Control of ZnO Crystal Morphology through Face Specific Adsorption

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Declaration

This is to certify that:

i. the thesis comprises only my original work towards the PhD,
ii. due acknowledgement has been made in the text to all other materials used,
iii. the thesis is less than 100,000 words in length, exclusive of tables, maps, bibliographies and appendices

__________________________
Nathan Johann Nicholas
Abstract

Many of the potential applications of ZnO are dependent upon either its overall shape (e.g. piezoelectric devices or LEDs), or the relative ratio of the different ZnO faces (e.g. catalysis). These applications have stimulated renewed interest in controlling the aspect ratio of ZnO crystals during their growth. One promising way to control the aspect ratio of ZnO crystals during hydrothermal growth is via the introduction of small organic molecules. Whilst there have been many studies showing that particular molecules affect ZnO crystal shape, few studies explain exactly how particular molecules influence growth. The overriding goal of the work contained in this thesis is to enhance understanding of how small organic molecules affect ZnO growth surfaces.

The first data section of this thesis investigates the mechanism for hydrothermal growth of ZnO in an ammonium hydroxide solution (a common synthesis condition). The products formed at 20–90°C and ambient pressure were characterised using Fourier Transform Infrared Spectroscopy (FTIR), X-ray Photon Spectroscopy (XPS), X-ray Diffraction (XRD) and Secondary Ion Mass Spectroscopy (SIMS). Under these conditions, the growth of ZnO occurs via the initial precipitation of \( \varepsilon \)-Zn(OH)\(_2\) (Wülfingite), which subsequently dehydrates, to form Würtzite ZnO. Isotope tracking experiments show that most of the oxygen atoms do not mix with water during the conversion from Wülfingite to ZnO, and thus that the reaction proceeds via conversion in the solid phase, as well as dissolution and re-precipitation.

The dissolution of ZnO, which is the complementary process to growth, was then studied in situ using Atomic Force Microscopy (AFM) under alkaline conditions. The etching of the three native surfaces of ZnO, (0001), (10\(\bar{1}\)0) and (000\(\bar{1}\)) was investigated. In aqueous NaOH solution the (0001) plane forms a stepped surface, whereas the (000\(\bar{1}\)) plane converts into more stable \{10\(\bar{1}\)\(\bar{1}\)\} planes. Dissolution of the (10\(\bar{1}\)0) plane leaves a combination of \{10\(\bar{1}\)\(\bar{1}\)\} and (0001) planes with \{10\(\bar{1}\)1\} risers. Dissolution in solutions containing both NaOH and trisodium citrate causes the (0001) plane steps to increase in number and reduce in height, and cause an overall increase in the rate of dissolution in the \{10\(\bar{1}\)0\} directions. The stability of the (0001) and \{10\(\bar{1}\)\(\bar{1}\)\} planes is attributed to their lower average number of surface oxygens per zinc tetrahedra (1 and 1.5 respectively) than the (0001) and \{10\(\bar{1}\)0\} planes (both having 3). This is because Zn tetrahedra with a lower number of exposed surface oxygen are more difficult to convert into a soluble Zn species as the Zn-O-Zn bonds of the
solid are not as exposed to solution. The formation of the meta-stable \{10\overline{1}1\} surfaces is caused by the dissolution of the edge of the (0001) plane.

The final section of this work large explored the adsorption of small organic molecules to single crystals of ZnO. Single crystals of ZnO were prepared such that the vast majority of a surface consisted of a single crystal plane, as shown by AFM, yet still retained the native hydroxide layer. The presence of the hydroxide layer was confirmed by XPS. The beam path of an infrared spectrometer was modified such that attenuated total internal reflectance spectroscopy could be performed on the faces of these crystals to determine adsorption to a single crystal plane. The results show that citrate strongly and selectively adsorbs to the (0001) face. Studies on the derivatives of citrate indicate that two carboxylate groups separated by three carbon atoms is the key structural component for adsorption to (0001) ZnO. Finally, these results show that ethylenediamine strongly and selectively adsorbs to the (10\overline{1}0) surface.

These findings show that small molecules strongly and specifically adsorb to different ZnO surfaces based on their chemical functionality and molecular shape. Furthermore by selectively adsorbing to a particular ZnO surface, a molecule encourages the preferential growth of that surface.
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The path one takes when doing a PhD can be described as many things; challenging, enlightening, exhilarating, frustrating, depressing, profound, and it is often all of these things simultaneously. However, there are those who help accentuate the positive qualities of a PhD, whilst offering help when the road takes a darker turn. And it is to those people I offer thanks, without you I would not be where I am now.

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1. Introduction
The spontaneous arrangement of randomly dispersed atoms and molecules into an ordered 3-dimensional solid seems like an impossible feat, yet it is seen all around us every day. From the formation of snowflakes on a cold winter’s day, to the brilliantly coloured gemstones that humans have coveted for millennia, these are all the result of the process of crystallisation. Whilst these examples still continue to be studied by scientists, nowadays there is greater focus on the growth of less glamorous, more technically useful crystals. Although crystals such as titanium dioxide, zinc oxide and gallium nitride may not be worth much for their appearance, it is their other properties that make them useful. These types of crystals can be in LEDs and other optical devices, electronic devices, as well as catalysts or biological and gas sensors.1-4

It is often the case that the suitability of these materials for a certain purpose is heavily dependent upon its overall shape.1 For instance in catalysis it beneficial to have very high surface area to volume ratios. However, it is often the case that only a certain face of the crystal is active. So the challenge then becomes to create structured materials with high surface area to volume ratios that are mainly comprised of the active face. Thus, the tailored growth of inorganic crystals has been a long standing goal for material scientists.

In this work the shape controlled growth of one particular inorganic crystal, zinc oxide was investigated. ZnO was chosen as it has a wide potential in many industries depending upon its shape.5-6 High quality crystals of many different shapes7 can be made from mildly basic aqueous solutions (pH around 11) at relatively mild temperatures of less than a 100°C. This makes the shape controlled hydrothermal growth of ZnO very attractive to industry, as it is low energy and environmentally benign system. Furthermore, there is an ever-increasing body of knowledge as to how the morphology of ZnO can be controlled by changing the conditions in which it is crystallised.

The primary goal of this work is to gain further understanding of the process of ZnO growth from solution, and how shape directing molecules influence this process. The hydrothermal growth of ZnO, like the majority of crystal growth, has been postulated to occur directly from solution. However, there is some evidence8-10 to suggest that ZnO forms from one or more metastable intermediates, both crystalline8-10 and amorphous.9 Hence, the determination of
the hydrothermal growth mechanism of ZnO must first be understood before the influence shape directing molecules have on this process can be determined.

With regard to shape controlled growth of ZnO, there have been many reports of different additives encouraging the growth of one or more ZnO crystal planes. These molecules are thought to selectively bind to a particular face of ZnO, lowering the energy per unit area, and thus encouraging the expression of that surface. Furthermore, the adsorbed molecule blocks growth units from being incorporated onto the face, thus hindering growth in the direction orthogonal to that crystal face (growth in a particular direction results in the growth of all adjacent faces, as illustrated by Figure 1.1). Whilst this theory has been demonstrated to be true for other systems (this is elaborated on in Section 2.6), it has not yet been confirmed for ZnO.

![Diagram of growth direction vs. growth of a crystal face](image)

**Figure 1.1:** Growth direction vs. growth of a crystal face. By growing in the ‘z’ direction (as indicated by the dotted lines), the adjacent ‘X’ surfaces increase in size, whilst the ‘Z’ surface remains the same size.

Furthermore, the features that allow a particular molecule to influence the growth habit of ZnO crystals are not well understood. If the key elements of known growth modifiers can be determined, it would then be possible to predict the activity of other potential growth directors, ultimately leading to the intelligent design of growth directing molecules that could be used to form ZnO crystals of any desired shape or aspect ratio.

In this thesis, Chapter 2 provides the background information required to place this work within the context of the greater scientific community. It begins with a review of the structure and properties of ZnO, before going on to classical crystal theory. Examples of previously reported shape-controlled growth studies on a variety of inorganic crystals are then reviewed. The chapter concludes with a comprehensive summary the factors that influence the growth of ZnO, with particular emphasis on the role of different additives on ZnO morphology.
The theory behind the experimental techniques used in this work, as well as their limitations is discussed in Chapter 3. This includes Atomic Force Microscopy, Fourier Transform Infrared Spectroscopy, X-Ray Diffraction, X-Ray Photoelectron Spectroscopy, Mass Spectrometry and Scanning Electron Microscopy. The development of a customised Attenuated Total Internal Reflectance FTIR system is also described.

The first experimental section, Chapter 4, investigates the mechanism by which the hydrothermal growth of ZnO occurs. How small molecules induce face specific growth cannot be fully understood until the general process by which ZnO grows under hydrothermal conditions is first determined. To investigate the hydrothermal growth mechanism of ZnO, powders were synthesised using a process known to create ZnO particles as a function of temperature between 90°C and 20°C. The composition of the products was studied using a variety of spectroscopic techniques and from these results a reaction pathway for the crystallisation of ZnO from solution was developed.

In Chapter 5 the focus shifts from ZnO growth to the complementary process of dissolution. The dissolution of ZnO single crystals with nominally (0001), (0001) and (1010) surfaces under basic conditions was studied in-situ using Atomic Force Microscopy. The influence of citrate ions on ZnO dissolution was also investigated. From these studies a mechanism by which the different faces of ZnO etch, as well as how citrate affects this process is presented.

In Chapter 6 the findings of the previous chapter are utilised to develop highly planar crystal surfaces, expressing primarily (0001) or (1010) planes. These surfaces were then used for molecular adsorption studies. An ATR-FTIR setup for the ZnO prisms available was also designed. Using this setup the interactions between two complementary growth directing molecules, trisodium citrate and Ethylenediamine, and the (0001) and (1010) surfaces of ZnO were studied. Furthermore, as citrate ions have three carboxylate groups that could interact with the surface, the adsorption of several derivatives of citrate were also studied, to gain more insight into functional groups active in face specific bonding.

Chapter 7 then summarises the major findings of this work, and makes recommendations on future studies that could be conducted to advance the work presented here.
2. Background & Literature Review

2.1. ZnO Structure

Many of the properties of ZnO that make it useful for a wide range of applications are related to its crystal structure. Crystalline ZnO can conform to either a Würzite, Zinc Blende, or Simple Cubic structure, depending on the production method. Natural ZnO exclusively forms hexagonal crystals with a Würzite structure (Figure 2.1), having a point group of C_{6v} (6mm). Würzite ZnO comprises hexagonally close packed alternating sheets of oxygen and zinc atoms, with every zinc atom being tetrahedrally co-ordinated to four oxygen atoms and vice-versa, as shown in Figure 2.1a. The three native faces of ZnO crystal are: the Zn-terminated (0001) plane (Figure 2.1c), the O-Terminated (0001̅) plane and the six equivalent non-polar {10̅10} planes (for an explanation of the Miller Index notation used in this work see Appendix 9.1).

![Figure 2.1: The structure of Würzite ZnO. (a) Projection along [10̅10] direction, showing the tetrahedral co-ordination of the zinc atoms (grey) and oxygen atoms (red). (b) Projection along [1̅120] more clearly showing the Zn-O dipole nature of the {10̅10} faces. (c) the (0001) surface, with the Zn atoms above the plane. (d) the (0001̅) surface, with the O atoms above the plane.](image-url)
2.2. Surface Structure of (0001), (000̅1) & (10̅10) ZnO

As this work is focused on molecular interactions occurring on different ZnO surfaces, it is important to know the surface structure of the native ZnO faces, both ideally and in solution. The following section contains a brief summary of different ZnO surface structures, both ideally and when hydrated. For a more in-depth review of the topic, including the adsorption of other small molecules besides water (such as H₂, CO, etc.) the reader is directed to a review entitled ‘The Chemistry and Physics of ZnO Surfaces’ by C. Wöll.¹³

2.2.1. (10̅10) ZnO

The six equivalent {10̅10} surfaces of ZnO are generally most stable of all ZnO surfaces, and as a result they form the majority of the crystal surface area (when grown under hydrothermal conditions without growth modifying molecules). The idealised bulk truncated structure of (10̅10) ZnO comprises of staggered layers Zn-O dipoles aligned in the [0001] direction as shown in Figure 2.2a. This configuration leaves the surface with each surface zinc atom and each surface oxygen atom with a vacant bond (also known as a ‘dangling bond’). The (10̅10) plane is also electrically neutral and has no net dipole moment¹³ (unlike the other native ZnO surfaces). It is for this reason that this surface is the most stable ZnO plane. Further to this, in-vacuo studies of (10̅10) ZnO have shown no significant surface reconstruction, with the surface remaining in the idealised (1 x 1) state.¹⁴-¹⁷

When the (10̅10) surface is hydrated (in-vacuo), studies have shown both experimentally¹⁵, ¹⁸-¹⁹ and theoretically¹⁴ that two different reconstructions of the (10̅10) surface co-exist, with the surface forming both (1 x 1) and (2 x 1) reconstructions. The (1 x 1) construction (Figure 2.2b) comprises of the adsorption of an intact water molecule to each surface zinc atom, with the oxygen dangling bond being stabilised by hydrogen bonding to the adsorbed water. For the (2 x 1) reconstruction, every second adsorbed water molecule in the (1 x 1) reconstruction dissociates, forming two surface hydroxide species (Figure 2.2c). As the difference between these two reconstructions is the dissociation of a water molecule, it been shown that at room temperature these two structures not only co-exist but are interchangeable, constantly switching between the two different reconstructions.²⁰

Whilst the hydrated surface structure of ZnO has been determined in-vacuo, how the surface reconstructs in solution is still to be determined. One would initially assume the structures
would be similar, as they both involve the interaction between water molecules and the ZnO surface. However in solution the termination of an oxide surface is dependent upon pH, as like most oxide surfaces, ZnO surfaces are amphoteric in nature (being able to either accept or donate one or more protons per surface group, depending on the solution conditions). The acid-base properties of the different ZnO surfaces has not been well characterised. It has been reported\textsuperscript{12} that the isoelectric point of ZnO powders, which are primarily composed of \{10\overline{1}0\} planes, is at about 9.5. This would indicate that the (10\overline{1}0) should also have an isoelectric point also around 9.5. AFM measurements on (10\overline{1}0) have shown\textsuperscript{21} the isoelectric point of the surface is 10.2 ± 0.2. However measurement of the surface potential by another group at pH = 11 showed that the surface is still positive.\textsuperscript{22}

![Figure 2.2: The surface structure of (10\overline{1}0) ZnO. (a) the bulk terminated structure, reproduced from Wöll\textsuperscript{13}. (b),(c) The hydrated (10\overline{1}0) surface, top and side views, showing the (1 x 1) (b) and (2 x 1) reconstructions, reproduced from Meyer.\textsuperscript{15} Grey atoms represent zinc, red atoms represent oxygen atoms originating from ZnO, blue atoms oxygen atoms originating from water molecules and white atoms represent hydrogen.]

2.2.2. (0001) ZnO

The bulk terminated (0001) surface of ZnO is comprised of a hexagonally close packed layer of zinc atoms each co-ordinated to three oxygen atoms below the plane (Figure 2.1c). Even though this surface is electrostatically unstable, studies have shown that the (0001) surface retains a (1 x 1) structure.\textsuperscript{23-26} Having said that, there is evidence\textsuperscript{27} of significant relaxation of the surface atoms (surface relaxation is when the surface atoms shift in position relative to the
bulk atoms with minimal changing their positions relative to each other) as well as the formation of a highly defective surface. STM (Scanning Tunnelling Microscopy) imaging of the (0001) surface showed the formation of triangular hillocks, as opposed to atomically flat planes. When hydrated, it has been shown that the (0001) surface again remains terminated by a (1 x 1) reconstruction, with the dangling bond of each of the zinc atoms being filled by a hydroxyl group. In aqueous solution, the isoelectric point of (0001) ZnO in solution has been found to be at pH = 8.7 ± 0.2 which almost an entire pH unit below the isoelectric point of ZnO powders. Further to this a separate study confirmed that at pH = 11 (the pH at which ZnO is typically grown) the (0001) surface is negatively charged.

2.2.3. (0001) ZnO
The (0001) surface is the only low index ZnO surface that deviates from the idealised bulk truncated structure. The bulk truncated structure of (0001) ZnO is the inverse of the (0001) plane, i.e. it consists of a layer of hexagonally close packed oxygen atoms, each co-ordinated to three zinc atoms below the plane (Figure 2.3a). This surface has been shown to relax to a (1 x 3) reconstruction, with every third row of oxygen atoms removed (Figure 2.3b). However, once hydrated the (0001) surface returns to a (1 x 1) surface structure, with every oxygen atom converted to a hydroxide as shown in Figure 2.3c. Furthermore, unlike the (0001) surface, the hydrated (0001) surface shows little relaxation of the atoms from their bulk terminated form. The charging behaviour of (0001) ZnO in solution to date has not been studied.

![Figure 2.3](image.png)

Figure 2.3: The surface structure of (0001) ZnO. (a) the bulk terminated structure (b) the stabilised (1 x 3) reconstruction of (0001) ZnO. (c) the hydrated (0001) surface. All images were reproduced from Wöll. Grey atoms represent zinc, red atoms oxygen and white atoms hydrogen.
2.3. ZnO Single Crystals: Properties & Applications

Whilst ZnO powders have been used industrially for various purposes, such as a white pigment, UV blocker, etc, the use of tailored single crystal ZnO has yet to be commercially realised. This may change in the near future, as the properties of ZnO make it potentially useful in many different applications, which are described below.

2.3.1. Light Emitting Diodes

As ZnO is a semiconductor with a band gap of 3.37 eV (which corresponds to the emission of blue light at a wavelength of 375 nm) with an exciton energy of 60 meV there has been recent interest in the use of ZnO in LEDs.\textsuperscript{5,22,32-35} Whilst n-type ZnO has been successfully synthesised, the formation of p-type ZnO is proving difficult.\textsuperscript{36} However, it has been shown that ZnO single crystals can be used as a current spreader in LEDs, increasing the efficiency of existing LED systems.\textsuperscript{37} While both ZnO plates\textsuperscript{32} and rods\textsuperscript{35} have shown to suitable for use as LEDs, in order for ZnO to be used as a current spreader it needs to be grown as a thin film epitaxially on a GaN substrate.\textsuperscript{37} Due to the lattice match between GaN and ZnO this means ZnO must be grown primarily in the \{10\bar{1}0\} directions (i.e. as plates).

2.3.2. Solar Cells

As ZnO is a transparent semiconducting material with high electron mobility\textsuperscript{38-39} it is a candidate for use in dye sensitised solar cells (DSC’s).\textsuperscript{40} The key element to a highly efficient DSC is the interaction between the photosensitive dye and the charge carrier. When the dye is exposed to light it generates an electron. This electron is then promoted to the conduction band of the charge carrier, which then transports it to the anode. Factors such as surface area of the charge carrier (higher surface area means more dye sensitive molecules can be adsorbed), transfer between the dye and the carrier, as well as the recombination rate (i.e. how readily the generated electron recombines with the positively charged dye molecule) all affect the efficiency of the DSC.\textsuperscript{40} Whilst ZnO particles have been used in DSC’s\textsuperscript{41}, reports have shown that substrates comprised of oriented ZnO nanowires show more potential for use in DSC’s.\textsuperscript{6,38-39,42}

2.3.3. Piezoelectric Devices

As a result of its structure, ZnO crystals contain a permanent dipole moment (that is there is a permanent separation of charge within each unit cell of the crystal), making the crystals piezoelectric. Therefore, when a stress is applied to ZnO crystals (by bending, compression, etc.) a voltage difference develops across the crystal. This means that ZnO crystals have the
potential to act as micro/nanoscale batteries. Piezoelectric devices can also be used as nanometre scale actuators. In a reverse of the previous application, when a voltage is applied across a piezoelectric crystal, the crystal deforms, elongating in the direction of the dipole moment. This elongation is relative to the size of the crystal (as the applied voltage causes a distortion of the unit cell dimensions), and increases with an increase in applied voltage (up to a point).

The piezoelectric property of ZnO has been exploited by several groups to generate electronic devices, including one group that has incorporated ZnO fibres into a cloth matrix, leading to the potential of clothing that can generate power when worn. In order for ZnO to function effectively as a piezoelectric device, the crystal must be grown primarily along its permanent dipole moment, i.e in the [0001] direction. This means that ZnO nanowires are particularly suited to this purpose.

2.3.4. Sensors
ZnO substrates have shown some potential for use in solid state gas sensors. Solid state gas sensors function by measuring changes in electrical conductivity as the target molecule adsorbs to the sensor. Cd-doped ZnO nanowires have shown excellent sensitivity and response time to ethanol.

2.3.5. Catalysis
ZnO based powders have been shown to act as a catalyst for the conversion of CO\(_2\) and water to methanol. However, ab-initio modelling has shown that CO\(_2\) and water only becomes reactive when adsorbed to the (10\(\bar{1}\)0) surface. Therefore to increase the catalytic activity, whilst simultaneously reducing the amount of catalyst needed, ZnO powders with high aspect ratios are desired.
2.4. Crystal Growth from Solution

The spontaneous formation of a regular solid phase from a liquid medium, can occur in one of two ways: solidification from a melt, or precipitation from solution.\textsuperscript{49} If the liquid phase is comprised of a pure substance and crystallisation is induced by lowering its temperature to below its melting point, the resultant solid is said to have been formed from a melt. An obvious example of this process is the formation of ice from water at 0°C, but it equally applies to more complex systems such as cooling of a molten salt or polymer melts.

The second method, solution precipitation, occurs when the chemical potential of a species in solution exceeds the saturation potential, or ignoring the chemical activities, the concentration exceeds the saturation concentration. The formation of solid silver chloride (AgCl) by mixing aqueous solutions of silver nitrate (AgNO\textsubscript{3}) and potassium chloride (KCl) is a classic example\textsuperscript{49} of precipitation from solution.

Solution precipitation will be the focus of the rest of this discussion. The phenomenon of crystal growth from solution can be separated into the following processes,\textsuperscript{49-51} supersaturation, nucleation, growth and aging, which are discussed in the following sections.

2.4.1. Supersaturation

All solids when immersed in a liquid dissolve to some extent. The degree in which dissolution occurs is usually expressed in terms of a solubility product $K_s$. Once the system reaches equilibrium it is said to be saturated with respect to the solid. The solubility product for the generalised binary ion equilibrium:

$$A_x B_y \rightleftharpoons xA^{n+}_{(aq)} + yB^{m-}_{(aq)} \text{ (Reaction 2.1)}$$

is:

$$K_s = [A^{n+}_{(aq)}]^{x}_{eq}[B^{m-}_{(aq)}]^{y}_{eq} \text{ (Equation 2.1)}$$

assuming an ideal solution, and ignoring the activity coefficients (a valid assumption as, in most crystal growth systems, the solubility of the precipitate is low). The subscripts eq refer to equilibrium concentrations. It should be noted that due to electrical neutrality the ratio of $x:y$ is equal to the ratio of $m:n$.

If, after establishing equilibrium, the concentration of one of the ions is increased, then solution becomes supersaturated and, above a certain degree of supersaturation, a solid
precipitate forms. As this precipitate forms, the dissolved ion concentration decreases, which lowers the free energy of the system.

Supersaturation can be induced by four different ways; altering the temperature (in most cases solubility increases with temperature), decreasing the fraction of solvent (via evaporation), increasing the concentration (as illustrated by the silver chloride example previously) or changing the solvent conditions (by introducing another solvent). It is also possible to induce supersaturation by increasing the system pressure, but this has only a small effect on supersaturation and it is often impractical to implement.

When the system is supersaturated it is no longer at equilibrium, the solute concentrations can be expressed as the function $\Pi$, defined by Equation 2.2, where the concentrations of $A^{n+}$ and $B^{m-}$ are now independent of each other and above their equilibrium values:

$$\Pi = [A^{n+}]^x [B^{m-}]^y$$ (Equation 2.2)

The degree of supersaturation (i.e. how far removed from equilibrium the system) is then defined as:

$$S = \left(\frac{\Pi}{K_{sp}}\right)^{1/(x+y)}$$ (Equation 2.3)

Thus $S = 1$ for a saturated solution and $S > 1$ for a supersaturated solution. The degree of supersaturation is an important parameter in crystal growth. If $S$ only exceeds one by a small amount, the rate of nucleation is low (so few crystals form) and crystal growth rate is slow, but the crystals tend to be more uniform in size and have fewer defects. On the other hand, if the degree of supersaturation is high, the nucleation and growth processes occurs so rapidly that the atoms being incorporated into the crystal lattice do not have time to adopt the lowest energy state, resulting in a faceted crystal faces, and the formation of non-native faces or branched crystals that have a large number of defects.

2.4.2. Nucleation

Nucleation is the initial formation of a crystal. It can either occur by the spontaneous clustering of dissolved constituents, eventually forming small, pure, solid crystals (homogeneous nucleation) or the constituents can form nuclei by adsorbing to small particulate contaminants, if present (hetero-nucleation). In this process the energy required to form the surface of the crystal is offset by the reduction in the degree of
supersaturation of the system. For the simplest case of crystallisation of a spherical particle of radius \( r \) it can be shown\(^{53} \) that the change in Gibbs Free Energy as a function of crystal radius is given by Ostwald-Freundlich equation (the crystal growth equivalent Gibbs-Thompson equation):\(^{54} \)

\[
\Delta G = \frac{-4\pi r^3}{3V_c}kT\ln(S) + 4\pi r^2 \quad \text{(Equation 2.4)}
\]

where:
- \( \Delta G \) = Change in Gibbs free energy of crystal formation
- \( r \) = Radius of the nucleus
- \( \sigma \) = Surface energy of the nucleus
- \( V_c \) = Unit cell volume of the nucleus
- \( z \) = number of molecular units per unit cell
- \( k \) = Boltzmann constant
- \( T \) = Temperature

When Equation 2.4 is plotted as a function of \( r \) (Figure 2.4) it can be seen that below a certain crystal size (\( r^* \), the critical crystal radius) the growth of a crystal is unfavourable as \( \frac{d\Delta G}{dr} \) is positive. However above the critical nucleus size the continued growth of a crystal is energetically favourable. The size of the critical nucleus is determined by setting \( \frac{d\Delta G}{dr} = 0 \):

\[
r^* = \frac{2\sigma V_c}{zkT\ln(S)} \quad \text{(Equation 2.5)}
\]

Substituting \( r^* \) into Equation 2.4 the activation energy of crystallisation (\( \Delta G^* \)) can be determined:

\[
\Delta G^* = \frac{16\pi^3\sigma V_c^2}{3(3z\ln(S))^2} \quad \text{(Equation 2.6)}
\]

This reduces to:

\[
\Delta G^* = \frac{\sigma}{3} \varphi^* \quad \text{(Equation 2.7)}
\]

where \( \varphi^* = \) surface area of the critical nucleus = \( 4\pi(r^*)^2 \).

So far only a spherical crystal has been considered. Whilst this is relevant for the condensation of a liquid drop from vapour (i.e. the original Gibbs Thompson equation), it is irrelevant for crystal growth. This is because crystals are confined to fixed geometries based on the crystal structure. Furthermore if the crystal structure is anisotropic the different surfaces will have different surface energies. After accounting for the different surface energies, Equation 2.7 becomes:\(^{53} \)

\[
\Delta G^* = \frac{1}{3} \sum_n (\sigma_n \varphi_n^*) \quad \text{(Equation 2.8)}
\]
where \( \sigma_n \) and \( \varphi_n \) are surface energy and surface area (respectively) of a particular crystal face.

As stated earlier, supersaturation of the system is the key factor influencing nucleation. From Equation 2.6 it is evident that the activation energy for homo-nucleation is inversely dependent upon the square of \( \ln(S) \). Also from Equation 2.5 the size of critical nucleus is inversely dependent upon \( \ln(S) \). Therefore, the higher the degree of supersaturation, the smaller the initial nucleus becomes, whilst simultaneously becoming easier to form. This leads to the rapid generation of a greater number of nuclei. The nucleation rate can be modelled using the general kinetic equation:\(^{54}\)

\[
\dot{N} = N_0 e^{-\frac{\Delta G^*}{RT}} \quad \text{ (Equation 2.9)}
\]

2.4.3. Growth

Once a crystal nucleus has been formed, and the degree of supersaturation is low, the crystal will continue to grow, rather than new nuclei forming from solution. Crystal growth can be separated into the following processes: diffusion of the growth unit from solution to the crystal surface, incorporation of the growth unit into the lattice and any resultant reactions, and finally, the diffusion of any by-products into the bulk solution.\(^{49, 52, 55}\) In the case of hydrothermally grown ZnO the last stage, diffusion of by-products, is not relevant as water is

![Figure 2.4: Change in Gibbs free energy as a function of crystal size for different degrees of supersaturation. At the critical radius \( r^* \) growth of crystals becomes favourable. As the degree of supersaturation is increased, the critical radius and activation energy decreases.](image-url)
produced when aqueous Zn(II) ions form ZnO. Furthermore, this work focuses on selective growth of particular faces, in which case diffusion to and from all faces should be similar.

After a growth unit has diffused from the bulk to the crystal surface it usually must undergo some form of change before being able to be incorporated into the crystal. This could be a partial or complete dehydration of the dissolved complex, a reaction with the crystal surface to form a continuous network, or the adoption of a specific conformation/orientation. A simplified example of this can be demonstrated by what must occur on an atomic level in order for zinc oxide to form from solution. Zinc ions form tetrahedral complexes in solution. At pH 11 (which is the condition used for optimal crystal growth as ZnO solubility is at a minimum) exists primarily as Zn(OH)$_2$(H$_2$O)$_2$. Therefore, in order to become ZnO it must undergo both dehydration and reaction via the overall equation:

$$\text{Zn(OH)}_2(\text{H}_2\text{O})_2(\text{aq}) + \text{ZnO}_\text{(s)} \rightarrow 2\text{ZnO}_\text{(s)} + 3\text{H}_2\text{O}(\text{l}) \quad \text{(Reaction 2.2)}$$

The adsorption site is another factor affecting crystal growth. This could be the location in which a growth unit adheres to on a surface, or for an anisotropic crystal, which face it adsorbs to. For instance if the simplest case of an isotropic simple cubic structure (as illustrated in Figure 2.5) is considered, then as the crystal is growing a crystal front will appear (a crystal front is the surface perpendicular to the primary direction of growth), offering several sites which a new unit could be incorporated into, either (A) forming a new front, (B) propagating an existing front or (C) consolidating the crystal front. It is obvious that (C) is the most energetically favourable, as no new faces are formed, whereas (B) and (A) create 2 and 4 new unit faces respectively, and the formation of new faces results in an increase in surface energy.
Figure 2.5: Different adsorption sites for a growth unit (denoted by a dark grey top) being incorporated onto a crystal surface. A) Adsorbs onto the face creating a new front and consequently four new surfaces, B) Adsorbs onto an edge, propagating the crystal front and creating two new surfaces and C) Adsorbs on a corner, consolidating the crystal front without creating any new surfaces. The crystal growth front is highlighted in light grey.

From this it would appear that crystal growth would have a tendency to occur in planar waves, with a new layer being able to form if there was sufficient driving force to encourage (A)-type attachment.\textsuperscript{51} This simplistic model however, ignores the fact that crystals do not form into perfect lattices, but instead often form with defects in the crystal structure. These defects can be caused by factors such as the dynamics of dissolution/adsorption, stresses that develop (especially in epitaxial growth) and the incorporation of impurities into the lattice. The defects are important to the process of crystal growth as they usually offer a low energy binding site which encourages crystal growth. In particular it has been shown that the emergence of a screw dislocation (that is when a crystal plane becomes split so that it simultaneously occupies two planes) would allow perpetual low energy sites for growth perpendicular to that plane, via a spiral propagation mechanism (Figure 2.6).\textsuperscript{49,51}
2.4.4 Anisotropic Crystal Growth

So far only isotropic crystal growth has been discussed, with no mention of what occurs when the crystal structure is anisotropic. The concepts from Section 2.4.3 still apply, but do not predict why a particular face can grow preferentially when the crystal structure is anisotropic. To understand why this preference occurs, consideration must be given to the thermodynamics and kinetics of crystal growth.

It is often observed that anisotropic crystal growth occurs in such a way as to minimise the free energy of the system, i.e. the lowest energy faces form the majority of the surface area.\textsuperscript{49-51} This is most clearly shown by the Wulff Rule\textsuperscript{53} which states that, at equilibrium, ratio of surface energy ($\sigma$) to distance from the centre of the crystal ($h$) is constant for each face, i.e.

\[
\frac{\sigma_n}{h_n} = \frac{2kT}{\gamma c} \ln(S) \quad \text{(Equation 2.10)}
\]

or, as the degree of supersaturation does not depend on crystal face,

\[
\frac{\sigma_1}{h_1} = \frac{\sigma_2}{h_2} = \frac{\sigma_3}{h_3} \quad \text{etc. (Equation 2.11)}
\]

If the relative surface energies of the different faces of a crystal are known, this relation also allows the equilibrium crystal habit to be calculated. For instance consider a crystal with the relative surface energies listed in Table 2.1. To determine the equilibrium crystal habit a plot of the crystal vectors is constructed (called a Wulff construction). The start of each vector is taken to be the same point (as this point is at an arbitrary location, the origin is typically used), the direction of each vector is normal to the surface it represents, and the length is...
proportional to the surface energy. The surface orthogonal to the vector is drawn (at the vector end) and the smallest resulting closed polyhedon represents the equilibrium crystal habit. An example using the values in Table 2.1 is given as Figure 2.7.

<table>
<thead>
<tr>
<th>Crystal Face</th>
<th>Relative σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>±(100)</td>
<td>2.5</td>
</tr>
<tr>
<td>±(010)</td>
<td>1.0</td>
</tr>
<tr>
<td>(001)</td>
<td>2.0</td>
</tr>
<tr>
<td>(001̅)</td>
<td>0.6</td>
</tr>
<tr>
<td>±(110), ±(110̅)</td>
<td>2.3</td>
</tr>
<tr>
<td>(011), (011̅)</td>
<td>1.5</td>
</tr>
<tr>
<td>(101), (101̅)</td>
<td>2.1</td>
</tr>
<tr>
<td>(011), (011̅)</td>
<td>0.5</td>
</tr>
<tr>
<td>(011), (011̅)</td>
<td>1.7</td>
</tr>
</tbody>
</table>

From Figure 2.7 it can be seen that the resultant 3D shape is comprised of the lowest energy faces in each direction. The higher energy faces that fell outside the enclosed shape and so are not expressed. Whilst the Wulff construction shows thermodynamically favoured crystal shape, the influence of kinetics on anisotropic crystal growth must also be considered.

Consider Figure 2.8 which illustrates the growth rates two crystal faces (001) and (011) at different times, with the length of the line indicating the size of the crystal face and the distance between successive lines indicating the growth rate of the crystal face. Even though the growth in the [100] and [010] directions is much slower than the growth in the [110] direction, the (100) and (010) faces are actually increasing in size, whereas the (110) face is decreasing, and would potentially disappear with time (being replaced by the (100) and (010) crystal faces). In this way the kinetics of the system that can also control crystal morphology with the face orthogonal to the slowest growth direction being dominant.
Figure 2.7: Wulff construction of an arbitrary crystal with the relative surface energies presented in Table 2.1. (a-c) 2D projections of the distance of the different surfaces from the crystal centre (grey dot). Dark arrows indicate the relative energies of each plane, dotted lines represent the crystal surfaces location within the projection plane, and solid line is resultant crystal shape, being the closed polygon closest to the crystal centre. (d) 3D crystal shape based of the Wulff construction, representing the equilibrium shape of the crystal.

However, the kinetics and thermodynamics are not totally independent. It is often the case that slowest growing faces is also the most stable, as any growth units being incorporated on these faces results in the formation of new surfaces that have a higher surface energy.\(^{55}\) The surface energy of a particular face is not solely controlled by atomic bonding and structure however, as solution factors such as pH, solvent and impurities can influence the relative energies of the different crystal faces, as explored in detail in for ZnO Section 2.8. So to summarise, the growth habit of anisotropic crystals is ultimately influenced by the grow rates of the different crystal faces, with the dominant face growing at the slowest rate. However, the growth rate is often determined by the thermodynamics of the system and so as a result the crystal adopts a conformation so that its surface energy is at a minimum.
2.4.5. Aging

Crystallization causes a decrease in supersaturation and thus a decrease in growth rate. Eventually this leads to the solution becoming saturated, allowing no further growth to occur. However, when crystals are present in a saturated solution, precipitation still occurs, it is merely balanced by the dissolution of the crystal. Thus there is no net change to the degree of solution saturation, but mass is still transferred between the solid and aqueous phases. This allows several different processes to occur (either in isolation or simultaneously) to reduce the energy of the system. These processes are collectively known as aging.

The most common process in aging is that of Ostwald Ripening.\textsuperscript{49, 53-54} Local differences in saturation and the timing of nucleation leads to the formation of crystals that are not of a uniform size. Thus in solution there will be a size distribution of crystals. As a consequence the smaller crystals, with their higher surface to volume ratio (and hence higher average free energy) will dissolve preferentially, allowing the larger crystals grow. This process ultimately leads to a net reduction in the surface area of the system (and as such a reduction in the free energy of the system). It is apparent that the system will continue this way until there is only a single crystal present, or every crystal in the system is the same size. Another consequence of ripening is the smoothing of surfaces as this will also reduce the free energy of the system.

Flocculation occurs via the colliding and subsequent joining of formed crystals, which lowers the free energy by reducing the overall surface area of the system and increases the magnitude of the van der Waal forces.\textsuperscript{49} This process occurs frequently in agitated systems, where any repulsions can be overcome by particle momentum, but is also apparent in
stagnant systems, in particular when fixed crystals are allowed to grow into contact with each other.

The final aging process that is common is the transformation from metastable phases.\textsuperscript{49} During the crystallisation process it is possible for a less stable, kinetically favourable crystalline phase (or phases) to form in favour of the lowest energy thermodynamically favourable state. Then with time the initial solid phase transforms into the thermodynamically favourable crystalline state. The most common examples of this are seen at high temperatures and pressures as under these conditions the atoms are more energetic and therefore more easily able to overcome the understandably high activation barrier preventing the transformation to the more stable solid. An example of this is the conversion of the metastable anatase titania to the more stable form of rutile titania when heated to over 550°C.\textsuperscript{57}

At lower temperatures this transformation can still occur, though it usually takes a very long time. However there are some systems, in particular those observed in nature, where it can occur on a relatively short time frame. For instance it has been reported\textsuperscript{58-62} that marine creatures, such as mollusks, urchins, starfish etc. create complex structures of calcite and aragonite by first creating an amorphous calcium carbonate intermediate. This amorphous intermediate form of calcium carbonate then transforms, in the presence of certain biological molecules (typically proteins) to form crystalline CaCO\textsubscript{3}. This process can occur at biological temperatures (20° to 40°C) and the resultant structure is highly susceptible to the influence of other chemical species present during crystallization.\textsuperscript{58-60} The possibility of ZnO growing by this mechanism (when grown under hydrothermal conditions) is explored in Chapter 4 of this thesis.
2.5 Adsorption to Surfaces

As stated previously, the thermodynamics of the surfaces formed during crystallisation play an important role in determining how the crystal will form, and which crystal faces will be expressed. It has also been suggested that the presence of foreign molecules in the system can alter the surface energy of particular faces by adsorbing to them. This can be shown to be true via the Gibbs Adsorption Equation, which relates Surface Excess (Γ) to Surface energy (σ), and the bulk concentration of the adsorbing species (c):

\[ \Gamma = -\frac{1}{RT} \frac{d\sigma}{d\ln(c)} \] (Equation 2.12)

Here it is assumed that there is only one solute (with unit activity) and the surface excess of the solvent is zero. From this it can be seen that if the adsorbing molecule reduces the surface tension of a solid surface (i.e. dσ is negative), the molecule will adsorb to the surface, thereby increasing the surface concentration (or surface excess). Equation 2.12 can be used to determine the surface excess provided surface tension is known. The surface tension as a function of concentration of adsorbing species can either be obtained experimentally or through modelling.

There are two common surface adsorption models, the Langmuir Isotherm and the Freundlich Isotherm. The Langmuir isotherm is the classical adsorption model that assumes that each adsorption site is equivalent, that a maximum of a single monolayer can form and that there are no lateral interactions between the adsorbed molecules. It relates surface coverage (Θ, expressed as a fraction of occupied sites vs. available sites) to bulk concentration (c) and the adsorption equilibrium constant \( K \) via:

\[ \Theta = \frac{Kc}{1 + Kc} \] (Equation 2.13)

The Freundlich Isotherm is a modification on the Langmuir Isotherm that accounts for the possibility of many different types of adsorption sites with different energies. The Freundlich Isotherm is a power-law adsorption model of the form:

\[ \Theta = K_f c^n \] (Equation 2.14)

where \( n \) is a fitting parameter, \( n \leq 1 \).

For both the Langmuir and Freundlich Isotherms \( K \) can be related to the standard free energy of adsorption (\( \Delta G^\circ \)) on the surface, though in the Freundlich it represents the ‘average’ energy of adsorption:

\[ K = \exp \left( \frac{\Delta G^\circ}{RT} \right) \] (Equation 2.15)
The structure of the molecular species is a key factor in determining its ability to adsorb to a specific surface, and hence influence the growth rate of one or more crystal surfaces. In particular, the interactions between a surface active molecule and a particular surface can be influenced by:

*Binding Strength:* The interaction of the binding species with the crystal surface on an atomic level is largely going to determine how rapidly exchange is going to occur between an adsorbed molecule and a growth species or solvent molecule. An obvious example of this is the fact that a dissociated carboxylic acid group, with a formal negative charge is going to form a stronger bond then a simple OH alcohol group to a positive surface. Furthermore, the specific chemistry involved in these surface interactions will also contribute to the binding strength of a molecule to a crystal surface. For instance, acids bind poorly to surface hydroxyls present on silicon, whereas alcohols and silanols interact quite strongly, as can bind to the surface via condensation reactions.

*Surface Chelation:* If the molecule binding to surface has multiple potential interaction sites there is the possibility that these sites could bind to several different surface atoms simultaneously, thereby making the molecule harder to remove once adsorbed. These binding arrangements could involve a single charge site interaction (e.g. a carboxylate group could bind to the surface through one or two oxygen atoms), or multiple interaction sites (e.g. if a molecule had two amine groups it could bind to two different charge sites simultaneously).

*Molecule/Surface Registry:* In order for a molecule to bind to the surface at more than one site, the geometry of the molecule must be complementary to the geometry of the surface. This means that an adsorbing molecule must be able to adopt a conformation such that the active binding groups are at a similar distance to that of the distance between interaction sites on the surface. Furthermore, the conformation the molecule adopts must be a low energy conformation, with minimal strain being introduced by binding to the surface.
2.6. Anisotropic Inorganic Crystal Growth from Solution

Generally, the anisotropic growth of crystals can be achieved by either exploiting the innate anisotropy of certain crystal structures or by restricting the growth of the crystal in certain directions by use of a template.\(^1\) As this work pertains to the growth of an inherently anisotropic crystal, the rest of this section shall focus on this form of anisotropic growth. For a detailed overview of template directed growth, the reader is directed to a review on anisotropic growth by Younan Xia et al.\(^1\) While the fundamental concepts of anisotropic growth due to inherent crystal anisotropy has already been discussed, this section illustrates some particular examples of how the shape of anisotropic crystals can be tailored.

2.6.1. Calcium Carbonate

Calcium Carbonate (CaCO\(_3\)) can conform to a vast array of shapes and phases in nature, as organisms can tailor the shape of CaCO\(_3\) crystals to build complex structures such as shells or spines.\(^64\) As such the reproduction of these shapes under laboratory conditions has garnered a lot of interest over the years. Whilst CaCO\(_3\) crystals with the scale and complexity found in nature still eludes researchers, significant insight has been gained in CaCO\(_3\) morphological control in general. There are three different methods by which the shape of CaCO\(_3\) may be influenced; by controlling which polymorph of CaCO\(_3\) forms, by the introduction of soluble shape directing molecules and by restricting growth via the use of templates or self-assembled macromolecular structures.\(^65\)–\(^66\) Whilst it is thought that all three methods are implemented simultaneously in nature,\(^67\) this section will focus on the first two methods only, as they are the most relevant to the work contained within this thesis. For a more comprehensive review of the topic (including templated growth) the reader is directed to the review articles by Meldrum\(^66\) and Cölfen.\(^65\)
CaCO$_3$ can conform to several different crystal structures, each with their own crystal habit. The most common forms of CaCO$_3$ are calcite, aragonite, vaterite and amorphous. The structures of the three main crystalline forms of CaCO$_3$ (calcite, aragonite and vaterite) are given as Figure 2.9. Calcite, the most thermodynamically stable form of CaCO$_3$, has a face-centred rhombohedral unit cell (Figure 2.9a) and typically forms parallelepiped (distorted cubic) crystals. Aragonite, which is slightly less stable than calcite, has an orthorhombic unit cell (Figure 2.9b) and typically forms needle-like crystals elongated in the [001] direction. The least stable crystalline CaCO$_3$, vaterite, has a hexagonal crystal structure (Figure 2.9c) and often forms spherical polycrystalline clusters. The amorphous form of CaCO$_3$ is very unstable and rapidly converts into one of the more stable forms of CaCO$_3$, however there is strong evidence to support that it is an essential intermediate in biological CaCO$_3$ growth.

As calcite, aragonite and vaterite have different crystal habits it is obvious that CaCO$_3$ morphology can be controlled by encouraging the formation of one particular polymorph. Whilst the selection between these different polymorphs can occur in the typical manner (i.e. by varying synthesis temperature and pressure, or the degree of supersaturation), the introduction of certain additives during crystal growth can also help stabilise the less favourable forms of CaCO$_3$. The most well-known case is when CaCO$_3$ is formed in the presence of magnesium ions, which retards the growth of calcite (by the incorporation of
Mg$^{2+}$ ions into the crystal lattice) and encourages the formation of aragonite (which does not incorporate Mg$^{2+}$ ions into its crystal lattice). Another example of morphological control by polymorph selection is when CaCO$_3$ is formed in the presence of simple alcohols which prevent vaterite from converting into calcite.

The incorporation of different molecules into the growth medium can also be used to change the morphology of a particular type of CaCO$_3$. A striking example of this is the growth of calcite in the presence of L/D-aspartic acid (L/D-Asp) reported by Orme et al. They found that while both L-Asp and D-Asp caused the (114) and (014) planes to convert into a series of higher index planes (designated as \{hk0\}), resulting in curved crystal faces, as shown in Figures 2.10b-d, L-Asp preferentially binds to the (114)/(104) step, whereas D-Asp preferentially binds to the (014)/(104) step. This encourages the growth of (014) plane over the (114) plane (for D-Asp, the opposite is true for L-Asp) resulting in the formation of asymmetric crystals as shown in Figures 2.10d and 2.10e.

The influence of dicarboxylic acids of different lengths on calcite formation has also been investigated by Mann et al. It was found that di-carboxylic acids encourage the formation of \{104\} planes. Furthermore this effect was more pronounced with shorter dicarboxylates, with malanoic acid (HOOC-CH$_2$-COOH) having the greatest effect. The authors believed there were different mechanisms at work, with malonic acid occupying charge sites (i.e. it was replacing CO$_3^{2-}$ on certain faces, disrupting crystal growth in that direction), whereas the larger molecules were adsorbing only due to electrostatic attraction.
As a way of determining how organisms form the complex CaCO₃ structures found in nature, CaCO₃ has been grown in the presence of soluble proteins extracted from biological CaCO₃ samples. However, due to their complex nature, the proteins used are often poorly characterised (especially in regards to secondary and tertiary structure under experimental conditions) and so the mechanism by which the macromolecules affect CaCO₃ is hard to determine. To remedy this, the growth of CaCO₃ in the presence of either block copolymers or poly-peptides has been previously performed. These molecules present properties similar to the proteins found in nature, but are simpler in structure and so are easier to model. One of the most interesting results from this work was the use of poly-(aspartate). CaCO₃ grown in poly-(aspartate) resulted in the formation of spherical aggregates which occasionally had hollow helical protrusions (Figure 2.11). These aggregates were mainly comprised of vaterite and, when etched, it appeared as if the structures initially formed from an external membrane, which subsequently grew inwards (as opposed to the normal mode of crystal growth, which is outwards from a central core). The mechanism by which poly(aspartate) helps form these fantastical structures was attributed to a combination of sequestering and concentrating of ionic species, whilst hindering the nucleation and growth of calcite, to encourage the formation of vaterite.
2.6.2. Calcium Oxalate Monohydrate

There has been significant research into the effects of biological molecules, such as citrate and peptides, as well as others, on the morphology of calcium oxalate monohydrate (COM). As COM is the primary component of kidney stones, determining how molecules present in urine influence the growth of COM is crucial to understanding how to mitigate kidney stone growth. The De Yoreo group have been major contributors to this field, combining in-situ AFM growth studies and molecular modelling simulations to investigate the binding of citrate and peptides with large amount of aspartic acid residues. One of their key findings is that citrate molecules preferentially bind at the intersection of the (101) and (101) surfaces of COM, causing a dramatic increase in step density (i.e. the number of steps per area) on the (101) surface. They also predicted the stabilization of a new surface, (120). This was confirmed experimentally by the radical change of surface morphology on the (101) face as shown in Figure 2.9. They also confirmed that citrate inhibits growth of the oxalate terminated, negatively charged (010) face, but to a lesser degree.
For the larger peptide molecules, which have more –COOH functional groups, it was found that the overall peptide structure was more important in determining the effectiveness of a molecule as a growth inhibitor, rather than the overall COOH content. When comparing two different 27-residue peptides with the formula (DDDS)₆-DDD or (DDDG)₆-DDD (where D = aspartic acid, S = serine, G = glycine) the elongated hydrophilic DDDS peptide was proven to be a more effective growth inhibitor (in every direction) than the slightly hydrophobic DDDG. The difference in activity was attributed to greater conformation flexibility of DDDS in solution, allowing it to bind to more surface sites, thereby inhibiting growth. From this work the overriding conclusion is that the activity of a molecule as a growth inhibitor is strongly dependent upon the matching of geometry of the molecule to the surface of the crystal, with charge interactions playing a lesser role.
2.6.3. Indium Hydroxide/Oxide

In the absence of growth modifiers In(OH)$_3$ typically forms regular cubic crystals.\cite{97,100}

However, when the solution conditions, such as temperature,\cite{98,99,101} emulsion composition\cite{99,100,102} pH\cite{103} or applied potential\cite{98} are modified, other shapes such as rods,\cite{98,100,103} fibres,\cite{101} sheets\cite{98,100} and ellipsoids/spheres\cite{98,103} have been successfully synthesised. The more complex shapes formed (i.e. fibres, ellipsoids and spheres) are not pure crystals but rather agglomerates of In(OH)$_3$ rods that are either oriented (in the case of wires) or in a random array (spheres and ellipsoids).\cite{103} This indicates that In(OH)$_3$ single crystals form two general morphologies; either cubes or rods (in which the crystals are elongated in the [100] direction).\cite{99-100} This elongation is often induced by reducing the amount of organic phase relative to the aqueous phase and the emulsifying agent.\cite{99-100} As the growth rates of the different faces of In(OH)$_3$ are similar (as is evident in the fact that the anisotropic crystal structure produces isotropic crystals) changes to the solution conditions can dramatically alter the relative growth rates.\cite{100}

The formation of the more technically useful In$_2$O$_3$ is achieved by heating either In(OH)$_3$ or InOOH (which can be formed under similar conditions to Zn(OH)$_3$\cite{102}) crystals to 150-400°C.\cite{99,104} During this conversion it has been shown that In$_2$O$_3$ retains the morphology of the parent In(OH)$_3$ or InOOH crystals.\cite{104} This indicates that controlling the morphology of the precursor In(OH)$_3$ or InOOH leads to the control of In$_2$O$_3$ crystals. Further to this the crystal structure of In$_2$O$_3$ is dependent upon the precursor, with In(OH)$_3$ producing the more common cubic form, whereas InOOH forms hexagonal In$_2$O$_3$.\cite{99}

2.6.4. Cadmium Selenide

The final example of shape-controlled growth by the use of additives is cadmium selenide (CdSe). CdSe is a structurally similar material to ZnO, as both naturally form a Würtzite crystal structure. It has been shown by Peng and co-workers\cite{105-106} that the shape of CdSe quantum dots can be tailored by the introduction of phosphorous based ligands into the reaction mixture. Usually quantum dots are spherical in nature but by introducing hexylphosphonic acid rod shaped quantum dots can be formed. Molecular modelling performed\cite{106} by the above authors demonstrated that the phosphine and phosphate functional groups displayed the greatest binding energy to the [10 10] faces, thereby encouraging the formation of these faces. This result is interesting because it has been shown experimentally that phosphate ions encourage (0001) growth in the similar system of ZnO.
2.7. ZnO Morphologies Produced via Hydrothermal Growth

Typically, when ZnO is grown under hydrothermal conditions it adopts a hexagonal prism crystal shape. The ZnO crystal structure is anisotropic, so the rate of growth in all directions is not the same. The rapid growth direction of ZnO is [0001], with the slower growth directions being <10\bar{1}0>. This results in an elongated crystal shape with the crystal surface being primarily comprised of the \{10\bar{1}0\} faces (as shown in Figure 2.12a). However, as the aspect ratio (defined as \(L/D\), \(L\) being the length of the crystal, \(D\) being the width), and indeed its overall shape, is very sensitive to the condition of the solution it has been grown in it is difficult to give a ‘typical’ aspect ratio for ZnO crystals (\(L/D\) ratios between 5\(^{107}\) and 40\(^{22}\) have been reported for ZnO crystals grown without modifiers). It is much more prudent to discuss trends in aspect ratio with variation of different system parameters. The parameters varied are typically; the degree of superstation, solution pH, or the introduction of different ionic species/molecules into the growth medium. By adjusting these parameters a wide range of ZnO aspect ratios (0.1 < L/D < 100)\(^{22}\) as well as a variety different shapes can be produced, as illustrated by Table 2.2 and Figure 2.13. Each of the different observed morphologies is separated into characteristic groups and shall be discussed presently.

![Figure 2.12: ZnO crystals with two different aspect ratios (L/D). (a) ZnO typically grows primarily in the [0001] direction leading to elongated crystals. (b) A ZnO crystal where the primary growth directions are <10\bar{1}0> leading to a crystal with a lower aspect ratio.](image)

The first type of shape to be discussed is that of rods and wires. This morphology is characterised by an elongation of the crystal in the [0001] direction, creating crystals with very small diameters and high aspect ratios. Rods typically have smaller aspect ratio compared to wires, and grow uniformly in one direction. Wires tend to have very high aspect
ratios (L/D > 150 have been reported\textsuperscript{11}) but often formed ‘kinked’ structures with the crystal bending and twisting as it grows.

ZnO crystals described as plates or sheets tend to have much lower aspect ratios (L/D < 1 is common), whilst generally retaining their hexagonal morphology. They are formed when the primary growth direction is switched from [0001] to the <10\bar{1}0> directions. This is typically achieved by severe reduction in growth in the [0001] direction,\textsuperscript{107} as opposed to increasing the growth in <10\bar{1}0> directions.

![Figure 2.13: Examples of the different types of ZnO morphology observed during hydrothermal growth. (a-i) Rods,\textsuperscript{108} (a-ii) Wires,\textsuperscript{109} (b) Plates,\textsuperscript{110} (c) Hexagonal Pyramids,\textsuperscript{111} (d) Granules,\textsuperscript{107} (e) Tubes (using hydrothermal electrodeposition),\textsuperscript{112} (f) Rings,\textsuperscript{113} (g) Stars,\textsuperscript{114} (h) Trees (thermal using en/H\textsubscript{2}O co-solvent)\textsuperscript{115}]

The formation of ZnO crystals with surfaces that are neither (0001) or (10\bar{1}0) has been reported by Uekawa.\textsuperscript{111} By using LiOH (instead of the more common NaOH) as source of hydroxide ions, they were able to generate crystals that had a flat hexagonal base with six sides that taper to a point at the top of the crystal. Unfortunately as it was not the focus of their work but rather an interesting side note, they did not determine the orientation of these new surfaces.

When growth in all directions is decreased, the resultant morphology is usually described as being granular in nature. These structures tend to be highly faceted, with no particular face dominating. This structure is most often seen in systems that are heavily agitated, and have a high degree of homo-nucleation occurring, whether this is due to a high degree of supersaturation, or the presence of a non-face specific growth inhibitor.\textsuperscript{7}
Table 2.2: Different morphologies of ZnO formed during hydrothermal growth in the presence of different chemical species

<table>
<thead>
<tr>
<th>Shape</th>
<th>Characteristic Surface</th>
<th>Functional Group/s</th>
<th>Additive</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple Shapes</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>R-NH₂</td>
<td></td>
<td>118</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R-NH₂/R₂-NH</td>
<td></td>
<td>118</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R₂-NH</td>
<td></td>
<td>119</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R₃-N</td>
<td></td>
<td>120</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R₄-N⁺/COOH/R₃-N</td>
<td></td>
<td>120</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-CF₂-O⁻/-SO₃</td>
<td></td>
<td>109</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Composite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B) Platelets, Sheets</td>
<td>(0001)</td>
<td>Cation</td>
<td>Cd²⁺, Cu²⁺, Mg²⁺, Ca²⁺, PO₄³⁻, Citrate, Maleate, Tartarate, Phenolphthalein, EDTA (pH ≈ 7), DTPA (pH &lt; 11.5), TEA, PAM-COOH, Docusate, PSS, Arabic Gum</td>
<td>22, 126-127, 12, 107, 110, 128-130, 129, 129, 129, 119, 119, 116, 120, 131, 113, 107, 130, 132</td>
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<tr>
<td></td>
<td></td>
<td>Anion</td>
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<td></td>
<td></td>
<td>-COOH</td>
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<td>-COOH/R₃-N</td>
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<td></td>
<td>-OH/R₃-N</td>
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<td></td>
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<td>-CO-NH₂/-COOH</td>
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<td></td>
<td></td>
<td>-SO₃</td>
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<td></td>
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<tr>
<td></td>
<td></td>
<td>Composite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C) Hexagonal Pyramids</td>
<td>unknown</td>
<td>Cation</td>
<td>Li⁺</td>
<td>111</td>
</tr>
<tr>
<td>D) Granules</td>
<td>multi</td>
<td>Cation</td>
<td>Li⁺, PAA, SDS</td>
<td>116, 129, 116, 129</td>
</tr>
<tr>
<td>E) Tubes</td>
<td>(1010)</td>
<td>R-NH₂</td>
<td>EDA</td>
<td>112</td>
</tr>
<tr>
<td>F) Rings</td>
<td>(0001)</td>
<td>-CO-NH₂/-SO₃</td>
<td>PAA</td>
<td>131, 113</td>
</tr>
<tr>
<td>Complex Stuctures</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G) Trees/Rotors</td>
<td>(1010)</td>
<td>Various</td>
<td></td>
<td>115, 133</td>
</tr>
<tr>
<td>H) Stars, Urchins, Flowers,</td>
<td>(1010)</td>
<td>Various</td>
<td></td>
<td>111, 114, 116-117, 134</td>
</tr>
</tbody>
</table>
The two stage process that leads to the formation of ZnO tubes or rings is similar, with the difference being on the shape of the precursor crystal formed in the first stage. Initially either ZnO rods or platelets (depending if tubes or rings are formed, respectively) are formed. Then, with time the solution conditions change such that the formed crystals begin to dissolve. This dissolution could be caused purely by Ostwald ripening, or by including a molecule that decomposes over time, changing the pH so that the system becomes undersaturated with respect to ZnO. The conditions must also be set such that the core on the rod/plate preferentially dissolves. This is accomplished by the introduction of a species that adsorbs to the outer surfaces, protecting them from dissolution (in most cases this is the species used to direct the shape of the crystal during the first stage). The resultant shape is a hollow, thin walled crystal either with a high (tubes) or low (rings) aspect ratio.

The final category ZnO morphology observed is broadly classified as complex structured ZnO. These structures are usually an assembly of several different crystal grains that have oriented in a particular fashion. They have been further separated into two different subgroups, classified by their overall shape. The first type is often labelled as ‘flowers’, or ‘urchins’. It is comprised of several ZnO spines growing radially out from a central nucleate, with each of the spines being oriented in the [0001] direction. The variation between urchins, flowers, stars, etc. is fairly arbitrary, but in general stars tend to have fewer spines per nucleate than flowers, while the spines of both tend to be of a moderate aspect ratio. Rotor/tree shaped ZnO structures are characterised by a central crystal ‘trunk’ (primarily grown in the [0001] direction) that has a series ‘branches’ that grow regularly out of the {10\bar{1}0} planes. Each of these branches have been shown to be growing in the [0001] direction even though they are growing out of the {10\bar{1}0} planes of the original crystal.

These complex shapes can be formed by several different mechanisms. The most obvious is the random aggregation (and subsequent growth) of several nucleates, which would lead to randomly oriented spines. Due to the inherent crystal symmetry, however, it is often the case that the nucleates agglomerate in an ordered fashion, resulting in a more ordered complex crystal structure. Similar structures are also possible if the crystal is grown from an intermediate species that is more isotropic in structure. Finally, in systems with a high degree of supersaturation, it is possible for differently oriented homo-taxial growth (or nucleation) to
occur, resulting in crystal twinning or, in the case of Figure 2.13i, multiple offshoots from a central crystal.

It has been touched on briefly when discussing the different morphologies how different solution conditions can influence the aspect ratio, and indeed the overall shape of ZnO crystals. However, to properly understand how to control the growth of ZnO crystals, the influence of different solution conditions needs to be examined more thoroughly.

2.8. Factors Affecting Morphology of Hydrothermally Grown ZnO

2.8.1. pH Effects
Due to the solubility of ZnO as a function of pH (Figure 2.14) hydrothermal growth of ZnO typically occurs in the limited pH range of 9 – 13. Outside of this range the solubility of ZnO becomes too high, making crystallisation harder to achieve. In addition there is an increased possibility of co-precipitation of other zinc species, resulting in poor crystal quality. Within the pH 10.5 – 11.5 range it has been showed that an increase in pH leads to a decrease in aspect ratio of epitaxially grown ZnO rods, particularly in the lower half of the pH range. This decrease in aspect ratio was attributed to a change of the surface charge of the growing crystal, making growth in the [0001] less favourable.

![Figure 2.14: The phase stability diagram for H2O–ZnO as a function of pH at 25°C. Reproduced from Yamabi.](image)

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2.8.2. The Addition of Complexing Agents
Another way to control the degree of supersaturation the system is to add an additional component (called a complexing agent) into the system to increase the solubility of the solid. A complexing agent functions by forming a new, more soluble complex in solution. The presence of a complexing agent can affect crystal growth in several ways. Most obviously it alters the degree of supersaturation in the system, the effects of which have already been covered. However, it also changes the nature of the species in solution, and therefore can affect the growth process by changing the ion complex that is incorporated into the crystal lattice. This could lead to a change in the relative growth rates of different directions, depending on the compatibility between the new ion complex and the different surfaces of the crystal.

For hydrothermal growth of ZnO the two most common complexing agents used are either hexamine (C₆H₁₂N₄) or ammonia. Ammonia increases Zn²⁺ solubility by forming [Zn(NH₃)₄]²⁺. This complex is less stable with increasing temperature, leading to the retrograde solubility of ZnO. Thus ZnO can be grown by forming the soluble zinc-amine at low temperature, which will then precipitate out as ZnO if the solution temperature is increased.

The role of hexamine however is not as clear. It has been postulated that hexamine acts as a shape directing molecule (Section 2.8.5). However, other literature assume that hexamine decomposes into CH₂O, NH₄⁺ and OH⁻ ions during growth. These ions keep the degree of supersaturation low throughout the growth process, thereby limiting nucleation, and encouraging growth in the [0001] direction. It is possible that both mechanisms are occurring simultaneously, as the presence of hexamine in the system encourages an increase in the aspect ratio of the formed ZnO crystals.

2.8.3. Ionic Effects
Due to the nature of the hydrothermal growth process it is often required to introduce different ionic species that are not directly involved in the growth process into the system. These ions could be introduced as the counter-anions present in the zinc salt precursor, or the counter ion of acids/bases used to adjust the pH. Whilst these ions should ideally have no influence on the morphology of ZnO it is not always the case.

When metal ions (Cd(II), Cu(II), Mg(II), Ca(II)) which form positive complexes at pH 11 were introduced into the growth medium, it was observed that the resulting ZnO crystals
tended to form short crystals with a surface primarily consisting of (0001)/(000̅1) planes. The reverse trend was observed when negatively charged metal ion complexes (Al(III), Ga(III), In(III)) were introduced into the system, as these ions increased the aspect ratio of ZnO crystals, creating crystals with a high area of {10̅10} planes. This trend was attributed to the specific adsorption of the complexes to the oppositely charged ZnO surfaces. This was supported by surface charge measurements done using an AFM colloidal probe technique, which showed, at pH 11, the (0001) face is negatively charged and the (10̅10) is positively charged (however recent work has cast doubt on this\textsuperscript{21}).

The influence of different alkali metals on ZnO morphology has also been studied by two different groups. Chittofrati\textsuperscript{116} compared ZnO grown in equivalent amounts of LiOH, NaOH, and KOH. They found that compared to NaOH (the most common hydroxide used) that crystals grown with KOH had a significantly increased aspect ratio. The crystals grown with LiOH however, tended to form granules with no specific shape. These results were contrary to the work by Uekawa,\textsuperscript{111} who found that as the cation (Na, K, Cs) became larger the resultant ZnO crystals became more irregular, but in general there appeared to be a decrease in crystal size. However, they also noted that LiOH was a special case, but observed the formation of hexagonal pyramidal crystals instead of granules. Thus the presence of alkali metals in the growth medium, particularly the presence of Li\textsuperscript{+} (which is thought to influence the nucleation of ZnO\textsuperscript{111}), can influence ZnO morphology, but as of yet no definitive trend has been observed.

Finally, the influence of anions has not been widely investigated. However, it has been reported that the inclusion of phosphate ions tended to reduce the aspect ratio of ZnO\textsuperscript{126-127}.

2.8.4. Shape Directing Additives
Another way to change the aspect ratio of ZnO crystals is via the introduction of a surface active species into the growth system. This differs to the introduction of a complexing agent mentioned in the previous section (though they may also function as a complexing agent, e.g. hexamine) in that the introduced species alters the surface properties of a particular face of the forming solid, not just the solution conditions. Usually only a small amount of additive (µM to mM) is required to affect a dramatic shift in aspect ratio. This makes altering the growth process in this way attractive for industrial applications, as not only is a small amount required, but can be applied to a wide range of solution conditions. Table 2.2 summarises different types of ZnO morphology reported by various groups, as well as the additives used
to accomplish the particular morphology (chemical structures of the additives are given in Appendix 10.2). Examples of the different morphologies are given in Figure 2.13. For further detail into the experimental conditions used the reader is directed to the comprehensive review article by Kawano and Imai.

From Table 2.2 a trend between the functional groups of the additive and the face it encourages expression of can be seen. In general, amines tend to form crystals with increased areas of \((10\overline{1}0)\) planes, whereas carboxylic acids, phosphate ions, and, to a lesser extent, sulfonyl groups tend to form crystals with increased areas of \((0001)\). This trend is not true for all members of a particular functional group though. Yahiro et al.\(^\text{129}\) showed that the geometry of a carboxylic acid is key in determining whether or not it will encourage \((0001)\) growth as maleate, the cis- isomer of \(1,2\) butenedioate is surface active, but the trans- isomer, fumarate, and unsaturated equivalent, succinate, was not. Amines seem to be less sensitive to structural changes within the molecule as it been observed that primary to tertiary amines all encourage \((10\overline{1}0)\) growth. The surface activity of quaternary amines, however, has had mixed reports. Maiti\(^\text{125}\) reported the thinning of nanorods grown in the presence of CTAB, whereas Chittofrati\(^\text{116}\) reported that CTAB had no influence on ZnO morphology.

Molecules containing both amine and carboxylic acid groups, such as ethylenediaminetetraacetate (EDTA) was studied by DiLeo et al.\(^\text{119}\). They found that the ZnO morphology could be tuned by varying the pH. At lower pH values plates tended to form, whereas at higher pH values needle like crystals were observed. For EDTA the pH at which this transition occurs was not clear, with the pH region between 8 and 11 producing ZnO powders of variable morphology. Whereas the more complex molecule diethylenetriaminepentaacetate (DPTA), with three tertiary amine and five carboxylic acid moieties, had a much sharper transition point with the morphology switching from platelets to rods at about pH = 12.

The introduction of pyranine, a sulfonated aromatic dye, into the growth solution produces a rather unique morphology of ZnO. Typically the introduction of a shape directing molecule containing sulfonyl groups causes hindrance of growth in the \([0001]\) direction resulting in the formation of regular hexagonal ZnO plates\(^\text{131, 113}\) (as the six \{10\overline{1}0\} faces are equivalent, the growth in each direction is equal). Rather than this typical hexagonal platelet morphology though, pyranine tends to form ZnO wires\(^\text{109}\). These wires, however, are not oriented along
the [0001] direction (like wires formed using amine based compounds), but seem to be oriented along different {10\overline{1}0} directions, forming a winding structure. The mechanism for forming this type of wire is not immediately obvious. However, as this structure was grown homotaxially, the authors attributed the formation to incomplete surface coverage of the pyranine on the (0001) plane. This led to the random formation of small islands on the (0001) surface that eventually coalesced into the observed wires.
3. Experimental Techniques, Apparatus & Applications

3.1. Fourier Transform Infrared Spectroscopy

Infrared Spectroscopy can be used to study the chemical functional groups present within a sample. As infrared light is similar in energy to the spacing of vibrational energy levels of molecular bonds it is able to be absorbed by the sample. The wavelength of IR that will be absorbed is dependent upon the bonding atoms (e.g. C-H, or N-O), the type of bond (single bond, double bond, etc.), the symmetry present within the molecule and the vibration mode (Figure 3.1). IR spectroscopy is also sensitive to any changes to the force constants of a vibrational mode, whether it is caused by change in oxidation/acid state, solution conditions and even molecular conformations. It is for these reasons that IR spectroscopy is a powerful tool for not only identifying compounds but also for monitoring any change that occurs within the system, such as chemical reactions or adsorption to surfaces.

![Figure 3.1](image-url)

Figure 3.1: The different possible deformation modes of a tri-atom group.

As IR light is absorbed by the different vibration modes of a molecule these different vibration modes should be mentioned in detail. The vibration modes for three connected atoms in molecule (in order of decreasing energy) are shown in Figure 3.1. IR vibrations are categorised into two groups, the higher energy stretching modes and the lower energy bending modes. A stretching vibration is when an atom moves along the same axis as the bond, causing the bond length to expand and contract. When two atoms, which are both bonded to a central atom undergo this vibration they can either be in phase (where both bonds are elongated and contracted at the same time, Figure 3.1b), which is known as a symmetric vibration, \(v_s\), or the bonds can stretch out of phase in an antisymmetric stretch \(v_a\) (Figure
3.1a). The bending modes occur when the motion of the atoms is not co-incident with the bond axis. When the deformation occurs such that the atoms remain within the plane of the molecule it is either a rocking deformation, \( \delta \), (when the angle between atoms is unchanged, Figure 3.1c) or a scissoring deformation, \( \gamma \), (when the angle between the atoms increases and decreases periodically, Figure 3.1d). When the deformation is out of the plane it is either a wagging, \( \omega \), (when the distance between the end atoms remains constant, Figure 3.1e) or twisting, \( \tau \), (when the distance between the end atoms changes, i.e. the atoms travel in opposite directions, Figure 3.1f). Whilst these vibrations have been considered separately, in reality they are all occurring simultaneously. Therefore, it is possible that different vibration modes can couple together, resulting in one mode shifting to higher frequency, whilst the other drops to a lower frequency.\(^{140}\) This usually occurs with the lower energy vibrations, such as the wagging and rocking vibrations as they are of similar energy.\(^{140}\) Also, not all vibration modes are IR active in every molecule, as the IR activity of a molecule-functional group is dependent upon its symmetry.\(^{139-141}\)

Whilst it has been stated that factors that influence the strength of a bond also influence the IR wavelength that is absorbed, the exact relationship has not been defined. This is because to do so is quite an involved process, as not only the movements of the atoms connected to a central atom that need to be considered, but the movements of all the atoms in all directions, as well as any interactions occurring from nearby molecules, etc.\(^{139}\) A first order approximation of the relationship between the bond strength \((K)\), the mass of the atoms and the absorbed IR frequency \((\bar{\nu})\) for the stretching frequency for two atoms can be obtained, however, by considering the atoms and the bond as a simple harmonic oscillator. Using this approximation, Equation 3.1 can be derived:\(^{139-142}\)

\[
\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{m_r}} \quad \text{(Equation 3.1)}
\]

where \(m_r\) is the reduced mass and defined as:

\[
\frac{1}{m_r} = \frac{1}{m_1} + \frac{1}{m_2} \quad \text{(Equation 3.2)}
\]

where \(m_1\) and \(m_2\) are the atomic masses of atom 1 and 2 respectively. Eq. 3.1 is valid for any system whose potential energy varies quadratically with the dynamical variable (in this case, position).\(^{139, 142}\)
3.1.1. Instrumentation

As IR spectroscopy depends on IR absorption at different wavelengths (or frequencies) it would be expected that an IR spectrometer would operate in a similar fashion to traditional UV-Vis spectroscopy, where the intensity of the light after it passes through the sample is measured for different wavelengths separately. However, instead of a single wavelength at a time, FTIR Spectrometers emit all wavelengths within a certain range (which is dependent upon the IR source, but typically is in the range of 0.75 µm to 300 µm) at once. To be able to simultaneously measure these different wavelengths a special setup is required. A typical FTIR spectrometer setup is given as Figure 3.2.

Figure 3.2: Schematic setup of an FTIR.

The IR light from the source is collected and collimated (made linear) and transmitted into an interferometer. The interferometer (formally a Michelson Interferometer\textsuperscript{139}) is the essential component of FTIR spectrometer. It is comprised of a semi-reflective beam splitter (made from an IR transparent material, typically a KBr crystal), a fixed mirror and a moveable mirror, arranged as per Figure 3.2. Once the collimated light enters the interferometer it strikes the beam splitter. Ideally half the light is reflected from the beam splitter to the fixed mirror, whilst the other half is transmitted through the beam splitter to a mirror that is
oscillating in the beam direction (i.e. the distance between the movable mirror and the beam splitter changes with time). The light reflects off both mirrors, returning to the beam splitter, where the two different beam paths recombine and are sent to the sample compartment. The light reflected from the fixed mirror will have a constant path length with time, whereas the light that strikes the moving mirror will have a different path length, depending upon position of the mirror when the light hits it. Thus when the two beams recombine they will no longer be completely in phase (except when the movable mirror is at the same distance as the fixed mirror from the beam splitter). This causes the two beams to either constructively or destructively interfere with each other. The intensity of the recombined beam will therefore become a function of the position of the moveable mirror.

Once the IR beam leaves the interferometer, it is focused on the sample (by various different means which are discussed later) where some of the IR light is absorbed. The remaining light is then collected and focused onto an IR detector which measures the intensity of the IR across all frequencies simultaneously (i.e. the absolute intensity of the beam). Whilst several different types of detectors are available, a common detector for the mid IR range (4000 to 700 cm\(^{-1}\), with cm\(^{-1}\), called wavenumbers, being equivalent to frequency) is a liquid nitrogen cooled MCT (mercury cadmium telluride) detector, which is the type of detector used in this work.

The plot of beam intensity vs. mirror position is known as an interferogram. As the IR beam consists of many different frequencies of IR light, the different frequencies will interfere with each other to different degrees, and as such the intensity of the interferogram will vary as a series of peaks and troughs as the different IR frequencies go in and out of phase as the mirror moves. If the interferogram undergoes a Fourier Transformation the interference pattern can be resolved into a spectrum of intensity vs. frequency. However, in order to measure the absorbance spectrum of a sample it needs to be compared to the background conditions. Thus a background scan must first be recorded. Then if the intensity ratio between sample spectrum and the background spectrum (as a function of frequency) is taken the absorbance spectrum can be generated.

A Discrete Fourier Transform is applied to the interferogram (specifically the Cooley-Turkey algorithm of the Fast Fourier Transform\(^{139}\)), with the sampling points determined by the interference pattern of a monochromatic HeNe laser that is transmitted co-linearly with the IR beam. As the data points on the interferogram are collected discretely the resolution of the
resultant IR spectrum is dependent upon the ability to accurately resolve the position of the moveable mirror. Thus higher scan resolutions (that is the number of points per scan) can be achieved by either slowing the velocity of the mirror (thereby increasing the scan time), or increasing the distance the mirror travels (making the equipment larger). The advantages of using this method of data collection over the more traditional one wavelength at a time are mainly related to the experimental time.\textsuperscript{139, 141-142} As all wavelengths are measured in the time otherwise taken to measure a single wavelength, the collection time is dramatically reduced. This improves the accuracy of the spectrum as there is less chance of factors such as thermal drift affecting the measurement. Furthermore as all the wavelengths are measured at once, the use of filters to select single wavelengths is not required. This improves the signal to noise ratio as less of the signal is lost during measurement.

As mentioned previously, there are several different ways the IR beam can be made to interact with the sample. The following were techniques used in this work:

3.1.2. Transmission FTIR
Transmission FTIR is perhaps the simplest and most common form of IR measurement. In transmission FTIR the sample is mounted in an appropriate fashion and placed directly in the beam path so that the IR absorbance of the material can be measured. If the sample is a liquid it is contained in a fluid cell consisting of two IR transparent windows (e.g. single crystal NaCl, CaF\textsubscript{2} or ZnSe) that are separated by a spacer of known thickness. By varying the thickness of the spacer (and by extension the sample thickness or absorbance length) an appropriate signal strength can be obtained. If the sample is a powder, in order for it to be suitable for use in transmission FTIR it must be mixed with an IR transparent material (typically KBr) and pressed into a clear disc. This reduces the amount of light scattered by the powder, which would result in only a small fraction of the incident light would making it to the detector.

In this work the transmission spectra presented in Chapter 6 were obtained by this method using a PIKE Transmission Fluid Cell using CaF\textsubscript{2} windows (transmission range 0.2 to 6 \textmu m) at a separation of 0.05 \textmu m.
3.1.3. Diffuse Reflectance FTIR
Another option for measuring the IR spectrum of powder samples is to use a diffuse reflectance FTIR (DRIFT) accessory. In DRIFT the powder sample is diluted with KBr and packed loosely into an open small volume (< 1 cm$^3$) vessel. The vessel is placed into the DRIFT accessory where the incident beam focused onto the surface of the powder. The IR beam is then transmitted and scattered throughout the sample. The scattered light that is not absorbed by the sample is collected and focused by an off-axis parabolic mirror (positioned above the sample) before being sent to the detector. The DRIFT method has the advantage of measuring the IR spectrum of the powder in its natural state, without it being subjected to the high pressures required to press it into a clear disc. However, the relative intensities of the peaks can become distorted due to the scattering, particularly at higher wavenumbers. To account for this an IR spectrum obtained using DRIFT must undergo a secondary transformation known as a Kubelka-Munk transformation.$^{142,143}$ The transformation is given by Equation 3.3:

$$f(R) = \frac{(1-R)^2}{2R} = \frac{\epsilon_0}{s} \text{ (Equation 3.3)}$$

Where $R$ is the absolute reflectance of the sample, $\epsilon_0$ is molar absorption coefficient and $s$ is the scattering coefficient.

The IR spectra of the powders synthesised in Chapter 4 were measured by diffuse reflectance FTIR using a PIKE EasiDiff Accessory, which has a 45° angle of incidence.

3.1.4. Attenuated Total Internal Reflectance Fourier Transform Infrared Spectroscopy
When using transmission FTIR on samples in solution the absorbance of the entire sample is measured. Whilst this is beneficial when performing bulk IR studies, it is undesirable for interfacial studies, as the contribution from the molecules at the interface is relatively small compared to the contribution from the molecules in bulk solution. These contributions from the bulk can be significantly reduced by using Attenuated Total Internal Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR).$^{142}$ In ATR-FTIR the IR beam is transmitted through a prism made from an IR transparent material (e.g. ZnSe) that is in contact with the solution. The beam enters the prism at an angle such that incident light reflects off the prism:solution interface a number of times before exiting the prism, as shown by Figure 3.3c.
Figure 3.3: The different occurrences when light travels from a high refractive index medium to a low index medium. (a) below the critical angle the light passes through the interface, bending away from the normal. (b) at the critical angle the light travels along the interface. (c) above the critical angle total internal reflectance occurs generating an evanescent wave at the interface.

Usually, when light passes through an interface the light changes trajectory. The degree of this change is dependent upon the angle at which it strikes the interface and the refractive indices of the materials at that interface, as given by Snells Law (Equation 3.4):

\[ n_1 \sin \theta_1 = n_2 \sin \theta_2 \]  

where \( \theta_1 \) is the angle (from the normal) that the light strikes the interface, \( \theta_2 \) is the angle refraction, and \( n_1 \) and \( n_2 \) are the refractive indices of their respective mediums.

If the light is passing from a high refractive index medium to a low index medium there is an angle of incidence where the angle of refraction will equal 90° (i.e instead of passing through the interface, the beam will travel along the interface, as shown in Figure 3.3b). This angle, known as the critical angle, \( \theta_c \), is given by Equation 3.5.

\[ \theta_c = \arcsin \frac{n_2}{n_1} \]  

Above the critical angle the light will not pass through the interface, but rather will reflect off it. Under these conditions the light can undergo total internal reflection within the high refractive index medium. Whilst under principles of classical physics no light is being
transmitted into the second medium, quantum mechanics shows that indeed some light is transmitted through the second medium. When light undergoes total internal reflection there exists a finite quantum mechanical probability that the light striking the interface can temporarily ‘jump’ to the other, ‘forbidden’ side of the interface. This results in the formation of an evanescent wave at the interface as shown by Figure 3.3c. The intensity of the evanescent wave decays exponentially with distance from the interface. This means that the majority of the light is at or near the interface, with only a small portion of the light penetrating the bulk of low index medium. The degree in which the evanescent wave extends from the interface is usually defined by the penetration depth, $d_e$, which is the distance from the surface where the intensity has decreased to a factor of $e^{-1}$ from its original intensity, and is given by Equation 3.6:

$$d_e = \frac{\lambda}{2\pi \sqrt{n_1^2 \sin^2 \theta_1 - n_2^2}}$$

(Equation 3.6)

The typical penetration depth of an evanescent IR wave is about 100 to 200 nm. The effective path length ($l_e$) of the evanescent wave (i.e. the equivalent sample thickness in transmission) can be approximated by multiplying the penetration depth by the number of reflections ($N$), i.e:

$$l_e = N d_e$$

(Equation 3.7)

From Equation 3.6 it can be seen that as the angle of incidence increases the penetration depth will decrease, making the evanescent wave more surface selective. However increasing the angle of incidence also decreases the number of reflections through the prism, meaning a balance must be struck between surface selectivity and signal intensity.

As an evanescent wave is sensitive to changes at the interface, whilst remaining relatively insensitive to changes within the bulk, ATR-FTIR can be used to probe molecular interactions occurring between the surface of the prism and the solution, with minimal interference from molecules in bulk solution. Given that ZnO is nominally IR transparent in the 4000 – 500 cm$^{-1}$ range, it seems that ATR-FTIR is perfect for investigating the interactions between shape directing molecules and the different faces of ZnO. However, due to the unavailability of suitably large single crystals of ZnO (commercial ATR prisms are typically about 10 mm x 10 mm x 50 mm in size, whereas the largest single crystal of ZnO that was readily available was only 0.5 mm x 10 mm x 10 mm), there were some technical difficulties to overcome.
The main problem in using such a small prism is getting a high enough throughput of IR light through the prism to be able to resolve an absorbance spectrum. This problem was largely overcome by using a combination of lenses and parabolic mirrors to focus a high intensity IR beam to a spot size of ca. 3 mm. The custom setup used to achieve this is shown as Figure 3.4.

![ATR-FTIR Experimental setup used in Chapter 6](image)

Figure 3.4: ATR-FTIR Experimental setup used in Chapter 6. (a) the custom setup used to change the IR beam path (dotted line indicates the original beam path). A convergent IR beam is focused into a ZnO ATR prism in contact with a solution containing the adsorbing molecule. The exiting beam is collected using an off axis parabolic mirror focusing it on a MCT detector. (b) cross section of the fluid cell perpendicular to the beam path.

The spectrometer used for this work was a Varian 670 FTIR, which is designed to produce a convergent IR beam. Upon leaving the interferometer the collimated light strikes a concave focusing mirror causing it to converge. The sample is then typically placed at the focal point of the beam. Due to the negative spherical aberration of the mirror (that is the focal length of the mirror increases with radial distance from its centre, as illustrated in Figure 3.5) the focal point of the mirror is not a tight spot, but rather about 2 cm in diameter. This aberration also causes a low intensity region to appear in the centre of the beam after the focal point. This low intensity region meant that conventional bevelled edge ATR was not an option.
To make this system suitable for use with a small prism, the first step was to reduce the focal point to a size that is comparable to the thickness of the ZnO prism (i.e. 0.5 mm). This was ultimately accomplished by placing a ZnSe biconvex lens at the focal point of the beam. This reduced the beam diameter at the focal point (i.e. the spot size) to 2-3 mm. Whilst this is still significantly larger than 0.5 mm it was found to be the smallest practical size the beam could be reduced to. A ZnO prism contained within a customised fluid cell, shown in Figure 3.4, was placed after the ZnSe lens, and oriented such that the IR beam nominally struck the prism normal to the surface. As the beam was convergent with the intensity being maximum (after the focal point) towards the edge of the beam (Figure 3.5), it meant the majority of the light entered the ZnO prism in such a way that the beam was striking the ZnO:water interface within the fluid cell at angles above the critical angle ($\theta_c \approx 42^\circ$ for the ZnO:water interface at 20°C). Thus most of the beam underwent total internal reflectance. However, the IR beam strikes the ZnO:water interface at a range of angles. This means the penetration depth of the evanescent wave could not be controlled or quantified to any substantial degree as it would be a weighted average of the different penetration depths resulting from the different IR incident angles. This was not found to be a problem however, as the absorbance spectra were similar in intensity between repeat experiments, and the contribution from bulk solution was observed to be minimal.

The fluid cell itself is comprised of two Teflon (PTFE) halves that sandwich a single crystal ZnO prism. To prevent the presence of PTFE peaks in the IR spectra, and aid in sealing the fluid cell, gold gaskets were placed between the ZnO Prism and the fluid cell. The two halves of the fluid cell were able to be filled either independently (for absorption studies on the (0001) face) or in series (for absorption studies on the (10\bar{1}0) face).
Whilst reducing the spot size allowed a sufficient amount of the IR beam to enter the prism, it also caused the divergence of the beam after the focal point to increase. This increased the portion of the beam that underwent internal reflectance, as by increasing the divergence of the incident beam, the angle at which the beam struck the ZnO:water interface is also increased. However, it also meant that the beam was more divergent after leaving prism, therefore making it harder to re-focus the beam on the IR detector. To minimise the IR loss due to this divergence, the off axis parabolic mirror (i.e the collecting mirror in Figure 3.2) and the detector were moved closer to the fluid cell (and the ZnO prism). This is another reason why the spot size of the incident IR beam was not reduced further, as it would have resulted in more signal loss of the IR beam leaving the prism.

The final modification made to the system was made on the basis of space considerations. In order to fit the above modifications into the confines of the sample chamber the focal point of the IR beam had to be shifted. This was done by using two flat, gold coated mirrors to shift the focal point closer to the entry side of the sample chamber.

3.2. Atomic Force Microscopy

The Atomic Force Microscope (AFM) is a flexible tool capable of producing nanometre scale 3D topographic detail of a wide range of samples. It is also capable of measuring short range forces.\(^{144}\)

The basic components of an AFM are; a flexible cantilever, a laser, a photodiode, three piezo scanners, and a P.I. (Proportional, Integral) feedback controller as illustrated by Figure 3.6.\(^{144}\)

In imaging mode, a flexible cantilever with a sharpened tip is brought in contact with the sample surface. The tip is then traced over the sample surface in a raster fashion using two piezoelectric manipulators (X-Y piezo scanners, oriented horizontally). As the surface topography changes the deflection of the cantilever will change accordingly. For instance, if the sample height increases, the tip will be pushed by the surface, causing the cantilever to deflect away from the surface (referred to as positive deflection). The changes in deflection of the cantilever are measured by reflecting a laser off the top of the cantilever onto a four quadrant photodiode. As the deflection of the cantilever changes, the position of the laser on the photodiode will change. This will change the relative intensity readings on the four quadrants, thus by measuring the intensity difference between the top half and the bottom half the change in deflection of the cantilever is known. The changes in deflection are
compensated for by either lifting (for positive deflection) or lowering (for negative deflection) the cantilever by varying the voltage applied to third (Z-) piezo scanner which is oriented vertically. Therefore by measuring the changes in applied voltage to the Z-piezo as a function of tip position (recorded by measuring the applied voltage on the X-Y piezos) the topography of the sample can be measured.

Figure 3.6: Schematic of an AFM. Sample topography is measured by changes in deflection of a flexible cantilever as it is traced over the sample.

AFM imaging can be classified broadly into two different modes; static (contact mode) and dynamic (tapping mode), the difference being how the tip interacts with the surface. In static imaging mode the tip is in direct contact with the surface and the sample topography is measured by the changes in cantilever deflection as it is ‘dragged’ across the surface. As the tip is in contact with the surface, the tip is less prone to influences from surface forces and the medium in which the image was taken (e.g. air vs. water) resulting in a clearer representation of the surface, and it is often used for measuring the topography of simple, hard surfaces. However, the constant contact with the surface can lead to wearing of the tip, and so lowering the resolution of the scan.

In tapping mode the cantilever is held above the surface and oscillated near its resident frequency. The amplitude of oscillations can be varied such that the cantilever either remains above the surface (non-contact mode) or the cantilever is held in intermittent contact with the
surface. As the separation between the cantilever and the surface decreases, the amplitude of the cantilever vibrations will become more dampened. So by adjusting the height of the cantilever to maintain a constant amplitude, the topography of the sample can be determined. Further to this, by monitoring changes in the phase of the oscillations as the tip passes over the sample, the composition of the sample can be observed. Due to the tips limited contact with the surface, tapping mode imaging is best suited for use with soft or deformable samples, and is the primary mode used when studying biological samples. However, it is more prone to generating artefacts, as the things such as surface forces or hydration layers can influence the image.

AFM imaging, whilst useful for small scale measurements, is not without its limitations. The sampling area available is usually only up to 100 by 100 µm and, due to the nature of the measurement, very rough samples can be difficult to image accurately. Also the image resolution is limited by the sharpness of the tip, which is prone to degradation when imaging hard surfaces.

In addition to an imaging tool, the AFM can also be used for quantitative force measurements, as any force applied to the cantilever will subsequently cause a change in the deflection of the cantilever. The relationship between the applied force \( F \) and subsequent deflection \( x \) can be quantified using Hooke's law given as Equation 3.8.

\[
F = kx \quad \text{(Equation 3.8)}
\]

where \( k \) is a constant of proportionality known as the spring constant and is dependent on the physical properties of the cantilever. As the cantilever is on the order of tens of micrometres thick it is sensitive to forces of a very small magnitude, therefore the AFM is capable of measuring forces on the molecular scale, particularly in regard to surface forces. This allows such properties as surface charge/potential, Van Der Waals forces and capillary action to be measured. Additionally if the tip is functionalised, i.e. if a molecule is chemically grafted to the tip, such things as protein unfolding, molecular adhesion strength, and molecule interactions can also be quantified.

The AFM studies conducted in this work were performed using Veeco NP Silicon nitride tips with a spring constant of 0.43 N/m (nominal tip radius of 20 nm) in contact mode.
3.2.1. Dissolution Studies
In Chapter 5 the dissolution of the different faces of ZnO, (0001), (0001̅), and (10̅10), was studied in-situ under basic conditions. To achieve this, a modification of the traditional AFM fluid (using an Asylum Bioheater Fluid Cell) cell setup was used (Figure 3.7). A piece of single crystal ZnO (usually ca. 3 x 3 mm) was mounted in the fluid cell on a gold coated (200nm) glass plate with heat sensitive glue (Epon 1004, Hexicon Specialty Chemicals), which was previously found to be insoluble in high pH aqueous solutions. The glass was coated in gold to limit the solubilisation of silica species which may contaminate the sample. Once assembled, the fluid cell was filled with water via the fluid loading port so that the sample could be imaged before etching. At \( t = 0 \) the water was exchanged with the etching solution (either 2 M NaOH or 2 M NaOH with 100 mM trisodium citrate) at a rate of 5.7 mL/min for 1 minute with the effluent being removed from the system. During the experiment the etching solution was circulated between the fluid cell (\( V \approx 1.5 \) mL) and storage reservoir (\( V = 100 \) mL) via a peristaltic pump at 0.25 mL/min (4.2 µL/s) to keep the degree of undersaturation approximately constant during the experiment, whilst keeping the flow rate low enough in order to minimise erosion due to flow.

Figure 3.7: Fluid cell setup used in Chapter 5. To keep the degree of supersaturation approximately constant through the experiment the fluid was circulated between fluid cell and a large reservoir.
3.3. Scanning Electron Microscopy

The Scanning Electron Microscope is an instrument first created in 1932 to break the diffraction limit of conventional optical microscopy, allowing objects below 1 µm in size to be visualised. This is possible because an SEM doesn’t use light to probe the surface but rather monitors the interactions between an electron beam and the sample surface. In this way the SEM can be used to image surface features to a resolution of about 50 nm. This makes the SEM a convenient tool for imaging samples that are too small for traditional microscopy, but too large for Atomic Force Microscopy or Transmission Electron Microscopy.

The principal feature of an SEM is its focused electron beam. The beam is formed by collecting electrons from a source (referred to as an ‘electron gun’) which are passed through a series of condensing lenses, focusing the beam down to a spot size of 0.5 to 5 nm. The electron beam is typically of an energy range of 0.5 to 40 keV and scans the surface in a raster pattern. As the beam scans across the sample the electrons interact with the sample in different ways and by monitoring these different interactions, topographic and compositional information about the sample can be obtained. The two main interactions used in SEM imaging are the formation of secondary electrons and backscattering of the electrons, each of which give different information about the sample. A simplified schematic of an SEM showing the key features, as well as the different sample interactions is given as Figure 3.8.

Secondary electrons are formed as the incident electrons collide with the surface, transferring part of their energy to the atoms in the surface layers of the sample. This causes the emission of low energy (typically on the order of 5 eV) ‘secondary’ electrons from the sample. These secondary electrons are then collected (using positively charged grid over the secondary electron collector) and the electron count (i.e. intensity) as a function of sample position is recorded. As these electrons are low energy, they are only able to escape from the topmost layers (< 10 nm) of the sample. As the sample topography changes, the intensity of secondary electrons also changes, with the higher surface regions generating more secondary electrons. So the surface morphology can be represented by a plot of the intensity vs. position, with the taller features appearing to be brighter. However, it should be noted that the received signal is not strictly topographic as it also has contributions from the optical properties of the sample.
Figure 3.8: Schematic of a SEM. A beam of electrons is focused onto the sample. The intensity of the electrons that are knocked out the sample is measured and from this the sample topography is determined.

Electron backscattering occurs when an incident electron has a near normal elastic collision with a surface atom (i.e. the angle of incidence is almost 0° from the normal). The reflected electrons are then captured by a detector mounted around the incident beam. As the chance of an electron reflecting off the surface is dependent upon the mass of the atom (with heavier atoms more likely to cause back scattering) the backscattering image is able to give atomic compositional data, with regions of the sample containing heavier atoms appearing brighter than the areas with lighter atoms.\(^{148}\)

Due to the nature of SEM it is only capable of imaging solid samples under high vacuum. Furthermore, the sample must be conducting, as the SEM causes the surface to become electrostatically charged. Unless the sample is conductive as it is bombarded with electrons this charge will increase making the sample appear brighter, making the surface features less distinguishable. Non-conducting samples must be coated in a conductive material, such as gold, carbon (graphite) or platinum before they can be imaged. This unfortunately can lead to sample damage (particularly for delicate biological samples) as well as the loss of surface detail or formation of artefacts if the sample is not coated uniformly. Fortunately as ZnO is a
semiconductor the samples could be imaged by mounting them on conductive tape with no further treatment.

3.4. X-Ray Diffraction

X-ray Diffraction (XRD) is a simple technique for determining the structure of crystalline components of a sample. Whilst several different configurations of x-ray diffractometers (and the complementary system of x-ray spectrometers) are available, they all contain the same essential elements; an x-ray source, an x-ray detector and a goniometer. Figure 3.9a depicts a schematic for the most common type of diffractometer, a vertical θ/θ Bragg-Brentano Diffractometer. In this orientation the sample is fixed whilst the x-ray source and detector are mounted on synchronised goniometers, so that they are both at an angle of θ from the sample. The other most common orientation is a θ/2θ (Figure 3.9b), where the x-ray source is fixed and the sample rotates by θ and the detector moves by 2θ to maintain the correct geometry between the source, detector and sample surface.

Figure 3.9: Schematics of different types of XRD. (a) vertical θ/θ Bragg-Brentano XRD. Source and detector move in sync, relative to a fixed sample. (a) vertical θ/2θ Bragg-Brentano XRD. Source remains fixed, sample is rotated by θ, detector is rotated by 2θ to maintain geometry. (c) XRD powder diffraction. As a powder consists of an ‘infinite’ random array of crystals, all XRD peaks are expressed simultaneously as concentric rings at any incident angle.

The basic principle behind XRD is that when a solid sample is irradiated with x-rays some of the x-rays will be scattered in an elastic fashion by the atoms within the sample. This is possible because x-rays have a wavelength that is comparable to the diameter of an atom. As the x-rays penetrate the entire sample, the x-rays can scatter from electrons (electron-deficient portions of the Bravais cell are invisible) surrounding the atoms at different sample depths, as illustrated in Figure 3.10. This results in the x-rays with different path lengths (i.e.
The x-rays travel different distances, depending upon position of the atom upon which it was scattered. The different path lengths lead to phase differences in the scattered x-rays which usually results in destructive interference (Figure 3.10b), nullifying the rays. However, when the difference in the path length of the x-rays is the same distance as an integer value of the incident x-ray wavelength, constructive interference occurs resulting in the amplification in intensity of the scattered rays in that direction. An example of constructive interference scattering is shown as Figure 3.10a, as expressed by Bragg’s Law (Equation 3.9):

\[ 2d \sin \theta = n\lambda \] (Equation 3.9)

Figure 3.10: X-Ray scattering by atoms within a crystal structure for two different wavelengths. (a) constructive interference occurs when the wavelength is an integer value of the path difference \( n\lambda = |AB| + |BC| \). (b) destructive interference occurring as the path length is not equal to \( n\lambda \).

From Bragg’s Law it can be seen that for a certain atomic spacing there is only going to be a single incident angle (between 0° and 90°) where constructive interference will occur. This assumes monochromatic incident x-rays as any change in incident wavelength will result in a shift in peak position (in Equation 3.9, if \( d \) is constant, any change in \( \lambda \) will change \( \theta \) accordingly). If the intensity of the scattered x-rays is measured as a function of incident angle (by convention denoted as 2\( \theta \) as both the x-ray source and the detector move by \( \theta \) during measurement) any observed peaks can be correlated to the different spacing between the atoms within the sample. However, as crystals are three dimensional structures, measuring the atomic spacing in only one direction is not going to yield enough information to determine the crystal structure. Therefore to determine the structure of an unknown crystal (and by extension the dimensions of the unit cell of the crystal) diffractograms must be produced at different sample orientations. Whilst this is method is still used to determine the structure of an unknown compounds (particularly complex biological structures, such as proteins) nowadays XRD is primarily used for identifying the composition of a sample by comparing the diffractogram of a sample against known (theoretical or measured) diffractograms.
So far only XRD for a single crystal has been mentioned, whereas powder XRD was used exclusively throughout this work. This is because the principles behind single crystal diffraction also hold true for powder diffraction, albeit with a few minor adjustments. In powder XRD, ideally, the incident x-rays will strike crystals that are oriented in every possible way equally. Therefore, the scattered x-rays (that undergo constructive influence) will appear for every crystal orientation simultaneously. Thus the diffraction peaks will appear as discrete concentric rings instead of singular points, still at their respective values of 2\(\theta\) (as shown in Figure 3.9c). This can be thought of as the same as if single crystal was rotated through every possible angle, with the resulting diffractograms being overlaid. Powder XRD relies on assumption that every crystal orientation appears equally in the sample. This is not always true, as quite often the crystals can pack with some degree ordering. This means that the intensities of the powder XRD peaks can be dependent upon the sample orientation. To diminish these effects it is quite common to ‘smooth’ the diffraction peaks by rotating the sample about its central axis during data collection.

If a powder sample contains more than one crystalline phase, either from different crystal structures of the same material (e.g., a mixture of rutile and anatase titania) or a mixture of different materials, the resulting diffractogram would be the combination of the diffractograms for each individual phase. This is because at an angle where constructive interference occurs for one phase, the other phases will still experience destructive interference (assuming the peaks do not overlap). This is equivalent to two different peaks appearing simultaneously from different crystal orientations in a pure powder sample. Hence XRD can be used to analyse the phase composition of a composite sample. Furthermore the amount of each phase present can be determined quantitatively if the amount of one phase in the sample is known. Usually this is accomplished by mixing the unknown sample with a known amount of another material that is not usually present (i.e., introducing an internal standard).

One limitation of powder diffraction is that it has a substantially lower signal to noise ratio than the single crystal diffraction. As the incident x-rays are being scattered in all directions simultaneously the intensity for any given peak will be substantially lower than for an equivalent peak in single crystal XRD. To counter this powder diffractometers often use a divergent incident beam, making the reflected beams convergent (focusing at the detector) thereby increasing the measured intensity. This therefore increases the signal to noise ratio of
the diffractogram.\textsuperscript{149, 151} Another, limitation of XRD in general is that it can only performed on crystalline samples, as amorphous samples, by definition, lack the long range ordering needed to produce a enough constructive interference to produce a XRD peak.

3.5. X-Ray Photoelectron Spectroscopy

X-Ray Photoelectron Spectroscopy (XPS) is one of the most useful techniques for probing the elemental composition and bonding of the surface of a sample. XPS utilises the photoelectric effect to determine not only the atoms present, but also their bonding configuration. The basic setup of an XPS is given as Figure 3.11. Monochromatic x-rays of a known wavelength are radiated onto the sample surface under ultra-high vacuum. Monochromatic K\textsubscript{α} x-rays are typically obtained from either an aluminium (1486.7 eV) or magnesium source (1253.6 eV). The x-rays are absorbed by electrons within the sample, which are subsequently ejected. The ejected electrons will have a kinetic energy (\(E_k\)) equal to the energy of the incident X-ray (\(h\lambda\), where \(\lambda\) = wavelength and \(h\) is Planck’s Constant), less the energy required to remove it from is atomic orbital (i.e. the binding energy, \(E_b\)), as illustrated by Equation 3.10:\textsuperscript{152}

\[ h\lambda = E_k + E_b \] (Equation 3.10)

As Equation 3.10 assumes that there is no energy loss with the system, an extra term, the work function, \(\varphi\), needs to be added (Equation 3.11). The work function is particular to the instrument (not the sample) and is used as an adjustable parameter to account for the energy losses occurring within the system.\textsuperscript{152-153}

\[ h\lambda = E_k + E_b + \varphi \] (Equation 3.11)

By measuring the kinetic energy of the ejected electrons the binding energy of the electrons can be determined. As the binding energy of the different atomic orbitals of an element are discreet values, the ejected electrons will have discrete kinetic energies. Furthermore the binding energy of the same orbital (e.g. the 1\textsubscript{s} orbital) for different elements will have different (discrete) values. Therefore by measuring the electron intensity as a function of kinetic energy, the elemental composition of the sample can be determined.\textsuperscript{152-153} Whilst in XPS the electron kinetic energy is measured, a typical XPS spectrum will be displayed as a function of binding energy rather than kinetic energy. This is because the kinetic is dependent upon the properties of the spectrometer (i.e. the incident x–ray wavelength and the work function) whereas binding energy is a fixed value.

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Figure 3.11: Schematic of an XPS. The sample is bombarded with x-rays, ejecting e\textsuperscript{−} from the different atomic orbitals of the elements within the sample. The e\textsuperscript{−} are collected, focused and selected on the basis of kinetic energy using a concentric hemispherical analyser (CHA).

As stated before XPS is a surface selective analytical technique. This is because only electrons from the top 1-10 nm of the sample are able to escape from the material.\textsuperscript{152} The penetration depth of the x-rays can be adjusted by adjusting the angle at which the x-rays strike the surface (\(\theta_T\) in Figure 3.11, known as the take-off angle, TOA). When the TOA is higher, the sample penetration is decreased, so composition of only the top 1-2 nm of sample is measured. Therefore by varying to TOA depth profiling of the sample’s surface can be achieved.

At depths greater than 10 nm electrons still become excited, but will either collide with electrons in other atoms (thus lowering their energy) or recombine with an electron vacancy formed by the ejection of another electron.\textsuperscript{152-153} A special case of the latter is the formation of Auger electrons. When an electron from a lower orbital is removed, an electron that occupies a higher energy orbital can drop down to fill the vacancy and in doing so gives off a photon. This photon can then be absorbed by one of the remaining higher orbital electrons, causing it to be ejected. This second ejected electron is an Auger electron, and is quite often visible in XPS spectra as a very broad peak.\textsuperscript{152} Auger electrons can also be used in the related technique of Auger Spectroscopy, which is not covered in this thesis.
So far XPS has only been stated as being capable of determining which elements are present in the sample. XPS is also capable of determining the bonding within the sample, as well as the oxidation state of any multivalent elements. If high resolution scans of a single orbital of a particular element are performed, the subtle shifts in orbital energies caused by differences in bonding configuration can be observed, even if the orbital itself is an inner shell orbital not directly involved in bonding. For instance the binding energy O1s orbital of oxygen is different for a metal oxide vs. a metal hydroxide (in both cases the O2p orbitals are involved in bonding). In addition, as the peak intensity for a particular element is directly related to the abundance of that element in the sample, XPS can be used for quantitative analysis (or, for pure samples, determining the empirical formula).152-153

As with every analytical technique XPS has some limitations. Like all high vacuum surface selective techniques, XPS is very sensitive to surface contamination and only suited to solid samples. Furthermore, as the sample loses electrons it becomes positively charged, causing the binding energy to slightly increase. Whilst charge compensation can be countered (by either earthing conductive samples, or by flooding non-conductive samples with an electron gun)152 it is often advantageous to have an internal standard. In many cases this internal standard is chosen to be adventitious carbon. Adventitious carbon is present on practically every surface that has been exposed to ambient air and has C1s peak at 285.0 ± 0.2 eV. Therefore by adjusting the work function so that the C1s(adventitious) peak is at this value the effects of charging (and various other more minor factors that can cause a peak shift) can be countered, and thus accurate results can be obtained. Another limitation of XPS is that it is insensitive to hydrogen and helium as, due to their small size and atomic number, the probability of X-ray adsorption is very low. As a result the presence of these elements (hydrogen in particular) has to be inferred based on the bonding of the other, heavier, elements present. The main drawback of XPS is, however, the time taken to obtain a spectrum. Whilst low resolution scan that sweep across a wide range of energies can be performed in a few minutes, high resolution scans of several different atomic orbitals can take hours, depending on the abundance of the element of interest within the sample (typical XPS resolution can be parts per million, but this usually requires a scan time on the order of hours to properly resolve the peak from signal noise).

A major contributor to the scan time (besides the peak resolution of trace elements) is due to the nature of detector. The electrons exiting the sample are collected and focused into a
concentric hemispherical analyser (CHA). As the name suggests, a CHA consists of two concentric hemispheres. A voltage difference across the hemispheres is applied (with the inner hemisphere having the positive potential) so that the electrons undergo a curved trajectory to the detector. However for a particular voltage only an electron with a specific velocity (and hence kinetic energy) will follow the correct trajectory to the detector. If the electron is moving too fast it will not undergo enough curvature and as such it will strike the outer (neutral) hemisphere, whilst slower electrons will curve too much and strike the inner hemisphere. Thus by varying the applied voltage across the CHA the electrons can be selected based on their velocity and hence kinetic energy. So to obtain an XPS spectrum the intensity at each energy interval must be determined sequentially. The collection time at each point must be constant and be dependent upon intensity of the weakest signal in order for quantitative analysis. Furthermore, multiple sweeps are averaged to reduce the signal to noise ratio of the spectrum. This leads to the aforementioned long collection times. Lengthy collection times can be a problem for delicate samples, which are constantly being bombarded by X-rays during the scan. Whilst this isn’t an issue for most inorganic samples, organic samples can often undergo degradation causing the XPS spectrum to change with time.

3.6. Secondary Ion Mass Spectrometry

In Secondary Ion Mass Spectrometry (SIMS) a beam of primary ions is generated and focused onto a sample under high vacuum. The primary ions collide with the sample, sputtering off atomic fragments of the sample (known as secondary ions). These fragments are filtered and separated on the basis of their mass (using a mass analyser) and projected onto an ion collector (either a faraday cup or electron multiplier) which converts the ions into a current that is then recorded. A simplified schematic of this process is given as Figure 3.12. There are two main operational modes of SIMS, dynamic and static.

3.6.1. Dynamic SIMS

In dynamic SIMS the primary ion beam continuously sputters material from the sample. The secondary ions are then usually separated using a magnetic/electrostatic mass analyser. The setup shown in Figure 3.12 is for dynamic SIMS. This type of analyser uses constant electric and magnetic fields (separately) to alter the trajectory of the secondary ions, based on their mass to charge ratio ($m/z$). As the ions enter the electric field (or magnetic field) they experience a force that causes the trajectory of the ions to curve. The degree of curvature an
ion experiences will depend on the inertia of the particle, and as such will be dependent upon its charge (which is typically \(\pm 1\)) and its mass. If the flight path (i.e. the path an ion must travel from the sample to the detector) from the sample to the detector is curved, ion selection can be achieved by varying the electric field strength. For instance, at lower field strengths lighter ions will undergo more deflection than heavier ions. Therefore heavier ions will not curve enough and so collide with the walls of the flight path. Hence only ions that experience the same degree of curvature as the flight path will reach the detector.

Figure 3.12 Schematic of a (dynamic) SIMS. The sample is bombarded with primary ions, causing the removal of different mass fragments. The fragments are collected and selected on the basis of their mass on charge ratio (m/z).

Dynamic SIMS is best suited for monitoring one particular mass peak with time. As the sample material is constantly being removed (as SIMS is an inherently destructive technique) by monitoring the signal from one mass (or, more usually, the signal from several different masses sequentially) with time, the composition of the sample can be determined as a function of depth, especially if imaging of the sample is done concurrently. Whilst one of the major drawbacks of dynamic SIMS is that the sample is destroyed during the measurement (as opposed to most other spectroscopic techniques that are non-destructive), the primary limitation with dynamic SIMS is that it is only capable of measuring one m/z value at a time. If several signals are to be monitored, each signal must be measured sequentially. So to monitor the depth profile of two different atoms the intensity of the first atom must be measured, then the mass analyser must be switched to select for the second
atom. This switching is non-instantaneous and so disrupts the system and as such it takes time for it to return steady state conditions. During this time however, the sample has continued to be degraded, and as such the measurement of the second atom occurs at a different depth than the measurement of the first atom. This limitation has largely been overcome for the monitoring of two signals by implementing a fast switching mechanism and a duel detector system, with each detector attuned for a specific mass.\textsuperscript{154}

3.6.2. Static SIMS
Unlike dynamic SIMS, static SIMS strength lies in its ability to measure the composition of the surface of a material. Instead of a primary ion source of constant intensity, static SIMS strikes the sample with a pulsed ion beam. With each pulse only (ideally) the very top surface layer of the sample is removed. The secondary ions then typically pass through a time of flight (TOF) mass analyser.\textsuperscript{152} A TOF mass analyser is also comprised of an electric and magnetic field (separately). However, unlike a magnetic/electrostatic mass analyser the electric field is not used to separate the ions by changing their trajectory, but rather causes them to accelerate without changing direction. Upon leaving the electric field the ions will undergo separation along the flight tube based on their exit velocities, as the acceleration from the electric field can be directly related to their change in kinetic energy.

Thus the time taken for the ion to reach the detector will be related to its mass, with lighter ions reaching the detector first. So if the ion count as a function of time (with $t = 0$ being when the primary ion pulse occurred) the elemental composition of the surface of the sample can be measured. This also has the advantage over dynamic SIMS that it is considered non-destructive, as only the topmost layer is removed. However, as only the topmost layer is removed the measurement is very sensitive to the presence of surface contamination. Furthermore, whilst depth profiling of the sample can still be performed, due to the minute amount of material removed by each primary ion pulse, the etching rate of the sample is very slow, making depth profiling very time consuming.

The limitations of both static and dynamic SIMS can be avoided by combining the two techniques. In this hybrid version two different primary ion beams are used, one to etch the surface (as in dynamic SIMS) and a secondary, pulsed beam (static SIMS) to measure the composition of the sample at the bottom of the formed crater. This compromise allows faster, complete compositional analysis of the sample, but at the expense of detail as a function of depth. This is because instead of continually measuring the composition as a function of
depth (as with dynamic SIMS), the composition is measured at discreet sample depths (and naturally as the frequency of these points increases, so does the experimental time).\(^{152}\)

There are also some general limitations in SIMS (regardless of the mode) which should be highlighted. Firstly, SIMS is only suited to solid samples that can handle high vacuum conditions. Furthermore, if the sample is non-conducting the sample must be bombarded with electrons (or positive ions depending on the charge of the primary ion) to neutralise the built up charge the sample experiences. Also the choice of primary ion source affects the resulting compositional spectra, as different primary ion sources (particularly positive ions vs. negative ions) produce different mass fragments. The greatest limitation of SIMS however is that quantitative analysis of the sample is not possible without the use standard samples.\(^{152}\) Whilst this is easily accomplished when performing an isotopic analysis, using SIMS to determine the quantitative composition of an unknown sample is very difficult.

### 3.7. ZnO/ Zn(OH)\(_2\) Powder Synthesis

In Chapter 4 the growth mechanism of ZnO under hydrothermal conditions was studied by synthesising Zn-based powders at different temperatures. The synthesis of these powders was done as follows: Zinc hydroxide/oxide powders were prepared by drop-wise addition of 0.5 M Zn(NO\(_3\))\(_2\)(aq) to a covered, continuously stirred, 0.3M NH\(_4\)OH solution that had been pre-heated to the required reaction temperature. At the start of the addition a white powder is seen to form, but quickly dissolves as it is mixed throughout the solution. Whilst this initial powder could not be isolated and studied, it is suspected that this powder forms due to the presence of a localised area of supersaturation before the drop is fully mixed into the solution. When the solution becomes fully saturated with zinc ions the precipitate begins to form, and remains. Once the addition was complete, the suspensions were allowed to mature for 20 min before vacuum filtration at the reaction temperature. During this time no additional powder was seen to form. The precipitates were then washed with water and dried in a desiccant chamber containing silica gel for 48 hours at room temperature. All experiments utilized a standard 0.3 M NH\(_4\)OH solution prepared at at 20°C which had a measured pH of 11.3. Solutions were sealed and then heated to the desired temperature. As the formation of Zn(OH)\(_2\) consumes OH\(^-\), the addition of Zn(NO\(_3\))\(_2\) solution leads to a decrease in pH over the course of the reaction.
4. The Mechanism for Hydrothermal Growth of ZnO

4.1. Introduction

As shown in Section 2.7, a significant body of work has been generated on the effects of small molecules on the aspect ratio of zinc oxide crystals, but only a relatively small amount of work has addressed the fundamental question of how these molecules affect the growth. The first stage of understanding their effect, and the subject of this chapter, is to understand the mechanism for hydrothermal growth of crystalline ZnO.

Previous work has already suggested that Zn(OH)$_2$ is an intermediate in ZnO growth, but there is debate as to the form (crystalline vs. amorphous) and the mechanism by which it converts to ZnO. Shaporev et al. showed that zinc hydroxide can be formed from basic aqueous zinc solutions at low temperatures, and that these subsequently form ZnO once heated to a high enough temperature. Based on these observations, they proposed a growth mechanism by which ZnO forms from several Zn(OH)$_2$ intermediates (both crystalline and amorphous) depending on the solution conditions. McBride et al. also proposed that a zinc hydroxide intermediate occurs during the formation ZnO, but did not determine whether the transformation from hydroxide to oxide occurred by dissolution-precipitation or via solid phase transformation.

Several different forms of Zn(OH)$_2$ have been isolated under various conditions and, of these phases, only ε-Zn(OH)$_2$ (Wülfingite) is known to form large, pure crystals in nature. The unit cells of Wülfingite and Wurtzite ZnO appear to be very different: ZnO is a hexagonal close packed structure, whereas Wülfingite is orthorhombic. In both structures, however, the Zn(II) ion is tetrahedrally co-ordinated to four oxygen atoms, with each oxygen bridging four zinc tetrahedra ZnO, whereas in Wülfingite each oxygen bridges only two zinc tetrahedra. This yields a much lower density of Zn atoms in Wülfingite (Figure 4.1). This is reflected in the large difference in mass density: 5.6 g cm$^{-3}$ for ZnO compared to 3.1 g cm$^{-3}$ for ε-Zn(OH)$_2$. 
Figure 4.1: Crystal structures of Wülfingite (left) and Würzite ZnO (right), projected along the [010] and [0110] axes respectively. The large red sphere represents oxygen, the small grey sphere represents zinc and the small white sphere represents hydrogen.

The overall reaction for conversion of Zn(OH)$_2$ to ZnO is:

\[
\text{Zn(OH)}_2 (s) \rightleftharpoons \text{ZnO} (s) + \text{H}_2\text{O} (l) \quad \text{(Reaction 4.1)}
\]

The free energy difference for reaction 4.1 at room temperature from Wülfingite to ZnO, is $\Delta G^{\circ}_{298} = -1.13 \text{ kJ/mol}$.\textsuperscript{159-160} This free energy difference is very small, \( \sim -0.5 \, kT \), indicating that while Wülfingite does spontaneously convert to ZnO at room temperature and in pure water, only a small change in Gibbs energy, e.g. from a change in temperature, or the activity of water, is required to change the direction of the reaction. For example, Reaction 4.1 will be pushed to the right by adding ions to the solution that decrease the activity of water. At higher temperatures, e.g. 70°C, where ZnO growth is more commonly performed, the Gibbs–Helmholtz equation gives an estimate of $\Delta G^{\circ}_{343} = -2.5 \text{ kJ/mol}$ (assuming the literature value\textsuperscript{159-160} of $\Delta H^{\circ}_{298} = 8.2 \text{ kJmol}^{-1}$ is constant up to 70°C), which is still a very low energy difference.

### 4.2. Experimental

**Chemicals**

The chemicals used in this work were: 99% zinc nitrate hexahydrate (Sigma Aldrich), 28.89% ammonium hydroxide solution (Fisher Scientific), and water purified by an Elix then a Millipore system (resistivity 18.2 MΩcm$^{-1}$). The Millipore system removes dissolved carbonate. Enrichment studies were performed using 98% $^{18}$O water (Medical Isotopes, Inc).
**Powder Synthesis**

Zinc hydroxide/oxide powders were synthesised by the procedure described in Section 3.7.

**Fourier transform infrared Spectroscopy (FTIR)**

Spectra of the synthesised powders were collected on a Varian 670 FTIR Spectrometer using a Pike EasiDiff diffuse reflectance accessory with 128 scans at a resolution of 4 cm\(^{-1}\), with KBr powder as a background.

**X-ray photoelectron spectrometry (XPS)**

The elemental composition of each synthesised powders was determined using a Perkin-Elmer PHI 5400 spectrometer with a Mg K\(_{\alpha}\) photon energy of 1253.6eV. The source was run at 250W (12.5 kV and 20 mA).

**X-Ray Diffraction (XRD)**

The work performed in this chapter used three different X-Ray Diffractometers. The data presented in Figure 4.2 were obtained at the Australian Synchrotron using the 10-BM-1 Powder Diffraction beamline at a 15kV X-Ray source, with a Mythen PSD detector at 4 positions (110°, 109°, 81.5°, 81°) yielding a merged scan range of 1° to 110° with no gaps. Data was obtained using a wavelength of 0.82645Å, which was converted to 2\(^{\circ}\) values consistent with \(\lambda=1.5418\text{Å}\), for ease of comparison between the different XRD spectra and reference spectra in literature. Samples were mixed with corundum in a 1:1 mass ratio to allow quantitative comparison of peak heights between samples.

Low resolution scans were measured using either a Panalytical Xpert Pro DY 2693 using a 45kV, 40mA X-Ray source (\(\lambda=1.5418\text{Å}\)), with a 0.5° slit, a scan range of 10° to 90° with a step size of 0.030° and a time/step of 10 sec (Figure 4.6), or a Bruker AXS D8 Advance using a 40kV, 30mA X-Ray source (\(\lambda=1.5418\text{Å}\)), with a 0.6° slit, a scan range of 10° to 90° with a step size of 0.030° and a time/step of 0.5 sec (Figure 4.9). Samples were also spun at 15 rpm during measurement to remove any orientation effects.

**Secondary Ion Mass Spectrometry (SIMS)**

The ratios of \(^{16}\text{O}\) to \(^{18}\text{O}\) in \(^{18}\text{O}\)-enriched samples of Zn(OH)\(_2\) or ZnO were determined using a Cameca IMS-7f Geo Universal Magnetic Sector spectrometer, with a 15kV Cs\(^+\) source at 36°, and a 30 \(\mu\text{m}\) diameter spot size. A mass resolution of 2000 m/\(\Delta\)m was used to distinguish \(^{18}\text{O}\)\(^-\) from (H\(_2^{16}\text{O}\))\(^-\).
Scanning Electron Microscopy (SEM)

Scanning electron micrographs of the synthesised powders were taken using a LEO (Zeiss) 1550 Schottky field-emission SEM using a source electron energy of 5 keV and an in-lens detector. Samples were coated with 2 nm of gold to enhance contrast.

4.3. Results & Discussion

4.3.1. The Formation of ε-Zn(OH)$_2$ & ZnO as a Function of Temperature

To investigate the effect of temperature on synthesis products, individual samples were prepared by combining Zn(NO$_3$)$_2$(aq) and NH$_4$OH(aq) at a single constant temperature of 20°C, 50°C, 60°C, 70°C, 80°C, or 90°C, and then characterised by XRD, FTIR, and XPS.

![Figure 4.2: X-Ray Diffractograms of the zinc compounds synthesised at different temperatures (synchrotron)](image)

(a) 20°C sample has ε-Zn(OH)$_2$ labelled and ZnO peaks on the 70°C sample. Higher Miller-index peaks have been omitted for clarity. Al$_2$O$_3$ was introduced into the samples for quantitative analysis. (b) Enlargement of the range 2θ = 30.5°– 35.5°.
Figure 4.2 shows the XRD spectra of the synthesised products as a function of increasing synthesis temperature. From Figure 4.2a it can be seen that below 60°C Wülfingite is the major product, with increasing amounts of ZnO forming as the temperature is increased (Figure 4.2b). From 70°C and above it can be seen that only ZnO is formed. Also looking at the peak width of the Wülfingite vs. ZnO it is evident that the ZnO grain size is smaller than that of Wülfingite, however, formal average grain size analysis using the Scherrer Equation cannot be performed as the crystals are larger than 100 nm in size (as shown later in Figures 4.10 and 4.11).

The results of XRD are confirmed by IR of the bulk crystal, shown in Figure 4.3. From 20 to 60°C, there are two peaks at 1086 cm\(^{-1}\) and 1039 cm\(^{-1}\), which have previously been attributed to Zn-O-H bending vibrations in Zn(OH)\(_2\).\(^{161}\) There are also two large, broad bands centred around 3305 cm\(^{-1}\) and 3203 cm\(^{-1}\) which are similar to O–H stretching bands that have been observed for many compounds containing hydroxide groups.

Figure 4.3: FTIR spectra of the zinc compounds synthesised at different temperatures. Each temperature has been arbitrarily offset in Absorbance so that the spectra do not overlap.

For powders synthesized at temperatures greater than 70°C, the IR spectra of the Zn compounds do not contain the Zn-O-H bending peaks (as proven by peak deconvolution), and instead contain a shoulder with a broad peak at 900 cm\(^{-1}\). Furthermore, the O–H stretching bands have decreased in intensity and are shifted to a higher frequency range (3400 cm\(^{-1}\) to
3550 cm\(^{-1}\)), which is tentatively attributed to either a surface reconstruction of the oxide into a hydroxide species (which is supported by the XPS data), or water trapped within the powder. The data at temperatures greater than 70°C are consistent with the formation of ZnO, which is IR transparent in the range 3500–1000 cm\(^{-1}\). Thus, the IR spectra are consistent with the formation of Zn(OH)\(_2\) at synthesis temperatures below 70°C and ZnO above 70°C.

It should be noted the presence of three peaks 2300 cm\(^{-1}\) and 2000 cm\(^{-1}\) in the Wülfingite samples cannot be fully explained. They appear to be consistent with the presence of an crystalline ammonium (NH\(_4\)) salt\(^{162}\), which is not likely, as the crystals were synthesised under basic conditions, and the XPS analysis showed no nitrogen present in the sample.

XPS was used to further investigate the effect of synthesis temperature on the nature of the product. Low resolution scans across a wide energy range showed that carbon, oxygen and zinc were the only elements present at the surface of the samples. This indicates that neither the ammonia, nor the nitrate ions used in the synthesis were incorporated into the crystals during growth.
for the 50°C, 70°C and 90°C samples. In the 20°C sample, we attribute the peak at 530.0 eV to a carbonate species, and this was confirmed by the presence of the corresponding peak at 289.1 eV in the C1s spectrum. The exact carbonate species could not be confirmed from the FTIR as the carbonate region (1700 cm\(^{-1}\) to 1400 cm\(^{-1}\)) contained peaks attributed to the presence of hydroxide species.

The XPS spectra show that, as the synthesis temperature increases, the surface composition changes. From 20°C to 60°C the surface is 70 – 75 % zinc hydroxide, with the ZnO content of the sample synthesised at 50°C being 20 %. In the sample synthesised at 20°C 16 % of the oxygen content is due to the presence of a carbonate species. Whereas from 70°C to 90°C, the surface is 65 – 67 % zinc oxide, with 26 – 29 % of the sample surface remaining a zinc hydroxide species. The water content in the samples was consistently about 5 – 6 %, with the exception of the sample synthesised at 20°C, which had a higher water content of 13%.

Whilst the shift in major product from Zn(OH)\(_2\) to ZnO as the synthesis temperature was increased is consistent with the (bulk) XRD and infrared spectra, the presence of a zinc hydroxide species at higher synthesis temperatures is not. As XPS is a surface selective analytical technique, whereas XRD and FTIR sample the entire specimen, this hydroxide peak is only on the surface, and so is most likely due to surface hydroxylation of ZnO. It should be noted that the Zn 2p\(_{3/2}\) peak does not shift in accordance with the O1s peak, remaining at 1022.3 eV for all temperatures.

![Figure 4.5: O1s XPS spectra of the zinc compounds synthesised at 20°C, 50°C, 70°C and 90°C. The grey line is the acquired data, the dotted line is a curve fit. The curve fit is the sum of Gaussian contributions from: the O1s peak of water (532.9 eV to 533.3 eV), Zn-OH (531.9 eV to 531.5 eV), Zn-O (530.5 eV) and CO\(_3\) (530 eV), which are show as black lines.](image)

The XPS results differ from those presented by Sepulveda-Guzman et al. who reported XPS spectra consistent with the formation of ZnO rather than Zn(OH)\(_2\) at 60°C.
this apparent discrepancy may be due to differences in synthesis procedure. First, sodium hydroxide was used in their work whereas ammonium hydroxide was used here. It has been reported\textsuperscript{10, 135-136} that the ammonium ion is influential in the hydrothermal synthesis of ZnO and different products can be formed\textsuperscript{10} at 60°C by use of NaOH or NH\textsubscript{4}OH. Second, in the work by Sepulveda-Guzman et al the product was held as a suspension at 60°C for a much greater time (3 hours) than in our work (20 minutes), so it is possible during that time the zinc hydroxide could have converted to zinc oxide. The latter possibility will be examined in the next section.

Based on the IR, XPS and XRD data presented in this section, it is concluded that the major product by the previously described hydrothermal synthesis (Section 4.2) is $\varepsilon$-Zn(OH)$_2$ below 70°C, and ZnO above 70°C.

4.3.2. The Conversion of $\varepsilon$-Zn(OH)$_2$ to ZnO

It has now been shown that the synthesis temperature determines which of Wülfingite or ZnO is the predominant synthesis product after 20 minutes. It has not been established however, whether Wülfingite is formed as intermediate which then converts into ZnO or is merely a side reaction that becomes less favourable as the temperature increases (the term “intermediate” is used here to describe a substance that is formed along the reaction coordinate, not a product that is spatially located in between two other materials). X-ray diffraction is the most decisive technique for determining the product, but it is difficult to perform X-ray diffraction on a liquid-phase reaction. Therefore progress of the reaction could only be analysed by removal of the product at discrete time intervals. The reaction pathway for single temperature, 50°C, was chosen and individual samples were studied after a set period of time. At lower temperatures ZnO was not observable within a reasonable time, and at 70° or above Wülfingite was not seen to form.

Two nominally identical syntheses were performed at 50°C. One was removed, filtered and dried after 20 minutes and the other after 140 h at 50°C. Both were examined by XRD. Figure 4.6 shows that when the sample was held at 50°C for only 20 mins, the major product was Wülfingite, whereas when the sample was held at 50°C for 140 h, the major product was ZnO. The reaction was not monitored between 20 mins and 140 h, so the 140 h should be considered to be an upper bound for the reaction time. The results at 50°C are consistent with the mechanism in which first Wülfingite is formed and then converts to ZnO. The results in
Figure 4.2 are then explained by an increase in temperature increasing the rate at which Wülfingite converts into zinc oxide: a higher temperature leads to the systematic increase in ZnO product seen in Figure 4.2b. An alternative hypothesis is considered in the next section.

Figure 4.6: X-ray Diffractograms for the Zn powders synthesised at 50°C, with varying hold time. (a) Reaction for 20 min and (b) Reaction for 140 h. High index reflections have been omitted for clarity.
4.3.3. Determining the Reaction Pathway for the Conversion of \( \varepsilon \)-Zn(OH)\(_2\) to ZnO

Now that it has been established that Wülfingite can convert to ZnO under hydrothermal conditions, the next step is to elucidate the conversion pathway. Two possible hypotheses are illustrated in Figure 4.7:

(A) *Formation of ZnO from Wülfingite via dissolution and re-precipitation.* Wülfingite dissolves (reaction –1 in Figure 4.8) and re-precipitates as ZnO from the dissolved zinc species (reaction 2 in Figure 4.8).

(B) *Formation of ZnO directly from Wülfingite in the solid state.* Solid state phase transformation accompanied by dehydration as shown in path 3 in Figure 4.8.

It is important to differentiate between these two hypotheses as they give a different role to Wülfingite in the hydrothermal growth of ZnO. If the process proceeds via route (A) then one could encourage ZnO growth by hindering the growth of Wülfingite (as Wülfingite formation is a competing reaction) whereas if ZnO forms primarily from Wülfingite via solid state reaction (route B) then hindering the formation of Wülfingite would also hinder the growth of ZnO.

To confirm that Wülfingite can convert to ZnO in the solid state the conversion was performed in the absence of a liquid medium. A sample of dry Wülfingite powder, synthesised at 50°C, was baked in a dry oven at 70°C for 140 h. The x-ray diffractograms of the starting and product materials (Figure 4.8) show an increase in ZnO product, thereby confirming that Wülfingite can convert to ZnO via a solid state transition. Comparing to
similar reactions in aqueous solution (70°C, 20 minutes, Figure 4.2) and (50°, 140 minutes, Figure 4.6), we see a smaller degree of conversion in the dry state. This indicates that the conversion of Wülfingite to ZnO could be occurring via both pathways simultaneously.

![X-ray diffractograms](image)

Figure 4.8: X-ray diffractograms of the powder synthesised at 50°C (a) before and (b) after heating at 70°C for 140 hr under dry conditions. ZnO reflections are labelled.

To determine which pathway is favoured in the transformation of Wülfingite to ZnO, the oxygen atoms were tracked via isotope labelling. To do this, a sample of Wülfingite that contained 10% molar oxygen fraction of $^{18}$O was prepared by hydrothermal synthesis in 10% H$_2^{18}$O at 50°C for 20 minutes. $^{18}$O is a stable isotope of oxygen, so it can be used to trace the origin of oxygen atoms in ZnO through measurement of the isotopic contribution. The Wulfingite crystals were removed from the 10% H$_2^{18}$O by filtration. The Wülfingite crystals (ca. 5 mg) were then immersed in water (5 mL) with the natural abundance of $^{18}$O (0.2%) at 70°C for 140 h to allow it to convert to ZnO. The reaction was not done in the normal growth liquor (i.e. 0.3 M NH$_4$OH) to prevent additional ZnO precipitating from the growth liquor due to the retrograde solubility of Zn$^{2+}$ in ammonia solutions.$^{56}$

Because of the excess of water, the mole fraction of $^{18}$O in the total system (solid plus liquid) was 0.22% (calculated using a basis of 5 mg of 10% $^{18}$O Zn(OH)$_2$ immersed in 5mL 0.2% O$^{18}$ H$_2$O), so if the Wülfingite converts solely via solution (pathway (A)), we would expect a mole fraction of 0.22 in the resultant ZnO (ignoring the small isotopic effect on equilibrium.
constants). As the hydroxide and water ligands of Zn(II) ions exchange rapidly with water in aqueous solution,\textsuperscript{168} it is assumed that any dissolved zinc species will come to isotopic equilibrium with the solution before re-precipitation can occur. Similarly, if the ZnO were formed exclusively via the solid phase, with no solution exchange, then it would be expected that the ZnO \textsuperscript{18}O content would be close to 10\%. SIMS analysis showed that the \textsuperscript{18}O content of ZnO product was 6.8\%, demonstrating that about 2/3 of the oxygen atoms in the ZnO originate from the Wülfingite crystals. The remaining 1/3 were incorporated from the solution. This result is shown as Experiment 1 of Table 4.1.

To check the isotope tracing experiment, the enrichment of the starting phases was reversed, with a 0.2\% \textsuperscript{18}O Wülfingite converted to ZnO in 98\% \textsuperscript{18}O water at 70ºC for 140 h. The final crystals contained 42\% \textsuperscript{18}O, (Experiment 2 in Table 4.1) so 57\% of the oxygen in the final crystals originated in the Wülfingite. The final crystals here are also ZnO and thus it is concluded that 57–68\% of the oxygen atoms of ZnO originates in the Wülfingite.

As the previous experiments were both done under stagnant conditions, the possibility of poor mixing influencing the origin of the ions in ZnO had to be considered. When the experiment was done with vigorous mixing, the percentage of Wülfingite that converts to ZnO via the solid state was similar to the conversion under stagnant conditions, with 69\% solid state conversion observed (Experiment 3 Table 4.1).

Table 4.1: \textsuperscript{18}O content of ZnO prepared under various conditions

<table>
<thead>
<tr>
<th>Initial Solid</th>
<th>Stirring</th>
<th>% \textsuperscript{18}O</th>
<th>Solid State Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Initial Product</td>
<td>Raw\textsuperscript{A}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Solid Liquid Av. A Solid\textsuperscript{B}</td>
<td></td>
</tr>
<tr>
<td>1 Wülfingite</td>
<td>no</td>
<td>9.98 0.2</td>
<td>0.22 6.8</td>
</tr>
<tr>
<td>2 Wülfingite</td>
<td>no</td>
<td>0.2\textsuperscript{E} 98</td>
<td>97.8 42</td>
</tr>
<tr>
<td>3 Wülfingite</td>
<td>yes</td>
<td>0.2 98</td>
<td>97.8 30</td>
</tr>
<tr>
<td>4 ZnO</td>
<td>no</td>
<td>0.2 98</td>
<td>97.8 5.9</td>
</tr>
</tbody>
</table>

\textsuperscript{A} A\textsubscript{v} = (\textsuperscript{18}O \% x amount \textsuperscript{18}O)\text{solid} + (\textsuperscript{18}O \% x amount \textsuperscript{18}O)\text{liquid}

\textsuperscript{B} Measured by SIMS

\textsuperscript{C} raw = product solid / initial solid. Calculated for \textsuperscript{18}O in exp. 1 and \textsuperscript{16}O in exps 2–4.

\textsuperscript{D} =raw/(1–0.059). This figure subtracts the estimated surface exchange to give the estimated fraction of the bulk that exchanges.

\textsuperscript{E} the natural abundance of \textsuperscript{18}O in water is 0.2\%.

\textsuperscript{F} using unstirred control for stirred experiment.

A small complication arises in interpreting these isotopic exchange experiments. ZnO is quite soluble at the conditions of the isotope studies (ca. 10\textsuperscript{-5} M in pure water at 70ºC\textsuperscript{56}), which means that there is always some exchange of the ZnO material with Zn(II) ions in solution (path -2 in Figure 4.8). Thus, even if an entire crystal of Wülfingite converted to
ZnO in the solid state, the zinc and oxygen atoms in that ZnO crystal would still undergo exchange with the solution, so the rates of conversion via solid state described above (57–68%) are an underestimate. To estimate the extent of surface exchange of oxygen in the ZnO crystal a sample of 0.2% $^{18}\text{O}$ ZnO crystals was placed in solution and allowed to equilibrate in 98% $^{18}\text{O}$ water under the same conditions for the same period of time as the previous $^{18}\text{O}$ experiments (Experiment 4 Table 4.1). In this control experiment, about 5.9% of the atoms exchanged from the solid ZnO. This shows that surface exchange alone cannot account for the observed degree of conversion via the solution state. However, if this degree of surface exchange is taken into account (as noted by the final column of Table 4.1), it is apparent that about 60–73% of the ZnO arises from the Wülfingite directly.

In addition to surface exchange, direct precipitation of ZnO from solution will always occur in a solution that is equilibrated with Wülfingite, as the solubility of Wülfingite is greater than that of ZnO (7.6 mM vs. 4.6 mM) under conditions where Wülfingite spontaneously converts to ZnO. This means that, during the reaction of Wülfingite to ZnO, the solution will remain supersaturated with respect to ZnO, whilst being saturated with respect to Wülfingite, which would encourage direct growth of ZnO from solution.

If surface exchange and surface precipitation occur, then there should be variation in $^{18}\text{O}$ composition within each final crystal. This was tested by analysing the sputtering profiles from the SIMS experiments. Figure 4.9 shows the depth profile for Experiment 4, Table 4.1. At the start of sampling, when more of outermost layers of the crystals are sampled, the experimentally observed $^{18}\text{O}$ content is close to that of the solution (98%) in which the ZnO was prepared. SIMS sputters material from the surface, so higher sample numbers sample material that has been exposed by earlier sputtering. The term ‘sample numbers’ is used here instead of sample penetration depth because penetration depth cannot be accurately gauged for powders. However, it is estimated that about 10 nm of sample surface is removed between each measurement. Therefore as the individual crystals (both Wülfingite and ZnO) are greater than 100 nm in size several measurements would be performed on any one crystal, and hence any effects due to packing or start-up can be neglected. Furthermore, as the size of the crystals is small (< 10 μm) relative to the sampling spot of the SIMS (30 μm) contributions from both the bulk and the surface of the sample will still occur, even at higher sample numbers. The $^{18}\text{O}$ content in the higher sample numbers is much closer to the $^{18}\text{O}$ content in the Wülfingite crystals (0.2%). These steady state values at high sample number give a good
indication of the average $^{18}\text{O}$ content throughout the whole crystal and are the values shown in Table 4.1.

The key point from this work is that the SIMS samples that consisted of more of the interior of the ZnO crystal contained much more oxygen from the original Wülfingite crystal. This is again consistent with a mechanism in which the interior of each crystal underwent a solid–solid reaction, whereas the exterior exchanged or precipitated from solution. If the ZnO formed purely by dissolution/re-precipitation there would be little variation with sample number and the $^{18}\text{O}$ content would be close to that of 0.2% i.e. the natural abundance of water, as it was present far in excess to the $^{18}\text{O}$ enriched Wülfingite.

![Graph](image)

Figure 4.9: Depth profile of $^{18}\text{O}$ content in ZnO measured by SIMS in Experiment 2, Table 4.1. Low sample numbers sample only the surface whereas high sample numbers sample a mixture of surface and bulk. ZnO was prepared from 0.2% $^{18}\text{O}$ Wülfingite in 98% $^{18}\text{O}$ H$_2$O.

In support of the findings from the SIMS experiments the chemical composition as a function of depth below the surface of the particles was measured by varying the take-off angle during an XPS experiment. When the take-off angle (TOA) is decreased, the sampling depth is increased. The O$_{1s}$ signal from the Wülfingite prepared at 50°C (Figure 4.11a and b), shows an increase in the in Zn-O (530.4 eV) and water (533.3 eV) peaks, relative to the Zn-OH (531.9 eV) peak as the sampling depth is increased. Thus the inner material is richer in ZnO and water. The presence of both ZnO and water beneath the surface of the Wülfingite crystal strongly suggest that conversion from Wülfingite to ZnO is occurring within the bulk of the crystal, rather than at the surface. In particular, the extra water on the interior is very telling. Normally one would expect more water on the surface of a substance that had been immersed
in water, but here water is a by-product of the formation of ZnO from Wülfingite (Equation 4.1), so the water on the interior is consistent with ZnO formation on the interior. It should be noted however, that the O1s signal from ZnO synthesised at 70°C showed no variation in composition with penetration depth, (Figure 4.10c and d) which is contrary to our expectation if an outer hydroxide-rich layer existed.

As further evidence of that Wülfingite converts to ZnO at 50°C via both the solid state and dissolution precipitation mechanisms changes in the crystal morphology were monitored as a function of time. Figure 4.11 shows that initially (Figure 4.11a) the sample is primarily comprised of clusters of Wülfingite crystals that are approximately 1 - 5 µm in size. Furthermore, Figure 4.11h confirms the presence of ZnO nuclei that are about 500 nm in length. As the reaction progresses it was observed that the large Wülfingite clusters break up into single crystals, which then break up into smaller ZnO clusters that remain about 1 µm in size. Also as the reaction progresses it is seen that the ZnO nuclei grow and the Wülfingite surface becomes cracked and pitted.

These observations would suggest that single Wülfingite crystal does not convert to a single ZnO crystal, but rather the conversions causes the Wülfingite crystals to break up into smaller crystals. This is not surprising given the density difference between Wülfingite and ZnO. However, given that the system was vigorously stirred and the original size and morphology of the original single Wülfingite crystals is maintained even after long reaction times (e.g. even after 100 h, as observed Figure 4.11f) a pure dissolution/re-precipitation mechanism is not a valid explanation. Rather, a reaction mechanism where the Wülfingite crystals break
apart into smaller crystals as they undergo both solution/re-precipitation and solid state conversion appears to satisfy the SEM observations. This also goes to explain the smaller ZnO crystals that were shown in the XRD analysis.

Figure 4.11: (a-g) SEM images of Wülfingite crystals converting to ZnO at 50°C for different reaction times. Samples were taken from one reaction batch at the noted time intervals. Scale bar is 1 µm (a-g). Enlargement (scale bar 250 nm) of the Wülfingite surface at 0 h (h) and 100 h (i) showing the enlargement of the initial ZnO nuclei and pitting of the Wülfingite surface over time.

4.3.4. Implications for Using Small Molecules to Control Growth Morphology
Elucidation of the mechanism of ZnO formation affects the interpretation of previous experiments, which studied the effect of small organic molecules (e.g. trisodium citrate) used to control the aspect ratio of ZnO crystals during hydrothermal synthesis (Section 2.8.5). The assumed mechanism has been that strong adsorption of the small organic molecule selectively to one face of the crystal caps growth selectively in the direction of the normal to that face.\textsuperscript{11, 107, 121} That mechanism inherently assumes that the ZnO crystal surfaces are in direct contact with solution. The results presented here cast doubt on this assumption. The experiments (in the absence of small organic molecules) are consistent with a mechanism in which Zn(OH)\textsubscript{2} forms first, then mainly transforms to ZnO without exchanging with solution. Whilst Wülfingite was not observed at higher temperatures ( >60°C ) it is assumed that this is due to
the rate of formation of Wülfingite becoming slower than the rate of conversion of Wülfingite to ZnO. Hence the formation of Wülfingite becomes the rate limiting step. This suggests that the differences in ZnO crystal aspect ratio observed in the presence of small organic molecules may arise from interactions between shape directing molecules and a Zn(OH)$_2$ surface rather than with a ZnO surface. Thus, hypothesis proposed in this chapter is similar to the previously suggested hypothesis, except that selectivity of the small organic molecules acts on Zn(OH)$_2$ rather than ZnO.

This hypothesis assumes that by increasing the synthesis temperature the rates of reaction of the formation of Wülfingite and conversion of Wülfingite to ZnO change relative to each other. However, given that the conversion of Wülfingite to ZnO is occurring by two competing pathways; solid to solid conversion and solution to solid precipitation, it is possible that increasing the temperature alters the balance between these two processes, making the direct growth of ZnO from solution dominate. In this case the pre-existing theory holds true. To test whether shape directing molecules influence the formation of Wülfingite two samples were prepared at 50°C, one in 0.3 M NaOH, the other in 0.3 M NaOH and 10 mM trisodium citrate. The morphology of the resulting Wülfingite crystals were studied with the SEM and are given as Figure 4.12. To test if the citrate ions affect the conversion of Wülfingite to ZnO two samples of the Wülfingite prepared at 50°C without citrate were dispersed in water at 70°C and converted to ZnO in the presence and absence citrate (10 mM) via the same procedure outlined in Section 4.2. The resultant morphology is also given in Figure 4.12.

Comparing the Wülfingite samples grown with and without citrate it is evident that citrate alters the morphology of Wülfingite. Without citrate (Figure 4.12a) Wülfingite forms large faceted polyhedral crystals on the order of 10 µm in size that have relatively smooth surfaces (some star shaped nuclei of ZnO are present on the surface). The sample grown with citrate (Figure 4.12b) also forms large crystal clusters that overall are similar in dimensions to the sample grown without citrate. However, the cluster appears to be comprised of small interlocking platelets of Wülfingite about 1 µm in size and 100 nm thick, rather than the large, solid crystals formed without citrate.

When Wülfingite is converted to ZnO (Figure 4.12c) in water only it is apparent that the star shaped ZnO nuclei present in the original sample grow along the [0001] direction forming a
network of urchin shaped clusters. Again overall this cluster retains the original Wülfingite crystal shape. This is also true for the sample converted in the presence of citrate ions. However this time (Figure 4.12d) the clusters form tight agglomerates with high amounts of (0001) plane, which is expected for ZnO grown in the presence of citrate.

Figure 4.12: Morphology of Wülfingite and ZnO synthesised under different conditions. Wülfingite synthesised at 50°C (a) without citrate and (b) with 10 mM citrate. ZnO originating from (a) after being converted at 70°C for 140 hr (c) in water and (d) in 10mM citrate. This demonstrates that citrate influences both the formation of Wülfingite and the conversion to ZnO on the surface. All scale bars represent 1 µm.

These results appear to cast doubt on the solid to solid conversion of Wülfingite to ZnO as the resulting crystal shapes dramatically different. However, overall the clusters retain the same a shape similar in dimensions to the original Wülfingite sample. Also given that the only crystal surface can be seen, it is entirely possible the centre of the cluster, which forms the bulk of the material, converted via the solid phase, whilst the surface of the crystal (and hence the apparent topography) is affected by growth from solution. Based on the
observations made here it is evident the citrate molecules are influential on directing the shape during the formation of Wülfingite, as well as the conversion of Wülfingite to ZnO.

4.4. Conclusions

During the hydrothermal growth of ZnO from Zn (II)\textsubscript{aq} in 0.3 M NH\textsubscript{4}OH solutions at T<70°C Wülfingite (\(\varepsilon\)-Zn(OH)\textsubscript{2}) is the first stable crystalline compound formed. After a period of time, the Wülfingite dehydrates to form ZnO. The transformation from Wülfingite to ZnO was observed to occur primarily via a solid state to solid state reaction within the interior of the crystal, with the outer surface layers of ZnO forming directly from, or exchanging with, solution. Therefore, the ZnO growth surface at lower temperatures is comprised of a hydroxide species. At higher synthesis temperatures the degree of ZnO that forms from solid state may be less. Furthermore, citrate was found to influence the morphology of the initially grown Wülfingite, as well as affecting the morphology during the conversion of Wülfingite to ZnO.

Acknowledgements

Special thanks goes to those who helped with the data collection and analysis at the various locations this work was done: Frank Cromer (XPS), Mr. Mark Styles and Dr. Carolina Tallon Galdeano (XRD, Synchrotron), Tongan Jin (XRD), Dr Jerry Hunter (SIMS) and Dr. Steve McCartney (SEM).
5. Differential Etching of ZnO Native Planes under Basic Conditions

5.1. Introduction

Having established the hydrothermal growth mechanism of ZnO, the focus of this work temporarily shifts to the complementary process of dissolution. Even though there has been a increasing interest in controlling the shape of ZnO during growth (Section 2.8.5), comparatively little attention has been given to the so called ‘top down’ approach of controlling ZnO shape by etching. This is surprising as etching not only has the potential to create shapes that are difficult to achieve via growth methods (such as the formation of ZnO nanotubes\(^{112,169}\)), but also can produce surfaces of ZnO\(^{170}\) that are normally absent during growth.

Previous work on the wet etching of ZnO focussed on how the different surfaces respond to acidic\(^{170-175}\) conditions. The majority of these studies used ex-situ techniques, which give good insight into products of etching, but are limited in their ability to show the etching mechanism. One exception to this is the work by Valtiner et al,\(^{26,176}\) who have performed in depth studies of the in-situ etching of single crystal ZnO under both acidic\(^{26}\) and basic\(^{176}\) conditions. They showed that under alkaline conditions (pH>14) the (0001) plane is stabilized by hydroxide adsorption, and dissolution proceeds at crystal step edges. There have been only a few studies on the effect of small molecules on the ZnO dissolution process, and so far these have only been studied ex-situ.\(^{170,174,177}\)

In this work the in-situ dissolution of three polished faces of ZnO, (0001), (000\(\bar{1}\)) and (10\(\bar{1}0\)), is studied under basic conditions. The effect of citrate, a known growth modifier\(^{10-12,30,34,35}\), on ZnO dissolution is also investigated. A mechanism of dissolution is developed, including the influence of citrate.
5.2. Experimental

Chemicals
Solid NaOH (Sigma Aldrich) used in this work was AR Grade (99%+ purity) and used as received with no further purification. The solvent for all solutions is Millipore purified water (resistivity 18.2 MΩcm⁻¹).

Atomic Force Microscopy
ZnO single crystals (10 mm x 10mm x 0.5 mm SPC Goodwill) were obtained cut and polished perpendicular to the [0001], [000\overline{1}] or [10\overline{1}0] directions. In this work, the sample nominally normal to the [0001] direction is referred to as the Zn-terminated basal plane ZnO. The sample nominally normal to the [000\overline{1}] direction is referred to as the O-terminated basal plane ZnO and the sample nominally normal to the [10\overline{1}0] as the prismatic plane ZnO. The Miller Indices (0001), (000\overline{1}) and (10\overline{1}0) will be used to refer to the actual crystalline planar surfaces.

Scanning Electron Microscopy
Ex-situ images were obtained under high vacuum using an FEI Quanta Scanning Electron Microscope (ESEM) with an accelerating voltage 5 kV at a working distance of 9.7 mm and a spot size of 2.0 nm. Samples were mounted on conductive tape with no pre-treatment.

5.3. Results

5.3.1. Etching the Zn-Basal Plane ZnO with 2M NaOH
The (0001) polar plane is the most characterised native face of ZnO due to it being the primary growth direction for ZnO, especially during epitaxial growth. Figure 5.1 shows the time evolution of the nominally Zn-terminated basal plane ZnO during etching. AFM images on a 10 μm-scale of the Zn-terminated basal plane ZnO before etching (Figure 5.1a) shows that the surface is quite flat (2.8 nm rms roughness over 100 μm²) and is characterised by a series of thin scratches that arise from the manufacturer’s polishing process. At higher magnifications (Figure 5.1e) it is obvious that the surface does not consist of molecularly smooth planes, instead it is comprised of irregular features on the order of 3 nm high and 100 nm in diameter. For convenience, this sample is referred to as Zn-terminated basal plane ZnO, but it is clear that there are no large areas of (0001) facets on the sample.
Once the Zn-terminated basal plane ZnO is exposed to 2M NaOH two different types of dissolution occur. Initially dissolution pits form in the [000\bar{1}] direction at certain locations on the plane. It has been previously reported that dislocations occur primarily in the [0001] direction for hydrothermally grown ZnO.\textsuperscript{12, 178} As dissolution occurs preferentially at defect sites, it is concluded that a dislocation is present at the point of origin of a dissolution pit. This explains why dissolution in the [000\bar{1}] direction only is seen to occur at specific points,
and why these points often occur in lines corresponding to the deeper scratches initially present on the surface. As the etching in the [0001] direction occurs, material is also removed along the <10\bar{1}0> directions parallel to the (0001) plane surface. The newly revealed terraces extend away from the dislocation sites forming stepped, hexagonal pits as seen in Figure 5.1g. These pits continue to increase in size, expanding away from the dislocation in the {10\bar{1}0} directions and are the main method by which the ZnO crystal dissolves.

As dissolution continues, the steps become less frequent but increase in height. The steps seen in the AFM images (Figures 5.1a to 5.1f) are on one side of a hexagonal dissolution pit, and there are similar steps going in the other five directions, as is evident in Figure 5.1g. Under etching conditions, the basal plane becomes rougher (i.e. there is greater variation in height across the sample) over larger areas (100 μm²) but locally, i.e. the area between the steps, is very smooth. The continuing presence of the (0001) plane during dissolution and the observation that dissolution into the Zn-terminated basal plane ZnO only occurs at dislocation sites implies that the (0001) plane itself is stable (i.e. has a low surface energy) in the highly alkaline solution.

The orientation of the step risers (the planes that are formed when a step is created) can be not be easily approximated by studying the AFM cross section presented in Figure 5.1h. The orientation of the dissolution front (that is the orientation of the riser) is not perpendicular to the (0001) plane and so is not purely (10\bar{1}0) plane, but rather it is at an incline making it a higher index combination of (0001) and (10\bar{1}0) planes. This inclination cannot be attributed to an imaging artefact caused by tip convolution. As the leading face of the AFM tip is inclined at an angle of about 15° relative to the [1000] direction (as the steps are large enough they are likely to be imaged by the side of the cantilever as it travels across the surface, rather than the tip which usually images the surface), the tip convolution will lead to images with the (10\bar{1}0) plane at an angle of 105° relative to the (1000) plane. However, Figure 5.1h shows that the angle is approximately 150°, making the riser some combination of to a (10\bar{1}X) planes. The stability of these (10\bar{1}X) planes are confirmed by their continuing presence when ex-situ SEM were performed (region enclosed by dots in Figure 5.1g).
5.3.2. Etching the Zn-Basal Plane ZnO with 2M NaOH & 0.1M Trisodium Citrate

During crystal growth, citrate hinders growth in the [0001] direction and therefore leads to formation of crystals containing large areas of (0001) and (000$\bar{1}$) planes. Here in-situ AFM imaging was used to examine the effect of citrate on the dissolution of ZnO. The sample was initially etched with 2 M NaOH solution (without citrate present) to remove the defect-rich surface layers that etch quickly and are particular to each sample. Figure 5.2 shows a time series of AFM images of a Zn-terminated basal plane ZnO sample as it dissolves in the presence of citrate. From Figure 5.2 it can be seen that the stepped structure is maintained, but the average step height decreases and there is a commensurate decrease in the spaces between the steps, as highlighted by the comparative cross-sections presented in Figure 5.2d.

Figure 5.2: Effect of citrate ions on the dissolution of the Zn-terminated basal plane ZnO. (a) – (c) time series of 10 µm by 10 µm AFM scans in the presence of 2M NaOH and 0.1M trisodium citrate. (d) step profiles over 4 µm showing how citrate increases the step density and reduces the average step height. Note, that the sample designated as $t = 0$ has previously been etched in 2 M NaOH (without citrate) for 4 hours.
5.3.3. Etching of O-Basal Plane ZnO with 2 M NaOH

The next ZnO face to be studied was the O-terminated basal plane ZnO, which is nominally normal to the [000\(\overline{1}\)] direction. Figure 5.3 shows the time evolution of the O-terminated basal plane ZnO as it etches in the presence of 2M NaOH. The first thing to note is that the polished sample is locally rough and there are no large planes of (000\(\overline{1}\)) so the term O-terminated basal plane is used to designate the sample. After a short etching time (less than 1 hr) the sample is predominantly comprised of smooth (000\(\overline{1}\)) planes, with the occasional small hexagonal pyramidal pit. As time progresses the small hexagonal pyramidal pits grow rapidly, reducing the amount of (000\(\overline{1}\)) plane present and making the previously (000\(\overline{1}\)) surface very rough on the 10 \(\mu\)m-scale after about 3 h. At this time most of the sample terminates in the higher index planes which make up the sides of the pits (Figures 5.3e and f). The presence of these pits suggests that these higher index planes are more kinetically stable than the (000\(\overline{1}\)) face in basic solution. The sides of the pits appear to be quite smooth, with the occasional ridge due to the incorporation of the shallow dissolution fronts that rapidly spread across the surface in the early stages of dissolution. The Miller indices of these newly formed faces are not able to be determined at this crystal orientation because the linear dissolution rate of the pits is again similar to the scan speed. Each image takes about 8 minutes to capture, so the dimensions of the pits change during this time, making them appear distorted.

5.3.4. Etching of O-Basal Plane ZnO with 2 M NaOH & 0.1 M Trisodium Citrate

Unlike the other samples the O-terminated basal plane ZnO sample was etched in a solution of 2 M NaOH and 0.1 M trisodium citrate, without pre-etching in a purely 2 M NaOH solution. This was done for two reasons. First the rate of etching of (000\(\overline{1}\)) ZnO was seen to occur more rapidly than for the other faces. Secondly the etching process causes the (000\(\overline{1}\)) plane to transform into a different set of planes. Consequently, if the sample was pre-etched there would be very little (000\(\overline{1}\)) plane present, with only a limited time frame to study the influence of citrate on (000\(\overline{1}\)) plane dissolution.

When the O-terminated basal plane ZnO sample was etched in 2M NaOH and 0.1M trisodium citrate there were no observable difference in morphology or etching rate when compared to the sample etched in 2 M NaOH only. Therefore it is concluded that trisodium citrate has no influence on the etching of (000\(\overline{1}\)) ZnO.
Figure 5.3: Time series of AFM scans showing the in-situ dissolution of the O-terminated basal plane ZnO in 2 M NaOH. (a) 5 µm by 5 µm image of a typical O-terminated basal plane ZnO surface before etching. (b) to (d) 20 µm by 20 µm scans showing the evolution of the stable semipolar planes. (e) 40 µm by 40 µm scan showing the (000\bar{1}) plane has almost completely reconstructed after 3 hr. (f) Ex-situ SEM showing the formation of hexagonal dissolution pits across the entire ZnO surface.
5.3.5. Etching of Prismatic Plane ZnO with 2 M NaOH

Etching of the (0001) and (000\bar{1}) faces occurs primarily in the \(< 10\bar{1}0 >\) directions. Thus more insight into the dissolution process can be obtained by directly observing the dissolution of the (10\bar{1}0) face. Another reason for interest in etching of this face is that \{10\bar{1}0\} surfaces are the primary surfaces produced during hydrothermal growth. Therefore understanding how the \{10\bar{1}0\} dissolve is key to understanding how ZnO crystals will dissolve in general.

The as received prismatic plane ZnO appears similar to the as received (0001) plane shown in Figures 5.1a and e. The time progression of etching of the prismatic plane ZnO in 2 M NaOH is shown in Figure 5.4. After 4 hours (Figure 5.4a) it is apparent that the prismatic plane ZnO primarily reconstructs into trenches. These trenches appear to be running in the [1\bar{1}20] direction with one side being the (0001) plane and the other the higher index plane observed during the dissolution of the (000\bar{1}) surface. This is highlighted by the corrugated nature of what was formerly the (10\bar{1}0) plane as shown in greater detail in Figure 5.4g. The planes forming the sides of these trenches are stable across most of the surface except where a dislocation is believed to be present as no further dissolution in either the [0001] or [000\bar{1}] directions is seen to occur (as highlighted by the invariance with time of the trench marked by the (*) in Figure 5.4a and cross sections along the [0001] direction presented as Figure 5.4i). However at dislocation sites (assumed to be parallel to the [0001] direction) dissolution does continue to occur as evident by the large pits formed. At these sites it can be seen that the dissolution occurs initially in the [000\bar{1}] direction, with newly exposed (0001) plane forming the stepped structure that appears to propagate away from the dislocation in the \(\pm [1\bar{1}20]\) directions. However, ex-situ SEM imaging (Figure 5.4h) show that the dissolution front on one side of the dislocation is comprised of (10\bar{1}1) and (01\bar{1}1) planes, marked by a white bar and black dot respectively (the other side is comprised of (10\bar{1}1) and (0\bar{1}11) planes). Thus the apparent propagation in the [1\bar{1}20] direction is merely the resultant combination of etching of the (10\bar{1}1) and (0\bar{1}11) dissolution fronts. This is further heightened by the fact that dissolution in the [\bar{1}010] direction (into the crystal) is limited by the stable high index plane that is formed opposite the (0001) plane, marked by a white triangle on Figure 5.4h. The SEM images also confirm the presence of the (10\bar{1}1) surface near the dislocation.
The high index plane (the surface of the etch pit opposite the (0001) planes, indicated by the white triangle in Figure 5.4h) is not only stable but also stationary (i.e. no dissolution parallel to the plane is occurring). As a result the orientation of this plane can be determined from the height trace without interference from the surface etching during the image scan. From the AFM profile it was determined that the orientation of this high index plane is close to (10\overline{1}1), when errors introduced by the tip width, thermal drift and sample tilt were accounted for.

5.3.6. Etching of Nominally Prismatic ZnO with 2 M NaOH & 0.1 M Trisodium Citrate
When the prismatic plane ZnO (which has been pre-etched with 2 M NaOH) is etched in 2 M NaOH and 0.1 M trisodium citrate the results are consistent with observations made during the (0001) and (000\overline{1}) plane dissolution experiments. The (10\overline{1}1) plane remains unaffected by the presence of citrate and the (0001) plane steps become smaller and more frequent. This results in a subtle change in the morphology of the etch pits, which will be discussed in the next section.
Figure 5.4: Time series of 50 µm by 50 µm AFM scans showing the in-situ dissolution of the prismatic plane ZnO. (a-c) dissolution in 2 M NaOH (a = 4 hr, b = 5 hr, c = 6 hr). (d-f) After 6 hr the etching solution was changed to 2 M NaOH and 0.1 M trisodium citrate (d = 1 hr after addition of citrate, f = 2 hr, g = 3 hr). Dashed line on (a) indicates the location of the height traces measured in the [0001] direction presented in (i). (g) 5 µm enlargement of the reconstructed (1010) surface (rotated 90°). (h) Ex-situ SEM image showing the dissolution habit in the pit. The (1011) plane is marked by a white triangle, the (1011) by a white bar and the (0111) by a black dot (i) Time series of cross sections through the dashed line in part (a) (curves for (a) and (f) have been labelled). Black lines show the cross section with 2 M NaOH only (a-c) and light grey show the cross sections for dissolution in 2 M NaOH and 0.1 M citrate (d-f).
5.4.Discussion

5.4.1. Estimating the Relative Dissolution Rates in the [000\(\bar{1}\)] & [10\(\bar{1}0\)] Directions using the observations made from the dissolution of (10\(\bar{1}0\)) ZnO

The observations of the dissolution pits on the prismatic plane ZnO can be used to estimate the relative dissolution rates in the two principal dissolution directions (along the dislocation and away from the dislocation). The rate of dissolution in each of these directions can be quantified unambiguously for each pit as they can be related to a fixed position on the sample (the stationary (10\(\bar{1}1\)) plane). As the angle formed at the top of a dissolution pit is the result of two different dissolution events (dissolution along the defect and away from the defect) it can be used to determine the relative dissolution rates. For instance, if the rate of dissolution away from the defect increases it would cause the angle to widen (becoming a greater value). This method also has the advantage of not being affected by the size of the dissolution pit or by the merging of different dissolution fronts. Two examples of this angle are shown in Figure 5.5. Table 5.1 shows the dissolution angle for three different etch pits as a function of time. Each of the etch pits started growing at different times and thus have different “ages”, which are also shown in the table. The age of the pit was obtained by plotting the distance the dissolution front has advanced along the dislocation (i.e. in the [000\(\bar{1}\)] direction) with time and extrapolating back to zero distance. This gave the time of origin of a dissolution front which could be subtracted from the experimental time to give the age of a dissolution front.

From Table 5.1 it can be seen that the angle near the apex of the triangle is approximately the same for each etch pit and is constant over time. Figure 5.4 shows that the dissolution rate in the \(<10\bar{1}0\)> directions slows as a section of the dissolution pit aged (i.e. as the section etched away from the dislocation over time). This can be attributed to the observation that the average step height increases as a section ages. It should be noted, however, that even though the etching rate decreases as a front ages, the dissolution rate for different sections of the same age is constant. Because the angle formed at the apex of the triangle is constant as the front advances along the dislocation (in the [000\(\bar{1}\)] direction), the etching rate away from the dislocation (in the \(\pm[11\bar{2}0]\) directions) also remains constant for any particular age. This means that as the crystal etches along the dislocation, the lateral dissolution rate (in the \(\pm[11\bar{2}0]\) directions) at any specified distance near the dislocation is the same at any given time, but as it propagates away from the point of origin the etching rates slows. This is
another advantage of using the angle formed at the dissolution front to determine the relative dissolution rates in the [000\bar{1}] and ±[1\bar{1}20] directions, as it averages across steps of different ages, but maintains the same age range with time. As stated in Section 5.3.5, dissolution in the [1\bar{1}20] direction occurs by removal of atoms from two different [10\bar{1}0] directions. Thus the rate of dissolution in the < 10\bar{1}0 > directions is related to the dissolution rate in the ±[1\bar{1}20] directions.

Figure 5.5: 2D projection of Figure 5.4b reproduced in grey-scale, illustrating the dissolution angle represented in Table 5.1. The dissolution angle gives an indication of how fast a dissolution front is advancing along a defect, relative to how fast it is propagating away.

When citrate ions are added into the system, the average dissolution angle increases from 153 ± 6° to 170 ± 2°. This indicates either an overall increase in lateral dissolution (in the ±[1\bar{1}20] directions) or hindrance of dissolution along the dislocation (in the [000\bar{1}] direction).

However, from the AFM cross sections (Figure 5.4i between the 18 µm and 35 µm marking on the x-axis scale) it is apparent that the etching rate along the dislocation remains constant before and after citrate addition. Therefore it must be concluded that the citrate ions increases the overall dissolution rate in the ±[1\bar{1}20] direction, and as such the < 10\bar{1}0 > directions.
Table 5.1: Change in dissolution front angle with time and solution composition.

<table>
<thead>
<tr>
<th>Etchant</th>
<th>Dislocation</th>
<th>Time (hr)</th>
<th>Age* (hr)</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 M NaOH</td>
<td>1</td>
<td>2.32</td>
<td>1.15</td>
<td>154</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>2.97</td>
<td>1.80</td>
<td>152</td>
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<td></td>
<td>1</td>
<td>3.05</td>
<td>1.89</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3.88</td>
<td>3.03</td>
<td>146</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>4.93</td>
<td>4.08</td>
<td>146</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>6.17</td>
<td>5.31</td>
<td>154</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3.88</td>
<td>1.15</td>
<td>156</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>4.93</td>
<td>2.20</td>
<td>161</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>6.17</td>
<td>3.44</td>
<td>162</td>
</tr>
<tr>
<td>2 M NaOH 100mM Citrate</td>
<td>3</td>
<td>7.42</td>
<td>4.69</td>
<td>170</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>8.47</td>
<td>5.74</td>
<td>168</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>9.52</td>
<td>6.79</td>
<td>172</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>10.32</td>
<td>7.59</td>
<td>169</td>
</tr>
</tbody>
</table>

*Age was determined by measuring the advancement along the dislocation with time and extrapolating back to zero distance.

5.4.2. The Dissolution of ZnO in General Under Basic Conditions

Having studied the etching of the Zn- and O- terminated ZnO samples, as well as the prismatic ZnO surface, some general comments can be made. The (0001) and \{10\overline{1}\} planes are stable as large areas of these faces are maintained throughout the etching process. The \{10\overline{1}1\} planes are partially stable, forming the dissolution front, and the (000\overline{1}) and (10\overline{1}0) planes are unstable, restructuring into other planes.

The soluble species under basic conditions investigated in this work are \([\text{Zn(OH)}_4]^{2-}\). As such each zinc atom dissolving must be tetrahedrally coordinated by four hydroxide ions. Due to stoichiometry, on average, only one of the oxygen atoms in the complex can come from the dissolving crystal and so the other three must come from water or hydroxide molecules. In order to liberate the zinc atom, a number of oxygen–zinc bonds must be cleaved. This cleavage is likely by hydrolysis reaction with hydroxide anion attacking a zinc–oxygen bond.

To understand what makes a ZnO surface stable in alkaline conditions, observed stability of a particular crystalline plane was compared to the number of surface oxygens per zinc tetrahedra present on the plane. In this work surface oxygens are defined as any oxygen coordinated to less than four zinc atoms.

The oxygen stabilised, unreconstructed ZnO planes observed in this work are presented as Figures 5.6a and 5.6b. As in-vacuo studies\textsuperscript{13} of hydrated ZnO have shown that the (1000), (10\overline{1}0), and (000\overline{1}) planes undergo a (1 x 1) hydroxylation, it is assumed that the dangling bonds on the surface zinc atoms have been filled with oxygen atoms for all the
surfaces observed in this work (whether they are present as a hydroxide or oxide species). If the number of surface oxygens (as denoted by the dark red oxygen atoms in Figure 5.6) per zinc atom (Table 5.2) is considered, it can be seen that stability is inversely dependent upon the number of oxygens present on the surface, per zinc atom. This makes sense from a mechanistic point of view. To go from a solid state lattice to a dissolved species the zinc ions must go from being tetrahedrally co-ordinated by oxygen atoms (that are also tetrahedrally co-ordinated to other zinc atoms), to tetrahedrally co-ordinated by hydroxide ions (at the pH these studies were conducted). So it is logical that the solubilisation of ZnO occurs more readily at the surfaces where the Zn–O–Zn bonds are more exposed. This makes the bonds easier to convert into hydroxides species. Thus the surfaces with the greatest number of surface oxygens per zinc atom will dissolve more easily. A similar trend was observed by Palacios-Lidón et al.\textsuperscript{179} for acid etching of high index planes. However, their analysis focused on the oxygen dangling bonds density as the reason for the observed trend, which does give good agreement with the results observed in this work (shown in Table 5.2). While oxygen dangling bonds density is important for dissolution under acidic conditions (as they are likely sites for proton interaction) it cannot explain the same observed trend for dissolution under basic conditions because hydroxide ions are unlikely to bond to a surface oxygen.

![Figure 5.6: The atomic structure for the oxygen stabilised bulk terminated ZnO projected along the [11\(\bar{2}\)0] direction, showing the surface oxygens for each of the different low index faces described in this work. Grey represents zinc atoms, red oxygen and dark red surface oxygen. Note as (10\(\bar{1}\)0) is equivalent to (1010), (101\(\bar{1}\)) is equivalent to (10\(\bar{1}\)1)](image)

The availability of surface oxygens to be converted to hydroxide species does not fully explain the appearance of the \{10\(\bar{1}\)X\} planes during the dissolution process. As the crystal etches into the (0001) plane along a dislocation, a series of \{10\(\bar{1}\)0\} planes is exposed. These \{10\(\bar{1}\)0\} planes should reconstruct into (0001) and \{10\(\bar{1}\)\} and cease propagating in the
directions, as was observed for the prismatic plane studies. Therefore the \{10\bar{1}X\} should not form. If an edge-wise dissolution mechanism is considered, however, it can be seen how the \{10\bar{1}X\} planes are formed. If a zinc tetrahedra is removed at the edge where the (0001) and (10\bar{1}0) planes meet (highlighted by the dotted triangle in Figure 5.6a), it results in the formation of a (10\bar{1}1) plane. The subsequent dissolution of this face by removal of a Zn tetrahedra from the newly formed (10\bar{1}1)/(10\bar{1}1) edge results in an increase in area of the (10\bar{1}1) plane. Thus the \{10\bar{1}1\} planes would continue to form in preference to the \{10\bar{1}0\} planes (having fewer surface oxygen) as the (0001) plane etches. Furthermore, the \{10\bar{1}1\} planes are easier to form than the more stable \{10\bar{1}1\} planes, which would require the removal of a zinc tetrahedron from the base of a step, at the junction between the (0001) and (10\bar{1}0) planes (i.e. the removal of a zinc tetrahedra from an inner corner). From this it can easily be seen that if this edgewise dissolution process continues then the (10\bar{1}1) surface could be etched in this way forming even higher index surfaces that result in the observed multifaceted (101X) surface.

Table 5.2: the number of exposed surface oxygens per zinc tetrahedra for the different faces of oxygen stabilised ZnO observed in this work.

<table>
<thead>
<tr>
<th>ZnO Surface</th>
<th>Exposed O per Zn Tetrahedron</th>
<th>O Dangling Bonds per nm²</th>
<th>Stability in 2 M NaOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0001)</td>
<td>1</td>
<td>32.8</td>
<td>Stable</td>
</tr>
<tr>
<td>(10\bar{1}1)</td>
<td>2.5*</td>
<td>26.0</td>
<td>Stable</td>
</tr>
<tr>
<td>(10\bar{1}1)</td>
<td>3</td>
<td>15.6</td>
<td>Semi-Stable</td>
</tr>
<tr>
<td>(0001)</td>
<td>3</td>
<td>10.9</td>
<td>Unstable</td>
</tr>
<tr>
<td>(10\bar{1}0)</td>
<td>3</td>
<td>5.9</td>
<td>Unstable</td>
</tr>
</tbody>
</table>

* The (101 ± 1) planes have two different zinc tetrahedra configurations with a different number of surface oxygens, and so an averaged value is used.

† here (10\bar{1}1) is used as an example of the (10\bar{1}X) facets

Consideration is now given to the observation that the step height on the Zn-terminated basal plane ZnO increases as it ages. There are only two ways for a step to increase in size during dissolution. Either etching occurs into the plane at the base of the step (i.e. etching occurs spontaneously into a plane, rather than at an edge), or several smaller macro steps must combine to form a larger step. As dissolution into the plane was only observed at specific sites (attributed to the presence of dislocations) it must be concluded that the general increase in step height (on the (0001) plane) observed must be due to the coalescence of smaller macro steps. Assuming material is removed from the outer corner of a step (as outlined previously) primarily in the [10\bar{1}1] direction, it results in the movement of the step in the [10\bar{1}0]
direction (which was the observed direction of step propagation). As smaller macro steps are initially formed and are seen to propagate faster, it follows then that the rate at which a step propagates must decrease with step height. If step propagation were independent of height, there would be no change in step height with time. If larger steps propagated faster there would be little chance of step coalescence, as the larger steps are seen to occur at the top of a dissolution pit on the (0001) surface and coalescence could only occur when the top step propagates slower than those below it. This agrees with the hypothesis that dissolution of the (0001) plane is governed by etching rate in the [10\overline{1}1] direction. As the dissolution front will advance in the [10\overline{1}0] direction as each (10\overline{1}1) layer is removed, the area of (10\overline{1}1) (and by extension the step height) will govern the etching rate in the [10\overline{1}0] direction. For instance, consider two different steps given in Figure 5.7, one that is two zinc tetrahedra high (step a) and one that only single tetrahedra high (step b). After four units have been removed (in the numbered order), step a will have advanced two units in the [10\overline{1}0] direction, whilst step b will have advanced four units, thus the step that is smaller in height advances faster. This example assumes that the rate of removal of each zinc tetrahedra is the same for each step, which given they are chemically the same and are exposed to the same solution conditions, is not unreasonable.

It is easy to see that if step heights were reversed (i.e. step a was 1 unit high and step b 2 units) step b would have merged with step a forming a new step that would be 3 units high. This mechanism is only valid if (1) the step etches at the (0001)/(10\overline{1}1) edge, and (2) the etching of a single step occurs primarily in the [10\overline{1}1] direction. If the first assumption was invalid, and dissolution occurred anywhere on the (10\overline{1}1) plane, then pitting would be observed on the (10\overline{1}1) plane (from Figure 5.1g and Figure 5.4h we can see that pitting does not occur) and there would be no dependence of step height on etching rate, which is contrary to the results shown by Figures 5.4a-c and 5.4d-f). If the second assumption was invalid, and the etching of a step occurred primarily in the [10\overline{1}0] direction (i.e in Figure 5.7 for step a the 2nd and 3rd tetrahedra to be removed were switched) then we would see a reduction in height of small steps with time, which was not observed.

This theory however cannot explain one simple observation, that is, after the removal of the first tetrahedron steps 2 and 3 should be identical and so should begin etching together creating a changing dissolution front that becomes shallower with time (i.e. the riser becomes larger in area for a given step height). This is not observed however, as both this and
previous work has shown that the dissolution riser remains the same over time. Therefore the simplistic model presented does not fully explain the method by which step dissolution and coalescence occurs. Having said that though, this hypothesis still explains the observations made in this work, it cannot fully explain why they happen though. More work would be needed before this phenomenon is fully understood.

Figure 5.7: Demonstration of how step height influences lateral etching rate. Step (a) is twice the height of step (b) and so propagates in the $[10\bar{1}0]$ direction at half the speed. The numbers represent the order of removal of the Zn tetrahedra and (x) marks the original location of each step.

5.4.3. The Effects of Citrate on the Dissolution of ZnO

The results presented in this chapter shows that the citrate molecules only influence the dissolution of (0001) ZnO. It has been well established that citrate encourages the expression of (0001) ZnO during growth. It is thought that citrate selectively adsorbs to the (0001) plane thereby hindering growth normal to this plane. $^{12, 107, 110, 128-130}$

As seen in Figures 5.2 and 5.4d-f, citrate ions cause a reduction in average step size. As there is no growth possible in this system (as the solution is undersaturated with respect to ZnO) the reduction in step size must be due to the splitting of a larger step into smaller ones. Therefore it is speculated that citrate is adsorbing specifically onto the (0001) plane makes the formation of (0001)/(10\bar{1}1) edges more favourable. This increase in the number of steps then explains the increased rate of etching in the $< 10\bar{1}0 >$ directions observed in Figure 5.4.
By splitting a larger step into smaller ones, each smaller step is going to begin to etch independently (as the etching in the [10\bar{1}0] direction is governed by the presence of (0001)/(10\bar{1}1) edge) and so the overall etching rate in the <10\bar{1}0> directions would increase. At the dislocation site however, it can be seen (Figure 5.4h) that there is no (0001) plane present, and so the citrate will have no affect the etching rate near the dislocation. Due to the different spacing of the atoms, the citrate ions are not likely to bind to the \{10\bar{1}1\} planes in the same manner as they appear to do on the (0001). Thus they are unlikely to affect the dissolution of the {10\bar{1}1} planes, which is consistent with the observations made in this chapter.

5.5. Conclusions

From the in-situ dissolution studies of the Zn-terminated, O-terminated and prismatic planes of ZnO the following observations were made:

- The dissolution of ZnO occurs primarily by etching at linear defects that are consistent with dislocations that run parallel to the[0001] direction.
- The (0001) and \{10\bar{1}1\} planes are stable under alkaline conditions, with the semi-stable \{10\bar{1}1\} planes forming the main dissolution front. The \{10\bar{1}0\} planes reconstructs into the stable (0001) and \{10\bar{1}1\} planes, whilst the (000\bar{1}) plane reconstructs into \{10\bar{1}1\} planes, forming many hexagonal pyramidal pits.
- As the stable faces have the least number of surface oxygen atoms per zinc atom, it is concluded that surface stability is dependent upon the ability of the surface zinc atoms to be converted from the solid oxide network to the soluble tetra-hydroxide complex.

These observations are consistent with the hypothesis that etching proceeds in the \{10\bar{1}0\} directions via the continual removal of edge atoms in the <10\bar{1}1> directions. The addition of citrate molecules results in an increase in the number of steps on the (0001) plane, thereby increasing the number of edges and increasing the net rate of dissolution in the <10\bar{1}0> directions.
6. Specific Adsorption of Growth Directing Molecules on ZnO Surfaces

6.1. Introduction

As stated in Section 2.8.5, the shape of ZnO crystals can be influenced by the introduction of small molecules during the hydrothermal growth process. Amines (primary, secondary, and tertiary) tend to encourage (10\(\overline{1}0\)) growth, whilst carboxylic acids tend to express (0001). When both groups are present it has been found that the crystal shape could be altered depending on pH.

Many of these crystal growth studies have been done in isolation, without studying what determines the activity of a growth directing molecule. One notable exception is by Yahiro et al., who systematically studied the influence of various derivatives of citrate on (0001) growth. They found that succinate (butanedioate) does not cause an increase in the growth of the (0001) plane but maleate (the cis isomer of butenedioate) does. Furthermore the trans isomer of butenedioate, fumarate, did not. From this it is evident that the 3-D structure of a molecule is key to its ability to act as a growth modifier.

Researchers hypothesize that the action of the small molecules is to adsorb selectively to particular crystal faces and thereby to decrease the energy of the face, or block access of incoming Zn-containing solution species (i.e. growth units) to that face. If a molecule is adsorbed onto a particular face it would prevent growth in the direction normal to that face, whilst growth in other directions is relatively unhindered. For example, adsorption to the (0001) face is expected to hinder growth in the [0001] direction allowing growth in the \(< 10\overline{1}0 >\) directions to continue, producing larger areas of the (0001) face and therefore a crystal with a low aspect ratio.

The principal aim of this chapter is to determine whether there is a correlation between adsorption of a particular molecule to a particular face, and the aspect ratio of crystals grown in the presence of that molecule. Before this goal could be achieved, it was necessary to (a) develop a method to selectively measure the adsorption to a single face and (b) produce crystals with large areas of a particular face. Attenuated total internal reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was chosen to measure the selective adsorption because ZnO is transparent in the frequency ranges of interest, whereas the small molecules and water have adsorption bands. However, only small ZnO crystals (10 mm \(\times\) 10 mm \(\times\) 0.5...
mm) are available and considerable effort was required to adapt an FTIR spectrometer to establish a light path into and out of the crystal to produce evanescent waves. A second issue is that ATR-IR probes large areas (several mm²) of crystal, so it was necessary to produce crystal surfaces that were predominantly a single crystal face over this area.

The adsorption of two different shape directing molecules: a carboxylate, trisodium citrate, and an amine, ethylenediamine (EDA) was studied. Citrate is a tri-carboxylate molecule that has been reported to encourage the growth of ZnO with large areas of (0001) faces, whereas EDA is a simple amine that has previously been used in growth studies. Furthermore as citrate is a tri anion, the adsorption of three different derivatives of citrate, sodium acetate, disodium succinate and disodium glutarate was studied to better understand which carboxyl groups in the citrate ion are involved in adsorption. The structures of the different molecules are given in Table 6.1.

These molecules were also chosen because they have a simple structure and are easily identifiable by IR spectroscopy. Furthermore, IR can determine whether the adsorbing molecule interacts directly with a surface Zn atom (an “inner spheres complex”) or indirectly via water or hydroxide groups (an “outer sphere complex”).

Table 6.1: Structures and concentrations of adsorbates investigated

<table>
<thead>
<tr>
<th></th>
<th>Citrate</th>
<th>Acetate</th>
<th>Succinate</th>
<th>Glutarate</th>
<th>EDA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>10 mM</td>
<td>30 mM</td>
<td>15 mM</td>
<td>15 mM</td>
<td>10 mM</td>
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<tr>
<td>High</td>
<td>100 mM</td>
<td>300 mM</td>
<td>150 mM</td>
<td>150 mM</td>
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</tbody>
</table>

FTIR has previously been used to probe the interactions between small molecules and mineral surfaces. Kubicki et al. studied the adsorption of various carboxylic acids on slurries of different alumina-silicates, correlating the observed IR spectra with theoretically calculated spectra for different bonding arrangements of the functional groups. They observed that small differences in mineral structure (such as that between Kaolinite, Illite and Montmorillonite) affects the adsorption of different carboxylic acids. They also found that chemical impurities within the samples (such as the presence of iron ions) can encourage adsorption. Another study by Biber and Stumm demonstrated salicyclic acid adsorption on different aluminates and iron (III) oxide suspensions. By comparing the peak positions of the
adsorption spectra of salicylic acid to minerals with different elemental compositions but similar structures, such as corundum (α-Al₂O₃) and hematite (Fe₂O₃), they found that the elemental composition was more crucial than surface geometry in determining how carboxyl groups bond to mineral surfaces, as different bonding arrangements were determined for the aforementioned minerals. Furthermore, different forms of the same mineral, such as α-Al₂O₃ and δ-alumina, produced different adsorption spectra. The difference in adsorbance onto δ-Al₂O₃ and γ-Al₂O₃ was not as pronounced however.

Whilst both these studies demonstrate how changes in mineral structure and composition can influence molecular adsorption, they were performed using multi-faceted samples (powders). Therefore it is impossible to determine which faces the molecules were adsorbing to, and hence the specifics of the interactions between the molecule and the surface.

6.2. Experimental

Solution Preparation: The chemical species and concentrations used in this work, are shown as Table 6.1. A constant concentration of carboxylate groups was used in the experiments (except in EDA solutions). All solutions were prepared using AR Grade (purity 99+% Aldrich) chemicals dissolved in 99% D₂O (Cambridge Isotopes). All chemicals, with the exception of the glutarate, were used without further purification. Disodium glutarate was prepared by reaction of glutaric acid with 2 equivalents of NaOH (e.g. 15 mM glutaric acid with 30 mM NaOH). The solvent was then evaporated at ca. 70°C and the residual powder resuspended in an equivalent volume of 1mM NaOH in D₂O. The presence of the carboxylate group (as opposed to the carboxylic acid group) was confirmed using FTIR. All other solutions were made directly using 1mM NaOH in 99% D₂O (referred to as the background solution). The pH of an equivalent solution in H₂O was found to be 10.7. As every pKa of the carboxylic acids used in this work were well below pH 10 there was no significant shift in pH of the solutions (± 0.1) when the sodium salts were added, with the exception of disodium glutarate which could vary by about ± 0.5.

Sample Preparation: 10 x 10 x 0.5 mm ZnO single crystals (MTI Corporation) of (0001) or (1010) orientation were etched for 5 minutes in a 1 M NaOH solution, rinsed with ethanol/water then annealed in an open air furnace (Barnstead Thermolyne 48000) for 5 hours at 1000°C (ramp rate 5°C/min). After annealing the samples were further etched for 1
minute (1 M NaOH) then rinsed with ethanol/water to remove any contaminants formed during annealing.

**Adsorption Studies:** ATR-FTIR adsorption studies were performed using a customised ATR setup discussed in Section 3.1.4 using a Varian 670 FTIR spectrometer. Single crystal substrates of either (0001) or (10\(\bar{1}0\)) ZnO were exposed to background solutions (1 mM NaOH in 99% D\(_2\)O) for at least 90 mins to allow the system to come to equilibrium. For a particular chemical species (listed in Table 6.1) the spectrum was measured at two concentrations. The lower concentration was injected into the fluid cell using a disposable syringe and periodic scans were taken until equilibrium was reached (i.e. after several consecutive IR scans showed no change). The second, higher concentration solution was then injected and allowed to come to equilibrium. After the adsorption of the higher concentration had reached equilibrium, the fluid cell was flushed with background solution, allowing the desorption of the molecules from the surface to be monitored. If negligible desorption occurred the cell was flushed a second time. All FTIR scans were taken as an average of 64 scans taken at a resolution of 2 cm\(^{-1}\).

As both faces of a (10\(\bar{1}0\)) crystal are the same, both sides were exposed to solution (in series) and the spectrum is the sum of spectra from both sides. As a key feature of a dipolar crystal like ZnO is that the (000\(\bar{1}\)) and the (0001) surfaces of the crystal are different, the adsorption studies on the (0001) surface were done differently. Initially, both sides were exposed to background solution. All subsequent fluid exchanges were then done on the (0001) side only. This was done so that the absorbance spectra of the molecules adsorbed onto the (0001) surface could be determined unambiguously without interference from adsorption to the (000\(\bar{1}\)) face.

For comparison, the transmission spectrum of the different compounds was taken at the higher concentrations listed in Table 6.1 using a PIKE transmission cell under the same conditions as the absorbance spectra (64 scans at 2 cm\(^{-1}\) resolution).

**Atomic Force Microscopy (AFM):** Imaging in air of the (0001) and (10\(\bar{1}0\)) ZnO prism topography before and after annealing was performed using an MFP3D Atomic Force Microscope (Asylum Research) using Veeco NP Cantilevers. Images were obtained at a scan rate of 1 Hz with 512 scan lines and 512 scan points, regardless of the scan size.
X-ray photoelectron spectrometry (XPS): The surface composition of the ZnO prisms before and after annealing was determined using a Perkin-Elmer PHI 5400 spectrometer with a Mg Kα photon energy of 1253.6eV at 45° angle of incidence. The source was run at 250W (12.5 kV and 20 mA).

6.3. Results & Discussion

6.3.1. Preparation of Planar ZnO Surfaces.
The (0001) and (10\bar{1}0) ZnO prisms were received pre-cut and polished to roughness of < 10 Å. This manufacturing process leaves the crystal surface covered with fine scratches over large length scales (as shown in Figures 6.1a and 6.1c), but on the nanometre scale (as shown by Figures 6.1e and 6.1g) the surface is either amorphous or consists of many high Miller Index planes. For example, the as received (0001) prisms had very little area of (0001) face, and as such, were unsuitable for experiments to determine whether adsorption occurs specifically to the (0001) face. It was therefore necessary to produce large areas of (0001) face, which was achieved by the process described in the experimental section of this chapter. After treatment the crystal surfaces became stepped over large areas (Figures 6.1b and 6.1d) but the surface of each step became smooth on the nanometre scale (Figures 6.1f and 6.1h). The formation of steps led to the appearance of unwanted crystal planes (i.e. the planes that form the riser of the step). However, these unwanted planes constituted a minor fraction of the total surface area of the crystal: less than 1% of the total surface area of the (0001) crystals and less than 0.4% non {10\bar{1}0} planes for the (10\bar{1}0) crystal. The total area of the other planes present in each sample was calculated by manually measuring the step height and length of each step from the AFM height traces and then summating the resultant step areas. This area was then compared to the area of the AFM scan (which gives the total area of the desired plane) to give the percentage of non-plane in the sample. This process was repeated for different scan sizes and different samples (of the same orientation) and the results showed surprisingly little variation; the (10\bar{1}0) samples were between 0.3 and 0.4% non-(10\bar{1}0) and the (0001) were between 0.1 and 0.8% non-(0001).

It should be noted that annealing reduced the presence of any surface hydroxide layers, as evidenced by the decrease in the hydroxide peak (532.2 eV) relative to the oxide peak (530.2 eV), from 67% to 48% relative abundance, in the XPS spectra (Figure 6.1i and 6.1j). However, the continuing presence of the hydroxide peak after annealing indicates that the
Adsorption studies were conducted on the native hydroxide layers of the different ZnO surfaces.

Figure 6.1: (a-d) 10 µm x 10 µm AFM images of the (0001) and (1010) ZnO prism surfaces before (a,c) and after (b,d) annealing. Insets are (e-h) 1 µm x 1 µm enlargements of (a-d). Height scale is 10 nm for images (a) and (c), 40 nm for (b) and (d) and 5 nm for (e-h). (i, j) O1s XPS spectra for the (0001) surface before (i) and after (j) annealing, showing a reduction in hydroxide content (532.3 eV) from 67% before annealing to 48% after annealing.

As individual prisms were used for more than adsorption study, it was necessary to remove adsorbed organic species and contaminants. Between experiments, the prisms were exposed to UV light for 2 hours and then etched for 1 minute in 1 M NaOH, and then rinsed with ethanol/water to remove any residues. This process did not alter the surface morphology in any measurable way.

6.3.2. Adsorption of Citrate onto (0001) & (1010) ZnO.
Citrate is known to inhibit growth normal to the (0001) ZnO faces. The FTIR spectra of the carbonyl region for the adsorption of citrate on (0001) and (1010) ZnO is given as Figure 6.2. The spectrum of citrate in solution was taken using a transmission cell and has been included for comparison (it should be noted that the ATR spectra are distorted relative to
transmission spectra due to the wavenumber dependence of refractive index). The ATR spectrum for (0001) ZnO does not change much when the bulk solution concentration is changed from 10 to 100 mM, which shows that the spectrum is dominated by the adsorbed species, and not the bulk solution (otherwise the absorbance peak would have increased with increasing bulk concentration). For free citrate ions in solution there are several peaks observed in the region of 1750 cm\(^{-1}\) to 1250 cm\(^{-1}\). There are three observed carboxylate peaks;\(^{182}\) the COO\(^{-}\) symmetric stretch (\(\nu_s(\text{COO}^-)\)) is comprised of two peaks with a major peak at 1394 cm\(^{-1}\) and a minor peak at 1410 cm\(^{-1}\), and the broad peak at 1579 cm\(^{-1}\) is attributed\(^{183}\) to the COO\(^{-}\) antisymmetric stretch (\(\nu_a(\text{COO}^-)\)). The out-of-plane deformation of the O-H group (\(\delta(\text{OH})\)) present on the central carbon is at 1303 cm\(^{-1}\). The final peak at 1270 cm\(^{-1}\) is attributed to a combination of methylene (CH\(_2\)) wagging and twisting vibrations.

![Figure 6.2: FTIR spectrum of citrate in D\(_2\)O solution, and adsorbed on (0001) and (10\(\overline{1}0\)) ZnO. 10 mM (light grey lines) and 100 mM (dark grey lines). Dotted lines indicate the spectrum after desorption. Dashed vertical lines added as a guide for the peak positions of citrate in solution. The background spectrum for all spectra is 1mM NaOH in D\(_2\)O](image)

For citrate adsorbed on the (0001) plane it can be seen that \(\nu_a(\text{COO}^-)\) forms two distinct peaks; one consistent with the antisymmetric stretch of aqueous citrate at 1581 cm\(^{-1}\) (49%).
and a new peak at a higher wavenumber of 1623 cm\(^{-1}\) (51%). A summary of the details of the peak deconvolutions can be found in Section 9.3. The appearance of this second peak indicates that the (0001) plane of ZnO is directly influencing the carboxylate groups present. The large shift in wavenumber (ca. 40 cm\(^{-1}\)) is consistent with the formation of an inner sphere complex between the surface and the citrate molecule through one or more carboxyl groups. It is interesting to note that the COO\(^-\) symmetric stretches are less sensitive to the influence of the (0001) ZnO surface, with both peaks exhibiting a small shift of 10 cm\(^{-1}\) towards a higher wavenumber.

Figure 6.3: Different inner sphere complexes between a carboxylate and a ZnO surface

The fact that the \(\nu_{as}(\text{COO}^-)\) peak shifted to a higher wavenumber, increasing the distance between the antisymmetric and symmetric peaks (\(\Delta\nu\)), indicates that at least one COO\(^-\) group has formed a mono-dentate inner sphere complex with the surface\(^{141}\) (that is a single oxygen of a carboxyl group is bonding to the surface, Figure 6.3a). In contrast, bridging and bi-dentate complexes tend to move the antisymmetric and symmetric peaks closer together. A mono-dentate complex is also consistent with the surface structure of (0001) ZnO. On the (0001) surface the zinc atoms in ZnO are tetrahedrally co-ordinated with three oxygen atoms below the plane, with the fourth bond being a terminal hydroxyl group, the presence of which has previously been reported,\(^{176}\) and is confirmed by the XPS spectrum given in Figure 6.1j. Furthermore as the surface has a net negative charge (the isoelectric point of (0001) ZnO is 8.7\(^{26}\)) the terminal hydroxyl groups will be mainly deprotonated (making it a terminal oxide species). As the COO\(^-\) group cannot form an inner sphere complex with a negatively charged oxygen, it follows that the COO\(^-\) group must be replacing the surface oxide species, forming a mono-dentate complex with the surface Zn atom. However, it is also possible that as there are still going to be positively charged surface sites (as above the isoelectric point there will still be some positively charged sites, it is merely that, on average, there are more negatively charged sites) the carboxylates are binding to the positive sites.
The symmetric COO$^-$ stretch also appears to have a shoulder between 1450-1500 cm$^{-1}$. This can be deconvoluted into a new peak at 1490 cm$^{-1}$ and comprises about 18% of the symmetric peak area. This peak is attributable to either a bridging or bi-dentate complex.

The adsorption spectrum for citrate (100 mM) on (10\bar{1}0) plane ZnO shows a slight broadening of the COO$^-$ antisymmetric stretch, again towards a higher wavenumber. This peak can be de-convoluted into a major peak at 1581 cm$^{-1}$ (73%) and a smaller peak at 1622 cm$^{-1}$ (27%). The presence of this second peak is attributed to adsorption of the citrate to the small amount of (0001) plane that is present in the (10\bar{1}0) plane sample. It is also possible that citrate molecule preferentially adsorbs at the edge of the (0001) and (10\bar{1}0) planes, although after the samples were rinsed the citrate desorbed from the mainly (10\bar{1}0) plane, whereas the citrate remained bound to the mainly (0001) plane sample, even after repeated rinses.

Another potential site for interaction between the citrate molecule and the ZnO surface is the alcohol group present on the central carbon of the citrate molecule. From Figure 6.2 it would appear that the OH out-of-plane deformation remains more or less unaffected by both the (0001) and (10\bar{1}0) planes. However, as the spectral range of the system was limited to a minimum of 1200 cm$^{-1}$ any changes in the –OH peak could cause the peak to shift outside of this range, or be disguised by the fluctuations in the spectra that appear near the edge of the range.

6.3.3 Adsorption of Acetate, Succinate and Glutarate onto (0001) & (10\bar{1}0) ZnO
As from the spectra in Figure 6.2 it is evident that citrate binds to the (0001) plane of ZnO through one or more carboxylate groups; the next step is to determine the structural features of citrate that enable this binding. To this end the adsorption of three different derivatives of citrate was studied (see Table 6.1): acetate (one carboxylate group), succinate (1,2-dicarboxyl), and glutarate (1,3-dicarboxyl). Figure 6.4 shows the IR absorption spectra of 30 mM and 300 mM sodium acetate (30 mM and 300 mM carboxylate concentration) to (0001) plane ZnO. The spectrum of acetate in solution was taken using a transmission cell and has been included for comparison. First, there are no shifts in peaks, showing that the (0001) ZnO plane does not have a strong influence on the acetate carboxylate. Second, there is a large difference in absorption between the spectra obtained at 30 mM and 300 mM showing
that the adsorption of acetate to (0001) is either very weak or non-existent (the adsorption is not saturated at 30 mM, as it was for citrate at 10 mM). Finally the fact that the acetate ion easily rinses off the (0001) surface indicates that a single carboxylate group does not have a strong affinity for the surface.

Figure 6.4: FTIR spectrum of sodium acetate in D$_2$O solution, and adsorbed on (0001) ZnO. 30 mM (light grey lines) and 300 mM (dark grey lines). Dotted lines indicate the spectrum after desorption. Dashed vertical lines added as a guide for the peak positions of sodium acetate in solution. The background spectrum for all spectra is 1mM NaOH in D$_2$O

Since a mono-carboxylate did not adsorb greatly at 30 mM, it is interesting to determine if two carboxylic acid groups are necessary for adsorption. Succinate has two carboxylate groups that have the same spacing (two carbons) as the central and terminal carboxylates on citrate (see Table 6.1). The IR spectra of succinate are shown in Figure 6.5 at concentrations of 15 mM and 150 mM (30 mM and 300 mM carboxylate concentration) on (10$ar{1}$0) and (0001) plane ZnO. The transmission spectrum of succinate in solution has been included for comparison. The most obvious difference to citrate is that there is a large difference in magnitude of adsorption between 15 mM and 150 mM. The desorption spectrum shows that most of succinate remains bound to the surface after rinsing. This shows that the larger
absorbance at 150 mM is actually surface bound demonstrating that the adsorption of succinate is not as preferential as citrate. Thus simply having two carboxylates separated by two carbons is not sufficient to produce citrate-like affinity for the (0001) face.

For succinate adsorbed on the (10\bar{1}0) plane it initially appears as though the symmetric peak has shifted down to a lower wavenumber of 1310 cm\(^{-1}\). Whilst this cannot be ruled out, the disappearance of the anti-symmetric peak after desorption, whilst the apparent peak at 1310 cm\(^{-1}\) remains suggests that this peak is an artefact. For the adsorption of succinate on the (0001) plane, it is noted that the antisymmetric stretch remains unaffected. The primary symmetric stretch at 1397 cm\(^{-1}\) however, is shifted to a higher wavenumber of 1435 cm\(^{-1}\). This shift is could be consistent with the formation of either a bridging (where each oxygen of a carboxyl atom is bonded to a different Zn atom, Figure 6.2b) or bi-dentate (where both oxygens are bonded to a single Zn atom, Figure 6.2c) complex formed between succinate ion and the surface. As stated before the (0001) surface is ideally likely to have only a single bonding site, so a bridging complex is the most feasible. It should be noted that previous work by Yahiro et al.\(^{29}\) showed that succinate does not promote the formation of large areas of (0001) faces. Therefore it would suggest that whilst succinate bonds to the surface, the bonding is not strong enough to significantly hinder growth in the [0001] direction.
Figure 6.5: FTIR spectrum of disodium succinate in D$_2$O solution, and adsorbed on (0001) and (10\(\overline{1}0\)) ZnO. 15 mM (light grey lines) and 150 mM (dark grey lines). Dotted lines indicate the spectrum after desorption. Dashed vertical lines added as a guide for the peak positions of disodium succinate in solution. The background spectrum for all spectra is 1mM NaOH in D$_2$O.

Citrate also has carboxylic acid groups that are separated by three carbon atoms (Table 6.1). Glutarate is the simplest dicarboxylate with the same spacing, so its adsorption was also studied. Figure 6.6 shows the ATR-IR spectra of 15 mM and 150 mM glutarate (30 mM and 300 mM carboxylate concentration) on (10\(\overline{1}0\)) and (0001) plane ZnO as well as the transmission spectrum. For both the (0001) and (10\(\overline{1}0\)) surface there are large changes in the spectrum between 15 mM and 150 mM showing that the adsorption is much weaker than for citrate, which had already reached saturation at about 10 mM. There are no peak shifts in the adsorption to (10\(\overline{1}0\)) plane suggesting that there is no specific interaction between (10\(\overline{1}0\)) ZnO and glutarate ions. Furthermore, whilst the peak on the (1010) surface is broader (FHWM of 23 vs. 45 on the main peak) it has broadened symmetrically about the same peak location as the transmission spectrum (as opposed to the symmetric peak with citrate which only broadened on one side of the peak). This means that the peak could still be fitted using a single Gaussian peak. Therefore it is concluded that this apparent broadening is an artefact.
caused from the variable nature of the IR beam. On the (0001) plane however, it is quite apparent that glutarate is interacting with the surface as the antisymmetric COO\(^{-}\) stretch present at 1556 cm\(^{-1}\) in solution has split into four distinct peaks at 1533, 1571, 1596 and 1624 cm\(^{-1}\). The loss of the peak at 1556 cm\(^{-1}\) demonstrates that there is no free carboxylate: both carboxylate groups are interacting with the surface. The presence of four distinct antisymmetric peaks may indicate that different succinate ions are in different conformations or bind to different types of surface groups. However, as for citrate, the majority of the new peaks are at higher wavenumber compared to aqueous glutarate ions, which again is consistent with the formation of mono-dentate complexes. The peak at 1533 cm\(^{-1}\) would be more consistent, however, with either a bridging or bi-dentate complex. It is interesting to note that the peak at 1533 cm\(^{-1}\) increases after rinsing, whilst the peaks at 1596 and 1624 cm\(^{-1}\) decrease. This would indicate that once the glutarate ions are removed from bulk solution, the surface ions are changing conformation so that more of the carboxylate oxygen atoms are bound to the surface (as a mono-dentate complex leaves one of the carboxyl oxygens free, whereas both oxygens are involved in either bridging or bi-dentate complexes). Considering now the adsorption of each of the carboxylates, it is clear that citrate adsorbs at the lowest concentration and does not desorb as easily as the other carboxylates. Thus it is concluded that the effects of citrate arise from more than just two carboxylates: the third carboxylate and possibly the hydroxyl group help cause the strong adsorption to the (0001) ZnO plane. In addition glutarate (1,3 dicarboxylate) also experiences a large change in the spectrum on adsorption, so adsorption of both the terminal carboxylate groups of the citrate ion are probably key to citrate adsorption.
Figure 6.6: FTIR spectrum of disodium succinate in D₂O solution, and adsorbed on (0001) and (10\(\overline{1}0\)) ZnO. 15 mM (light grey lines) and 150 mM (dark grey lines). Dotted lines indicate the spectrum after desorption. Dashed vertical lines added as a guide for the peak positions of disodium succinate in solution. The background spectrum for all spectra is 1mM NaOH in D₂O.

### 6.3.4 Adsorption of Ethylenediamine to (0001) & (10\(\overline{1}0\)) ZnO.

Solutions of 10 mM then 100 mM EDA were adsorbed onto (0001) and (10\(\overline{1}0\)) plane ZnO, and the resultant IR spectra are shown as Figure 6.7. The most obvious result is that the absorbance intensity in 10 mM EDA to (10\(\overline{1}0\)) ZnO is already high enough to clearly measure a spectrum, and is about 50% of the intensity at 100 mM. In contrast, adsorption to (0001) ZnO of the same solution is so low that the absorbance is not resolved. Only at 100 mM EDA does adsorption to (0001) get high enough for the EDA to be observed. So EDA adsorsbs much more strongly to the (10\(\overline{1}0\)) surface than the (0001) surface. Given that EDA encourages growth of (10\(\overline{1}0\)) faces\(^{115,117}\) this supports the hypothesis that specific adsorption to a face leads to the growth of that face. However, unlike citrate on the (0001) plane, the EDA is not strongly bound to the (10\(\overline{1}0\)) plane, as most of the EDA is removed by rinsing.
Figure 6.7: FTIR spectrum of EDA in D₂O solution and on (0001) or (1010) ZnO. 10 mM (light grey lines) and 100 mM (dark grey lines). Dotted lines are EDA spectrum after desorption.

The spectrum of EDA in solution was also examined. Even though the EDA is in D₂O, complete proton-deuteron exchange with solution does not occur: the broad NH₂ scissoring peaks are still present at 1584 and 1608 cm⁻¹. Whilst some exchange is bound to occur, it was not able to be monitored as the resultant N-D peak would be shifted to below the spectral cut off 1200cm⁻¹.²⁸⁴

The other peaks present are different vibration modes that were previously attributed²⁸⁴ to the out-of-plane deformation (δ(CH₂)), twisting (π(CH₂)) scissoring (γ(CH₂)) and wagging (ω(CH₂)) of the methylene groups, and are summarised in Table 6.2. When EDA is adsorbed onto the (10\{1\}0) plane, a dramatic change in the IR spectra is observed. The ω(NH₂) vibration shifts down to 1551 cm⁻¹, which is more consistent with the wagging vibration mode of an ammonium ion.²⁸⁴ This is further supported by the appearance of three peaks characteristic of an ammonium salt at 2496, 2420 and 2358 cm⁻¹.²⁶² In addition the δ(CH₂)
vibration at 1460 cm\(^{-1}\) remains, which shows EDA remains in a gauche confirmation,\(^{184}\) that is, presenting both amines to the same side of the molecule. All this is consistent with the idea that the lone pair of electrons on both amine groups of EDA are complexing with the (10\(\overline{1}0\)) plane. However, the exact nature of this complex is harder to identify. And as the isoelectric point of the (10\(\overline{1}0\)) plane has been reported as being 10.2.\(^{21}\) As the experiments presented here were conducted at pH = 10.7 it is likely that both hydroxide and negatively charged oxide species are present on the surface. Further adding to the complexity are previous reports\(^{19}\) that the hydrated (10\(\overline{1}0\)) ZnO surface is a combination of hydroxide (-OH) and hydrate (-OH\(_2\)) species. Therefore it is possible that the amine groups of EDA are bonding to either a hydroxyl group or replacing a water molecule to bind with a Zn atom, or possibly both.

Table 6.2: IR Peak Assignments for EDA between 1650 and 1300 cm\(^{-1}\)

<table>
<thead>
<tr>
<th>Ethylenediamine (EDA)</th>
<th>Peak Assignment</th>
<th>Aqueous</th>
<th>(0001)</th>
<th>(10(\overline{1}0))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\tau(CH_2)/\tau(-NH_2))</td>
<td>1325</td>
<td>-</td>
<td>-</td>
<td>1358</td>
</tr>
<tr>
<td>(\omega(CH_2))</td>
<td>1365</td>
<td>*</td>
<td>1402*</td>
<td>1415</td>
</tr>
<tr>
<td>(\omega(CH_2))</td>
<td>1410</td>
<td>1460*</td>
<td>1460</td>
<td></td>
</tr>
<tr>
<td>(\gamma(CH_2))</td>
<td>1502</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>(\gamma(CH_3))</td>
<td>1512</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>(\gamma(-NH_2))</td>
<td>1584</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>(\gamma(-NH_3)^\dagger)</td>
<td>-</td>
<td>1551</td>
<td>1551</td>
<td></td>
</tr>
<tr>
<td>(\gamma(-NH_2))</td>
<td>1608</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

* Peak assignment ambiguous due to spectral noise
† Peak consistent with scissoring of ammonium ion

To confirm whether EDA binds to Zn\(^{2+}\) in solution, the transmission spectra of EDA in a 100 mM Zn(NO\(_3\)_2 / 1 mM NaOH solution and 1 mM NaOH solution with no Zn(NO\(_3\)_2 were recorded. The addition of Zn ions did not affect the spectrum, so the results in Fig. 6.7 must be attributed to surface adsorption.

6.4. Conclusions

Citrate adsorbs more strongly to the (0001) face than to \{10\(\overline{1}0\)\} faces of ZnO, whereas ethylenediamine adsorbs more strongly to \{10\(\overline{1}0\)\} faces than to the (0001) face. For both citrate and ethylenediamine the adsorption is stronger to the face that grows large in the presence of that molecule. This supports the hypothesis that adsorption to a particular face encourages growth of that face. Furthermore, analysis of the ATR-IR peaks shows that the adsorption is strong enough to cause a significant change in the spectrum of citrate when
adsorbed to the (0001) face and of ethylenediamine when adsorbed to the (10\overline{1}0) face. That is, strong, inner sphere adsorption occurs for these combinations. This strong adsorption decreases the surface energy of the face, and would require energy to displace the adsorbed molecules, hindering addition of further growth units to these faces. This explains why growth normal to these faces is hindered when the molecules adsorb. The explanation is supported by the fact that after the organic molecules are removed from bulk solution, they remain on the solid: desorption has an activation energy. A detailed analysis of the derivatives of citrate show that the strong and selective bonding to the (0001) face occurs through all three carboxyl groups, though in different conformations.

These conclusions were made possible by the modification of a commercial infrared spectrometer to allow ATR measurements of small, thin crystals, and by the ability to prepare ZnO crystals with large areas of a single crystalline face.
7. Overview & Future Prospects

The first step in understanding how small molecules influence the hydrothermal growth of ZnO was to understand the growth process of ZnO in general. This is described in Chapter 4. By using multiple spectroscopic techniques to study the products formed during the hydrothermal growth of ZnO at different temperatures, it was found that ZnO is formed from a crystalline zinc hydroxide intermediate known as Wülfingite (\(\varepsilon\)-Zn(OH)\(_2\)). Then by \(^{18}\)O labelling experiments it was found that this intermediate converts to ZnO via two competing pathways; solid state conversion, and dissolution followed by precipitation. Furthermore, it was found that, under the conditions studied, the solid state conversion was the dominant process. The rate of conversion was seen to increase with increasing temperature such that, at temperatures greater than 70°C, the initial \(\varepsilon\)-Zn(OH)\(_2\) was not observable after 20 minutes. Therefore it is possible that at these higher temperatures ZnO forms directly from solution. Whilst this result is fascinating, and causes us to rethink our approach to controlled ZnO growth, it is only a beginning of the potential work in this field.

As it has been established that there are two pathways to from ZnO from Wülfingite, it would be interesting to see how the different solution conditions affect these two pathways. Future studies in this area could investigate how the relative reaction rates of the two pathways change when process variables, such as temperature, pH and choice of solubilizer (i.e. NH\(_3\) vs. Hexamine), as well as the consequences of varying the Zn(II):solubilizer ratio. In addition it would be interesting to see how growth-directing molecules influence the different stages of the growth process, and the resultant morphology. For example when using citrate to obtain the small aspect ratio crystals, is it better to arrange conditions where solid state conversion is predominant (and hence try and alter the morphology of the Wülfingite), or is it better to use a system where direct precipitation of ZnO is occurring (therefore try and directly alter the relative growth rates of ZnO)?

The next stage in this work was to investigate the complementary process of ZnO dissolution (Chapter 5). The dissolution of nominally (0001), (00\(\overline{1}\)) and (10\(\overline{1}\)0) ZnO surfaces under basic conditions was studied in-situ using Atomic Force Microscopy. From these studies it was found that etching originates mainly from dislocation sites running in the [0001] direction. Furthermore, the (10\(\overline{1}\)0) plane, which is the predominate face of hydrothermally
grown ZnO, is unstable at high pH reconstructing into a combination of (0001) steps (with 
{10\bar{1}1} risers) and smooth {10\bar{1}1} planes. The preferential formation of these planes was 
explained by considering the number of surface oxygens per zinc atom for each of the 
surfaces, with stability of a plane being inversely dependent upon number of surface oxygen 
atoms. The effect of citrate on the dissolution was also investigated, and it was found that 
citrate increases the number of (0001) steps per given area, and also reduces the average step height. Future studies could focus on the effects of other molecules (particularly those which have been shown to alter ZnO morphology) on the dissolution of different ZnO faces. Whilst this would be interesting, and potentially lead to the formation of other ZnO faces not normally expressed during growth, a more interesting direction for this work would be to use ab-inito modelling to simulate ZnO dissolution process. This process needs to be modelled to confirm the theories developed during this work, particularly with regards to the mechanism by which citrate molecules encourage (0001) step formation.

The final stage in this work was to bring the knowledge gained from the two previous 
chapters together to directly measure the face-specific bonding of growth directing molecules 
to the different ZnO surfaces. The first stage was to produce large areas of crystal surface that were predominantly a single crystal face, and were suitable for spectroscopy. A process involving dissolution and annealing led to the creation large areas of molecularly smooth, planar, ZnO surfaces, of a single crystal plane. These faces also retained their native hydroxide layer. These surfaces were then used in a customised ATR-FTIR spectrometer which allowed direct observation of face-specific binding (Chapter 6). Two complementary systems were studied, one that encourages (0001) growth (citrate) and one that encourages (10\bar{1}0) growth (ethylenediamine). From these studies specific bonding of growth-directing molecules on different ZnO faces was directly observed for the first time. Furthermore, by studying the bonding of different citrate analogues (acetate, succinate, glutarate), it was found that a critical structural element required for adsorption to (0001) ZnO was two carboxylate groups separated by three carbon atoms.

However, this is just the beginning of the potential studies in this area. There are many different known organic growth modifiers that could potentially be investigated with the system (see Table 2.2). A further advancement in this area could also be pH studies. As most of the functional groups active in bonding are acids/bases, it would be interesting to see how the degree of dissociation affects the bonding to the different ZnO surfaces (i.e. can a –
COOH group bond as effectively as a COO\(^-\) group). This would be particularly interesting for molecules that influence aspect ratio of ZnO crystals differently depending on the pH in which the crystals are grown (e.g. EDTA).

Whilst these studies have a great deal of potential, there are always going to be limited in the information they can yield about the bonding. Whilst the adsorption studies can show if specific bonding is occurring, the interactions between the molecule and the surface cannot be determined accurately. It would be much better to use ab initio modelling of the interactions between different growth directing molecules and the ZnO surfaces. By combining the experimental observations with theoretical calculations, the bonding configurations of growth directing molecules could be determined more precisely. This would invariably lead to determining exactly why a specific molecule is able to affect the crystal morphology, which would in turn lead to improved tailoring of chemicals that could affect the ZnO morphology.

In a broader scientific sense, this work could be expanded to investigate other systems. Whilst there would be significant technical difficulties to surmount (as there was in this project), the single crystal ATR-FTIR could be used to investigate face specific interactions between inorganic crystals and organic molecules for a wide range of systems. This could lead to greater insight into a myriad of systems in many different fields from material science to biology (such as protein-CaCO\(_3\) interactions, or the interactions between algae and glass for anti-fouling applications).
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9. Appendices

9.1. Miller Indices

As a significant portion of the work presented in this thesis relates to face specific properties of ZnO a brief explanation of the nomenclature used when describing different crystal faces is required.

The most common method for describing crystallographic directions is using the Miller index system. A Miller index is a vector represented by a combination of three, non-co-linear unit vectors $\mathbf{h}$, $\mathbf{k}$, $\mathbf{l}$, written as [hkl], that correspond to the directions of the crystal unit cell. This vector then defines a particular surface normal to the vector, written as (hkl). As an example consider a simple cubic unit cell, as illustrated by Figure 9.1. The three principal crystallographic directions for this cell are the three orthogonal Cartesian co-ordinates $\mathbf{h}$ = [001], $\mathbf{k}$ = [010], and $\mathbf{l}$ = [001]. The corresponding planes, (100), (010), and (001), represent three different surfaces of the unit cell, and, by extension the crystal itself. The other three faces of the crystal are defined by the surfaces normal to negative vectors, i.e. the face opposite (001) would be the (00 − 1), though negative Miller indices are conventionally denoted by a bar over the co-ordinate, instead of a negative sign, so (00 − 1) is written as (00\text{̄}1).

Miller indices can also be used to describe planes that are not surfaces of the unit cell. For instance, if a surface formed by cutting the unit cubic unit cell along the diagonal of a face of the unit cell, the resulting surface would be written as (110), (101) or (011), depending on which direction the cut was made. This new surface has different atomic arrangement to (100), as the atoms are now spaced either 1 or $\sqrt{2}$ units apart, as opposed to the (100) surfaces where each atom was separated by 1 unit. Further to this a different atomic spacing could be obtained by cutting along the body diagonal, exposing the (111) face. These atoms are $\sqrt{2}$ units apart and are in a hexagonal close packed arrangement as shown in Figure 9.1c. Higher index surfaces are surfaces formed from vectors that extend over more than one unit cell. These Miller indices are always expressed as integer vectors with no common denominator, i.e if the vector was one unit in the $\mathbf{h}$ direction and 0.5 units in the $\mathbf{k}$ the vector would be [210] not [10.50].
Figure 9.1: Examples of different surfaces of a simple cubic structure and the associated Miller Indices. The spacing of the atoms for each of the different low Miller index surfaces is also shown for comparison. (A) the native crystal surfaces of the unit cell. (B) the surface diagonal to a crystal face. (C) hexagonal close packed surface formed by the surface of the body diagonal of the unit cell. (D) Examples of higher Miller index surfaces formed over more than one unit cell.

Whilst Miller indices allow each face to be classified uniquely, it is quite common that in a crystal some of the faces will not be unique, i.e. they have the same atomic spacing and composition. In this case it is often convenient to refer to a family of non-unique faces as a single entity, written as \{hkl\}. Hence, in the case of the cubic structure in Figure 9.1 it is obvious that all the faces of the unit cell are equivalent, and so the (001), (010), (001),
(1\(\bar{1}\)0), (0\(\bar{1}\)0), and (00\(\bar{1}\)) faces are expressed as \{100\}, and the corresponding vector set as \(<100>\).

For crystals with hexagonal geometry it is convenient to introduce a fourth Miller index, \(i\), written as [\(hki\l\)], with \(h, k,\) and \(i\) in the x-y plane separated by 120° and \(l\) normal to the plane, as illustrated by Figure 9.2. As \(i\) is a redundant co-ordinate it can be expressed in terms of \(h\) and \(k\) such that \(i = -(h + k)\). ZnO has a hexagonal habit so it is this version of Miller indices that will be used in this work. The reason the \(i\) (the redundant index) is included in hexagonal crystal systems is to allow a family of planes (or directions) with geometric similarity to be expressed with a single, consistent set of values. For instance it is easy to see that the \((11\bar{2}0)\) and \((1\bar{2}10)\) planes are geometrically similar, but when written as \((110)\) and \((1\bar{2}0)\) their similarity is not as obvious.

![Miller Index system for hexagonal structures.](image)

Figure 9.2: Miller Index system for hexagonal structures. Due to symmetry there are typically three different types of surfaces: \((0001)\), \((10\bar{1}0)\), \((1\bar{2}0)\).

ZnO naturally forms a Würzite structure, with alternating hexagonally close packed sheets of oxygen and zinc. The native faces of are ZnO are \((0001)\) which is the Zn terminated basal plane, also referred to as the c-plane, \((00\bar{1})\) which is the O terminated basal plane, (also known informally as the c'-plane), and the set of six prismatic planes, \(\{10\bar{1}0\}\) also known as the m-plane.
### 9.2. Chemical Structures

Table 9.1: Chemical Names and Structures of growth modifiers listed in Table 2.2

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<tr>
<th>Chemical Name</th>
<th>Abbreviation</th>
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<td>Diethylenetriamine</td>
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<td>Diethylenetriaminepentacetic Acid</td>
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9.3. Carboxyl peak analysis

The carboxylate peaks presented in Chapter 6 were de-convoluted into separate Gaussian Peaks of the form:

\[ F(\lambda) = 2.5Ae^{-\frac{(\lambda-B)^2}{2C^2}} \] (Equation 9.1)

where:

A = Peak Intensity
B = Peak Wavenumber
C = Peak Width, which is related to the full half width maximum (FHWM) by the equation:

\[ FHWM = 2\sqrt{2 \log_2 2} C \] (Equation 9.2)

In each case the peaks were de-convoluted iteratively into the smallest number of peaks possible. This was done to minimise the interpretational bias of the data that results when the number of fitted peaks is increased. However, it is possible that the larger peaks are the result of several smaller peaks, but without some evidence, such as molecular modelling of the system, this cannot be proven. The area of each de-convoluted peak is given by:

\[ Area = AC\sqrt{2\pi} \] (Equation 9.3)

and is expressed as a percentage of the total peak area. Table 9.2 gives a summary of all the parameters used for the de-convolution of the antisymmetric and symmetric carboxylate peaks studied in Chapter 6.
Table 9.2: Symmetric and Anti-symmetric peak de-convolution

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<th>Peak Type</th>
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**Author/s:**
Nicholas, Nathan Johann

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**Date:**
2011

**Citation:**

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