reference to the central Zn atom at the origin.

To determine the local structure order defects, the coordination numbers of the Zn-O and Zn-Zn correlations are considered. For the as-synthesized powder, the coordination number obtained from the fitting analysis is 3.4 for the Zn-O correlation and a coordination number of 9.3 for the Zn-Zn correlation. These values were then compared to the coordination numbers for Zn-O and Zn-Zn correlations obtained from the refinement of the NIST standard. As shown in Table 6-8, the as-synthesized sample has a lower ratio of Zn-Zn correlations as compared to Zn-O and the NIST standard, indicating a *ca.* 25.9% decrease in coordination of Zn-Zn correlations. This suggests that zinc vacancies are present in the as-synthesized sample. The coordination numbers obtained at each annealing temperature are similarly compared with the coordination numbers of the NIST standard. At the higher annealing temperatures, the ratios suggest the presence of zinc vacancies in the system. Note that the ratios obtained at 600°C are too close to each other to make a conclusive finding. In this case, there could be a similar concentration of zinc and oxygen vacancies in the system. In summary, the GZO powder sample has a highly zinc deficient system from the EXAFS analysis of the Zn *K*-edge. This favours the hypothesis that the Ga³⁺ dopant is sitting in the tetrahedral Zn²⁺ site within the ZnO lattice.

6.8 Photoluminescence Spectroscopy of Ga-doped ZnO Powders Grown at pH 10.9

The photoluminescence measurements were carried out at room temperature to characterize the optical properties of the GZO powders. The PL spectra of the GZO powders are shown in Figure 6-25. The DLE was deconvoluted by Gaussian-fitting analysis and shown in Figure 6-26.

Figure 6-25: Room temperature PL spectra of GZO powders as-synthesized and after annealing at 200°C, 400°C and 600°C for 1 h in air.

Figure 6-26: De-convoluted defect level emission for (a) as-synthesized, and after annealing at (b) 200°C, (c) 400°C, and (d) 600°C.

The spectra obtained are similar to that of the undoped powders reported in Section 4.7. There is a near band edge (NBE) transition at *ca.* 3.25 eV, originating from exciton radiative recombination.²⁰⁷ In the as-synthesized sample, this PL NBE transition is weak, but upon annealing at 400°C, the peak becomes relatively sharper. As-synthesized ZnO usually consists of many lattice and surface defects acting as non-radiative centres and thus reducing the light emission from the ZnO samples.¹⁶¹ After annealing, these non-radiative defects are reduced and restructured, greatly enhancing the crystal structure leading to a reduction in the non-radiative recombination, and hence, an increase in the luminescence efficiency,¹⁶¹ shown by the sharp peak observed in the film annealed at 400°C. A broad deep level emission (DLE) is also observed at lower energies (higher wavelengths) due to impurities or structural defects. A deconvolution of the DLE was done by Gaussian fitting analysis, as shown in Figure 6-26.

For the as-synthesized powders, a mixture of green, yellow and red bands are observed centred at approximately 2.3 eV (540 nm), 2.0 eV (610 nm) and 1.8 eV (690 nm), respectively. The origin of the green band has been attributed to the presence of zinc vacancies.^{68,212} The yellow band has been attributed to the doubly charged oxygen vacancy.^{213,214} The red band edge is attributed to the presence of oxygen interstitials.^{213,215}

As the powders are annealed at higher temperatures, the green luminescence band is reduced and eventually becomes insignificant and nonexistent when the powders were annealed at 600°C. Concurrently, with the increase in annealing temperature to 600°C, there is the emergence of the red luminescence band which becomes evidently more prominent, centred at about 1.8 eV. This red DLE band is attributed to defects associated with oxygen interstitials.²⁰⁹

Figure 6-27: Correlation of the total integrated intensity of the PL spectra at each annealing temperature with the ratio of the integrated intensity of the NBE to DLE peak for sample S3.

Figure 6-27 shows the correlation of the total integrated intensity of the PL spectra at each annealing temperature with the ratio of the integrated intensity of the NBE to DLE peak. As annealing temperature is increases, the total integrated intensity increases, and the ratio of the NBE to DLE peak also increases, reaching a peak at 400°C. This represents a better crystalline quality of the ZnO sample at 400°C. At 600°C, there is an obvious decrease in the ratio of NBE to DLE, indicating more defects present.

Figure 6-28: Correlation of the integrated intensity variation of DLE of the GZO powders with annealing temperature and the respective peak position at each annealing temperature.

Figure 6-28 shows correlation of the integrated intensity variation of each of the de-convoluted bands with annealing temperature and the peak positions of the DLE at each annealing temperature for the GZO powder. It is seen that the DLE peak shifts to higher wavelength or to lower energy levels (i.e., red-shift) with increasing annealing temperature.⁶⁷ The red band is attributed to defects associated with oxygen interstitials.^{209,215} On the other hand, the green band which is attributed to zinc vacancies decreases with annealing temperature. This corresponds to the XAS results shown in Section 6.7.

6.9 *In Situ* Pair Distribution Function Analysis of Ga-doped ZnO Powders

To further establish the findings from the EXAFS data, total scattering experiments were performed. Total scattering is not atom specific and gives information on longer range order. The Fourier Transform of the measured data gives the pair distribution function (PDF). Details of the technique have been given in Section 2.4.6. The analysis performed was similar to that of the undoped powders as shown in Section 4.8.

Figure 6-29: Fourier Transformed $S(Q)$, generating *in situ* PDFs of the GZO powder (sample S3) from measurements at room temperature (RT), 200°C, 400°C and 600°C; and after cooling back to room temperature.

Figure 6-29 shows the Fourier Transformed $S(Q)$ which generates the PDF of the GZO powder (sample S3) from measurements at room temperature and at 200°C, 400°C and 600°C and after it is cooled to room temperature again. Intensities of all the Zn-Zn correlations are lower than that of the Zn-O correlations. This intensity difference is related to the temperature factor and the occupancy.

Figure 6-30: Comparison of the Fourier transformed $S(Q)$, or PDFs of sample S3 with ZnO NIST standard (S4) at room temperature (RT). The inset shows the enlarged area from 1.5 – 4.0 Å.

As seen from Figure 6-30, the intensities of the Zn-Zn correlation peaks are lower than the ZnO NIST standard for the GZO powder (sample S3), while the Zn-O correlation peaks have no change in intensity (specifically shown in the inset –red circle). Assuming that the ZnO NIST standard (SRM 674b) has the ideal stoichiometry of ZnO, the results obtained suggest that zinc vacancies are present in the as-synthesized GZO powder (sample S3) at room temperature.

Further analysis of the powders were attempted using PDFgui²²⁰. Data were first inputted into the programme PDFFit2 and PDFgui. The PDF function, $G(r)$ data were then studied. The total PDF, $G(r)$, of the ZnO samples at room temperature essentially contain structural information in real-space and are the Fourier Transforms of the reduced structure factor $Q[S(Q)-1]$. It uses similar

parameters, e.g. lattice parameters, atomic displacement parameters, occupancies etc. to those used in a Rietveld refinement but performs it on the real space $G(r)$ data. More details of the fitting analysis have been given in Section 2.4.6. Table 6-10 shows the refined structural parameters from *in situ* PDF fitting of X-ray total scattering data for sample S3.

Table 6-10: Refined structural parameters from *in situ* PDF fitting of X-ray total scattering data for the Ga-doped ZnO powder (sample S3).

S3	a = b (Å)	c (Å)	Vol. (Å ³)	Zn			O			Occupancy		Red. chi ²	Rw
				u11 = u22	u33	u12	u11 = u22	u33	u12	Zn	O		
RT	3.2477 (0.0012)	5.2189 (0.0040)	47.672	0.0049 (0.00012)	0.0058 (0.00041)	0.0024	0.0076 (0.00068)	0.0077 (0.0032)	0.0038	1.0194 (0.013)	0.8599 (0.031)	0.15	0.13
200°C	3.2540 (0.0015)	5.2259 (0.0049)	47.921	0.0083 (0.00021)	0.0096 (0.00075)	0.0041	0.0130 (0.0012)	0.0068 (0.0043)	0.0065	1.0214 (0.014)	0.8448 (0.033)	0.15	0.14
400°C	3.2603 (0.0018)	5.2272 (0.0059)	48.119	0.0122 (0.00032)	0.0131 (0.0011)	0.0061	0.0216 (0.0021)	0.0149 (0.0069)	0.0108	1.0134 (0.015)	0.8995 (0.039)	0.13	0.15
600°C	3.2646 (0.0022)	5.2258 (0.0066)	48.233	0.0163 (0.00043)	0.0163 (0.0014)	0.0081	0.0289 (0.0029)	0.0302 (0.01)	0.0145	1.0015 (0.015)	0.9884 (0.044)	0.12	0.15
Cooled to RT	3.2482 (0.0011)	5.2166 (0.0037)	47.664	0.0049 (0.00011)	0.0058 (0.0004)	0.0025	0.0070 (0.00061)	0.0035 (0.0023)	0.0035	1.0278 (0.012)	0.8011 (0.027)	0.16	0.13

Attempt was made to refine the occupancies of Zn and O. First we analyzed the ZnO NIST standard. From this best fit, the refinement yielded predominantly oxygen vacancies even at room temperature, which is difficult to rationalize. Ideally, the ratio of O to Zn should equate to 1, however the refinement revealed that this value deviates from 1 and yielded a ratio of 0.78. Therefore, it is not clear if the NIST standard contains oxygen vacancies in the system. This analysis procedure contains errors; however, in order to rationalize the remaining results, this value of 0.78 was taken as a base standard. Thus, comparing the occupancies of sample S3 with sample S4 (ZnO NIST standard SRM 674b), the ratios of O to Zn obtained for sample S3 was 0.84. The higher value as compared to sample S4 indicate more zinc vacancies in the real system as compared with the NIST standard. After annealing and cooling down to room temperature, the values become closer to that of the ZnO NIST standard. There is a possibility that zinc vacancies were annihilated during the annealing process. Furthermore, there is a high correlation between temperature factor and occupancy which may lead to an underestimate in the refined parameters of the PDF analysis. Thus, the values obtained for the occupancies of Zn and O may not be real and varies with the R-range of about a 10 Å distance. The reliability of the results obtained for the occupancies of Zn and O is greatly reduced. It is difficult to accurately model the structure without the information on the stoichiometry of the NIST standard.

Nonetheless, this high energy X-ray diffraction technique has enabled the study of defects within the lattice at the atomic scale as compared to observing only the microstructure from microscopy, and thus proves to be a useful technique in complementing the results obtained from X-ray absorption spectroscopy, which is a more reliable characterization technique.

6.10 Discussion

Ex situ XAS experiments of the GZO film clearly showed that the Ga^{3+} dopant in GZO film is residing in the Zn^{2+} lattice site. Ga^{3+} is substitutionally sitting in the tetrahedral Zn site and this is a plausible reason for the increase in carrier concentration in the Hall measurements as compared to the undoped ZnO film seen in Section 3.2.3. Similarly, the Ga^{3+} is found to be residing in the Zn^{2+} site in the GZO powders as shown from the XANES measurements at the Ga *K*-edge. Generally, a zinc deficient system was observed from the EXAFS analysis of the Zn *K*-edge GZO, especially when the sample was annealed *in situ*. This supports the hypothesis that the Ga^{3+} dopant is sitting in the tetrahedral Zn^{2+} site within the ZnO lattice.

Room temperature photoluminescence (PL) mapping studies showed the presence of a mixture of green, yellow and red bands in the as-synthesized GZO samples, indicating the presence of zinc vacancies and the doubly charged oxygen vacancy and a small concentration of oxygen interstitials. When the GZO powders were annealed in air at temperatures from 200°C – 600°C, there was a red-shift suggesting the presence of oxygen interstitials, and concurrently the reduction of the green band indicating the reduction in zinc vacancies. From XAS results, no information can be obtained about oxygen interstitials because the Zn central atom was probed. However, the presence of zinc vacancies is confirmed by XAS and PL mapping. Furthermore, an *in situ* pair distribution function (PDF) analysis showed that in the short to medium range structure order, zinc vacancies are present. This is shown by a reduction in the Zn-Zn peak intensities when compared with a ZnO standard (purchased from NIST, SRM 674b).

6.11 Conclusion of Chapter 6

This chapter investigated the local structure of GZO films and powders grown by a low temperature chemical bath deposition route. Synchrotron radiation experiments such as XAS and PDF has aided in the defect structure characterization of such films and powders. *Ex situ* XAS experiments of the GZO film and powders clearly showed that the Ga^{3+} dopant in GZO film is residing in the Zn^{2+} lattice site. Ga^{3+} is substitutionally sitting in the tetrahedral Zn site and this is a plausible reason for the increase in carrier concentration in the Hall measurements as compared to the undoped ZnO film. Generally, a zinc deficient system was observed from the EXAFS analysis of the Zn *K*-edge GZO films and powders, especially when the sample was annealed *in situ*. From the *in situ* pair distribution function (PDF) analysis, it was found that in the short to medium range structure order, zinc vacancies are present. This is shown by a reduction in the Zn-Zn peak intensities when compared with a ZnO standard (purchased from NIST, SRM 674b).

Thus, XAS and HEXRD have proven to be effective characterization tools utilizing synchrotron radiation, which can be used for the analysis of the short to medium range defect structure of materials. These results will potentially be valuable for the advancement of GZO for semiconducting TCOs in displays applications, etc.

Chapter 7

Summary and Future Work

The field of materials growth has in recent years progressed tremendously. This has allowed for new materials to be synthesized and studied through the use of advanced characterization techniques. Likewise, the advances in materials characterization have enabled new characterization techniques to be employed for its study. The development of synchrotron radiation has made possible a greater understanding of materials structure and elucidation of complex materials.

In this thesis, ZnO films and powders have been successfully synthesized through a low temperature aqueous solution route and characterized. All the samples were post-growth thermal annealed in air to enhance the electrical and optical properties. Defect characterization using synchrotron radiation based methods were performed on the samples. Specifically, X-ray absorption spectroscopy (XAS) and total scattering experiments yielding pair distribution function (PDF) was done in order to better understand the short to medium range order of the samples. As-synthesized ZnO is primarily *n*-type and this limits its use as a semiconductor material for device applications. The understanding of the role of defects within the ZnO system has provided useful insight for further exploitation of the material. The main conclusions drawn from this study are stated below:

1. ZnO films were grown on MgAl_2O_4 epitaxial substrates yield epitaxial films. The films exhibited excellent optical and electrical properties as shown from photoluminescence mapping measurements and Hall measurements, respectively. The annealed undoped ZnO films had carrier concentrations of the order of 10^{19} cm^{-3} . From XAS, it was found that zinc vacancies are predominantly present in the as-synthesized ZnO film. As the film is annealed at 200°C , there is an increase in zinc vacancy concentration. Further annealing the film at 300°C and 400°C seems to cause the appearance of oxygen vacancies. However, as the ratios obtained for the coordination numbers of Zn-O to Zn-Zn correlations are close to ideal, it can be said that there are about the same concentration of zinc and oxygen vacancies in the lattice. A possible reason for this could be the appearance of pores, formed by annihilation of cation and anion vacancies, which is observed at temperatures above 200°C . De-convolution of the defect level emission (DLE) peak of the room temperature photoluminescence (PL) mapping spectra showed a shift from green to yellow and red as the sample is annealed at higher temperatures. The green band is attributed to zinc vacancies, the yellow band to the doubly charged oxygen vacancies and the red band is attributed to oxygen interstitials. The red-shift suggests that the net zinc vacancy concentration decreases while there is an increase in oxygen interstitials as the film is annealed at higher temperatures. It is noted that the zinc vacancy increase seen by XAS is more reflective of the bulk while the zinc vacancy decrease as indicated by PL is more indicative of the surface, and this may be a reason why the results cannot be directly correlated.

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2. ZnO powders were synthesized at moderate pH as well as at higher pH mimicking the growth conditions for the films. The local structure of ZnO powders grown by various chemical precursor routes and at different pHs were investigated. XAS and PDF analysis found that ZnO powders grown at pH 8.0 have zinc vacancies predominantly present in the system. The ZnO powders grown at a higher pH of 10.9 using two different seeds (labelled sample S1 and S2), similarly contained zinc vacancies as seen from both *ex situ* and *in situ* XAS measurements. Room temperature PL mapping studies showed the presence of a green and yellow band in the as-synthesized ZnO samples, indicating the presence of zinc vacancies and the doubly charged oxygen vacancy, respectively. When the ZnO powders were annealed in air at temperatures from 200°C – 600°C, there was a red-shift suggesting the presence of oxygen interstitials. An *in situ* PDF experiment was carried out and was found that in the short to medium range structure order, zinc vacancies are present. This is shown by a reduction in the Zn-Zn peak intensities when compared with a ZnO standard (purchased from NIST, SRM 674b).

 3. ZnO nanorods were synthesized and pores were characterized using advanced transmission electron microscopy (TEM) techniques. Visible isolated pores were observed within the ZnO nanorods when the sample was annealed. From 3-D electron tomography reconstruction, it was found that the pores exist within the nanorods. In addition, increasing the annealing temperature or annealing for extended periods of time causes the pores to strive to reduce the total surface energy of the system by coalescing and in time, forced out of the morphology, as observed by an *in situ* TEM study. Further defect characterization was
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performed using XAS and found that zinc vacancies are predominantly present in the as-synthesized ZnO nanorods.

4. Ga-doped ZnO films were synthesized and found to have carrier concentrations of the order of 10^{20} cm^{-3} after post-growth thermal annealing. Ga-doped powders were similarly synthesized as well. These Ga-doped films and powders were characterized and from XAS, it was found that Ga^{3+} is sitting in the tetrahedral Zn^{2+} site and is being substituted in the lattice. This shows that Ga^{3+} is acting as a donor, generating one free carrier and increasing the carrier concentration of the Ga-doped ZnO film, as shown by Hall measurements.

Thus, it has been shown that defect characterization has aided in the understanding of ZnO synthesized by a low temperature aqueous solution method. XAS and PDF have served to be a very useful and applicable characterization tool to measure the local defect structure in thin films and powders, as well as the defect structural changes within the ZnO system as annealing proceeds. This enhances the knowledge of the defect structure of ZnO and will narrow the gap in realizing these ZnO films for device applications such as transparent conducting oxides (TCOs) and other applications such as in the optoelectronics field. In addition, advanced microscopy, such as TEM techniques, have allowed the observation of pores within ZnO nanorods. This will serve to be useful for controlling and inducing pores for increased surface area to volume ratio for catalysis and gas sensing applications. It has been demonstrated that XAS and PDF are useful characterization techniques for the understanding of the short and medium range order structures of oxides, such as ZnO. This understanding of ZnO short and medium range structure order will be invaluable for further development of optoelectronic device applications.

Recommendations for future work

Future studies on defect characterization will potentially enhance the knowledge and elucidate the structure-property relationships of such solution grown ZnO for use in the development of semiconductors in the optoelectronics field. Two possible studies are as follows:

1. *High temperature in situ synchrotron experiments on ZnO films*

High temperature *in situ* synchrotron experiments can be carried out to further understand the role of Zn vacancies in the ZnO films and powders. *In situ* EXAFS done during the heating of the ZnO film and powders can mimic the annealing conditions and data can be collected *in situ* to observe the changes in the short-range order of ZnO films during heating. This experimental data seek to confirm the supposition that Zn vacancies are present in the ZnO films and powders synthesized through a low temperature aqueous solution method. This can similarly be compared to the ZnO standard obtained from NIST.

2. *Hydrogen as a shallow donor in ZnO*

Van de Walle¹⁵⁰ made a theoretical calculation and concluded that hydrogen acts as shallow donor in ZnO, giving it its *n*-type conductivity. A useful study to further characterize ZnO would be neutron scattering, which may potentially be used to determine the position of H in ZnO lattice.

3. *Developing modelling and refinement techniques*

The use of more intense X-ray sources may allow an improvement of resolution for data collection, especially for resolving issues with self

absorption for film data collection. Further hardware and optic improvements may help in reducing the overall signal to noise of the spectra. Modelling methods and refinement techniques may be improved to allow the extraction of in-depth information, with less error for a more quantitative evaluation of the local structure order of such oxide materials, and alternative methods of refinement may potentially yield more accurate structural parameters.

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